A41F MCC: 3018 Thursday 1020h

2002 New England Air Quality Study II

Presiding: **E Williams,** NOAA Aeronomy Laboratory and CIRES**; B Talbot,** Institute for the Study of Earth, Oceans, and Space, University of New Hampshire

A41F-01 1020h

The Dominance of Organic Aerosols During NEAQS 2002

Timothy S. Bates[1] (206-526-6248; tim.bates@noaa.gov)

Patricia K. Quinn[1] (206-526-6892; Patricia.K.Quinn@noaa.gov)

Ann M. Middlebrook[2] (amiddlebrook@al.noaa.gov)

[1]NOAA Pacific Marine Environmental Laboratory, 7600 Sand Point Way NE, Seattle, WA 98115, United States

[2]NOAA Aeronomy Laboratory, 325 Broadway, R/AL 7, Boulder, CO 80305, United States

Aerosol chemical, physical and optical measurements were made aboard the NOAA RV Ronald H. Brown off the coast of New England during July/August 2002 as part of the New England Air Quality Study (NEAQS). Measurements (generally 20 to 100 km from the coast) were made downwind of urban centers (NYC, Boston) and rural areas, and in air masses that had not been in contact with land for several days ("marine"). On average during NEAQS, 72±9% of the dry aerosol mass sampled 18 m above the sea surface was in the < 1 μm fraction (size cut at 55% RH). This submicron fraction accounted for 84±14% of the aerosol light scattering. The major sub-micron aerosol components were ammonium sulfate and particulate organic matter (POM, defined here as 1.6 times the concentration of organic carbon). The ammonium to non-sea-salt (nss) sulfate ratio increased in the urban air masses. The mass ratio of POM to nss sulfate plus ammonium ranged from 0.38 to 8.8 with values generally higher in the rural/marine air masses. POM was the dominant aerosol component in 75% of the samples. Even considering the water associated with ammonium sulfate at ambient RH and assuming no water uptake of the POM, POM was often the major source of the regional haze. These data are similar to that found off the mid-Atlantic states during TARFOX but contrary to the current understanding that the New England haze is primarily a result of sulfate aerosol. The data raise two important questions: Are these data representative of "normal" conditions along the New England Coast? And, what is the source of the POM? We can not address the first question from our single cruise but will attempt to address the latter using other measurements made aboard the ship. We will address both questions during the summer of 2004 using ship and aircraft measurements in this region along with a more detailed study of the organic POM species.

URL: http://www.al.noaa.gov/NEAQS/

A41F-02 1035h

Non-Refractory Submicron Aerosol Mass Loadings during NEAQS

A M Middlebrook[1] (303-497-7324; amiddlebrook@al.noaa.gov); B M Matthew[1,2] (bmatthew@al.noaa.gov); M R Canagaratna[3] (mrcana@aerodyne.com); D R Worsnop[3] (worsnop@aerodyne.com); P K Quinn[4] (patricia.k.quinn@noaa.gov); J A DeGouw[1,2] (jdegouw@al.noaa.gov); C Warneke[1,2] (cwarneke@al.noaa.gov); P D Goldan[1] (pgoldan@al.noaa.gov); W C Kuster[1] (bkuster@al.noaa.gov); E J Williams[1] (ewilliams@al.noaa.gov); S A McKeen[1] (smckeen@al.noaa.gov)

[1]NOAA Aeronomy Laboratory, 325 Broadway, Boulder, CO 80305, United States

[2]University of Colorado, CIRES, Boulder, CO 80309, United States

[3]Aerodyne Research Inc, 45 Manning Rd, Billerica, MA 01821, United States

[4]NOAA Pacific Marine Environmental Laboratory, 7600 Sand Point Way NE, Seattle, WA 98115, United States

During the New England Air Quality Study (NEAQS) in July-August 2002, an Aerosol Mass Spectrometer (AMS) was deployed aboard the NOAA ship RONALD H. BROWN and collected 2-minute averaged data. The AMS, which measures non-refractory components of aerosol particles with aerodynamic diameters between roughly 40 and 1500 nm, produced particle mass spectra as well as aerosol organic, sulfate, ammonium, and nitrate mass distributions. A wide variety of air masses were sampled, including clean marine, clean continental, and polluted continental air masses. In general, the volatile particle composition was mostly organic and sulfate with lesser amounts of ammonium and nitrate and the mass loadings typically peaked around 400-600 nm in vacuum aerodynamic diameter. Although the AMS sulfate and ammonium concentrations were highly correlated with the sulfate and ammonium concentrations from the Particle into Liquid (PILS) instrument also deployed on the ship, the AMS and PILS nitrate concentrations were not correlated and at times anti-correlated. In contrast, the AMS nitrate and organic concentrations as well as the AMS nitrate and gas phase alkyl nitrate concentrations were highly correlated. These results suggest that organic nitrate was present in the submicron aerosol phase. The AMS organic concentrations were generally higher than the AMS sulfate concentrations, consistent with other shipboard measurements. Whenever the sulfate concentration increased, the organic concentration also increased, indicating that sulfate and organic aerosol growth are influenced by the same processes or that sulfate may play a role in organic aerosol growth. The exception to this pattern occurred during a sea fog event where the sulfate concentration increased and the organic concentration decreased, probably due to rapid aqueous phase sulfur oxidation and relatively less oxidation of organic compounds. Furthermore, the organic concentration often increased without concurrent increases in sulfate mass, indicating that organic and sulfate aerosol mass have different sources or that the processes involved in increasing organic concentrations can be independent of sulfur oxidation.

A41F-03 1050h

Aerosol Optical Properties in the Northeastern U.S. Plume Measured During NEAQS 2002

Patricia K Quinn[1] (patricia.k.quinn@noaa.gov)

Timothy Bates[1] (tim.bates@noaa.gov)

Derek Coffman[1] (derek.coffman@noaa.gov)

Theresa Miller[1] (theresa.miller@noaa.gov)

James Johnson[1] (james.e.johnson@noaa.gov)

[1]NOAA PMEL, 7600 Sand Point Way NE, Seattle, WA 98115

To assess the impacts of aerosols on air quality and climate downwind of the northeastern United States, extensive measurements of aerosol chemical, physical, and optical properties were made onboard the NOAA RV Ronald H. Brown during NEAQS 2002. These measurements included light scattering, hemispheric backscattering, and absorption by the aerosol at 450, 550, and 700 nm. These data allow for the calculation of the hemispheric backscattered fraction and single scattering albedo. Coupling the measured aerosol chemical composition and size distributions with a Mie scattering model allows for the calculation of the fraction of light extinction due to each chemical component. Aerosol optical depth (AOD) at 380, 440, 500, 675, and 870 nm also was measured. Mean values and variability of these parameters will be reported for the different urban plumes encountered along the cruise track from Charleston, SC to the Gulf of Maine. The aerosol forcing efficiency or aerosol forcing per unit AOD can be estimated from the single scattering albedo, hemispheric backscattered fraction, and AOD. Forcing efficiencies will be presented for the northeastern U.S. urban plumes and will be compared to values from European, Asian, and Indian plumes. In addition, aerosol mass scattering and absorption efficiencies, quantities which determine the magnitude of AOD, will be presented.

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

A41F-04 1105h

Identification of Plume Signatures from the NOAA Research Vessel Ronald H. Brown during NEAQS-2002

B. M. Lerner[1,2] (303/497-5296; blerner@al.noaa.gov); P. C. Murphy[1,2] (pcmurphy@al.noaa.gov); P. D. Goldan[1] (pgoldan@al.noaa.gov); W. C. Kuster[1] (bkuster@al.noaa.gov); C. Warneke[1,2] (cwarneke@al.noaa.gov); J. A. deGouw[1,2] (jdegouw@al.noaa.gov); E. J. Williams[1,2] (eric@al.noaa.gov)

[1]Aeronomy Laboratory/NOAA, 325 Broadway, Boulder, CO 80305, United States

[2]CIRES, University of Colorado, Boulder, CO 80309, United States

During the New England Air Quality Study (NEAQS-2002) a large number of trace gas species were measured aboard the NOAA ship Ronald H. Brown along the east coast of the U.S. Emissions from numerous sources were measured in the New York harbor area during a brief stop on the transit north. Urban emissions from the Boston area and from the New Hampshire/Maine coastal region, as well as emissions from biogenic sources, were frequently observed during the intensive study period in the southern Gulf of Maine. Moreover, numerous well-defined narrow plumes were sampled throughout the experiment, attributable to either marine vessel exhaust or point-source emissions from land-based sites at or near the coast. Measurements of SO2, NOy and CO2 mixing ratios in these plumes, along with back-trajectory analysis, were used to identify a number of these point-sources through comparison to emission inventory data available from the U.S. EPA. In this talk the types and characteristics of emissions source plumes encountered during the study will be presented. Part of the discussion will focus on the transport and transformation of these plumes within the marine boundary layer.

A41F-05 1120h

The Photochemical Impact of Oceanic Hydrocarbons on the Atmospheric Marine Boundary Layer over the Gulf of Maine

Oliver W. Wingenter[1] (505-835-6006; Oliver@nmt.edu); Karl B. Haase[1] (holstien@nmt.edu); Amy Harlow[1] (aharlow@nmt.edu); Gao Chen[2] (Gao.Chen-1@nasa.gov); Eric Williams[3] (eric@al.noaa.gov); Roger Jakoubek[3] (jakoubek@al.noaa.gov); Barkley C. Sive[4] (bcs@ccrc.sr.unh.edu)

[1]Department of Chemistry,New Mexico Institute of Mining and Technology, 801 Leroy Place, Socorro, NM 87801, United States

[2]NASA, Langley Research Center, Hampton, VA 23681-0001, United States

[3]Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80305, United States

[4]Climate Change Research Center, Institute for the Study of Earth, Oceans and Space,, University of New Hampshire, Durham, NH 03824, United States

The concentrations of nonmethane hydrocarbons (NMHCs), halocarbons, and alkyl nitrates were quantified in situ from the surface air and water aboard the NOAA R/V Ronald H. Brown during the New England Air Quality Study (NEAQS) using gas chromatography with flame ionization and electron capture detection. The highly reactive alkenes, ethene, propene, trans-2-butene, 1-butene, isobutene, cis-2-butene, and isoprene were always supersaturated in the coastal waters. The measured air and water concentrations were used along with air-sea gas exchange relationships to determine the sea-air flux of these alkenes. The fluxes served as input into a photochemical box model to assess the impact of marine hydrocarbons on local photochemistry, specifically ozone formation and destruction, under clean marine conditions. This study helps to establish coastal baseline conditions so that the magnitude of the impact on air quality under polluted condition can be put into context.

A41F-06 1135h

Comparison of Day- and Nighttime Oxidation of Biogenic and Anthropogenic VOCs Along the New England Coast in Summer During NEAQS 2002

Carsten Warneke[1,2] (1-303-497-3601; cwarneke@al.noaa.gov); Joost A. de Gouw[1,2] (jdegouw@al.noaa.gov); Paul D. Golden[1] (pgoldan@al.noaa.gov); William C. Kuster[1] (bkuster@al.noaa.gov); Eric J. Williams[1,2] (ewilliams@al.noaa.gov); Brian Lerner[1,2] (Brian.Lerner@noaa.gov); Steven S. Brown[1,2] (sbrown@al.noaa.gov); Harald Stark[1,2] (hstark@al.noaa.gov); Mattias Aldener[1,2] (maldener@al.noaa.gov); Roger Jakoubek[1] (jakoubek@al.noaa.gov); James M. Roberts[1] (jr@al.noaa.gov); Matt Marchewka[3] (marchewka7@yahoo.com); Fred C. Fehsenfeld[1,2] (fcf@al.noaa.gov)

[1]NOAA Aeronomy Laboratory, 325 Broadway, Boulder, CO 80305, United States

[2]Cooperative Institute for Research in Environmental Sciences (CIRES), 216 UCB, Boulder, CO 80309, United States

[3]Department of Chemistry, Western Michigan University, 3425 Wood Hall, Kalamazoo, MI 49008, United States

Volatile organic compounds (VOCs) and some of their oxidants (O_3, NO_3) were measured on board the NOAA research ship Ronald H. Brown along the coast of New England, downwind of New York, Boston and Portsmouth and large forested areas in New Hampshire, Maine, and Massachusetts in July and August 2002. The diurnal variations of isoprene, monoterpenes, and aromatics were mainly dependent on the abundance of the oxidants OH and NO_3 and on the emissions. Elevated mixing ratios of short lived VOCs were only encountered at the ship, which was about 1-6 hours downwind of the sources, when the concentrations of the oxidants were low. For the biogenic compounds this was generally the case during morning and evening hours, when the lifetime of the biogenics was long due to low OH and NO_3 concentrations. On the other hand, most anthropogenic VOCs do not react with NO_3 and therefore their mixing ratios remained elevated during the night. The products of isoprene oxidation, methyl vinyl ketone, methacrolein, and peroxymethacrylic nitric anhydride (MPAN) were on average higher than isoprene itself. Only during the transition periods from day to night, when oxidation rates were at a minimum, could isoprene exceed its products. The loss of the biogenic VOCs was dominated by reactions with NO_3, whereas the loss of anthropogenics came mostly from reactions with OH. The oxygenated VOCs are the major contributor to the OH loss, except in close vicinity of emission sources. The total loss of biogenic compounds during the night was so effective that after one night of transport they were in most cases completely reacted away, whereas the mixing ratios of the anthropogenic compounds remained high during the night. The pool of reactive hydrocarbons after one night was thus typically dominated by anthropogenic VOCs.

A41F-07 1150h

Nighttime NOx Loss during NEAQS

Steven S Brown[1,2] (303 497 6306; sbrown@al.noaa.gov); J. E. Dibb[3]; M. Aldener[1,2]; H. Stark[1,2]; M. Vozella[3]; S. Whitlow[3]; E. J. Williams[1]; B. M. Lerner[1,2]; R. Jakoubek[1]; T. R. Ryerson[1]; A. M. Middlebrook[1]; P. Quinn[4]; T. S. Bates[4]; J. F. Meagher[1]; A. R. Ravishankara[1,2]

[1]NOAA Aeronomy Lab, R/AL2 325 Broadway, Boulder, CO 80305, United States

[2]Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder, CO 80309, United States

[3]Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, NH 03824, United States

[4]NOAA Pacific Marine Environmental Laboratory, R/PMEL 7600 Sandpoint Way, Seattle, WA 98115, United States

Direct, in situ observations of NO3, N2O5 and HNO3 in the marine boundary layer during NEAQS have provided new insights into the nocturnal budget for NOx. Comparison between the behavior of these compounds in the NEAQS data set and from a continental site in Boulder, CO shows that N2O5 can act as both a reservoir for NOx and an efficient sink that converts it to nitric acid. The total removal of NOx pollution will depend strongly on the efficiency of these processes. Diurnal averages of NO3, N2O5 and HNO3 during NEAQS show that the nitric acid production during the night is comparable to that during the day, and that N2O5 hydrolysis reactions produce a significant quantity of gas phase nitric acid.

A41F-08 1205h

Regional Air Quality Forecasts during NEAQS-2K2: Comparisons with Observations

Stuart A McKeen[1] (303-497-5622; stu@al.noaa.gov); Georg A. Grell[2] (303-497-6924; grell@fsl.noaa.gov); John McHenry[3] (919-248-9237; mchenry@emc.mcnc.org); Steven E Peckham[2] (303-497-7978; steven.peckham@noaa.gov); Eric Williams[1] (303-497-3226; ewilliams@al.noaa.gov); Brian Lerner[1] (303-497-5296; B.Lerner@noaa.gov); J. William Munger[4] (617-495-5361; jwm@io.harvard.edu); Wayne M Angevine[1] (303-497-3747; wangevine@al.noaa.gov)

[1]NOAA Aeronomy Laboratory/CIRES, R/AL4 325 Broadway, Boulder, CO 80305-3328

[2]NOAA Forecast Systems Lab/CIRES, R/FS1 325 Broadway, Boulder, CO 80305-3328

[3]Environmental Modeling Center, Baron Advanced Meteorology Systems, Research Triangle Pk, NC 27709

[4]Harvard University, Dept. of Earth and Planetary Sciences, 20 Oxford Street, Cambridge, MA 02420

The results of two Eulerian-based air quality forecast models (AQFMs) are compared to observations collected during the summer of 2002 North East Air Quality Study (NEAQS-2K2) field campaign. The focus of the comparison is on ozone, and several other key photo-oxidants measured during July and August of 2002 at four AIRMAP surface sites in New Hampshire, the Harvard Forest site in central Massachusetts, and aboard the NOAA Research Vessel Ron Brown that was deployed along the northeast U.S. coastline. The air quality forecast models are NOAA Forecast System Laboratory's MM5-CHEM, and MCNC's Multiscale Air Quality Simulation Platform (MAQSIP). Each model provides forecasts of meteorology and gas-phase oxidants at three horizontal grid resolutions; the coarsest (45 km and 27 km) covering much of the United States, and the finest (5 km and 3 km) covering the Northeast U.S. The modeling systems are completely independent, with different grid structures, precursor emissions estimates, physical parameterizations, and photochemical mechanisms. Two types of model-measurement comparisons are presented; standard statistical measures of variance and model bias, and species-species relationships between key photochemical species. The standard statistical measures allow forecast skill for the six independent AQFMs to be analyzed in terms of model system, horizontal resolution, and lead time of the forecast. In terms of forecast skill, neither model platform is significantly better than the other, and nearly no improvement is seen with increased horizontal resolution. Model biases, however, are noticeably different between model platforms, model horizontal resolution, and distance from coastline. The comparisons between model and measured species-species relationships provide limited information on the reliability of specific model processes such as emissions and O_3 production efficiencies. The models generally reproduce species-species relationships between O_3, nitrogen oxides, and CO with some dependence on model horizontal resolution. Deposition of HNO_3 is shown to be a strong influence on relationships involving nitrogen oxides. These results allow recommendations to be made concerning AQFM formulation, further observations needed to assess individual model components, and provide a statistical base-line for further AQFM development in the Northeast U.S.

A41G MCC: 3016 Thursday 1020h

The Organic Aerosol Component: Impact on Reactivity, Optical Properties, Hygroscopicity, and Cloud-Condensation Properties II

(joint with AE)

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

A41G-01 1020h INVITED

Initial steps of particle formation and growth

Kari E. J. Lehtinen[1] (+358-9-19150711; kari.lehtinen@helsinki.fi)

Markku Kulmala[1] (+358-9-19150756; markku.kulmala@helsinki.fi)

[1]University of Helsinki, Dept. Physical Sciences P.O.Box 64, Helsinki 00014, Finland

Aerosol particles are ubiquitous in the Earth's atmosphere and influence our quality of life in many different ways. In urban environments, aerosol particles can affect human health through their inhalation (e.g. Wichmann and Peters, 2000). In the global troposphere aerosol particles are thought to contribute to climate change patterns (Stott et al., 2000; Ramanathan et al., 2001). Understanding these effects requires detailed information on how aerosol particles enter the atmosphere and how they are transformed before being removed by dry or wet deposition. Key processes in this respect are the formation of new atmospheric particles and their subsequent growth to larger sizes. Quantitative measurements of aerosol formation and growth rates have required the recent developments in instrumentation for measuring size distributions down to sizes as small as 3 nm in diameter (McMurry, 2000). However, the phase change between vapour and liquid will occur at smaller sizes, typically around 1 nm in diameter. Thus, e.g. DMPS/SMPS systems, which have cut off sizes of 3 nm, are not suitable for direct detection of nucleation and initial steps of the particle growth. Ion spectrometers are one class of experiments that can reach this important size range in which the initial formation is occurring (Hörrak et al., 2000). The ion spectrometers reveal the mobility spectrum, and thus also indirectly the size distribution, of atmospheric ions. Here were report the first field experiments where ion spectrometers (two of them) have been used together with DMPS to study formation and growth of aerosol particles focusing particularly in the initial steps of the growth. In principle the initial steps of the growth can occur via several ways: condensation of nucleating vapours, activation of soluble vapours (multicomponent nano-Köhler theory), heterogeneous nucleation or ion mediated particle formation (Yu and Turco, 2000). In this paper, we demonstrate how the analysis of ion distribution data, together with DMPS data, can result in useful hints concerning the mechanisms of the initial steps of particle formation in Hyytiälä, Finland. The initial analysis supports a hypotheses of formation of thermodynamically stable clusters (Kulmala et al., 2000), their subsequent growth by condensation of sulphuric acid molecules and further activation by soluble organic vapors, resulting in remarkably constant growth rates in the nucleation mode size regime. Much of the work has been done under EU-project CASOMIO. Horrak, U., Salm, J., and Tammet, H. (2000) J. Geophys. research D 105, 9291. Kulmala, M., Pirjola, L., and Mäkelä, J. M. (2000): Nature 404, 66. McMurry, P. H. (2000a): Atmos. Env. 34, 1959. Ramanathan, V., Crutzen, P. J., Kiehl, J. T., and Rosenfeld, D. (2001) Science 294, 2119. Stott, P. A et al.(2000) Science 290, 2133. Wichmann, H.-H., Peters, A. (2000): Phil. Trans. R. Soc. Lond. A. 358, 2751. Yu, F., and Turco, R. P. (2000): Geophys. Res. Lett. 27, 883.

A41G-02 1045h

Evolution of Organic-Carbon/Black-Carbon Nanoparticle Size and Mixing State Near the Point of Emission

Mark Z. Jacobson[1] (650-723-6836; jacobson@stanford.edu)

John H. Seinfeld[2] (626-395-4635; seinfeld@caltech.edu)

[1]Dept. of Civil and Env. Engineering, Stanford University, Terman M-31, Stanford, CA 94305-4020, United States

[2]Departments of Chemical Engineering and Environmental Science and Engineering, California Institute of Technology, 1200 E. California Blvd., Pasadena, CA 91125, United States

The regional and global radiative effects of fossil-fuel soot (black carbon plus organic matter) are predicted to depend substantially on its mixing state, and the mixing state begins to evolve at the point of emission. One set of field data (1) have shown that, within minutes of emission, the soot particle size distribution can evolve substantially, eliminating a 10-nm nucleation-mode peak, consisting mostly of organic matter, in favor of a larger peak around 40-50 nm, which may merge with the 70 nm emission peak of black carbon. Because the number of small particles in the data set decreased significantly while the number of large particles did not, it was hypothesized in that study that Brownian coagulation played a large role in the evolution of the nanoparticle size distribution. Here, it is found that Brownian coagulation, alone, is insufficiently fast to account for the observed rapid evolution of the size distribution. However, the enhancement of Brownian coagulation due to Van der Waal forces offset by viscous forces together with enhancement due to soot particle fractal geometry can account for a much greater share of the evolution. These processes were represented together with aerosol emissions, nucleation, condensation, dissolution, hydration, and chemistry among 10 aerosol size distributions and gas chemistry in a high-resolution three-dimensional numerical simulation examining the internal mixing of soot among multiple size distributions. Results suggest that coagulation is important, not only for rapidly mixing organic carbon/black carbon nanoparticles, but also for creating new distributions from the interactions of soot with background particles. (1) Zhu, Y., W. C. Hinds, S. Kim, and C. Sioutas, JAWMA, 52, 1032-1042, 2002.

A41G-03 1100h

Organic Aerosol Nucleation From the Oxidation Products of α-pinene

Tahllee Baynard[1,2] ((303) 497-5820; tbaynard@al.noaa.gov)

Jim Burkholder[1]

Edward Lovejoy[1]

A. R. Ravishankara[1,2]