A51A MCC: 3016 Friday 0800h

Atmospheric Nitrogen Deposition to Critical Estuary Habitats: The Bay Regional Atmospheric Chemistry Experiment (BRACE) II *(joint with B, OS)*

Presiding: **T B Watson,** NOAA Air Resources Laboratory**; N Poor,** College of Public Health, University of South Florida

A51A-01 0800h INVITED

Tampa Bay Regional Atmospheric Chemistry Experiment: Overview

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The Tampa Bay Estuary Program (TBEP) was formed in 1991 to assist in developing a comprehensive plan to restore and protect Tampa Bay in Florida, USA. An ecological indicator of the health of the Bay is the coverage of seagrasses, historically in decline, which are important to the aquatic habitat and food web of the bay. Seagrass decline is linked to excess of plant-stimulating forms of nitrogen to the bay, promoting algae growth, which shades out light needed to sustain seagrasses. One element of the TBEP is a private-local-state, multi-agency Nitrogen Management Consortium that seeks to limit nitrogen loading to the Bay to the 1992-1994 average. Present estimates suggest atmospheric deposition comprises 30% of the nitrogen budget of the Bay. This estimate was based, however, on limited ambient monitoring data and simple models, typical of such national estuary program efforts nationwide. In the Bay Regional Atmospheric Chemistry Experiment Florida DEP joined with TBEP to increase the intensity, sophistication and spatial scope of monitoring and modeling and provide better information on air quality in the Tampa Bay area. The result will be improved estimates of the effects of local and regional emissions of oxides of nitrogen (NOx) on the Bay and the benefits to be gained from implementation of emissions reduction strategies.

URL: http://www.hsc.usf.edu/publichealth/EOH/BRACE/

A51A-02 0815h

Texas Tech Uuniversity Measurements at BRACE Sydney Site, May 2002

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TTU measurements included semi-continuous monitoring of acid gases, gaseous ammonia and total soluble anionic constituents and ammonium in atmospheric particulate matter (with the 50 percent cut off in the collection/measurement system lying above 10 micron mass median aerodynamic diameter) with a 15 min time resolution and formaldehyde, hydrogen peroxide and methyl hydroperoxide measured with 10 min time resolution. Continuous measurements with response times of 90 s were also made of Hydrogen Peroxide and Formaldehyde on the NOAA Twin Otter Aircraft. Measurements at the Sydney site were made from April 26 through May 31st. Data and findings related to the atmospheric composition of the Tampa Bay Airshed will be presented. The pattern of HCl, particulate nitrate and nitric acid concentrations strongly suggest that at least in part, HCl formation is related to nitrate formation. This postulated reaction of nitric acid on coarse sea salt particles constitutes a dominant pathway for nitrogen deposition. The appearance of gaseous HCl is inversely related to relative humidity; this may be expected as well. The sulfate/ammonium equivalent ratio in equivalents is almost always greater than unity during weekdays suggesting that sulfate is only partially neutralized by ammonium. However, on weekends the same ratio approaches unity. The acidic nature of the fine particles in addition to the abundance of coarse sea salt NaCl also explains the almost exclusive presence of nitrate in the coarse PM fraction. Finally representative patterns of gases and particles will also be presented along with occasional observation of plumes from coal power plants, which passed directly over the Sydney site.

A51A-03 0830h INVITED

Gas Phase and Particulate Phase Organic Compositions at the Sydney Site During the 2002 Bay Regional Atmospheric Chemistry Experiment (BRACE)

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During the Bay Regional Atmospheric Chemistry Experiment (BRACE) in 2002, particle and gas phase organic compounds were routinely measured at the Sydney site east of Tampa. This was the most easterly (inland) site occupied during the study and could be characterized as a rural clean air site which provided the background site for the Tampa urban area. Aircraft measurements were also performed using canisters to follow the urban air plume. Because of the proximity of Tampa and the transport of the urban air mass eastward, periodic enrichment episodes where anticipated. Hourly measurements of C2-C12 NMHCs were performed using a system composed of a gas trap coupled with a GC/FID. Aerosol samples were also collected for organic speciation. PM2.5 and size-segregated samples were respectively collected with a high volume sampler and Micro Orifice Uniform Deposit Impactors (MOUDIs). All particulate matter (PM) samples were collected on a 24 hours schedule with the exception of a few days while shorter schedules were used for the PM2.5. Samples were extracted using a mixture of dichloromethane/acetone/hexane, concentrated down and analyzed using gas chromatography-mass spectrometry (GC/MS). Gas phase results showed that isoprene was consistently the most common NMHC present and constituted the bulk of the OH reactivity. The measurements will be put into the context of other continental background measurements. Linkages to organic aerosol formation will also be explored. Organic speciation of PM showed that the Sydney site was representative of a rural site for most of May 2002. Concentrations, especially for polycyclic aromatic hydrocarbons (PAH), compared well with PM2.5 data obtained from other rural sites within the Southeastern United States. Only a few days showed concentrations higher than typical rural sites but without reaching urban values.

A51A-04 0845h INVITED

Emission Rates of PM Constituents from Highly Time-Resolved Ambient Concentration Measurements: A New Paradigm in Air Pollution Management

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Highly-time resolved metals measurements were made in the Bay Regional Atmospheric Chemistry Experiment and at four other urban locations using the University of Maryland Semicontinuous Elements in Aerosol Sampler. Aerosol slurry samples were collected at 30-minute intervals, i.e., at periods short relative to changes in wind direction, and analyzed off-line by mutli-element graphite furnace Atomic Absorption Spectroscopy for up to 12 elements useful as markers of primary particle emissions of high-temperature combustion sources. At this resolution, the plumes of individual sources, including coal- and oil-fired power plants, and a battery recycling plant, were readily observed as excursions in time series profiles of the concentrations of the various marker elements. Over the scale of 40 km, wind and source angles are nearly identical when the former are relatively constant during the time required for plume transport. Herein, ambient data collected at the Sydney site were combined with available stack emission measurements of SO2, along with meteorological data in a pseudo deterministic least squares model in which ambient concentrations are reconciled with the products of emission rates and dispersion factors for known sources. The model encompasses horrizontal and vertical gaussian dispersion terms as constraints and is used to estimate estimate emission rates of the various species from the known sources. Ambient ground-level measurements made in the vicinity of the Sydney site will be presented along with some the model estimates of emission rates from various sources.

A51A-05 0900h

The Dry Deposition of Nitrogen and Sulfur Compounds During BRACE 2002

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During the 2002 Bay Regional Atmospheric Chemistry Experiment (BRACE) that was conducted in May, the conditional sampling method was used to measure the fluxes of nitric acid vapor, ammonia, and fine sulfate and nitrate aerosol. Annular denuders and filterpacks were used as collectors of the gases and aerosols in the "updrafts" and "downdrafts" during 4 hour runs from from which the concentrations and fluxes were determined. The fluxes of water, CO2, sensible heat and ozone were also determined using the eddy covariance method. These measurements were conducted at a grassland site location near the water treatment facility east of Tampa Bay near Sydney, Florida. Comparisons of concentrations with other measurement systems as well as an assessment of the daytime deposition velocities of the gases and aerosols will be presented.

A51A-06 0915h

Export of Atmospherically Derived Nitrogen in the Tampa Bay Watershed

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Several approaches are used to place bounds on likely fluxes of nitrogen to Tampa Bay, Florida that ultimately are derived from atmospheric deposition to the watershed. One approach compares ion ratios of total N and Cl in a number of north Florida watersheds to ratios in atmospheric deposition. Atmospheric deposition ion ratios were calculated based on wet deposition measured at NADP/NTN sites in north and central Florida and dry deposition estimates developed by Poor et al. (2003). Two key assumptions are inherent in the analysis: Cl is conservative (no sources other than atmospheric deposition contribute significantly to riverine Cl fluxes; nor are there significant sinks for Cl within the watershed other than surface runoff and groundwater recharge), and the only source of nitrogen is atmospheric deposition. This approach thus defines a minimum degree of N retention. Samples with K concentrations greater than 15 microequivalents per liter were screened to remove agricultural influences on nutrient export, resulting in average N retention estimates ranging from 41 to 81%. The data base analyzed included 22 different stream stations in Florida that are part of the USGS NASQAN stream water chemistry data base. Other approaches are based on simplified watershed mass balances computed from NASQAN flow and water quality measurements and atmospheric fluxes based on NADP wet deposition fluxes and dry deposition fluxes developed by Poor et al. (2003). For systems where atmospheric inputs of chloride balance riverine export (within +/- 20%), preliminary estimates of minimum N retention based on this approach range from 5 to 94% and likely reflect the limited hydrologic data available to estimate annual fluxes. The third approach is based on a critical examination of existing nutrient budgets for Tampa Bay, and defining the maximum contribution to indirect N loading to Tampa Bay from atmospheric deposition.

A51A-07 0930h

Aircraft Observations of the Tampa Urban Plume during BRACE: Transport, Photochemical, and Depositional Processes

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Staff from NOAA's Air Resources Laboratory conducted airborne measurements of trace gases and aerosols in the Bay Region Atmospheric Chemistry Experiment (BRACE) using the NOAA Twin Otter. The Twin Otter flew more than 90 hours in 21 flights in and around the Tampa metropolitan region in May, 2002, at altitudes of 60-3000 m MSL. Flights were conducted over rural and suburban areas, over the centers of Tampa and St. Petersburg, and over Tampa Bay and the Gulf of Mexico. The overall objective of the aircraft measurements in BRACE was to study the emission, transport, and photochemical transformations of nitrogen and other ozone precursors in the Tampa area. Continuous instrumentation was used to measure NO, NOX, NOY, HNO3, CO, SO2, O3, CH2O, and H2O2. A semi-continuous GC technique with luminol detection was used to measure PAN. Filter packs were used to make integrated measurements of nitric acid and inorganic aerosols in both fine and bulk aerosol size fractions. Stainless steel grab cans were filled during flight for post-flight analysis of NMHCs by GC/FID/MS. The urban plume was sampled under a variety of meteorological regimes, as it was advected by the prevailing winds over the Florida peninsula (with continuing input of natural and anthropogenic precursors along the advection path) and, in other cases, over the Gulf of Mexico, where additional chemical inputs were negligible and the plume was relatively unaffected by turbulent deposition processes. Case studies will be used to compare and contrast the photochemical processes in the plume under these different regimes. The observed relationships and variations of trace gas concentrations will be used to determine the efficiency of ozone production, as well as instances of NOX or VOC limitation. Sampling the plume at varying downwind distances, over both land and water, allows the determination of overall rates of photochemical ozone production, NOX and SOX oxidation, and estimates of depositional losses of trace species.

A51A-08 0945h

Studies of Tampa Bay Region Power Plant Plumes during the Bay Region Atmospheric Chemistry Experiment (BRACE)

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The NOAA Air Resources Laboratory made aircraft measurements of chemical and meteorological parameters during 21 flights of the NOAA Twin Otter as part of the Bay Region Atmospheric Chemistry Experiment (BRACE). BRACE was conducted in May 2002. The aircraft flew horizontal transects upwind and downwind of the urban area on 13 of these flights to characterize the urban and power plant plumes. Vertical profiles from 60 to 3000 m MSL were made on most flights. Profiles were made over the Gulf of Mexico, Tampa Bay, and various land sites. On many flights, transects were located immediately downwind of the urban region and power plants and at successive distances farther downwind to characterize the horizontal distribution and chemical processing of the plumes as they aged. At each distance, data was collected during multiple passes at different altitudes to characterize the vertical structure. Many of the downwind passes were flown over the Gulf where sources are limited and the plumes can be observed in relative isolation. The contribution of the power plant plumes are analyzed to determine changes in the vertical and horizontal distribution of the plumes; horizontal fluxes of NOx, NOy, and ozone; production of ozone; deposition rates; and changes on successive days of regional background and concentration maxima caused by the power plant emissions.

A51B MCC: 3018 Friday 0800h

Use of Inverse Modeling for Constraining Global Budgets of Atmospheric Trace Gases I *(joint with B)*

Presiding: **A M Michalak,** NOAA Climate Modeling and Diagnostics Laboratory**; W Peters,** NOAA Climate Modeling and Diagnostics Laboratory**; P P Tans,** NOAA Climate Modeling and Diagnostics Laboratory

A51B-01 0800h INVITED

Regional Carbon Flux Estimation by Inversion of Mesoscale Tracer Transport

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Estimation of carbon fluxes over large regions by tracer transport inversion at global scales is now well established in carbon cycle science, and several studies are now underway in the Europe, the US, and in Brazil to apply similar methods to regional studies over continental areas. Continuous measurements of CO_2 have the potential to better constrain regional CO_2 fluxes through temporal variations associated with synoptic and mesoscale meteorology, and this class of mesoscale inverse problem is expected to be very important in the upcoming North American Carbon Program. We are conducting a pilot study of mesoscale CO_2 inversions using a network of seven continuous analyzers in the region of a tall TV tower (WLEF) in northern Wisconsin. Here we report preliminary results of inverse modeling studies using the new data and experiments using synthetic data for the year 2000. The mesoscale inverse problem is complicated by the need to treat initial conditions, lateral boundary fluxes, and the interaction between mesoscale transport and heterogeneous surface fluxes. Some studies have used zoomed or nested grids in global models to resolve near-field transport, whereas others have specified lateral boundary fluxes from global models. We have taken the latter approach, and simulate tracer transport over a domain much larger than the area of the observations to keep lateral boundaries at a distance. We have simulated the entire year 2000 over a 100 km grid covering most of North America using the CSU Regional Atmospheric Modeling System (RAMS), with two nested grids (dx=20 km and dx=4 km). Meteorological boundary conditions are specified from the NOAA/NCEP reanalysis, with CO_2 mixing ratios at lateral boundaries from the mean of the global TransCom models after flux adjustment to match remote flask observations. We simulate the influence of upstream fluxes on hourly measurements of CO_2 mixing ratio at each tower using a Lagrangian Particle Dispersion Model that calculates thousands of back trajectories for each observation. Linear combinations of spatial and temporal variations of upstream surface fluxes were then scaled to provide optimum agreement with observations constrained by reasonable diurnal and synoptic variations. Our results highlight the importance of vertical resolution, subgrid-scale turbulence, and cloud-scale transports in determining upstream sources and sinks. Sources within one day's advective travel time of the receptor have a disproportionate influence on the estimated flux, which suggests that spacing of observational networks should be made with this metric in mind. Continuous measurements were found to exert significantly stronger constraint on upstream surface fluxes than subweekly vertical profiles.

URL: http://biocycle.atmos.colostate.edu

A51B-02 0815h

Top-down Constraints on North American Carbon Fluxes using CO2:CO Correlations from Aircraft Data

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We employ measurements of CO2, CO and CO2:CO correlations in conjunction with 3-D simulations from a global chemical transport model (GEOS-CHEM) to better constrain specific sources contributing to North American CO2 exchange. The CO2:CO emission ratio varies with efficiency of combustion and provides a characteristic signature of source region and source type, and in particular, of combustion versus biospheric influence. Our analysis of CO2:CO correlations in Asian outflow demonstrated the utility of these measurements in constraining the regional biospheric source of CO2 [Suntharalingam et al. 2003]. Here we employ observed correlations from aircraft campaigns (NOAA and NASA-GTE) over and around the North American continent in conjunction with CO2 and CO measurements from NOAA/CMDL surface sites. We use the GEOS-CHEM model, driven by our best emissions estimates, to identify influences of separate source regions on the CO2:CO measurements. Comparison of modeled and observed concentrations and correlations then enables evaluation of the a priori emissions distributions.

A51B-03 0830h

A First Attempt to use Variability at Synoptical Time Scales in Constraining Trace gas Emissions

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Global scale inversions of e.g. CO_2 fluxes from atmospheric observations normally employ simulated and observed mixing ratios, averaged over a monthly or yearly period. Reasons for this approach may be computational costs, the use of climatological meteorological fields, a limited number of observations, and a limited performance or resolution of the transport model. On or close to the continents it is expected, however, that concentration variations on the shorter time scales contain information about the emission distribution of the observed trace gas. The newly developed Adjoint Version of Tracer Model, version 5 (TM5) has been used to obtain tracer emissions based on 6-hourly averaged observations . TM5 is a global model that allows a two way nested zoom over specific regions. In the model version that is used here, a horizontal resolution of 1x1 degree is employed over Europe. The region of interest is the Mediterranean sea. Measurements taken there during the Minos campaign have been analyzed by using back-plumes' calculated with the adjoint TM5.

A51B-04 0845h

Emission Verification of Greenhouse Gases on the Sub-continental Scale Using Tall Tower Observations and Inverse Trajectory Modeling

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Inert (on the time scale of several days) greenhouse gases like CH_4, N_2O and SF_6 are almost ideal gases to model in trajectory models, as (photo)chemistry and uptake processes can be neglected. The forward and backward (inverse) calculations of atmospheric transport presented here have been performed by using a simple trajectory model, utilizing 3D 96 hour backward trajectory data based on ECMWF analysed windfields.