A41A MCC: 3018 Thursday 0800h

2002 New England Air Quality Study I

Presiding: **E Williams,** NOAA Aeronomy Laboratory and CIRES**; T Bates,** NOAA Pacific Marine Environmental Laboratory

A41A-01 0805h

Meteorological Review of Conditions Encountered During the Summer 2002 New England Air Quality Study (NEAQS)

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The New England Air Quality Study (NEAQS) was conducted during the period of July through August of 2002 with the measurement intensive phase occurring from 12 July through 10 August. The primary study area was along the seacoast of New England from Bar Harbor, Maine, southward. During this period, meteorological conditions were sufficiently favorable on approximately 35% of the days, so that pollution episodes with one-hour average ozone levels of more than 100 ppb were recorded at one or more regulatory sites in New England. Was this a typical summer for the region? What were the synoptic features associated with these elevated pollution events? This review will attempt to address these questions. Two general synoptic patterns tend to dominate this region during the summer months. The first is the so-called "Atlantic Return (AR)" pattern where a high pressure system (typically the Bermuda High) is well offshore to the southeast. A low pressure typically accompanies this pattern and is usually located towards the northwest over the Ontario or western Quebec provinces. This AR pattern usually has an associated southwesterly air flow component and was the prevailing synoptic pattern during the elevated pollution episodes. The second dominant feature is the "Continental High (CH)" pattern, characterized by high pressure to the northwest of the region and northwesterly flow. This pattern is usually associated with clean air days. The frequency of these two synoptic patterns was slightly more prevalent during the summer of 2002 than on average. Cold frontal passages usually marked the transition from AR to CH situations. Warm advection, sometimes accompanied by a warm front, and usually preceded the transition from the CH to AR pattern. The wind climatology for July-August 2002 based on ETA model analysis fields show the strong prevailing southwest and northwest flows associated with the AR and CH patterns, respectively. On the elevated pollution days, the southwesterly flow was indeed most typical. However, the next greatest frequency was shared equally between west-northwest and west-southwest flows. Examining 12- and 24-hour low-level backward trajectories from the Isle of Shoals off the coast of New Hampshire, the air source regions for elevated days were located in the single octant between the south and southwest 43 and 39 percent of the time, respectively. This octant implies that most have some over water trajectory components. Winds and trajectories at 1- and 2-km on these days and corresponding trajectories tended to be more westerly. Sea breezes occurred during some of the pollution episodes. Surface temperatures at nearly all coastal station and offshore buoys tended to be about 1 degree Celsius above normal in July and approximately twice that amount in August. The majority of onshore stations during the high pollution days had surface temperatures above 29 degrees Celsius. Precipitation at many of these sites was significantly less than normal in amount and frequency. Sea fog that can usually be expected on a few days near shore was virtually non-existent during the summer of 2002. Overall, the summer 2002 NEAQS weather was not too far from the average climatology. The normally dominant synoptic patterns were slightly more dominant than normal. Dirty air was usually associated with southerly to southwesterly low-level flow with an over water path and warmer temperatures.

URL: http://pscwx.plymouth.edu/NEAQS/archive.html

A41A-02 0815h

Coastal Boundary Layer Influence on Pollutant Transport in New England

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Air pollution episodes in northern New England often are caused by transport of pollutants over water and involve two crossings of the coast. Two such episodes in the summer of 2002 are examined (22-23 July and 11-14 August). In both cases, the pollutants that affected coastal New Hampshire and coastal southwest Maine were transported over coastal waters in stable layers at the surface. These layers were at least intermittently turbulent but retained their chemical constituents. The lack of deposition or deep vertical mixing on the overwater trajectories meant that the pollutant concentrations remained strong. In the 22-23 July case, the trajectories were relatively straight and dominated by synoptic-scale effects, transporting pollution to the Maine coast. On 11-14 August, sea breezes brought polluted air from the coastal waters inland in New Hampshire, adding significantly to already strong concentrations transported and/or produced by other means.

A41A-03 0830h

Pollutant Transport by the Nocturnal Low-Level Jet in New England

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High pollution events in northern New England often result from transport of pollutants from urban, industrial, and power-plant sources to the south and west. A key to being able to understand and forecast such events is thus the ability to characterize the strength and direction of the winds in the layer between the surface and 1 km above the surface. During the nighttime portion of the diurnal cycle, the flow in this layer is often dominated by a low-level jet (LLJ) that forms after sunset, in which the winds speeds peak at 100-500 m. When this jet is from a southwesterly direction over New England, it can bring minimally diluted pollutants into the Gulf of Maine the next day. From here the pollutants can continue inland into eastern Maine, or daytime sea-breeze circulations can carry them inland farther south (along the Massachusetts, New Hampshire, or southern Maine coasts). This study is a case showing such a scenario on the night of 4-5 August 2002 during the New England Air Quality Study (NEAQS). Wind-profiler data showed light southerly flow during the previous afternoon below 100 m, which had an easterly component at sites near the coast probably due to sea-breeze effects. After sunset this flow accelerated into a LLJ with maximum speeds of 11-13 m/s at 300-400 m. Layers of ozone aloft off the coast observed by an ozone-profiling lidar aboard the R/V Ron Brown could be traced back to the urban and industrial sources to the southwest. A sea breeze was not observed in New Hampshire the next day, and the southwesterly flow persisted. Thus, in this case, the major impact of the transport of polluted air was on the air quality farther north and east in Maine. The role of the LLJ was to carry pollutants faster than expected, and the veering of the jet through the night carried it farther east than expected, based on the winds at the surface or from winds measured before and after the nighttime period.

A41A-04 0845h

Vertical Structure of Ozone Over the Gulf of Maine Observed During NEAQS 2002: Implications for Air Quality in New England

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The main objective of the 2002 New England Air Quality Study (NEAQS) was to characterize and understand the chemical and meteorological processes that contribute to high-pollution events in northern New England, particularly in coastal areas of New Hampshire and Maine. The primary measurement platform of this study was the NOAA research vessel Ronald H. Brown, which spent about three weeks in July and August of 2002 in the Gulf of Maine and was equipped with an extensive set of chemical and meteorological sensors. Researchers at the NOAA Environmental Technology Laboratory deployed a vertically pointed lidar on the Ronald H. Brown to characterize the vertical structure of ozone and aerosols over the Gulf of Maine and to assess the representativeness of in situ chemical and aerosol measurements aboard the ship for the entire marine boundary layer. The lidar measurements showed that most of the time, particularly during onshore flow, ozone values at around 300 m MSL were significantly higher than at the surface, indicating that the surface and the marine boundary layer aloft were decoupled due to strongly suppressed vertical mixing in the stable atmosphere over the Gulf of Maine. Intermittent vertical mixing caused by mechanical turbulence was observed on a few occasions resulting in transient ozone spikes at the surface as ozone-rich air was mixed down. Under offshore flow conditions and when the Ronald H. Brown was close to shore, similar ozone values were registered aloft and at the surface, providing evidence that the convectively mixed boundary layer air coming off the land remained well-mixed over the coastal waters. Trajectory analysis using data from land-based and shipborne wind profilers was employed to track the elevated ozone plumes observed with the lidar. Back trajectories revealed that the high-ozone plumes encountered off the coast of northern New England originated predominantly in the Boston and New York City areas. In several cases, these high-ozone plumes aloft were transported back over land to coastal areas of New Hampshire and Maine by the large-scale flow or local land-sea breeze circulations. Surface monitoring sites showed an increase in ozone and other pollutant concentrations at the time of arrival of the elevated ozone plume, indicating that entrainment and down-mixing of pollutants from aloft contributed to higher surface pollutant levels.

A41A-05 0900h

Diurnal Characteristics of Surface-Level O_3 and Other Trace Gases in New England

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We use data from air quality monitoring sites operated by the Atmospheric Investigation, Regional Modeling, Analysis and Prediction (AIRMAP) program to examine the diurnal characteristics of O_3, CO, CO_2 and selected volatile organic compounds (VOCs) in the New England atmosphere. Throughout the year a nocturnal inversion forms several hundred meters above the surface on 25% of the days in winter with its frequency of occurrence increasing to 50% in summer. Below the inversion O_3 is typically depleted to zero while other gases including CO_2, alkanes and alkenes exhibit several-fold enhancements due to local emission sources. The daily time period with $O_3 < 5$ ppbv varies from < 0.5 to 21 hours, with a mean of 3.5 hours. Typically the depletion intervals are shortest in summer and last the longest in winter. The rates of nighttime depletion and daytime replenishment of O_3 are very similar, ranging from a few ppbv hr^{-1} to 25 ppbv hr^{-1}. Due

to the rural location of the AIRMAP sites, it appears that the depletion is mainly due to dry deposition with an occasional contribution of titration by NO. The relative enhancements of CO_2 and VOCs relative to urban tracers such as C_2HCl_3 and C_2Cl_4, which have minimal local sources, provides information on the magnitude and nature of natural and anthropogenic sources.

A41A-06 0915h

Regional Relationship between CO and O_3 in New England

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The seasonality and interannual variability in the mixing ratios of ozone (O_3) and carbon monoxide (CO) and their inter-relationship were investigated at the rural low elevation site Thompson Farm (TF) and the hill site Castle Springs (400 m above ground level) in southern New Hampshire using continuous observations (2001-2003) from the Atmospheric Investigation, Regional Modeling, Analysis and Prediction (AIRMAP) program at University of New Hampshire (UNH). Our results show distinct site-dependent characteristics in temporal variations on various time scales in O_3 and CO and particularly large interannual variability in fall and winter at both sites. The grouped O_3 and CO data, based on wind speed and direction over different time periods of the day, showed largely varying probability distribution functions (PDF). It was found that only 10% of the seasonal observations formed a positive O_3-CO linear correlation, leading to an estimate of 370 M moles d^{-1} for O_3 export from the northeastern U.S. This estimate is three times smaller than previous studies. We used a ratio analysis (NO/NO_y and NO_y/CO) to show that the linear O_3-CO relationships were a result of multiple processes rather than simply either photochemical or depositonal loss processes as proposed by previous work. One of the most important features of the O_3-CO relationship is the lower CO boundary, for which we attempeted to provide physical and chemical interpretations.

A41A-07 0930h

Propane and Light Alkene Enhancements at Thompson Farm: Impact on Local and Regional Ozone Production

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Continuous measurements of nonmethane hydrocarbons (NMHCs) at Thompson Farm in Durham, NH have revealed that large enhancements of propane (approximately 10-30 ppbv) are observed regularly at this sampling site. The large propane enhancements are associated with unique boundary layer dynamics causing an extremely low-level nocturnal inversion allowing for nighttime pollutant buildup. During these events, propane is the dominant NMHC with mixing ratios reaching levels that are at least 2-3 times larger than ethane. Further investigation has revealed that the propane events are not only occurring at Thompson Farm, but throughout the NH seacoast region; spanning an area from Brentwood, NH to Kittery, ME, yet is likely to be much more widespread. In addition, substantial increases in other reactive gases such as NO, CO, ethene, propene and the butanes are observed during these episodes, all of which largely impact daytime ozone production. Currently, the main source of the propane in this region remains unidentified. The local and regional impact on ozone production in New England from the large-scale propane and reactive alkene enhancements will be discussed.

A41A-08 0945h

Aerosol Mass Spectrometer measurements on board the DOE G1 during NEAQS

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An Aerosol Mass Spectrometer (AMS) was successfully deployed on board the DOE G1 research aircraft during the New England Air Quality Study (NEAQS), a multi agency campaign designed to characterize gas and aerosol pollutants passing through the northeastern U.S. and the outflow over the Atlantic Ocean. The addition of the AMS to the G1 instrument payload added the capability to collect real-time (seconds timescale) data on size and chemically speciated aerosol mass loadings for aerosol containing nitrate, sulfate, ammonium, chloride and organic species. Flight tracks were chosen to provide reasonable lateral coverage of the North Eastern region and important vertical profiles of ambient aerosol. Comparisons between the aerosol chemical properties measured from the G1 platform and similar aerosol properties measured at several ground sites, including on the Ron Brown research vessel, illustrate the layering of air masses and the varying sources and transportation pathways for particulate pollution. Ground level particulate measurements appear significantly influenced by regional sources. For example, bimodal organic carbon dominated size distributions consistent with freshly generated (automobile) emission were observed on flights that passed over NY city metropolitan area. In contrast, vertical profiles identify layers of high mass loadings of monomodal particulate sulfate aerosol accompanied by low SO2 levels that are consistent with aged/transported air. Back trajectory analyses correlate these observations with source emitters outside of the North Eastern region.

A41B MCC: 3016 Thursday 0800h

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

(joint with AE)

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

A41B-01 0800h INVITED

New Mass Spectrometric Tools and Their Application to Organic Aerosol Studies

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The organic fraction of airborne particulate matter is a complex mixture of compounds with a combined concentration on the order of 1 to 10 micrograms per cubic meter. Thousands of compounds may be present in a sample, with individual concentrations between about 0.1 and 10 nanograms per cubic meter. The complexity and low concentration levels associated with ambient samples carry over into laboratory investigations and present a significant analytical challenge. We have been exploring the use of new methods for off-line and on-line analysis of organic matter in particles to study aerosol reactions. Off-line analysis is performed with electrospray ionization and matrix-assisted laser desorption ionization in combination with exact mass measurements and tandem mass spectrometry. These methods have allowed us to characterize hundreds of high molecular weight compounds formed by secondary polymerization of the primary products of alpha-pinene ozonolysis. Polymerization provides a reasonable explanation of how the volatile primary products are able to partition to the particle phase. On-line measurements are made with an aerosol mass spectrometer that provides "soft" ionization (i.e. very little fragmentation) of organic compounds. Soft ionization is needed to reduce the spectral congestion that is normally observed from complex samples. On-line measurements permit reaction kinetics to be studied. Experiments currently underway that will discussed include the kinetics of acid-catalyzed polymerization in particles and the effect of surface organic layers on the reactive uptake of nitric acid into aqueous sodium chloride particles.

URL: http://www.udel.edu/chem/johnston/

A41B-02 0823h INVITED

Reactive Heterogeneous Chemistry on Organic Aerosols: Two Case Studies

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Two sets of laboratory studies will be discussed to illustrate the impact that heterogeneous chemistry involving tropospheric organic aerosols may have on both the gas-phase composition of the atmosphere and the chemical nature of the particles themselves. In the first case, the reactive uptake coefficient for the hydrolysis of dinitrogen pentoxide (N2O5) on organic aerosols has been measured in an entrained aerosol flow tube coupled to a Chemical-Ionization Mass Spectrometer (CIMS). The general observation is that the reaction on aqueous malonic acid aerosols behaves in an analogous manner to that on aqueous inorganic salts, i.e. the uptake coefficient shows a linear dependence on the particle water content up to 50% relative humidity (RH), at which point the effect saturates. In addition, there is evidence for the kinetics being dependent on both the size of the particles and the levels of dissolved nitrate. By contrast, the N2O5 hydrolysis kinetics on solid azelaic acid particles are too slow to be atmospherically significant, even at 85% RH. In the second case, the kinetics and product yields from the oxidation of liquid oleic acid by ozone have been studied in considerable detail, with emphasis on the quantification of gas-phase products (nonanal) by CIMS and water-soluble species by HPLC/Electrospray-Ionization Mass Spectrometry (azelaic acid, nonanoic acid). The atmospheric importance of these results will be discussed, in particular with respect to the role of organic aerosol oxidation as a source of cloud condensation nuclei.

A41B-03 0845h

Preparation And Characterization Of Organic Coatings Of Variable Thickness On Inert Cores And Their Chemical Reactions With Ozone

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Recent studies have emphasized the role of organic atmospheric particles in cloud formation, radiative forcing, and health effects. Quantification of these effects is limited because the compositions, morphologies, and chemical reactivities of organic particles are poorly understood. Laboratory studies are motivated to understand and quantify complex particles and their processes. A critical unknown is the heterogeneous chemistry that depends upon and leads to changes in the morphological and chemical complexity of the particles. Our work is focused on ozone heterogeneous chemistry as a general proxy for understanding the role of layer thickness and diffusivity in chemical transformations of surface and interior layers of complex particles. Our approach for preparing the particles is as follows. Polystyrene latex (PSL) particles are atomized into an aerosol flow. Oleic acid particles are formed by vapor condensation from a separate flow through a heated liquid reservoir. When the flows are mixed, the PSL and oleic acid particles are externally mixed. An oven having a linear hot-to-cold temperature gradient is employed to first evaporate the oleic acid particles in the hot region, which is followed by condensation in the cold region onto the surface of the PSL particles acting as heterogeneous nuclei. Internally mixed particles result. The apparatus capability is the controlled and reproducible generation of particles having 2 to 30 nm surface layers of oleic acid and 100 nm polystyrene latex (PSL) cores. The temperature of the reservoir,