ENVIRONMENTAL MONITORING, EVALUATION, AND PROTECTION: LINKING SCIENCE AND POLICY

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POSTER ABSTRACTS

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AIR QUALITY AND HEALTH

A METHOD TO EXTRACT AND INTERPRET ADDITIONAL AEROSOL ORGANIC CARBON FRACTIONS FROM THERMAL OPTICAL ANALYSIS OF FILTER-BASED DATA

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Fine particulate matter samples have been collected at seven different sites in New York State on a 1-in-3 day schedule for the Environmental Protection Agency (EPA) Chemical Speciation Network or CSN (formerly Speciation Trends Network).

According to the NIOSH analysis protocol for the TOT (Thermal-Optical Transmittance) method, six carbon fractions can be defined including OC1-OC4, OP and EC. (The OC1-4 fractions are associated with organic carbon of different volatility temperatures, the OP faction is associated with pyrolyzed organic carbon, and the EC fraction is identified with elemental carbon.) This study investigated these six carbon fractions in NY for 2006 and 2007 in order to see the seasonal variations related to carbon fractions.

From the analysis of aerosol carbon data in the $PM_{2.5}$ Speciation measurement, these data show relatively low concentrations of the lowest volatility fraction (OC1), which is consistent with a picture of the aerosol as being "well-aged" regional particles, as opposed to fresher, more volatile particles. The relatively high mass concentrations during the "warm" season (May-September) in the OC2-OC4 fractions are consistent with secondary organic aerosol (SOA) production and photochemical reactions producing lower volatility compounds. The relationships observed between carbon fractions and carbon concentrations between sites and seasons will be presented and analyzed in this presentation.

AIR QUALITY TRENDS AT WHITEFACE MOUNTAIN

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Trends in primary air pollutants (SO_2, NO_x, CO) and secondary pollutants (O_3, NO_2, NOy, and wet sulfate and nitrate deposition) based on measurements at Whiteface Mountain from 1990-2010 are presented. Whiteface Mountain is located in the northern part of the Adirondack State Park in upstate New York and is typically influenced by aged air masses that flow from the west and southwest, and transported emissions from source regions in the Midwest, or by very clean air associated with northerly flows. The measurements are predominantly made at the summit of the mountain at a level of 1,500 meters. Wet deposition measurements are collected at lower levels on the mountain (600m) and at other nearby locations as well.

Retrospective analyses of air quality and deposition trends are presented and compared with emission trends to determine consistency with implemented regulatory emission control actions. Such analyses demonstrate the utility of long-term environmental measurements in monitoring the efficacy of emission controls in achieving anticipated environmental/air quality outcomes, elements fundamental to establishing an "accountable" air quality management system.

Behavior of Ultrafine Particles and Related Particulate and Gaseous Species at Two Geographically Distributed Sites in New York City

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While there have been numerous short-term studies of ambient ultrafine particle behavior at single locations in urban environments, relatively little data has been gathered from long-term measurements at multiple geographical sites in such environments. In this study, ultrafine particle size distributions were measured at two locations in the New York State Air Monitoring Network at 15 minute intervals from June 2009 to June 2010, using an Ultrafine Particle Monitor (UFP Monitor, Model 3031, TSI, Inc.) designed for long-term ambient monitoring of six bins over the size range from 20 to 500 nm. The first monitor was installed at Queens College (QC), a well instrumented monitoring site representative of the New York City metropolitan area. Continuous monitoring of several gaseous and PM2.5 particle pollutant species was also conducted at this site. The second monitor was installed at Eisenhower Park (17 miles east of QC), a near-roadway site on Long Island located within 30 meters of a 4lane roadway and backed by unoccupied parkland, with various stationary sources also located in the vicinity. Data from the UFP Monitors at both sites are interpreted in the context of other collected particulate, gaseous, and meteorological measurements.

While ultrafine particle size distributions from both sites corresponded well with each other, the correlations of ultrafine particles at both sites with other particulate and gaseous species was highly dependent on particle size.

In particular, particle measurements in the 20-50 nm size bin exhibited little to no correlation with any of the other species, implying that there are no surrogates for ultrafine particles < 50 nm and they must be directly measured. For particles in the range from 50-200 nm, the correlation with species such as SO_2, NO_x, and particle-phase sulfate was highly dependent on seasonal behavior.

Carbon Electrode Materials for Electrochemical Sensing of Nitrogen Dioxide and Ozone

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Low-cost portable electrochemical sensors with carbon serving as the catalyst (the electrode) are developed for the purpose of enabling citizenship monitoring of air quality in terms of the concentrations of environmental pollutant gases, particularly nitrogen dioxide and ozone. The approach involves tailoring the carbon surface structure and chemistry through chemical, physical and thermal methods for selective gas sensing. The carbon materials are in powder form (e.g., graphite nanoplatelets) so that electrodes and other devices can be fabricated by standard processes. The project will involve the development of sensor materials and devices, laboratory and field testing of low-cost internet-connected sensors, evaluation of the effectiveness of citizen monitoring of air quality, and comparison of the performance of the low-cost sensors of this project and the high-cost monitoring equipment that is currently used for air-quality-index monitoring.

DEFINING SECONDARY ORGANIC ATMOSPHERIC AEROSOLS AT THE MOLECULAR LEVEL

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Traditionally secondary organic aerosols have been defined as chemical species containing one or more carbon atoms with functional groups containing one or two oxygen atoms and formed in the troposphere. The oxidization of the original carbon atom as the primary carbon species has been demonstrated in smog chambers and in field studies as reactions involving the hydroxyl radical, ozone and oxides of nitrogen in the presence of sunlight.

Our work on the molecular composition of polar (POC) and highly polar organic compounds (HPOC) associated with fine particles (nominal particle diameter < 2.5 micrometers, PM2.5) in the NY/NJ/CT region from 2002 to 2007 demonstrates the ubiquitous presence of oxygen-containing functional groups. Which compounds are secondary and which are primary emissions from the combustion of carbonaceous fuels (wood, diesel, gasoline, coal, biomass)? Which are primary emissions from biogeochemical processes? Which are formed from aqueous phase chemistry in cloud droplets?

This paper reports and summarizes individual chemicals and compound classes of POC and HPOC observed as fine PM in the NY/NJ/CT region. We discuss the potential of these compounds as secondary organic carbon species.

DESIGN AND PERFORMANCE ANALYSIS OF THE HIGH-FLOW DUAL-CHANNEL DIFFERENTIAL MOBILITY ANALYZER (HD-DMA)

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Accurate estimation of human health effects of ultrafine particles requires size distribution measurements, considering their spatial and temporal variability. Among all of the aerosol sizing instruments, the differential mobility analyzer (DMA) gives the greatest promise for accurate sizing and classification of ultrafine particles. Most of the commercially available DMAs (e.g., TSI 3081, 3085) have small sheath flows (~ 10 LPM) and correspondingly a small aerosol sample flowrate (~ 1 lpm), primarily because of the need to operate the instruments in a laminar flow regime. While several designs of DMAs operating with a high sheath flow have been introduced, the usage of these instruments has been limited to classification of particles smaller than ~ 20-50 nm. For measurements over a broad diameter range and with a high sample flowrate, a new high-flow dual channel differential mobility analyzer (HD-DMA) instrument design was recently introduced by our group. This instrument operates at relatively high flow rates (sheath flow ~100-300 lpm and sample flow ~ 20 lpm) while maintaining a low Reynolds number (~500) in the classification region. The reduced particle residence time in the classifier, associated with the high sheath flow, enables fast scan operation with this instrument (Dubey and Dhaniyala, 2008). The HD-DMA has a long classifier section length and, thus, a high upper mobility limit, which is possible because of the laminar nature of flow in this region. The HD-DMA is designed with two ports in the central rod, to simultaneously classify particles of two sizes. The dual-port design enables an extended measurement range and also faster size distribution measurements over an overlapping size range. The design and the performance of the new instrument will be presented. We will also discuss the future development of a compact ultrafine sensor based on electrical mobility measurements.

References:
Dubey P., Dhaniyala S. (2008). Analysis of Scanning DMA transfer functions. *Aerosol Sci. Technol*., 42: 544-555.

EMPIRICAL ESTIMATES OF SUMMER BACKGROUND OZONE LEVELS IN NEW YORK STATE

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Background concentrations for a certain region are usually defined as concentrations that would be observed in the absence of local anthropogenic emissions. Background represents regional transport into the area of concern as well as natural emissions. It is important because no amount of local controls can reduce average ozone concentrations below the background values.

Ozone background level is usually estimated indirectly by using ozone precursors and other pollutant markers ; low concentrations of nitrogen oxides and their oxidation products indicate low local ozone production. The method chosen for our study is by Lin et al. (Geophys. Res. Lett., 2000). They estimated background O_3 for Harvard Forest, MA as median value for the subset of data with CO or NO_y concentrations below 25th percentiles. For summertime conditions, median background corresponds to 25th percentile of the O_3 distribution. This empirical relationship is very useful since most of the ozone observation sites register only O_3 concentrations.

To establish applicability of the 25th O_3 percentile approach for New York, we have verified the method against one Maryland site (Beltsville) and one New York site (Pinnacle State Park) that have O_3, NO_y, and CO observations. The results are also verified using other available methods. Since the method works well for sites tested in and outside of New York, we have used data for the time period 1995-2010 to generate background ozone levels at all ozone (DEC) monitoring sites in New York State.

We find that for the 28 New York sites, summer background ozone levels are estimated to range from 30 to 45 ppb, with median value of 37 ppb. Some preliminary discussions of the spatial distribution of the background levels and its consequences for control strategies in New York are presented.

$PM_{2.5}$ CLASS III FEMS: PERFORMANCE EVALUATION AT QUEENS COLLEGE, NEW YORK

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The EPA designated several new instruments as Class III Federal Equivalent Methods (FEMs) for use in $PM_{2.5}$ ambient air monitoring. It was envisioned that the filter based Federal Reference Method (FRM) samplers, which have slow data turnaround and high operational costs, could be replaced with these new automated instruments. Monitoring agencies have been operating both FRM samplers for comparison to the NAAQS and older generation continuous mass monitoring instruments to produce the Air Quality Index (AQI) for health alerts and for air pollution forecasting. The new FEMs were designed to satisfy all of the $PM_{2.5}$ monitoring data needs.

The NYSDEC conducted an evaluation of the four available FEMs in Queens, NYC. The FEM samplers were operated from January through August 2010 alongside an FRM operating on a daily schedule. Comparisons were promising in the winter months but showed progressively poorer agreement towards warmer weather conditions with a significant high bias for some of the FEMs. The data demonstrated that the evaluation protocol used by the EPA for the Class III designation did not adequately predict the FEM performance in this urban environment during summer months.

The implications are that state and local monitoring agencies may be forced to choose between FEMs, which are less expensive to operate, but measure higher concentrations in warmer months or continue to operate filter based FRM samplers.

REPRESENTATION OF TEMPORAL FLUCTUATIONS IN POWER PLANT EMISSIONS IN AIR QUALITY FORECAST SIMULATIONS AND ITS EFFECT ON MODEL PREDICTIONS

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The New York State Department of Environmental Conservation (NYSDEC) has been performing model-based daily forecast of air quality since June 2005. The ability of any modeling system to accurately predict ozone and $PM_{2.5}$ air quality is dependent in part on the quality of the emissions used and the associated uncertainties. In an air quality forecasting context, the anthropogenic emissions

are usually annual average emissions that are then allocated to each hour based on typical temporal profiles for each source category. However, it is known that some source categories, such as electric generating units (EGUs), may exhibit significant temporal variations in emissions in response to weather conditions. In this study, we examine the sensitivity of model predictions to temporal fluctuations in EGU emissions, and evaluate approaches in refining the characterization of these emissions in an air quality forecasting context. Model sensitivity is examined through retrospective simulations of archived forecasted meteorological fields (NCEP WRF-NMM UTC 12z) for the summer of 2007 using EGU emissions derived from actual measurements by continuous emission monitors (CEMs), and using an average emissions inventory. The work showed significant differences between actual and average emissions (which coincided mostly with high temperature days) and non-negligible effect on ozone predictions. Consequently, we are testing an approach to refine the temporal characterization of EGUs in the context of an air quality forecasting simulation. This approach consists of quantifying possible relationships between energy demand forecasts in New York State and the EGU emissions. For NY State, energy load forecasts are provided, and made readily available, by the NYISO. The developed relationships would be applied to estimate/refine emissions of select EGUs for the summer 2007 period and compare against actual emissions. This poster will present the results of the model sensitivity simulations using the two different emission profiles, and the results and limitations of the methodology applied to refine the characterization of temporal variations in EGU emissions.

ROLE OF CERIUM-OXIDE DIESEL ADDITIVE ON EMISSIONS AND FUEL-EFFICIENCY OF A LIGHT-DUTY TRUCK

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The cerium oxide nano-powder is considered as an effective diesel additive to reduce the exhaust pollution and improve fuel efficiency. An experiment was designed to investigate the performance of CeO_2. The experiment was conducted with a GM Silverado diesel truck on a chassis dynamometer. The exhaust dilution ratio was maintained at 1:100 and the vehicle running speed was kept at 45 mph. The CO, CO_2, SOx and NOx gases were monitored. Real time particle size distributions were recorded by a Wide-Range Particle Spectrometer (WPS). Total particle counts were monitored by a water based particle counter (TSI 3781). The elemental carbon (EC) and organic carbon (OC) were collected on a quartz filter, and one Teflon filter collected the total mass of solid material. The results from regular diesel and regular diesel with CeO_2 additive were compared.

SOURCE APPOINTMENT OF AIRBORNE PARTICULATE MATTER IN ROCHESTER, NY

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Particle composition data from the Chemical Speciation Network (CSN), organic molecular marker measurements, particle number size distributions and other ambient pollutants were analyzed in this study. The measurements were conducted at the New York State Department of Environmental Conservation (NYSDEC) site in Rochester, the third largest city in New York State from October 2009 to October 2010. The particle composition and organic molecular marker data were 24-hour average mass concentrations and obtained for samples taken every third day. Meteorological data including wind direction, wind speed, ambient temperature, relative humidity, barometric pressure, and precipitation were also recorded in 1-hour intervals. The number size distributions of 10 to 500 nm particles and other pollutants, including $PM_{2.5}$, CO, black carbon (BC), Delta-C ($UVBC_{370nm} - BC_{880nm}$), SO_2 and O_3 were measured simultaneously and their concentrations were hourly averaged. Positive matrix factorization (PMF2) will be applied to each of the three datasets and different dataset combinations to identify the sources and their contributions to the airborne particulate matter (PM). Potential source contribution function (PSCF) and conditional probability function (CPF) analyses were used to locate the regional and local sources, respectively.

SOURCES AND HEALTH EFFECTS OF OXYGENATED PAHS

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Like PAHs, oxygenated PAHs (Oxy-PAHs), i.e. ketone and quinone—substituted PAHs—can be produced from combustion processes, but they may also form post emission via photo-oxidation, chemical oxidation, etc. Increasing usage of biodiesel could lead to a rise in the level of oxygenated PAHs in the air. EPA emission testing has observed decreases in emissions of elemental carbon, PAHs, nitrated PAHs, and increases in CO_2 emissions from the combustion of biodiesel, suggesting a more complete combustion process with the addition of biodiesel to conventional diesel fuel; however, there is evidence that emission of Oxy-PAHs will increase substantially. Previous data demonstrated that the increase of oxygen levels in coal tar resulted in a substantial increase in Oxy-PAH emissions during pyrolysis and combustion processes. Recently we observed high levels (>130 ug/g) of oxy-PAHs in soot emitted from a diesel truck engine running on fuel composed of 20% biodiesel and 80% diesel. Although the toxic effects of oxy-PAHs have not been fully characterized, data have shown that oxy-PAHs can induce oxidative stress, endocrine system disruptions, and cytotoxic effects in mammalian cell systems, as well as cause genetic changes by forming DNA-oxy-PAH adducts. Given the aforementioned issues raised above, it is critical to investigate the ecological and health effects of these compounds.

VARIATIONS AND TRENDS IN $PM_{2.5}$ MASS, SULFATE, AND CARBON CONCENTRATIONS AT A RURAL AND AN URBAN SITE IN NEW YORK STATE

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$PM_{2.5}$ mass and species concentrations using low volume samplers have been measured routinely at sites in New York State for more than a decade. We are analyzing this data for several sites to investigate both the overall trend in concentration and composition, and the year-to-year and season-to-season variations in these parameters. The sites chosen for this work are the rural station at Pinnacle State Park in Addison, NY; and the Queens College station in New York City. These two sites have an extensive array of continuous gas and aerosol phase pollutant measurements in addition to the filter samples used as the basis for this study. Over the past ten years, the annual average $PM_{2.5}$ mass concentrations have dropped about 3 $\mu g\ m^{-3}$ at each of the two sites. However, there are indications that much of this decrease has occurred in the sulfate and inorganic components as a result of a variety of SO_x and NO_x emission controls implemented under the 1990 Clean Air Act Amendments. Specifically, the decreases in $PM_{2.5}$ mass are mainly attributed to a decrease in particle sulfate (predominantly in summer) with a more modest decrease in particle nitrate in recent years. The carbonaceous component of the $PM_{2.5}$ has not decreased proportionally, and in some cases has increased. This raises many interesting questions about the future trends and toxicity of $PM_{2.5}$. Year-to-year and seasonal variations in the $PM_{2.5}$ mass and composition, while limiting our ability to determine precise trends, also can give insight into the origin of the PM and, in some cases, the overall chemical and dynamical processes controlling ground level concentrations.

VARIATIONS OF CARBON DIOXIDE WITHIN AN URBAN AREA: COMPARISON BETWEEN COMMERCIAL AND RESIDENTIAL LOCATIONS

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Urban areas have been identified as major contributors of carbon dioxide (CO_2) emissions to the atmosphere. Until recently, few studies have explored the fluxes of CO_2 within urban areas, with fewer still collecting simultaneous readings from multiple locations within the same urban area. In order to further examine the relationship of CO_2 levels and surrounding land use within urban environments, this study compares CO_2 fluxes and concentrations at two sites of different composition within Syracuse, NY: one within the commercial downtown district and the other in a residential neighborhood approximately 3.5 km apart. Both sites have collected CO_2 flux and concentration data from open path eddy covariance systems from June 2010 through May 2011. Preliminary

results show a strong diurnal cycle at both locations in different directions, suggesting local influences of traffic and vegetation. The downtown location has two rush hour peaks (maximum winter averages of ~36 µmol m^{-2} s^{-1} at 08:00 EST and ~39 µmol m^{-2} s^{-1} at 16:00 EST) visible in diurnal averages while the residential location has a midday dip in fluxes during the summer and fall months, with a minimum summer average value of ~11 µmol m^{-2} s^{-1} around 12:00 EST. Further examination shows variations at the downtown site between weekend and weekdays, suggesting a greater traffic influence compared to the residential site. The results of this study, in conjunction with traffic count measurements at the downtown site and high resolution land use cover maps, will give insight to the impact of traffic and land use within cities.

CLIMATE CHANGE

MAPPING CLIMATE CHANGE IN THE ADIRONDACKS: LOCAL-SCALE COMPARISON OF TREND MAPS BASED ON TWO HIGH-RESOLUTION GRIDDED DATA PRODUCTS

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High-resolution gridded historical climate (GHC) products offer the opportunity to map and interpret recent climatic changes at local and regional scales, where most research and decision-making occurs. Although many GHC products are now being used, relatively little has been done to compare these datasets or their estimates of recent change. In trend analyses of two 4-k temperature datasets for the US Northeast (1980-2009), we have found the most consistent and strong disagreements in coastal and high elevation montane areas. In this case study, we describe one of the strongest local-scale disparities found across the U.S. Northeast: the Adirondack Mountains of northern New York. Analysis found generally patchy disagreement in temperature trend maps across the climate-sensitive Adirondack region. One GHC dataset showed very rapid warming (up to 2°C decade-1) in the High Peaks Wilderness over the last three decades, while the other dataset showed relatively little change in temperatures. Such disparities are likely due to different input data and modeling methods used to generate the GHC datasets. The local-scale uncertainty caused by spatial disagreement between Adirondack climate change maps indicates the need to further investigate sources of bias in these GHC products before they can be reliably used in research and climate adaptation efforts.

ECOSYSTEMS AND ALTERNATIVE ENERGY

A COMPARISON OF THE TEMPORALLY INTEGRATED MONITORING OF ECOSYSTEMS AND ADIRONDACK LONG TERM MONITORING PROGRAMS IN THE ADIRONDACK MOUNTAIN REGION OF NEW YORK

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This paper compares lake chemistry in the Adirondack region of New York measured by the Temporally Integrated Monitoring of Ecosystems (TIME) and Adirondack Long Term Monitoring (ALTM) programs by examining the data from six lakes common to both programs. Both programs were initiated in the 1990s to track the efficacy of emission reduction policies and to assess the impacts of acid deposition on surface water chemistry. They now serve to inform on the emerging chemical recovery of these waters. The Adirondack TIME program utilizes a probability-based approach to assess chronic acidification in a population of lakes using one summer sample per year. The ALTM attempts to track changes in both chronic and episodic acidification across a gradient of lake types, using monthly samples. The ALTM has two important attributes that contrast with the TIME: higher temporal resolution (monthly versus once during the summer or fall), and speciation of aluminum. In particular, the ALTM provides inorganic monomeric aluminum (Al_{IM}), the fraction of Al that is most toxic. The monthly sampling of the ALTM includes the spring snowmelt period when acid neutralizing capacity and pH are near their lowest and Al levels are near their highest. We compare chemistry trends (1992-2008) for sulfate, nitrate, base cations, dissolved organic carbon, hydrogen ion, acid neutralizing capacity, and Al for the six lakes common to both programs. We also compare relatively high springtime Al_{IM} concentrations from the ALTM with relatively low summertime total Al concentrations from the TIME, showing that the ALTM program provides a more biologically-relevant indicator of the effects of acid deposition, illustrating the value of the complementary monitoring efforts in the Adirondack region.

A NEW CONCEPTUAL MODEL OF NITROGEN SATURATION BASED ON EXPERIMENTAL NITROGEN ADDITION TO AN OAK FOREST

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The dominant conceptual model of nitrogen (N) saturation in forests predicts the temporal patterns of key N cycling indicators as an initially N-limited forest is progressively enriched in N. We present the results from a long-term N addition experiment in an oak forest in southeastern New York State, USA, which do not conform to the predictions of the conceptual model in several ways. In contrast to the predictions of the conceptual model, the foliar N concentrations in the N-treated stands of our study increased to about 20% above the levels in the control stands and then remained essentially constant, and nitrogen leaching from the treated stands increased almost immediately after the start of the experiment, prior to the onset of elevated nitrification. Concentrations of N in soil solution of the N-treated stands peaked at over 150-fold greater than the concentrations in the control stands. There were no significant changes in potential net N mineralization. Tree mortality increased in the treated stands, but the tree mortality did not appear to be the primary cause of the excess nitrate leaching. Based on these results and those of other recent studies, we present a new conceptual model of the N saturation process focused on the mass balance of N rather than the temporal dynamics of N cycling indicators. The mass balance is characterized by inputs of N from atmospheric deposition and fertilization, internal sinks in the vegetation and soils, and outputs to leaching and gaseous losses. The key points of the conceptual model are 1) added N can flow simultaneously to all sinks and losses in the system, 2) the fate of the added N and the temporal patterns of flow of N depend on the strength of the sinks and the factors that control them, and 3) the movement of N to the various sinks determines how N saturation is manifested in the ecosystem. We distinguish *capacity* N saturation, in which the sinks in the vegetation and soil are zero or negative, from *kinetic* N saturation, in which the sinks are positive but lower than the N input rate. The sink strengths in the vegetation and soil have two components, one due to carbon (C) accumulation in the system and the other due to change in the stoichiometry (C:N ratio) of the pool. Further work quantifying the magnitudes and controlling factors for the N sinks will allow better prediction of the dynamics of N saturation in different types of forested ecosystems.

ADIRONDACK LONG-TERM MONITORING LAKES: A COMPENDIUM OF SITE DESCRIPTIONS, RECENT CHEMISTRY AND SELECTED RESEARCH INFORMATION

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The Adirondack Lakes Survey Corporation (ALSC) and the New York State Department of Environmental Conservation (NYSDEC) have compiled a compendium of site descriptions, recent lake chemistry and selected research information of the 52 Adirondack Long-Term Monitoring (ALTM) waters since the mid-1980s. This compilation is distributed free to the public on CDROM and via the web at www.adirondacklakessurvey.org and www.nyserda.org/programs/Environment/EMEP/finalreports.asp in Adobe PDF format. For each of the lakes, we provide descriptions of geomorphology; water chemistry summaries/time series (1992-2009); thumbnail summaries of historical and recent aquatic biota; fish stocking and netting histories; key intensive research studies; and watershed and land cover/use overviews in an easy-to-use desk reference format. The work is organized by watershed and supplemented with maps and tables to complete the overview for each of the ALTM waters. This work was designed to offer researchers, resource managers, policy makers, and the public an easy reference to the current research and chemistry at the diverse sites represented by the ALTM waters across the Adirondack Park.

ASSESSMENT OF LONG-TERM MONITORING PROGRAMS IN NEW YORK STATE

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Air pollutants such as nitrogen oxides, sulfur dioxide, and mercury have had significant impacts on the quality of lakes, rivers, soils, biota, and tree health throughout the Northeastern US. Some areas of New York State are particularly susceptible to environmental degradation, such as the Adirondack and Catskill regions, which receive some of the highest rates of acid and mercury deposition in the country. Long-term monitoring efforts have produced data sets that have been extremely valuable for evaluating changes over time in air pollution loads and effects on the environment.

It is important to reevaluate long-term monitoring programs to ensure that these programs remain efficient and effective. To our knowledge, a comprehensive evaluation of statewide long-term monitoring of acid and mercury deposition has never been undertaken in New York State. We are working with stakeholders to create a comprehensive database of long-term monitoring efforts in New York State, including monitoring of lakes, streams, soils, vegetation, and biota. These monitoring efforts include projects funded by a variety of federal and state agencies, private non-profit organizations, and academic institutions. Additionally, we are working to identify key science and policy questions to which the findings from long-term monitoring efforts can be applied.

We will undertake statistical analysis of select data sets to address the efficiency of monitoring efforts by identifying redundancies and gaps in monitoring efforts. After documenting data availability and identifying the policy needs for environmental monitoring, we can begin to analyze whether current monitoring practices are excessive (involving more effort than is justified by the results produced) and/or inadequate (producing results that are not sufficiently accurate or precise to meet policy needs). These analyses will include estimates of uncertainty in measurement and model parameters in order to most successfully answer key science and policy questions.

By summer 2012, we plan to have identified optimal, cost-effective monitoring options based on our inventory of long-term monitoring data sets and statistical analysis of select data sets. Ultimately this stakeholder driven, collaborative project will provide guidance for optimizing the efficiency and cost-effectiveness of long-term monitoring activities for sulfur, nitrogen and mercury in New York State.

CARBON OBSERVATIONS FROM CLOUD WATER AT WHITEFACE MOUNTAIN NEW YORK

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This poster will present observations associated with carbon found in cloud water samples collected from the summit of Whiteface Mountain New York. Since 1994, approximately 15% of the cloud water samples have failed the established ion balance test. Further, the vast majority of these ion imbalanced samples are shown to be anion deficient. We suspect, and as others have reported, this deficiency is largely from unmeasured organic acids. Organic acids may originate from natural and/or anthropogenic sources.

In 2010, total organic carbon (TOC) analysis was added to a subset of the cloud water samples collected. TOC concentrations determined for approximately 100 samples were observed in the range 0.5-27 mg/L.

FISH COMMUNITY CHANGES AND MERCURY IN ADIRONDACK LONG-TERM MONITORING LAKES

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Fisheries surveys have been conducted periodically by the Adirondack Lakes Survey Corporation in the 52 Adirondack Long Term Monitoring (ALTM) lakes. We compare fisheries community changes in 45 lakes conducted from 1994 to 2005 with an earlier survey from 1984 to 1987 for the purpose of examining the best methods for determining whether fish community responses are detectible over the average 14-year period between surveys, during which lake chemistry changes improvements from acidification have been documented. A second round of surveys (LTM2) was initiated for 2008 to 2012 with added investigations of mercury in yellow perch and brook trout.

We compare 45 lakes surveyed during 1994 to 2005 (LTM1) with earlier 1984 to 1987 (ALS) surveys: the ALS identified 147 fish populations and the LTM1 found a total of 176 resulting in 29 fish populations added during the average interval of 14 years between surveys. The median number of fish species populations increased from 3 to 4 per lake, the maximum number increased from 10 to 12 species.

Of the five fish population response classes, the largest group of lakes gained at least one species (n=15). The other species response classes were: no change in species (n=8 lakes); lost only (4 lakes); gained and lost (8 lakes); and 10 lakes had no fish present in either survey. We used a number of parametric and non-parametric statistics to identify relevant patterns. We developed a fish acid-sensitivity community index and discuss the limitations of using sensitive minnows and brown trout as indicator species.

We report preliminary findings on the 33 lakes that have been resurveyed (LTM2) to date (2008-2010) and present preliminary findings of fish community changes and mercury in water and fish tissue.

IMPORTANCE OF THE HYDROLOGICAL CHANGE ON THE DYNAMICS OF DISSOLVED ORGANIC CARBON AND NITROGEN AT **THE ARBUTUS LAKE WATERSHED IN THE ADIRONDACK MOUNTAINS OF NEW YORK STATE, USA**

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SUNY ESF

Dissolved organic matter (DOM) in terrestrial and aquatic ecosystems has several important components, with respect to a source of microbial activity, a cycle of energy and materials, and human health relevant to toxic metal (Al and Hg) and disinfection by-products, and its dynamics are closely related to hydrological and biological aspects of the watershed. For the last 30 years, both temperature and precipitation, which have been known as drivers in the change of DOM have significantly increased. But, dissolved organic carbon (DOC) and nitrogen (DON) at the inlet and outlet sites of the Arbutus Lake watershed showed no significant increase from 1984 to 2009. At the Archer Creek subcatchment (inlet site), there were, however, large fluctuations of annual DOC and DON concentrations, and their monthly patterns, which mirrored a seasonal aspect of forest catchments, appeared to be linked with climatic

and hydrologic factors or their interaction. Therefore, our aim is to investigate the effect of climate change on the dynamics of DOM at the inlet and outlet site of the Arbutus Lake watershed.

A stepwise linear regression was used to estimate the relationship between DOM and climatic and hydrological variables during growing (May to September) and early (October to January) and late (February to April) dormant periods. Estimated variables were daily discharge, daily temperature, average temperature for previous 7 days, daily precipitation, total precipitation for previous 7 days, and snow depth. The results suggest that DOC and DON responses to variables differed over periods and sites. Arbutus Lake plays an important role in the decrease of DOC, related to hydraulic retention time; however, in the case of DON, N cycle may appear to be another driver of the change of DON in the lake. In addition, through variation of DOC:DON ratios and stable C isotope values of DOC between the inlet and outlet site, algal production may contribute smaller than allochthonous DOC to the lake DOC. Our study provides that hydrological change induced from precipitation change may drive the major change of DOC, since monthly hydrological change vs. discharged-weighted DOC concentration provides fundamental information of understanding the dynamics of DOC export from the subcatchment and may highlight the importance of the change of discharge over years on the change of DOM.

MERCURY IN THE GREAT LAKES REGION: BIOACCUMULATION, SPATIOTEMPORAL PATTERNS, ECOLOGICAL RISKS AND POLICY

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A three-year bi-national effort examined mercury in the Laurentian Great Lakes region of North America. Data from aquatic and terrestrial biota as well as water, sediment, and air samples were synthesized. From this effort, the bioaccumulation and risks of methylmercury were examined, and the mercury policy in the region was explored. Key findings indicate that mercury in the region is still a pollutant of concern, and it poses a greater threat than previously recognized. The scope and intensity of the problem is widespread across the region, and mercury concentrations exceed human and ecological risk thresholds, specifically for inland waterbodies. In particular, the northern forested ecosystems are highly sensitive to mercury pollution as emissions and deposition are exacerbated by watershed and lake characteristics that lead to increased transport, methylation, and uptake of mercury. Additionally, encouraging results show mercury levels in the region have declined over the past four decades, coinciding with decreases in air mercury emissions. However, some fish and birds from certain locations have shown increased mercury concentrations in recent years and the reasons for these increases are not fully understood at this time. Adding further controls on mercury emissions is expected to lower mercury concentrations in the food web yielding multiple benefits to fish, wildlife, and people in the Great Lakes region, yet the timing and magnitude of the effects of future reductions is unknown. Collectively, this effort included more than 170 researchers who yielded 35 scientific manuscripts in the journals of *Ecotoxicology* and *Environmental Pollution*. This new and robust body of scientific findings strengthens the need for expanding existing monitoring efforts to better track progress in reducing mercury pollution.

MERCURY IN MACROINVERTEBRATES AND FISHES FROM STREAMS IN CONTRASTING SETTINGS: THE ADIRONDACKS (NY) AND THE COASTAL PLAIN (SC)

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Controls on mercury bioaccumulation in lotic ecosystems are not well understood. From 2007 to 2009, we studied mercury and stable isotope spatial patterns of macroinvertebrates and fish from two medium-sized (<80 km^2) forested basins in contrasting settings. Samples were collected seasonally from multiple sites across the Fishing Brook basin (FB_{NY}), in New York's Adirondack Mountains, and the McTier Creek basin (MC_{SC}), in South Carolina's Coastal Plain. Mean methylmercury (MeHg) concentrations in shredder and predator macroinvertebrate feeding groups, and mean total mercury (THg) concentrations within most fish feeding groups did not differ regionally. However, mean THg concentrations in game fish and forage fish, overall, were much lower in FB_{NY} (1300 and 590 ng/g dw, respectively) than in MC_{SC} (2300 and 780 ng/g dw, respectively), due to lower trophic positions of these groups from FB_{NY} (means 3.3 and 2.7, respectively) than MC_{SC} (means 3.7 and 3.3, respectively). Much larger spatial variation in topography and water chemistry across FB_{NY} contributed to greater spatial variation in biotic Hg and positive correlations with dissolved methylmercury and organic carbon in streamwater. Hydrologic transport distance (HTD) was negatively correlated with biotic Hg across FB_{NY}, and was a better predictor than wetland density. The small range of landscape conditions across MC_{SC} resulted in no consistent spatial patterns, and no discernable correspondence with local-scale environmental factors. This study demonstrates the importance of local-scale

environmental factors to mercury bioaccumulation in topographically heterogeneous landscapes, and provides evidence that food-chain length can be an important predictor of broad-scale differences in Hg bioaccumulation among streams.

Modeling the Trade-Off Between Calcium and Energy Acquisition for Reproducing Songbirds in Acidified Forests

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Birds require large amounts of dietary calcium to produce eggs and raise young. In acidified forests of the northeast, bird abundances and productivity can be limited by calcium availability, however it is unknown whether these observations are a direct result of insufficient calcium available for dietary intake or a result of trade-offs a bird must make between energy and nutrients. I used optimal foraging theory to model the potential trade-offs between calcium and energy acquisition by forest songbirds. I used the model to evaluate the cost of including calcium-rich food items at the expense of energy-rich food items because calcium-rich foods, like snail shells, have low availability, low energy content, and high handling time compared to energy-rich foods, like caterpillars. When calcium-rich food availability was high, birds were able to successfully lay eggs without reducing energy stores. When calcium-rich food availability was lowered, the energy stores of the birds were reduced, with each successive egg being laid with lower energy stores until either the birds died, stopped laying eggs, or laid eggs with thin eggshells. This simple model emphasizes the potential for trade-offs between calcium and energy to cause reproductive problems for birds in habitat with low calcium availability, like most northeastern forests.

Monitoring Bird and Bat Migration in the Thousand Islands Region of New York State

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The Biodiversity Research Institute initiated a study in August to October 2011 with the goal of providing the U.S. Fish and Wildlife Service (USFWS) with data on the migratory movements of birds and bats in the Great Lakes. These data will help the USFWS assess potential impacts of wind power proposals in the region, guide the siting of wind facilities, and minimize environmental impacts of wind energy development to bird and bat populations. This goal will be achieved through the following objectives: (1) quantify bird and bat migration on islands in the St. Lawrence River during both spring and fall migration seasons, including species, abundance, timing, and weather effects; and (2) apply newly developed analysis methods to NEXRAD radar images to characterize migration patterns at a regional scale, and to analyze arrival and exodus patterns at the five high priority islands of Grindstone, Carleton, Galloo, Stony, and Grenadier in the St. Lawrence and eastern Lake Ontario. Study methodologies include mist netting, visual surveys, and acoustic monitoring for birds and bats, and NEXRAD radar analysis of broad-scale migration movements throughout the Thousand Islands region. Preliminary results from the autumn 2011 field season are presented here. The study will continue in the spring of 2012.

Relationships Among Songbird Communities, Calcium Availability, and Acidic Deposition in the Adirondacks

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The depletion of soil calcium, an important macronutrient, by acidic deposition has been linked to changes in plant and invertebrate communities, as well as to reproductive declines in some avian species. However, studies limited to one or a few species have provided conflicting evidence on the importance of calcium as a limiting nutrient for birds. To investigate the effects of calcium depletion on overall avian abundance and diversity, we sampled avian communities at 14 sites representing a soil calcium gradient of upland northern hardwood forests in the Adirondack Mountains in New York. We found that some species may favor higher calcium sites with lower acidic deposition inputs for establishing breeding territories. However, there was no relationship between species richness and soil calcium concentration or acidic deposition levels. These results indicate that some species may be more sensitive to

acidic deposition than others. Future analyses will explore the effects of acidic deposition and soil calcium concentrations on overall avian abundance and on the abundance of avian guilds based on foraging strategy and dietary preference. The study may provide guidance for conservation efforts in the Adirondack Mountains, elucidating whether highly buffered sites may act as neorefugia for biodiversity by retaining potential for long-term acidification resistance and recovery.

RESULTS - LONG-TERM MONITORING AND ASSESSMENT OF MERCURY BASED ON INTEGRATED SAMPLING EFFORTS USING THE COMMON LOON, PREY FISH, WATER, AND SEDIMENT

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We used the common loon (*Gavia immer*), a top trophic-level piscivorous predator, as an indicator species to assess mercury exposure and risk in aquatic ecosystems in New York's Adirondack Park. We related loon mercury to reproductive success to evaluate the effects of mercury contamination on the population and to develop a hazard profile. We used mercury abiotic (water column and sediment) and biotic (common loon blood, feathers, and eggs; prey fish; crayfish; and zooplankton) levels from samples collected on 44 lakes over two years (2003 to 2004) to develop an exposure profile and quantitatively assess the ecological risk that mercury deposition poses to Adirondack waterbodies. Loons were sampled and monitored from 1998-2007. Food web mercury concentrations increased by many orders of magnitude from water to zooplankton to crayfish to fish to loons. There was a strong correlation between large and extra-large fish mercury and loon blood mercury. Lake acidity also correlated with mercury levels, with more acidic lakes exhibiting higher fish and loon mercury concentrations. Twenty-one percent of males and 8% of females were at a high risk of behavioral and reproductive impacts based on blood mercury exposure; 37% of male and 7% of female birds were at high risk based on feather mercury exposure. A Wildlife Criterion Value indicated that a water mercury level of 2.00 ng Hg/L or less is protective of male loons, while 1.69 ng Hg/L or less is protective of females. Female loons in the highest exposure category showed a 32% reduction and males a 54%, reduction in chicks fledged/year, compared to birds in the lowest exposure category. Quantile regression found a negative correlation between productivity and mercury for both female and male loon units, and indicated that (1) the maximum Adirondack loon productivity with negligible mercury exposure would be ~1.0 chick fledged/territorial pair; (2) productivity would be reduced by 50% when female or male blood mercury levels were 3.30 µg/g and 4.50 µg/g respectively; and (3) productivity would fail entirely when female or male blood mercury levels exceeded 6.80 µg/g and 8.96 µg/g respectively. Population model results indicated that the portion of the Adirondack loon population with high mercury levels has a reduced growth rate (λ = 1.0005), compared to low mercury birds (λ = 1.026). The results of this project will assist in the development of state and national policies and regulations that address the ecological injury mercury and other contaminants pose to freshwater ecosystems.

SPATIAL CONTROLS ON TOTAL AND METHYL HG IN THE UPPER HUDSON RIVER BASIN, NEW YORK, USA

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Surface water mercury concentrations, especially those of the neurotoxin methylmercury (MeHg), can vary widely across regional landscapes. Approaches are needed to better predict spatial variation in Hg species concentrations across heterogeneous landscapes that include mountainous areas, wetlands, and open waters. Here, we used multivariate regression to develop models to best describe the spatial variation of total Hg (THg) and MeHg concentrations across the 500 km^2 Upper Hudson River basin in the Adirondack Mountains of New York, an identified "hot spot" for freshwater Hg contamination. High spatial variation of about six-fold for THg concentrations and 40-fold for MeHg concentrations were present across this basin for synoptic samples collected during spring and summer of 2006 and 2008 at 27 sub-basins. THg, MeHg, dissolved organic carbon (DOC), and iron concentrations were significantly greater in summer than spring reflecting the increased influence of riparian areas dominated by wetlands during summer. Hg species concentrations were significantly related to percent wetland area and to DOC concentrations, but these relations were weaker in summer when only about one-third of spatial variation was accounted for by bivariate regression relations. In contrast, multivariate regression relations that included metrics of: (1) hydrogeomorphology such as slope and overland flow distance, (2) riparian/wetland area, and (3) open water, explained 66% to more than 90% of spatial variation in these data for each Hg species in each of the seasons. These metrics reflect the combined influence of basin morphometry and riparian soils on Hg source and transport, and the role of open

water as an Hg sink in this basin. Multivariate models based solely on these landscape metrics predicted Hg species concentrations as well as or, in some cases, better than models based on more expensive and time-intensive chemical and physical metrics, such as DOC concentrations and specific ultra-violet absorbance. Metrics derived from a digital elevation model, land cover, and hydrography show great promise for identifying areas of expected high Hg concentrations in waters and biota in the Adirondack region, and are likely applicable in similar glaciated riverine landscapes dominated by mountains, riparian wetlands, and lakes/ponds.

UNDERSTANDING THE MOLECULAR COMPOSITION OF HIGHLY POLAR ORGANIC COMPOUNDS IN CLOUD WATER AND FINE PARTICLES IN THE NORTHEASTERN U.S.

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Highly polar organic compounds (HPOC) comprise chemical mixtures found in cloud water and fine particles (nominal particle diameter < 2.5 micrometers, PM2.5). An understanding of the chemical composition of HPOC is key to developing better knowledge of cloud life cycles and the influence of organic carbon (OC) species on nanoscale to global scale atmospheric processes.
We report results of HPOC in fine particles sampled from the NY/NJ/CT region from 2002 to 2007 and cloud water collected from the top of Whiteface Mountain, NY during summer 2009. We compared distributions and abundances of approximately 20 HPOC markers. Low molecular-weight dicarboxylic acids with carbon numbers <10 and oxocarboxyic acids were common to both sample media and found in highest concentrations. The HPOC markers were compared to inventories of PM2.5 and cloud water reported in the literature. We discuss the sources for the HPOC present in the cloud water and PM2.5 from the northeastern U.S., which include combustion and photochemical processes, direct industrial emissions, and natural emissions of biochemical metabolites.

WATERSHED SULFUR BIOGEOCHEMISTRY IN THE ADIRONDACKS: SHIFT FROM ATMOSPHERIC DEPOSITION DOMINANCE TO CLIMATIC REGULATION

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North American atmospheric S emissions peaked in 1994 followed by a dramatic decrease that resulted in marked declines in sulfate (SO_4) concentrations in precipitation for many surface $_{2-}$ waters of the region. These changes in S biogeochemistry have important implications with respect to the mobilization of toxic and nutrient cations and the acidification of watersheds. We used the continuous long-term record for the outlet of Arbutus Lake (Adirondack Mountains of New York) from 1983 through 2009 as well SO_4 concentrations and fluxes from the Lake's $_{2-}$ major inlet (Archer Creek) and from two additional subcatchments (S14 and S15). Annual S budget discrepancies (SO_4) (flux in drainage waters minus total atmospheric S deposition) have $_{2-}$ become significantly more negative, indicating the increasing importance of the release of S from internal sources with time. We found that watershed wetness, as a function of $\log_{10}$ annual water flux, was significant and explained a large proportion of the annual variation in S budgets discrepancies but differed among the subcatchments of Arbutus Lake. The biogeochemical control of annual SO_4 export in stream water of these forested watersheds has shifted from $_{2-}$ atmospheric S deposition to climatic factors by affecting hydrologic conditions as found in other watersheds of the northeast U.S. and southeast Canada. This shift has important implications on the how climate is taking an increasing large role in affecting the water chemistry of this region.

BIOMASS AND BIOFUELS

CHEMICAL ANALYSIS OF WOOD PELLET FUELS FOR RESIDENTIAL WOOD COMBUSTION

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As states take actions to address climate change through increased use of renewable fuel sources, it is necessary to understand the potential air pollution, public health, and efficiency trade-offs, as well as the benefits. This poster provides information on the findings of a NYSERDA project that quantifies the elemental composition and other characteristics of various wood pellet brands found in the Northeastern U.S. to gain a better understanding of the variability within fuels and to identify elements of concern. It is important to assess the chemical composition of fuels used in residential space heating because emissions of particles and air toxics from this sector may be substantial and potentially much greater in the future. These results would also help to determine whether performance standards or other control measures should be developed to minimize the negative impacts associated with the use of solid biomass fuels. One hundred and thirty samples of wood pellets were purchased in five northeastern states (approximately 100 different brands, with duplicate brands purchased at different locations). Pellets are being analyzed to better understand emissions potential and determine if developing biomass fuel specifications, such as those that exist in Europe, could reduce the impacts associated with biomass combustion. Four categories of analysis are used: 1) basic characterization: calorific value, moisture content, ash content, and ash fusion; 2) ions: sulfate and chloride by IC; 3) trace metals by ICP-MS, and 4) mercury by volatilization onto a gold trap followed by CVAA analysis. Preliminary results show a wide range in levels of ions, trace metals, and mercury across the wood pellet brands tested.

CHEMICAL COMPOSITION OF WOOD CHIPS AND PELLETS

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Biomass combustion is gaining interest as a replacement for fossil fuels because it is a renewable resource and can be cost-effective as the price of fossil fuels rise. Increased wood combustion poses potential environmental problems related to air quality and ash disposal. Thus, there is reason to be concerned about trace metal concentrations in wood ash. The chemical composition of wood chips and pellets, mainly their ash content, varies depending on the nature of the plant species, where it grows (origin), fertilizers and pesticides used, addition of materials during biomass harvesting, transport, handling and processing, blending of plant species type, and the addition of waste wood that could have been painted or treated. There have been many small studies of the composition of woody biofuels. However, there has not been a large study of the wood chips and pellets analyzed using the same methods. In this study, about 132 wood pellet samples that include 100 different brands and some of the same brands purchased at different times and locations in northern New York and New England. Samples were purchased in five Northeastern states. In addition, 23 wood chips samples collected from different locations were also analyzed. The wood pellets and wood chips were analyzed for calorific value using a bomb calorimeter. Chloride and sulfate were determined by ion chromatography from the bomb washings. Trace elements in the ash were measured with ICP-MS and the mercury content in the wood was measured by direct analysis of the solid wood. The major component in wood is carbon that ranges from 45-50%, followed by hydrogen at about 6%. Other major elements in the decreasing order are nitrogen (N), calcium (Ca), potassium (K), sodium (Na), magnesium (Mg), manganese (Mn), iron (Fe) and aluminum (Al). Heavy metal concentration of cadmium (Cd), lead (Pb), arsenic (As), copper (cu) and cobalt (Co) were also determined. The distributions of these species will be presented along with estimates of the uniformity of pellets from single manufacturers.

EFFICIENCY MEASUREMENTS FROM HIGH EFFICIENCY WOOD BOILERS USING ASHRAE STANDARD 155P

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Thermal efficiency is the measure of heating performance of a commercial boiler set by Hydronics Institute (HI) and American Society of Heating, Refrigeration and Air Conditioning Engineers (ASHRAE 90.1-99). ASHRAE standard 155p is the new

performance evaluation protocol. This method provides a method for determining the thermal efficiency, including the partial load efficiency of individual commercial scale boilers. It also provides a method for determining application specific seasonal efficiency under steady state conditions. The standard is applied for space heating performance and is applicable to boilers with energy input values ranging from 300,000-12,500,000 Btu/hr. This procedure was applied to determine the efficiency of advanced wood combustion boilers installed at Clarkson's Walker Center and Wild Center, Tupper Lake, New York having output capacities of 514000 Btu and 1.7 million Btu/hr, respectively. Measurements were conducted during the heating season from January to March 2011 under steady state conditions for heating load demands. The efficiency ranged between 75% and 86% for a 150kW boiler and between 75% and 91% for the Wild Center Boiler. Boiler capacity has no significant effect on efficiency, but, the operating conditions such as fuel feed rate, outlet water temperature, and building demand did affect the results.

ENVIRONMENTAL, ENERGY, MARKET, AND HEALTH CHARACTERIZATION OF FOUR WOOD-FIRED HYDRONIC HEATER TECHNOLOGIES

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The proliferation of wood-fired hydronic heater technologies in the northern states has highlighted the lack of environmental, energy, market, and health information regarding these heating sources. The U.S. EPA and the New York State Energy Research and Development Authority (NYSERDA) addressed this data gap by testing four current and emerging technology hydronic heaters for emissions and energy-efficiency performance. The four units included a common, single-stage, split log combustor; a three-stage gasifier/combustor, a pellet fuel system, and a two-stage gasifier/combustor operating with heat storage. The daily heat load demand was supplied by a simulation program for a 2,500 ft^2 home during a Syracuse, NY winter. Energy transfer was by a chilled water heat exchanger. Measurements included emissions of particulate matter, elemental carbon, carbon monoxide, polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and polychlorinated dibenzodioxins/dibenzofurans (PCDDs/Fs) along with energy efficiency. HH units with cyclical damper operation to modulate heat release resulted in considerable increase in emissions upon damper opening and, at least for one unit, considerable nuisance odor. The split log units resulted in CO emissions ranging from 13 to 23 lbs per million BTU input (lbs/MBTUin) while the pellet unit was less than 2 lbs/MBTUin. These values compare to oil units at < 0.1 lbs/MBTUin. PM emissions were significantly higher from the single stage unit, ranging from about 5 to 15 lbs per Syracuse heat load day, than from the other three units, which averaged less than 1 lb/day. These PM values contrast sharply with oil-fired units at about 0.03 lbs per Syracuse day.

The market for residential wood-fired hydronic heaters was modeled with the MARKAL (MARKet ALlocation) energy systems model. Alternative market scenarios based on changes in unit efficiency, capital and operating costs, rate of technology turnover, and the cost of competing fuels for residential space heating showed that growth in the market for wood heat, in the absence of turnover to higher efficiency and lower emitting units, could lead to substantial increases in regional PM emissions. In addition to the MARKAL modeling, an engineering economic analysis was also performed to identify break-even points for different hydronic heating units and other wood/pellet heat alternatives. The results suggest that wood-fired hydronic heaters typically will be competitive with non-wood devices only where natural gas is unavailable and where wood can be obtained at very low or no cost. Even under these conditions, however, other wood devices, such as indoor high-efficiency wood boilers with hot water storage, can be a much more cost-effective option because of their higher efficiency.

Lastly, the health effects of hydronic heater emissions were evaluated with an exposure study for pulmonary and systemic biomarkers of injury and inflammation.

The results of this study are anticipated to be of value to New York State efforts to develop a high-efficiency, environmentally-acceptable biomass heating market of technologies and the U.S. EPA as it sets New Source Performance Standards for biomass-fired hydronic heaters.

FINE PARTICULATE MATTER CONCENTRATIONS IN OUTDOOR AIR NEAR WOOD-FIRED BOILERS

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Outdoor wood-fired boilers (OWBs) are growing in popularity but can emit considerable fine particle ($PM_{2.5}$) mass. During the 2007 and 2008 heating seasons, New York State Department of Health investigators conducted an air monitoring study to evaluate the potential for smoke from OWBs to increase outdoor air fine particle ($PM_{2.5}$) levels in residential neighborhoods. This was

accomplished by comparing $PM_{2.5}$ concentrations in air at residences near OWBs to levels in air at residences distant from OWBs, and then by determining if unusually elevated $PM_{2.5}$ concentrations reported in air at residences near OWBs coincided with wind conditions favoring local accumulation of OWB smoke (i.e., calm winds), downwind monitor status, or both. Geometric mean (GM) 5- or 10-minute average $PM_{2.5}$ concentrations were statistically significantly elevated at 5 of 6 nearfield monitors compared with their paired reference monitors. GM $PM_{2.5}$ level increases of 15, 17, 46, 74 and 187 percent were calculated. Relative odds of observing an extreme (>95^{th} percentile) $PM_{2.5}$ concentration event were 1.8- to 4.3-fold higher at the 5 nearfield monitors with elevated $PM_{2.5}$ levels, and increases were statistically significant. Calm (0 mph) winds were statistically significantly associated with increased relative odds of observing an extreme (>95^{th} percentile) $PM_{2.5}$ concentration difference (nearfield $PM_{2.5}$ minus reference $PM_{2.5}$) at 4 of the 5 sites with elevated $PM_{2.5}$ levels. Downwind status was statistically significantly associated with increased relative odds of observing an extreme $PM_{2.5}$ concentration difference at 3 of the 5 sites with elevated $PM_{2.5}$ levels. Alternative local sources of $PM_{2.5}$ (*e.g.*, chimneys, stacks and idling vehicles at the participants' homes; vehicles on roadways) were sometimes present between OWBs and air monitors, but alternative local sources did not appear to contribute substantially to elevated $PM_{2.5}$ concentrations at monitors near OWBs. Although these investigations considered only six residential locations near OWBs, study results indicated that OWBs can significantly increase $PM_{2.5}$ concentrations in outdoor air at nearby residences. The study did not employ regulatory air monitors, so measured $PM_{2.5}$levels were not compared to air quality standards. Nonetheless, the severity of adverse health effects associated with even short-duration elevated $PM_{2.5}$ air concentrations, along with the demonstrated importance of OWBs as sources of wood smoke and $PM_{2.5}$ in some residential settings, indicate that further efforts to reduce exposures to OWB-derived wood smoke and $PM_{2.5}$ are warranted.

MODEL FOR ASSESSING CARBON NANOPARTICULATE INHALATION EXPOSURE RISK: A PROTOCOL FOR COMBUSTION EMISSION ULTRAFINE NANOPARTICULATE TESTING

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The search for renewable and safe energy alternatives to replace fossil fuels has resulted in the development/use of many biomass fuels (solid biomass-wood, grasses, pellets; liquid biofuels-plant oils, ethanol), and new advanced-technology burners for biomass combustion. The success of these biomass fuels and more efficient burners depends on the production of nontoxic combustion emissions to insure public safety. Correlations have been found between human wood smoke exposure (homes and workplaces), and increases in cardio-respiratory morbidity, blood pressure and cataracts, as well as asthma and other respiratory ailments. Emission analyses from advanced technology biomass burners have shown significant reductions in large particulate-, and organic-, combustion emissions; however, little is now known about the remaining ultra-fine nanoparticulate (UFNP) emissions (<100 nm in size), and it is not yet possible to assess and predict whether these pose risks to human health. Ultimately, "health risk" will be the limiting factor for the success of these new energy systems. This poster describes our model protocol developed at Brookhaven National Laboratory for screening nanoparticulates (NPs) to assess their physico-chemical characteristics and their interactions with human lung epithelial cells. For this model we used single walled carbon nanotubes (SWCNTs) "as produced" from furnace material (containing Ni, graphene, amorphous carbon, nanoropes, SWCNTs and SWCNT-bundles); and acid/peroxide cleaned SWCNTs. To assess if these NPs changed following contact with surface waters (in the environment), NPs were aqueously aged in ultra-pure ~18MΩ water, sterile phosphate buffered saline, or fresh water with 5 mg/L Suwannee River natural organic matter (NOM)), and subsequently analyzed physico-chemically (FTIR, UV-VIS, DLS, SEM, TEM, x-ray microanalysis). Human muco-epithelial airway cell monolayers were exposed to NPs (2 and 3.5 hours) for viability testing and ultrastructural NP-cell imaging. Metal containing UFNPs proved highly destructive to human airway cells [even at reduced doses]. Metal-free SWCNTs were found to produce cell damage and necrosis due to (a) SWCNT surface oxidation; (b) direct contact of SWCNT-bundles with cell membranes (piercing vacuolar and plasma membranes); and/or (c) intracellular bioaccumulation of NPs. However, the aforementioned toxic responses to NPs and NP-agglomerates were ameliorated by NP aqueous aging in saline or NOM.

We are hoping to apply this described tested protocol for screening biomass combustion NPs collected from advanced technology biomass burners (using different biomass fuels), to identify and characterize physico-chemically and toxicologically combustion emission NPs. This should reveal if exposure to these NPs can pose a risk to humans via inhalation.

RENEWABLE FUELS ROADMAP AND SUSTAINABLE BIOMASS FEEDSTOCK SUPPLY STUDY FOR NEW YORK

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The need for a Renewable Fuels Roadmap was identified in the February 2008 Report of the Governor's Renewable Energy Task Force, which called for a Renewable Fuels Roadmap and Sustainable Biomass Feedstock Supply Study for New York (Roadmap). The Roadmap assesses the prospects for the expansion of biofuel production in New York State, focusing on resource availability and

economic and environmental impacts. In addition, the Roadmap solicited input from New York stakeholders to identify the most important social, economic, and environmental issues to make a renewable fuels industry socially, economically, and environmentally sustainable in the state. Assigned with the task of looking into the future for impacts from an industry that almost entirely does not exist at this writing, the Roadmap Team devised and implemented three scenario analyses. The scenario analyses were coordinated using an integrated set of computer models based on the best available data, combined with a set of expert judgments and assumptions where quantitative data were not available. These integrated computer models collectively provide feedstock, energy, economic, and environmental analyses of the three Roadmap scenarios. The Roadmap presents possibilities, identifies potential challenges, and outlines important technology and policy options that may be used to ensure that any expansion of a renewable fuels industry serves the social, economic and environmental goals for New York.

WOOD HYDRONIC HEATERS – EFFICIENCY AND EMISSIONS TESTING

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Interest is increasing in the use of wood-fired boilers for meeting space and domestic hot water loads in homes across the Northeast. While the increased use of this local fuel has benefits for regional greenhouse gas emissions, there is a concern that these benefits may come at the price of increased emissions of particulates and other pollutants. Combustion technologies and system configurations vary considerably and this is a rapidly emerging area. It is critically important that test methods accurately reflect the performance that these systems are likely to achieve in field operation and that new, low emission technologies be given due credit.

This presentation will describe the results of a review of the existing method of testing these heaters for efficiency and particulate emissions that was recently completed. The test method, potential sources for improvement, and areas with accuracy concerns are discussed. This test method has recently undergone a major revision, reflecting, in part, the efforts of this work and the major changes made are also reviewed.

Important questions remain about test loads relative to actual loads in typical homes, performance with large storage volumes (full storage), smaller storage volumes (partial storage), and fuel charging practices under low load periods, which can strongly affect the way that these units operate in the field.