south of Portsmouth Harbor, near the Isle of Shoals, and in the Boston Harbor area. Between Cape Ann and Newburyport, saturation anomalies for anthropogenic halocarbons of 100% for CFC-113, 140% for H-1211, 40% for methyl chloroform, and 15% for carbon tetrachloride were observed. Throughout the cruise, subsequent high levels of these compounds were found in the area. The findings suggest that there are local anthropogenic sources of these gases, which are draining into the Gulf of Maine from local rivers, harbors, or estuaries. Elevated level of methyl bromide, methyl iodide, bromoform, and chloroform were measured near the coast, and decreased with increasing distance. The distributions of the NMHCs were similar to the naturally produced marine halocarbons, suggesting similar sources. Supersaturation of alkyl nitrates were observed indicating an oceanic source of methyl nitrate, i-propyl nitrate, n-propyl nitrate, and 2-butyl nitrate, with the later three compounds reported here in ocean water samples for the first time.

A51D-0713 0830h POSTER

Non-Methane Hydrocarbon Measurements Aboard the NOAA Research Vessel Ronald H. Brown during the 2002 New England Air Quality Study (NEAQS 2002)

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During the NEAQS 2002 study, in-situ NMHC measurements were made aboard the NOAA research vessel Ronald H. Brown by a two channel automated gas chromatograph using both flame ionization and mass-spectrometric detection techniques. Five minute average samples were cryogenically trapped each 1/2 hour and analyzed immediately for C2 through C10 alkanes, C2 through C5 alkenes, C6 through C9 aromatics, C2 through C8 aldehydes and ketones, C1 through C5 alcohols and a variety of compounds of biogenic origin including 6 monoterpenes, isoprene and its primary oxidation products methacrolein and methylvinyl ketone. The relative contributions of these classes of compounds to OH photochemistry has been determined for air masses ranging from those showing significant anthropogenic influence to clean marine air. For the most anthropogenically influenced air masses, alkenes were observed to play a dominant role whereas oxyhydrocarbons, principally acetaldehyde, were observed to dominate under clean marine conditions. Both the NMHC measurements and back trajectory analyses indicated periods of significant influx into the New England coastal region of urban air masses showing elevated ozone levels from the Boston/Providence urban corridor. About as frequently, less photochemically mature air masses, depleted in ozone but laden with light reactive alkenes, were observed coming from the Portsmouth NH/Kittery ME coastal urban complex. Even in the presence of these anthropogenic plumes, biogenic hydrocarbons appear to dominate OH photochemistry in the New England region much of the time. Data demonstrating all of these conclusions will be shown.

A51D-0714 0830h POSTER

PAN-Type Compounds and Photochemistry in the NEAQS Environment

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Peroxyacyl Nitrates (PANs) were measured by capillary GC/ECD aboard the NOAA research ship, Ronald H. Brown, as part of the 2002 New England Air Quality Study (NEAQS). Peroxyacetyl nitrate (PAN), Peroxypropionyl nitrate (PPN), Peroxy-iso-butyryl nitrate (PiBN), and Peroxymethacryloyl nitrate (MPAN) were all measured simultaneously once every 10 minutes from July 12 through August 10, 2002. Calibration of the PANs was performed via acetone photolysis (PAN) and diffusion source (PPN and PAN) allowing for detection limits ranging between 5-10 pptv. Significant amounts of all the PANs were observed off of the coast of New England. These values are comparable to those obtained from past terrestrial ground site measurements. PAN mixing ratio was observed to be as high as 2.5 ppbv, while PPN and MPAN were seen to reach mixing ratios over 300 pptv. PANs thereby represent a significant NOx source to the New England marine boundary layer. The relative amounts of the PANs observed also indicate that the chemistry of the NEAQS sampling environment is impacted by the oxidation of both anthropogenic and biogenic hydrocarbons. The results from this investigation possibly indicate the in-situ production/destruction of PANs within the marine boundary layer.

A51D-0715 0830h POSTER

Measurements of HNO_3 on the NOAA Research Vessel Ronald H. Brown During NEAQS 2002

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Nitric acid was measured at 5 minute resolution with an automated mist chamber/ion chromatograph sampling/analysis system. More than 3000 measurements were made from 29 July through 10 August, 2002, mainly in the Gulf of Maine but also during the transect to South Carolina at the end of the cruise. Mixing ratios of HNO_3 varied over a wide range from day to day in response to synoptic conditions, with southeasterly flow bringing much cleaner air to the sampling region on several days. The maximum mixing ratio (7.1 ppbv) was observed in Boston Harbor, but the prevailing westerly flow carried regionally polluted air masses to the ship for most of the study, resulting in an overall mean HNO_3 mixing ratio of 1.1 ppbv. Pronounced diurnal variability was superimposed on these synoptic changes. Peak mixing ratios were observed each day around solar noon (mean for the interval 11:00 - 15:00 local time was 2.01 ppbv), with minima near sunrise and sunset. The morning hours between 6:00 - 8:00 almost always had the lowest HNO_3 mixing ratios each day, overall the mean during this period was 0.57 ppb. Interestingly, nitric acid increased after dark to a secondary maximum, averaging 0.98 ppbv for the 4 hours centered around midnight. The nighttime peak of HNO_3 was generally much broader than the daily maximum in the early afternoon, suggesting sustained production of HNO_3 in the dark (see Brown et al., this session).

A51D-0716 0830h POSTER

In-situ Measurements of NO_3 and N_2O_5 During NEAQS 2002

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During the New England Air Quality Study (NEAQS) 2002 campaign, nighttime chemistry of nitrogen oxides was studied through direct, in-situ measurements of NO_3 and N_2O_5 via cavity ring-down spectroscopy. The measurements were taken off the coast of the Northeast U.S. aboard the NOAA research vessel Ronald H. Brown. The marine boundary layer is a unique environment in which to observe chemical transformations occurring in polluted air masses advected from land over the ocean. Data are available for 17 nights of observations of these two compounds; their mixing ratios varied from the instrumental detection limit of 0.5 pptv (5 s average) to maximum values of 140 pptv for NO_3 and 1.5 ppbv for N_2O_5. Respective average mixing ratios were 17 and 84 pptv during nighttime hours for these two compounds. The combination of these observations with measurements of mixing ratios of other important trace gases, aerosols properties and composition, and meteorological data allowed for detailed analysis of NO_3 and N_2O_5 lifetimes and relevant sink chemistry for these compounds. Model calculations are used to illustrate the interconversion of nitrogen oxide compounds near sunset and sunrise.

A51D-0717 0830h POSTER

Field and Laboratory Measurements of Carbon Dioxide Mixing Ratios in Air Using the LI-COR LI-7000 CO_2/H_2O Analyzer

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Air measurements of CO_2 were made with a LI-COR LI-7000 CO_2/H_2O analyzer on the NOAA ship Ronald H. Brown during the New England Air Quality Study (NEAQS 2002) field campaign. This instrument is an improved version of the older model LI-6262 CO_2/H_2O analyzer, which uses a non-dispersive IR radiation absorption technique. During NEAQS, we operated the LI-7000 without temperature regulation, using a simple 2-point calibration scheme. An intercomparison between our measurements of atmospheric CO_2 mixing ratios and those measured by a more sophisticated method, using temperature-regulation and a multipoint calibration with a LI-6252 CO_2 analyzer (operated by AOML) shows generally good results ($[CO_2]AL = [CO_2]AOML \times 1.015\ (0.010) - 5.7\ (3.8)$ ppmv; $R^2 = 0.9889$) in highly variable air masses. During subsequent laboratory studies, we evaluated the instrument for the manufacturer's claims of improvement in signal noise, sample gas temperature equilibration and zero drift with temperature. Further work examined the instrument's susceptibility to rapid temperature changes, which has been previously demonstrated to introduce error of several ppmv $^{\circ}C^{-1}$ in the LI-6252. A change in the LI-7000 optical bench temperature of 12 $^{\circ}$C in 1 hour caused a sampling error of $\sim$3 ppmv CO_2. Therefore, our lab investigations indicate that the LI-7000 would benefit from a temperature-controlled enclosure, as is used by the AOML group.

A51E MCC: Level 2 Friday 0830h

2002 New England Air Quality Study IV Posters

Presiding: **B Talbot,** Institute for the Study of Earth, Oceans, and Space, University of New Hampshire**; T Bates,** NOAA Pacific Marine Environmental Laboratory

A51E-0718 0830h POSTER

Measurements of Marine Vessel Emissions

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Nitrogen and sulfur emissions from large marine vessels are a significant source of these species to the atmosphere. One estimate indicates that oxidized nitrogen from this source is at least 14% of all combustion emissions globally (1). More importantly, since approximately 70% of all ship emissions occur within 400 km of land (1) marine vessel emissions are of significance regionally in coastal areas and locally in ports. Marine vessel emissions are calculated from marine fuel usage and various emission factors, where sulfur emission factors depend on the sulfur content of fuel and nitrogen emission factors depend on the vessel engine type: slow-speed diesel, medium-speed diesel, and other (generally steam-turbine). Currently, the best available emission factors come from a Lloyd's Register of Shipping sponsored emissions research program. Measurements were made of emissions from engines during bench tests and from in-service marine vessels directly at the stack. While these results are the best available data, the significance of marine vessel emissions suggests that additional evaluation of emission factors be conducted. During the 2002 New England Air Quality Study (NEAQS 2002) the NOAA research vessel Ronald H. Brown was equipped with trace gas and aerosol monitoring instrumentation for the purpose of investigating the factors that affect air quality in coastal New England. As a part of that study, measurements were made of gaseous and particulate emissions from marine vessels, both in port and underway. This talk will present those results and relate them to current inventory estimates of marine vessel emissions. (1) Corbett, J.J., et al., Global nitrogen and sulfur inventories for oceangoing ships, J. Geophy. Res., 104, 3457-3470, 1999.

A51E-0719 0830h POSTER

Measurements by the DOE G-1 During the Summer 2002 NEAQS Study

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Brookhaven National Laboratory conducted a series of aircraft flights with the DOE G-1 aircraft during the Summer 2002 New England Air Quality Study (NEAQS). The principal objective of these flights was to conduct a regional survey of aerosol/oxidant precursors, aerosol mass loading, composition, and microphysics. Seven flights were made from July 8 - July 24 and on various days extended from central NY to the North Atlantic Ocean east of Boston. On two of the flights over the North Atlantic, measurements were made in conjunction with the NOAA research vessel the Ron Brown. To date, analysis of the aircraft data shows that- 1. Significant long-range transport of aerosol and trace gases from mid-western source regions to the Northeast and out over the North Atlantic can occur under certain commonly observed meteorological conditions. 2. Aerosol composition is a strong function of aerosol loading with sulfate dominating aerosol composition under high loading conditions and organics under conditions when the loadings were low; nitrate did not contribute significantly to aerosol composition under either circumstance. 3. Transport of pollutants from North American out over the ocean is vertically structured suggesting that much of this transport occurs well above the surface. In part, this phenomenon is caused by the presence of a strong temperature inversion that forms near the ocean surface.

A51E-0720 0830h POSTER

Chemical composition characterization by Particle-Into-Liquid Sampler during the New England Air Quality Study 2002 experiment

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An improved version of the particle-into-liquid-sampler (PILS) was deployed to study the aerosol chemical composition in the NEAQS 2002 field campaign. Major ionic species of aerosol particles smaller than 2.5 μm (PM 2.5) were analyzed by ionic chromatography. The SO_4^{2-}, NO_3^-, and NH_4^+ were quantified with a time resolution of three minutes. The soluble carbon species was analyzed by a total organic analyzer. The preliminary results were analyzed for better understanding of pollution sources and transport in New England area.

A51E-0721 0830h POSTER

Aerosol Acidity in the New England Coastal Atmosphere During Summer 2002

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Aerosol pH controls important multiphase chemical pathways in the atmosphere but absolute values are poorly constrained. As part of the New England Air Quality Study, aerosol pH was quantified based on multiple independent approaches and results were intercompared for consistency. Soluble, reactive trace gases with pH-dependent solubilities (HNO_3, NH_3, HCl, HCOOH, and CH_3COOH) were sampled with mist chambers. Size-segregated aerosols were sampled in parallel with cascade impactors and analyzed for major ionic constituents. H^+ was measured directly in minimally diluted, 5-μL spots on surfaces of impaction substrates with a flat-surface, field-effect transistor. Aerosol liquid water contents (LWCs) were calculated with hygroscopicity models. Aerosol pHs required to sustain the measured phase partitioning of each analyte were inferred based on corresponding thermodynamic properties and direct pH measurements were extrapolated to ambient LWCs. The ensemble of approaches yielded coherent results. Sea-salt pHs ranged from about 2 to the mid 4s and sub-μm aerosol pHs ranged from <1 to the mid 3s. The $H^+ + SO_4^{2-} \leftrightarrow HSO_4^-$ equilibrium strongly buffered aerosol pH in all size fractions.

A51E-0722 0830h POSTER

Aerosol Optical Properties at NEAQS 2002 From Lidar, Sunphotometer, and Integrating Nephelometer

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Optical measurements of aerosols were performed from the NOAA Research Vessel Ron Brown near the east coast of the United States for 3 weeks starting mid-July 2002. The instruments included a lidar (355 nm wavelength), a handheld sunphotometer (380, 440, 500, 675, and 870 nm), and an integrating nephelometer (450, 550, and 700 nm). Lidar extinction profiles are derived with constraint from the sunphotometer aerosol optical depth data when available. Typical extinction-to-backscatter values from these measurements for the same airmass types are used to retrieve extinction profiles at night and in cloudy periods. Temperature profile and wind shear data from radiosondes and vertical smoothness of the lidar backscatter profile are used to determine the vertical extent of the layer in which the aerosol particles can be considered well mixed. The fraction of the total column aerosol that is characterized by the near-surface in situ measurements is estimated from the lidar profile and depth of the mixed layer. Extinction values from the lowest gates of the lidar are compared with the nephelometer's aerosol scatter data when the atmosphere is apparently well mixed between the two heights. The optical characteristics for various sources (urban, rural, and maritime) are contrasted.

A51E-0723 0830h POSTER

The influence of the nitrate radical on the dimethylsulfide oxidation derived from field measurements during NEAQS (New England Air Quality Study)

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We present simultaneous measurements of nitrate radical (NO_3) and dimethylsulfide (DMS) from NEAQS (New England Air Quality Study). DMS is emitted from the ocean surface as a result of phytoplankton activity, whereas NO_3 is produced by reaction of ozone (O_3) and nitrogen dioxide (NO_2) in polluted air. Photolysis by visible light and rapid reaction with NO during daytime prevent NO_3 from building to significant concentration, except at night. The rapid reaction between NO_3 and DMS constitutes an important sink for the latter in the polluted marine boundary layer. We will show nocturnal profiles of both compounds as well as the anticorrelations between them. These data indicate that nighttime DMS oxidation by NO_3 under polluted conditions with high NO_3 concentrations in the north-east coastal region of the US and daytime oxidation by OH are comparable. We will discuss the influence of transport and mixing of fresh emissions into marine air on the observed anticorrelations based on trajectory calculations and tracer measurements to distinguish between transport effects and reactions.

A51E-0724 0830h POSTER

An Overview of the Nighttime Aerosol/Oxidant Plume Experiment (NAOPEX)

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The Nighttime Aerosol/Oxidant Plume Experiment was designed to characterize aerosols (number density, geographic distribution, physical characteristics) and trace gases coming from the greater Boston area at night between July 29 and August 8, 2002. Aircraft flights below 1500m MSL measured upwind/downwind characteristics of the urban plume and included Lagrangian measurements made in conjunction with tetroon releases within the plume. We focus here on just the upwind/downwind characteristics of the plume, with the Lagrangian results to be presented elsewhere. Statistically insignificant variations in aerosol number density, O_3, and CO downwind of Boston were found under conditions of westerly flow, although large (50%) increases in downwind NO_y were measured. Much bigger upwind/downwind differences were found in O_3 and CO when sampling under light and variable wind conditions although the downwind NO_y levels were much less (increase of only 15%), and were not associated with any measurable increase in the NO_x relative to observations made under westerly flow. There was, in general,

little evidence of the Boston plume at aircraft sampling heights, which suggests a greatly reduced potential for long range transport of the urban plume within the free troposphere over the Atlantic.

A51E-0725 0830h POSTER

Vertical variations of boundary layer chemistry in the urban environment of Boston

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Boundary layer chemistry in urban areas is often strongly influenced by surface emissions of NO_x and VOCs. Vertical mixing in combination with chemical transformations leads to distinctive vertical profiles of reactive trace gases. Chemistry, therefore, varies with altitude in the lowest 50 m, in particular in the stable nocturnal boundary layer. The influence of vertical mixing on chemistry in the lowest part of the boundary layer is often not accurately described, and a better understanding is needed to improve our ability to model urban air pollution. During the NEAQS/NAOPEX field campaign in July-August, 2002, vertical distributions of NO_2, O_3, HONO, HCHO, NO_3, and several other trace gases were measured in the lowest 10 - 50 m of the atmosphere with a long-path differential optical absorption spectroscopy instrument in a residential area in Boston, MA. Various meteorological parameters were also monitored at the same location. Clear vertical trace gas concentration gradients were observed. In particular, during nights with strong stabilities, nocturnal boundary layer chemistry was clearly altitude dependent. Positive gradients of O_3 and NO_3 developed as a result of the fast chemical reactions with NO emitted at the surface. Negative NO_2 and HONO gradients point to the vertical variation of the heterogeneous NO_2-HONO conversion process, suggesting the importance of heterogeneous chemistry at the ground and building walls. With the transition from the stable boundary layer to a convective layer after sunrise, the vertical profiles regressed. However, vertical gradients of HCHO and O_3 were observed in the afternoon on most days of this study. The observations suggest that ground-based emissions and fast photochemistry can lead to vertical profiles of trace gases in an urban boundary layer even during daytime. The vertical stratification of boundary layer chemistry, which depends on many factors including mixing strength, fast photochemistry and the emission strength, will be discussed.

A51E-0726 0830h POSTER

Lagrangian Measurements of Aerosols and Oxidants in the Boston Urban Plume During the NAOPEX 2002 Campaign

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Heterogeneous chemical processes involving trace gases and aerosols are poorly understood and are expected to play an important role at night. As part of the New England Air Quality Study (NEAQS), the Nighttime Aerosol/Oxidant Plume Experiment (NAOPEX) was designed to study the chemical evolution and interaction of ambient urban aerosols and trace gases in the absence of photochemistry. Lagrangian measurements of trace gases (O3, NOx, NOy, VOCs, CO) and aerosols (size distribution and composition) were made with the Department of Energy's (DOE) G-1 aircraft in the nocturnal residual layer downwind of greater Boston area. On clear nights with offshore flow, a superpressure, constant-volume balloon (tetroon) was launched from a coastal site into the Boston plume around sunset to serve as a Lagrangian marker of urban air parcels as they moved out over the Atlantic Ocean. The tetroon carried an instrument payload of about 2.5 kg that included a GPS receiver, radiosonde and ozonesonde. Latitude, longitude, altitude, temperature, pressure, relative humidity and ozone concentration data were transmitted in real-time to a receiver on the ground as well as one onboard the G-1 aircraft. About an hour after the launch, when the tetroon was outside the restricted Class B airspace, the G-1 aircraft made the first flight to make more comprehensive measurements in the vicinity of the tetroon. New GUI-based Lagrangian flight planning software onboard the G-1 was used in intercepting and maneuvering the aircraft near the tetroon. About five hours after the tetroon launch, after it had gone out of range of the ground station (but before sunrise), the G-1 made the second flight to make another set of measurements in its vicinity. Here, we report on the two flights made between 20:00 EST July 30 and 02:00 EST July 31. Analyses of the Lagrangian aerosol and trace gases dataset suggest evidence of heterogeneous activity and aging of aerosols. Vertical profiles of (O_3 + NO_y) concentrations in the vicinity of the tetroon were found to be anti-correlated with aerosol number density, and the slope of the linear regression fit decreased as a function of time, suggesting destruction of ozone in the presence of aerosols. Potential mechanisms that may explain this behavior will be presented and their implications will be discussed.

A51E-0727 0830h POSTER

Vertical Concentration Profiles of Nitrous Acid in the Boundary Layer: Comparison of Observations and 1D Modeling Results

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Nitrous acid, HONO, is an important precursor for OH radicals in the polluted atmosphere. HONO accumulates in the nocturnal boundary layer (NBL) and its photolysis at sunrise is often the dominant OH source at the ground. Although it is well known that HONO is formed by the heterogeneous conversion of NO_2, the surfaces involved in this process have not been clearly identified. The concentrations of HONO also depend strongly on the stability of the NBL. Many of the uncertainties about HONO formation in the atmosphere originate in the poorly understood role of the various urban surfaces and the influence of vertical mixing, which can lead to strong vertical concentration gradients of both HONO and NO_2. In recent years we have performed several field experiments to study the NO_2 - HONO system in the polluted boundary layer (e.g. TEXAQS, 2000, NEAQS/NAOPEX, 2002). In all studies we measured vertical concentration profiles of NO_2, HONO, and various other trace gases in the boundary layer by Differential Optical Absorption Spectroscopy continuously throughout the night and the following morning. Here we present a comprehensive analysis of the vertical distribution of NO_2 and HONO in these urban environments. The observations will be compared with results from a one-dimensional chemical transport model in order to investigate the influence of the ground, building surfaces, and aerosol on the formation of HONO. The altitude dependence of the early morning OH formation will also be discussed.

A51E-0728 0830h POSTER

Source Attribution of Aerosols during the Baltimore PM Supersite in 2002 from Lidar, a Turbulence Sensor, and Back-Trajectory Analysis

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During the Baltimore PM Supersite experiment highly time and size resolved concentrations of urban PM2.5 and its constituents were collected year round in 2002. Intensive measurement periods were conducted in the spring (March/April) and summer (July 1 - August 15). During those periods a backscatter lidar and a 3D sonic anemometer turbulence sensor provided information on vertical extent of the mixed layer, turbulence characteristics in the mixed layer, and entrainment dynamics. These data together with back trajectory calculations and radiosonde soundings allow good descriptions of the aerosol constituents and source attribution. A total of eleven high PM episodes are analyzed. The Canadian forest fire smoke event of July 6 - 8 is captured in great detail and other exemplary events for coastal air pollution are presented.

URL: http://www.jhu.edu/dogee/mbp/supersite2001/index.htm

A51E-0729 0830h POSTER

A New Wind Profiler Trajectory Tool for Air Quality Studies

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The Cooperative Institute for Research in Environmental Sciences, the NOAA Environmental Technology Laboratory (NOAA/ETL), and the Science and Technology Corporation have developed a new online tool for producing forward and backward trajectories from hourly wind profiles measured by a network of boundary-layer wind profilers. The tool is intended to aid scientists and forecasters in the planning and execution of field operations during the 2004 Northeast North Atlantic Air Quality Study. This study will involve an international consortium of agencies and will include upwards of a dozen of research aircraft and the NOAA research vessel Ronald H. Brown. The purpose of this talk is to demonstrate the tool and collect feedback from scientific investigators, which we will use to modify the tool before the 2004 field study. In addition, we will present preliminary results from the 2002 New England Air Quality Study that demonstrate the value of using continuous profiler observations instead of numerical model initialization fields to calculate trajectories for the meteorologically complex coastal zone of New England. The trajectory tool uses the horizontal wind profiles measured by the profiler network that are collected in near-real time and archived at NOAA/ETL's facility in Boulder, Colorado. The vertical velocities are not used because of large uncertainty in the profiler's vertical velocity measurement. To calculate hourly trajectory positions, the horizontal winds are interpolated in space using an inverse distance squared weighting. Users may request altitude ranges for the trajectories as well as start and end times and trajectory starting/end points. Trajectories are plotted on a two dimensional map background and are color coded by their respective altitude range.

A51E-0730 0830h POSTER

Quantification of Ozone Formation Metrics in Southeastern New Hampshire During NEAQS 2002

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Ozone formation metrics are calculated using ambient measurements taken during NEAQS 2002 at the Thompson Farm sampling station in rural southeastern New Hampshire. The metrics include the O3 production rate (OPR), O3 production efficiency (OPE), and reactivity (R). OPR is calculated as the rate of formation of peroxy radicals or the rate of conversion of NO to NO2. In each method, the rate calculated is assumed to be the rate-limiting step in O3 formation. OPR values illustrate the relative importance of chemical and transport mechanisms in leading to peaks in O3. OPE is defined as the ratio of the OPR to the rate of loss of NOx (assumed to be the HNO3 formation rate) and demonstrates the moles of O3 formed per mole of NOx emitted. A second method for calculating OPE gives a temporally averaged OPE by regressing O3 mixing ratios against NOy-NOx. Lastly, individual R values indicate the time scale for peroxy radical formation from reactions between CO or other reactive organic gases (ROGs) and OH. R for an individual gas is the product of its mixing ratio and reaction rate constant with OH.

Total R is the sum of the individual values. Mixing ratio data for NO, NOy, O3, and CO are collected at 1-minute resolution. Temperature and jNO2 are also measured at 1-minute resolution. However, ten-minute averages of these parameters are used to coincide with ten-minute averages of ROG mixing ratios measured once per hour. Only data that coincide with sufficient sunlight intensity to ensure the photostationary state are used. A zero-dimensional version of a photochemical mechanism is used to estimate mixing ratios of relevant HOx radicals. Results show OPR and R values that are very low compared to other locations. OPR peaks during midday. R peaks earlier and later in the day and tends to be dominated by short-chain hydrocarbons. The low values of OPR indicate that peaks of O3 in this location are likely a result of the mixing of O3-rich air transported from higher levels of the atmosphere or other areas. The relatively high OPE values for this location confirm that the air in southeastern New Hampshire is typically NOx-limited.

A51E-0731 0830h POSTER

Ozone Prediction for the 2002 Air Quality Forecasting Pilot Program Using a Hybrid (Lagrangian-Eulerian) Photochemical Model

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The Hybrid Single-Particle Lagrangian Integrated Trajectories with a generalized non-linear Chemistry Module (HY-SPLIT CheM) model has been developed to calculate the spatial and temporal distribution of different chemical species in the lower troposphere over a regional scale. The simulation relies on a Lagrangian particle approach to compute transport, dispersion and deposition; and uses an Eulerian framework to represent chemical transformations of different air contaminants. HY-SPLIT CheM has been configured to simulate 48-hour ozone mixing ratios for the eastern United States. Air concentrations are computed based upon a 1/2x1/2-degree resolution grid and 10 vertical layers. Emissions of volatile organic compounds (VOCs) and nitrogen oxides (NOx) are based upon the Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system. The forecast simulations only include pollutant sources between 25-50 N latitude and 65-100 W longitude. Transport and dispersion is computed using meteorological fields from the Mesoscale Model Version 5 (MM5) model with a horizontal resolution of 45 km, once each day, based upon the 0000 UTC forecasts (to 48 h). The Carbon Bond IV chemical mechanism is used to simulate the photochemical smog formation. Each calculation is started with all the lagrangian particles that are on the domain at the model's initialization time as computed from the previous day's simulation (yesterday's 24 h forecast). Pollutant particles may accumulate for up to 72 h before termination, although most of them are advected off the grid prior to reaching their age limit. The ability of HY-SPLIT CheM to simulate ozone mixing ratios is evaluated by comparing calculated ozone mixing ratios against measured values for a 25-day period (5-29 August 2002). HY-SPLIT CheM is the first operational implementation of the particle-in-grid approach applied to air quality forecasting. This model constitutes a feasible tool for ozone prediction due to its speed and low cost of implementation.

A51E-0732 0830h POSTER

Numerical air quality forecasts made at NOAA/FSL during NEAQS 2002

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The 2002 New England Air Quality Study (NEAQS) was an intensive effort to investigate the chemical and meteorological factors that contribute to poor air quality in the costal New England region. The campaign combined efforts of numerous educational institutions as well as federal, state, and local agencies. Data were collected from an extensive network of ground sites, from the NOAA research vessel Ronald H. Brown, and from the DOE G-1 aircraft. Although many of the ground stations routinely collect data year-round, the period of most intensive measurements was from July 12 through August 10, 2002. This presentation will discuss the configuration and real-time production from numerical guidance in use at NOAA/FSL. The numerical model used during NEAQS is a fully coupled atmospheric and chemistry forecast model (MM5-Chem). The atmospheric model is the Pennsylvania State University/National Center for Atmospheric Research Mesoscale Modeling System Version 5 (MM5). The chemistry model includes the RADM2 chemical mechanism, photolysis, biogenic and anthropogenic emissions and dry deposition. Data analysis is being conducted for three high-ozone events observed along the New England coast, 21 - 22 July 2002, 3-5 August 2002 and 12-15 August 2002. Comparisons are being made between MM5-Chem, observational data and retrospective simulations using other air quality forecast models. The analysis shows that, in general, the various numerical models produce similar results. However, small, but potentially significant, differences in the forecasted boundary layer wind speed and direction, as well as the temperature and moisture profile can result in large differences in regional ozone forecasts. For example, the residual boundary layer originating at the coast of New England and out over the Gulf of Maine was often predicted by MM5 to be warmer, more humid and shallower than what was observed. The resulting temperature and moisture profile is more stable than observed and restricts vertical mixing of pollutants off of the New England coastline.

A51E-0733 0830h POSTER

Evaluations of the Eta, RUC, WRF and MM5 Meteorological Models During NEAQS 2002

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During the summer of 2002 several NOAA Research laboratories (Environmental Technology Laboratory, Aeronomy Laboratory, Forecast Systems Laboratory) collaborated with the National Weather Service, including the National Centers for Environmental Prediction (NECP), on a project to assess and improve forecasts in New England using a regional testbed approach. During this project arrays of special research grade instruments were deployed throughout New England by NOAA Research, including seven 915 MHz wind profilers with RASS, cloud ceilometers, and surface meteorology stations that included solar and net radiation. Measurements from these instruments were compared against predictions made by operational and research forecast models, including the Eta, RUC, WRF and MM5 models. Model/observation comparisons were made on an hourly basis in real-time during the experiment. Results from this project will be presented, focusing on phenomena that most directly affect pollutant transport and mixing, including boundary layer depth, sea-breeze representation, and mesoscale transport.

URL: http://www.etl.noaa.gov/programs/2002/taq/verification/

A51E-0734 0830h POSTER

The Accuracy of Solar Irradiance Calculations Used in Medium Range Forecast Models

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During the 2002 New England Air Quality Study the NOAA Environmental Technology Laboratory (ETL) made radiative transfer observations at the University of New Hampshire, Thompson Farm Air Chemistry Site. We measured upward and downward solar irradiance, upward and downward IR irradiance, and aerosol optical depth at 412, 500, 675 and 862 nm from 18 July through 31 August 2000. We evaluated the solar irradiance forecasts made by both the National Center for Environmental Prediction (NCEP) operational ETA model and the Pennsylvania State University National Center for Atmospheric Research Mesoscale Model 5 (PSU/NCAR/MM5) Air Chemistry Model using the ETL observations. Our observations show that aerosol optical depths exceeding 0.8, accompanied the surface ozone events of 22-23 July and 11-15 August. The comparisons between the solar irradiance observed at Thompson Farm and the ETA and MM5 forecasts for 11-15 August ozone events suggest that the lack of sophisticated aerosol physics in both forecast models can cause the models to produce excessive clear-sky downwelling irradiance. 50-80 W m-2 forecast errors characterize the comparison. Similar comparisons conducted by ETL for Nashville, TN, Houston, TX and the Central Valley of California suggest that the radiative imbalances in models using the Lacis and Hanson solar irradiance parameterization are largest in regions impacted by the aerosols embedded in the East Coast industrial pollution plumes. We will show results that suggest that once the aerosol optical depth exceeds 0.1 the models typically forecast excessive downwelling solar irradiance. We will also present comparisons between JNO2 measured at Thompson farm with the 412 nm sun photometer measurements.

A

A51F MCC: Level 2 Friday 0830h

The Organic Aerosol Component: Impact on Reactivity, Optical Properties, Hygroscopicity, and Cloud-Condensation Properties IV Posters *(joint with AE)*

Presiding: **G D Smith,** University of Georgia**; T Mentel,** Institut für Chemie und Dynamik der Geosphäre Juelich

A51F-0735 0830h POSTER

Scanning Transmission X-ray microscopy Imaging of Aerosol Particles

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Scanning transmission x-ray microscopes (STXM) are used to image a diversity of carbon and metal containing items such as biofilms in soils, magnetic materials, polymers and meteorites. Studies on particles collected on SiO2 filters from biomass burns in Flagstaff, Arizona and individual aerosols collected in South Africa on TEM grids are underway at beamlines 5.3.2 and 11.0.2 at the Advanced Light Source of Lawrence Berkeley National Laboratory. Sub micron particles are imaged in the transmission mode over the energy range of 280 - 1900 eV. Spectromicroscopic studies on individual particles using near edge x-ray absorption fine structure (NEXAFS) probe multiple species within or on the same particle. In (STXM) an X-ray beam is focused with a zone plate onto a sample and the transmitted radiation is detected. Since the signal is obtained in the transmission mode, optically thin samples are required. Hence, atmospheric aerosols with submicron thickness and diameter are well suited for this method. Near edge spectra of various elements were scanned in step sizes from 0.1-0.5 eV around characteristic absorption edges, creating 2 dimensional images at each energy. While STXM images are taken with a lower spatial resolution (currently 40 nm) than microscopies such as scanning electron microscopy, transmission electron microscopy, and atomic force microscopy, detailed chemical information with spatial distributions, and oxidation states is obtained. A particular focus of this work is to obtain more detailed information on the type of carbons, multiply, or singly bonded and whether or not carbon is bonded to oxygen. The ultimate goal is discrimination between organic and black carbon within individual aerosol particles and determining if organic carbon, black carbon, and metal species are distributed homogeneously