

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

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**POSTER ABSTRACTS**

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## **ECOSYSTEM RESPONSE TO SULFUR, NITROGEN AND MERCURY**

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### **MERCURY IN FISH FROM NEW YORK STATE LAKES**

Howard A. Simonin, New York State Department of Environmental Conservation

A 4-year study surveyed 131 lakes across New York State beginning in 2003 to improve our understanding of mercury and gather information from previously untested waters. Our study focused on largemouth and smallmouth bass, walleye and yellow perch, common piscivorous fish shown to accumulate high mercury concentrations and species important to local fisheries. Fish from Adirondack and Catskill Forest Preserve lakes generally had higher mercury concentrations than those from lakes in other areas of the state. Variability between nearby individual lakes was observed, and could be due to differences in water chemistry, lake productivity or the abundance of wetlands in the watershed. We found the following factors impact mercury bioaccumulation: fish length, lake pH, specific conductivity, chlorophyll-a, mercury concentration in the water, presence of an outlet dam and amount of contiguous wetlands. Data from 12 Adirondack lakes were used to evaluate mercury trends in fish over time, and indicated an average decline of 16% in yellow perch mercury concentration over the past 15 years. Project data were used by the New York State Department of Health to issue new fish consumption advisories on numerous lakes and a new region-wide advisory for the Adirondack and Catskill Parks.

### **NEW YORK DEPARTMENT OF ENVIRONMENTAL CONSERVATION'S PROGRAM TO MONITOR MERCURY WET DEPOSITION AND SPECIATED AMBIENT MERCURY IN TWO URBAN AREAS**

Dirk Felton, Oliver V. Rattigan, Kevin Civerolo, Steve DeSantis, Patrick Malone

Over the past decade the largest reductions in anthropogenic mercury emissions have occurred from the municipal waste combustion and medical waste incineration sectors. During this same period, emissions of mercury from coal-fired utilities have not changed much. However, mercury emissions from this sector are expected to decrease in the coming years as a result of Clean Air Mercury Rule legislation. As these planned reductions are phased-in, it is important to monitor ambient concentrations and deposition of mercury to establish baseline levels. The NYSDEC is initiating a two year program to monitor air concentrations of elemental, divalent, and particle-bound mercury as well as weekly wet deposition of total mercury at two urban locations in New York State – Bronx and Rochester. Ancillary measurements of co-pollutants such as SO<sub>2</sub>, O<sub>3</sub>, CO, PM<sub>2.5</sub>, acid deposition, and meteorological parameters are currently made at these locations, which will help aid in source attribution analyses. These urban Mercury measurements will also be compared to similar measurements made at rural locations in upstate New York to better characterize mercury pollution across the state.

### **RETENTION, TRANSFORMATION, AND POTENTIAL LONG-TERM EXPORT OF MERCURY FROM WETLANDS TO SURFACE WATERS IN THE ADIRONDACK REGION, NEW YORK, USA**

Jason Demers, Cornell University

Wetlands are important controls of inorganic mercury and methyl mercury flux to surface waters. Research suggests that greater area of wetlands within a watershed is often correlated with greater amounts of dissolved mercury and methyl mercury in associated surface waters and fish; however, the importance of wetland type is seldom considered. This study quantifies differences in mercury biogeochemistry in individual wetlands of varying hydrologic setting in the western Adirondack region of New York, USA. Herein, we compare the pool size, flux, and residence time of mercury and methyl mercury in headwater wetlands perched at the top of their watersheds, with riparian wetlands lower in the landscape.

The pool size of mercury was greater in the top 50 cm of peat in riparian wetlands as compared with headwater wetlands, and the molar ratio of Hg:C shows that 2-4x more Hg per unit C was retained in these riparian wetlands. Mercury concentrations in peat porewater were consistently greater in headwater wetlands than in riparian wetlands during the non-growing season when water table levels were high. MeHg concentrations peaked at the end of the growing season, when water table levels were low. Riparian wetlands were spatial and temporal hotspots of

dissolved mercury and methyl mercury production, whereas headwater wetlands were less dynamic. Riparian wetlands provided the greatest flux of mercury and methyl mercury from wetlands to surface waters when compared to other wetlands within the same watershed. The residence time of mercury in riparian wetlands was >200 years, whereas the residence time of mercury in headwater wetlands exceeded 500 years. Differences in the flux of mercury from wetlands was primarily determined by the hydrology of the different wetland types, rather than by the concentration of mercury in porewaters. Based on the residence time, the magnitude of the flux of mercury from wetlands should not rapidly change with changes in atmospheric deposition of mercury.

#### **ASSESSMENT OF METHYLMERCURY AVAILABILITY IN BATS IN NEW YORK**

Dave Yates, Tim Divoll, David Evers, Jeff Loukmas, and Robert Taylor  
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More than half of the species of bats in the U.S. can be characterized as at least occasionally foraging over water and on emergent insects. There have been very few exposure investigations of exposures of bats to metals. For a variety of reasons relating to their natural history and vulnerability to some human impacts, an alarming 56 percent of the U.S. bat species were either listed as endangered or were under consideration for listing as of 2001. Bats comprise about one-quarter of the mammalian species and constitute a substantial proportion of the mammalian biological diversity in the United States. Bats have the highest percentage of endangered or candidate species among all the mammals in the United States. We present findings from an effort to evaluate mercury (Hg) exposure in various species of bats (*Myotis* sp.) from New York State. We sampled 96 bats obtaining fur for Hg analysis. The samples were analyzed for total Hg (95% Hg fur is MeHg). We found 16% of the bats sampled had Hg concentrations in their fur above the lowest observed effect levels in dosed mice. This study demonstrates the use of bats as bioindicators for atmospheric and point source contaminated areas.

#### **SONGBIRDS AS INDICATORS OF ENVIRONMENTAL MERCURY LOADS IN NEW YORK**

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It is established that avian piscivores in aquatic ecosystems accumulate high levels of mercury that affect reproduction and behavior. Breeding avian invertivore populations in a terrestrial ecosystem may be suffering the negative effects of multiple stressors such as habitat fragmentation, acidic and mercury (Hg) deposition, as well as other human-caused environmental changes. The effects of air pollutants, available calcium and sensitive habitats in breeding avian invertivores, such as Red-eyed Vireo, Palm Warbler and Wood Thrush, in northeastern forests are examined. In 2005-2007, we collected soil, litterfall, invertebrates and bird tissues (blood and feather) to test for mercury. We show results for avian invertivores at greatest risk, links to mercury deposition stations and songbird mercury loads, comparison of mercury loads to other terrestrial species, habitats and geographical areas at risk, soil calcium availability and mercury, and other factors that contribute to mercury contamination in songbirds.

#### **DYNAMICS OF HG IN FOREST WETLAND ECOSYSTEM IN THE ADIRONDACK REGION OF NEW YORK, USA**

Pranesh Selvendiran, Syracuse University

The losses of mercury (Hg) were studied in two forest wetlands in the Adirondack region on New York; one a riparian wetland and the other an abandoned beaver meadow wetland. Upland inputs, wetland pore waters and drainage losses of total mercury (THg), methyl mercury (MeHg) and other relevant water chemistry parameters have been measured monthly since August 2004. In addition gaseous losses of elemental Hg (Hgo) have been studied. The primary objective of this ongoing project is to conduct mass balances of THg and MeHg and evaluate seasonal patterns in Hg dynamics in these wetlands. The mean concentrations of THg and MeHg (1.9 and 0.04 ng/L, respectively; n = 28) of waters draining upland watershed into the wetlands are generally low. In contrast, elevated concentrations of THg and MeHg are (2.9 and 0.19 ng/L; n = 84) observed for waters draining the wetland sites. A strong seasonal pattern is observed for both THg and MeHg in wetlands. During the warm season (May – Nov), MeHg concentrations are strongly correlated with increasing DOC ( $r^2 = 0.72$ ) and decreasing SO<sub>4</sub><sup>2-</sup> ( $r^2 = 0.77$ ). During the cold season (Dec – Apr), concentrations of MeHg in wetlands are relatively low and showed no relation with DOC or SO<sub>4</sub><sup>2-</sup>. In contrast, concentrations of THg are strongly correlated with increasing DOC ( $r^2 = 0.79$ ), and

decreasing  $\text{SO}_4^{2-}$  ( $r^2 = 0.84$ ) during both cold and warm seasons. Evidence of MeHg production within wetlands is corroborated by high percentage of MeHg present in wetland pore water (23% of THg), compared to wetland surface water (7% of THg). Rate of evasive loss of Hg<sub>0</sub> from wetland surface exhibited marked temperature-dependent variations. Gaseous Hg<sub>0</sub> flux showed net deposition to the wetland surface during early morning and in the evening. In contrast fluxes increased showing net emissions during the day with increases in solar radiation. Over the 12-hr study period net emissions averaged 1.12 ng/m<sup>2</sup>/hr. Temporal patterns of evasion suggest that Hg<sub>0</sub> loss is largely mediated by photo reduction.

### **RESPONSE OF YELLOW PERCH (*PERCA FLAVESCENS*) IN ADIRONDACK LAKES TO CHANGES IN ATMOSPHERIC DEPOSITION OF MERCURY AND STRONG ACIDS**

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Over the last two decades, fish with elevated concentrations of mercury (Hg) have been observed in remote lakes, including the Adirondack region of New York. Studies across eastern North America have shown that fish Hg concentrations increase with decreases in lake pH. Recent controls in emissions of sulfur dioxide have resulted in some improvement in the acid-base status of Adirondack lakes. In addition, decreases in atmospheric Hg deposition have also occurred. In 1992-93 a survey of 25 lakes in the Adirondacks, representing diverse watershed and geochemical characteristics, was conducted to analyze patterns of Hg in the water column and yellow perch. The same 25 lakes were resurveyed in 2005-06 to evaluate if changes in lake concentrations of Hg species or fish Hg have occurred. Changes in water chemistry and fish Hg concentrations varied by lake. In general, pH and acid neutralizing capacity levels were greater, while sulfate concentrations were lower compared to the 1992-93 survey. Both total Hg (Hg<sub>T</sub>) and methyl Hg concentrations have decreased in almost all of the lakes since 1992-93. In both the original and most recent survey, concentrations of Hg<sub>T</sub> in perch increased with age, length, and weight. The decline in Hg fish tissue across age classes of yellow perch was lake dependent, with 12 lakes showing decreases in concentration, 6 lakes showing increases in concentration and 7 lakes exhibiting no change. These data suggests that some lakes have responded to decreases in SO<sub>2</sub> and/or Hg emissions over the past decade.

### **MERCURY ACCUMULATION IN SESTON ACROSS A RANGE OF LAKES IN THE ADIRONDACK MOUNTAINS, NEW YORK**

Ryan Adams, Syracuse University

Mercury content was measured in seston from nine lakes in the Adirondack Mountains of New York State that exhibit a range of physical and chemical characteristics. Fractionation of mercury (Hg) bound to particulate matter was conducted to identify the possible roles that seston density and dissolved aluminum have on Hg accumulation in various seston size classes (0.2-2 μm, 2-20 μm, 20-200 μm, and >153 μm). Total dissolved aluminum Al (<0.45 μm) significantly predicted Hg concentrations in the 20–200 μm size class and also was positively correlated with Hg concentrations in the other three sizes. Seston density was negatively correlated with seston Hg concentrations and significantly predicted Hg levels in the 0.2-2 μm size class. These results suggest that surface water aluminum concentrations and seston density influence Hg accumulation at the base of aquatic food chains.

### **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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Dr. Michale Glennon – Wildlife Conservation Society’s Adirondack Program  
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The Wildlife Conservation Society’s Adirondack Loon Conservation Program, in conjunction with BioDiversity Research Institute, NYS Department of Environmental Conservation, the Natural History Museum of the Adirondacks, and the Audubon Society of New York, used the Common Loon (*Gavia immer*) as an indicator species to assess the mercury exposure and risk in aquatic ecosystems in New York’s Adirondack Park. A mercury hazard

profile was developed based on the blood mercury levels in 261 loons (151 adults, of which 77 were male and 74 were female, and 110 juveniles) sampled on 80 lakes from 1998-2006. Adult and juvenile loons living on acidic lakes had significantly higher mercury levels than did loons on non-acidic lakes. Thirteen percent of the loons sampled had elevated mercury levels, and were at risk for behavioral changes, with potential impacts to their survival and reproductive success. Although there was a significant negative trend in reproductive success with male or female loon mercury levels, there was not a statistically significant difference in the average number of chicks fledged by high mercury loons vs. low mercury loons. However, loons living on acidic lakes fledged significantly fewer (42%) loon chicks than did loons on non-acidic lakes. Additional analyses in process include a mercury exposure profile, wildlife criterion value, and a population model for Adirondack loons. Results of this project will provide a scientific foundation for policy makers to make informed decisions regarding the regulation of airborne pollutants and the management of wildlife and freshwater ecosystems, based on reproductive impacts to a piscivorous predator at the top of the aquatic food web.

#### **A GEOSPATIAL ASSESSMENT OF MERCURY BIOACCUMULATION AND TROPHIC TRANSFER IN AMPHIBIAN POPULATIONS FROM THE NORTHEASTERN UNITED STATES**

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Nina Schoch, Wildlife Conservation Society, Adirondack Program  
David P. Braun, The Nature Conservancy

Mercury contamination in the United States is well-documented and continues to be a public-health issue of great concern for certain sectors of the global human population. Documentation of the pervasiveness of this contaminant is a first step toward understanding the potential environmental health and ecological implications of mercury pollution. Identifying broad scale distribution patterns of mercury bioaccumulation can convey to regulators that certain ecosystems may be degraded and require development of policies and regulations that may reduce mercury emissions, and ultimately, improve air and water quality. Spatial and temporal variability in watershed, trophic, and within stream sorption complexity likely has important influences on the bioavailability, bioaccumulation and biomagnification of mercury in lotic ecosystem biota. Watershed system variation and trophic complexity encompass interactions from both within streams and between the watercourse and the adjacent terrestrial landscape, including riparian habitat zones. The relationship between catchment conditions, aquatic-terrestrial linkages, and cross-habitat subsidies of energy is relatively well established in stream ecology, however the potential ecotoxicological implications of these linkages are not well studied, especially for species such as stream amphibians which may be sensitive to environmental degradation and reduced water quality. Worldwide amphibian declines are well documented and population declines have been attributed to a wide array of anthropogenic stressors including habitat loss and degradation, UV-B radiation, contaminants such as mercury, and multiple stressor effects, including pesticides, global climate change, and disease. Amphibians play an important role in many aquatic and terrestrial environments, and therefore their declines may have negative effects on ecosystem functions.

Here we report mercury bioaccumulation data from the continental United States with a special emphasis on the ecotoxicological effects of mercury exposure in amphibians inhabiting the northeastern region. The effects of regional disturbance mechanisms (i.e., acidification, calcium additions, fire, and forest removal practices) on mercury cycling are also discussed.

#### **NITRATE ISOTOPES AS TRACERS OF NITROGEN CYCLING PROCESSES IN WATERSHEDS OF VARYING LAND USE IN NEW YORK**

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Human activities have greatly accelerated the global nitrogen (N) cycle during the past 150 years. Nitrogen is an essential nutrient, but when available in excess of ecosystem demand, can contribute to such problems as acidification, eutrophication, and climate change. Atmospheric N contributes significantly to N loads in rivers and estuarine ecosystems. In many estuaries such as Long Island Sound and Chesapeake Bay, eutrophication is a concern that is being actively addressed through nutrient control policies. These policies are dependent on estimates of the impact of various N sources on river N loads to the estuaries. Dual isotope analysis of nitrate ( $\text{NO}_3^-$ ) can provide insight to the relative roles of various  $\text{NO}_3^-$  sources such as atmospheric deposition, human and animal

waste, and fertilizer. In this study, we analyzed the dual isotopes of  $\text{NO}_3^-$  in stream watersheds in New York that included forested, agricultural, and suburban land uses to better quantify the processes and cycling rates of these various  $\text{NO}_3^-$  sources. Atmospheric  $\text{NO}_3^-$  was rapidly transformed in these ecosystems as indicated by  $\delta^{18}\text{O}-\text{NO}_3$  values in forested, suburban, and mixed land use watersheds that indicated an immediate source from soil nitrification. The proportion of direct atmospheric N increased markedly in the suburban stream during high flow conditions, when impermeable surfaces and storm sewers transmitted unaltered N rapidly to the stream. The agricultural streams showed a  $\text{NO}_3^-$  source most likely from animal waste. The  $\text{NO}_3^-$  concentrations and dual isotope values showed a seasonal pattern of change consistent with denitrification, which removed  $\text{NO}_3^-$  that would otherwise have been transported downstream. These results show how the  $\text{NO}_3^-$  isotope signal is modified under seasonally-varying conditions, and also provide insight to the role of human-engineered changes to the landscape on the cycling of  $\text{NO}_3^-$ .

#### **AN ISOTOPIC TRACER OF STATIONARY SOURCE $\text{NO}_x$ EMISSIONS ACROSS THE MIDWESTERN AND NORTHEASTERN UNITED STATES**

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Global inputs of  $\text{NO}_x$  are dominated by fossil fuel combustion from both stationary and vehicular sources and far exceed natural  $\text{NO}_x$  sources. However, elucidating  $\text{NO}_x$  sources to any given location remains a difficult challenge, despite the need for this information to develop sound regulatory and mitigation strategies. We present results from a regional-scale study of nitrogen isotopes ( $\delta^{15}\text{N}$ ) in nitrate in precipitation across 33 sites in the Midwestern and Northeastern USA. We demonstrate that spatial variations in  $\delta^{15}\text{N}$  are strongly correlated with  $\text{NO}_x$  emissions from surrounding stationary sources, and additionally that  $\delta^{15}\text{N}$  is more strongly correlated with surrounding stationary source  $\text{NO}_x$  emissions than pH,  $\text{SO}_4^{2-}$ , or  $\text{NO}_3^-$  concentrations. Although emissions inventories indicate vehicle emissions are the dominant  $\text{NO}_x$  source in the eastern USA, our results suggest that wet  $\text{NO}_3^-$  deposition at sites in this study is strongly associated with  $\text{NO}_x$  emissions from stationary sources. This suggests that large areas of the landscape potentially receive atmospheric  $\text{NO}_y$  deposition inputs in excess of what one would infer from existing monitoring data alone. Moreover, we determined spatial patterns in  $\delta^{15}\text{N}$  values are a robust indicator of stationary  $\text{NO}_x$  contributions to wet  $\text{NO}_3^-$  deposition, and hence a valuable complement to existing tools for assessing relationships between  $\text{NO}_3^-$  deposition, regional emission inventories, and for evaluating progress towards  $\text{NO}_3^-$  reduction goals.

#### **QUANTIFYING ATMOSPHERIC NITROGEN SOURCES WITH NEW STABLE ISOTOPE TECHNIQUES: WHAT HAVE WE LEARNED?**

Carol Kendall (USGS), Emily E. Elliott (USGS – now University of Pittsburgh), Douglas A. Burns (USGS), Elizabeth W. Boyer (UC-Berkeley)

Increasing inputs of reactive nitrogen (N) to ecosystems in the northeastern USA have been linked to many environmental concerns, including acidification of ecosystems, accumulation of N in groundwater, and eutrophication of waterways. The role of atmospheric N deposition is of particular interest to land managers and policy makers, as rates of atmospheric N deposition in the northeast are among the highest in the nation. The sources of atmospheric N deposition include industrial, automotive, and agricultural emissions, and data regarding the relative contributions of these sources are needed in order to develop sound strategies for managing and understanding the effects of these and other N inputs to the landscape.

Recent advances in isotopic techniques allow researchers to quantify sources of N at finer spatial and temporal scales than have been possible with isotopic and mass balance budget approaches employed to date. Recent research suggests that different anthropogenic sources of N often have characteristic  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$  and/or  $\Delta^{17}\text{O}$  values, thus potentially allowing researchers to use the isotopic composition of nitrate in streams to estimate how much of the nitrate was derived from power plants, automobiles, row crops, and animal sources.

The overall goal of the NYSDERDA-EPRI-USGS project “Quantifying Atmospheric Nitrogen Sources with New Stable Isotope Techniques” has been to use novel isotopic methods for measuring  $\Delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ , and  $\delta^{15}\text{N}$  in nitrate to address two related research questions: (1) Can the isotopic composition of nitrate be used to quantify the relative contributions of different sources of atmospheric N to precipitation (e.g., distinguishing between stationary, automotive, and agricultural sources)?; and (2) Can the isotopic composition of nitrate be used to quantify the relative contributions of different sources of anthropogenic N to land and surface waters in New York’s watersheds (e.g., distinguishing between atmospheric, fertilizer, and wastewater N)? Our approach involves the analysis of the isotopic composition and water chemistry of wet and dry precipitation and surface water samples from a variety of environmental settings within New York’s watersheds. This poster is aimed at showing our progress with answering this first question.

### **WHY DO DIFFERENT ANTHROPOGENIC SOURCES OF ATMOSPHERIC NITRATE HAVE DISTINCTIVE ISOTOPIC SIGNATURES?**

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Do different sources of atmospheric nitrate (power plants, vehicles, agricultural emissions) have distinctive isotopic signatures? To answer this question, we conducted a national survey of nitrate isotopes in wet deposition samples collected throughout the USA from 156 NADP sites. Archived samples from the year 2000 were pooled into bimonthly composites and analyzed for  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ , with a subset analyzed for  $\Delta^{17}\text{O}$ . In this poster, we present our current thoughts about why the different sources have distinctive isotopic signatures, focusing mainly on oxygen isotopes of nitrate.

Our original conceptual model was based largely on (1) Heaton’s 1990 paper that showed that  $\text{NO}_x$  emissions from power plants in South Africa had  $\delta^{15}\text{N}$  values significantly higher than exhaust from vehicles, and (2) anecdotal data from several studies showing higher  $\delta^{15}\text{N}$  and/or  $\delta^{18}\text{O}$  values of nitrate in precipitation downwind of areas dominated by power plants. Our model proposed that atmospheric nitrate derived from near-surface sources (e.g., vehicle and biogenic emissions) would obtain  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  signatures predominantly from near-surface  $\text{O}_2$  produced by photosynthesis (avg +23 ‰), whereas  $\text{NO}_x$  exiting power plant stacks would circulate higher into the atmosphere and obtain nitrate  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  signatures predominantly from tropospheric  $\text{O}_3$  (+95 ‰ and +35 ‰, respectively). We speculated that the source discrimination seen in  $\text{NO}_x$  emissions would be maintained in the atmospheric nitrate ultimately derived from it, despite potential isotopic fractionation during conversion to nitrate. Furthermore, because of the likelihood of temporal and spatial variation in the compositions of  $\text{NO}_x$  exiting individual combustion engines due to changes in temperature, fuel types, and other operating conditions, we suspected that source signatures would best be determined after the  $\text{NO}_x$  had been converted to nitrate. Hence, we proposed to determine source signatures primarily from statistical analysis of a large set of wet deposition samples, instead of using emission samples.

The most striking aspect of our data is the distinct but different spatial patterns shown by the  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ , and  $\Delta^{17}\text{O}$  values. We observe strong correlations between  $\delta^{15}\text{N}$  and power plant  $\text{NO}_x$  (Elliott et al., in press), suggesting this source is well mixed relative to vehicle emissions, which appear to be largely deposited near roadways. Several recent papers have developed models to explain seasonal nitrate isotopic variations in wet and dry deposition in localized areas. In general, these models explain the variations in terms of seasonality in oxidative reactions in the atmosphere, not source signatures. We will evaluate these models and our original conceptual model with our various large data sets, and present the current state of our understanding of the isotopic signatures of different sources and how they are established during combustion, transport, mixing, and atmospheric reactions during the conversion of  $\text{NO}_x$  emissions to nitrate in deposition.

### **REPRESENTATIVENESS OF ADIRONDACK LONG-TERM MONITORING LAKES AND RECOVERY FROM ACIDIFICATION**

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Seventy Adirondack lake watersheds, extrapolated to the regional population, were studied to assess changes in acid-base chemistry and biology in response to changes in acidic deposition. The effort involved field sampling to develop a statistically representative soils database, model projections using the MAGIC and PnET-BGC models to classify lakes according to their sensitivity to changes in atmospheric sulfur (S) and nitrogen (N) deposition, and evaluation of the extent to which Adirondack Long-Term Monitoring (ALTM) lakes are representative of the regional population.

Monitoring data indicate that lake water chemical recovery is ongoing in many lakes as acidic deposition levels decline. However, our modeling results suggested that, for many Adirondack lakes, chemical recovery might fail to continue in the future. We simulated that many low-acid neutralizing capacity (ANC) lakes would actually reacidify under emissions control regulations in place at the time of development of this modeling effort. This response was due to projected continued declines in mineral soil % BS within the lake watersheds. Continued chemical recovery of lake water was suggested, however, under more stringent emissions controls.

We developed empirical relationships between lakewater ANC and the species richness of zooplankton and fish, based on available data. These relationships were then applied to PnET-BGC model hindcast and forecast projections to generate estimates of the extent to which changes in species richness might accompany projected chemical changes. The median inferred loss of zooplankton species from 1850 to 1990 was two, with some lakes inferred to have lost up to six species.

Ignoring other factors that might influence habitat quality, we estimated that the median EPA Environmental Monitoring and Assessment Program (EMAP) study lake had lakewater acid-base chemistry consistent with the presence of five fish species in 1850, prior to the onset of regional acidic deposition. Twenty percent of the lake population was estimated to have pre-industrial lake water ANC consistent with supporting fewer than 4.1 fish species. By 1990, these median and 20th percentile values for estimated fish species richness had been reduced to 4.6 and 2.0 species, respectively. The 20% of the lakes that were most acid-sensitive were simulated to change ANC in the future to an extent consistent with a further loss of 1.3 fish species by 2100 under the Base Case Emissions scenario (reflecting regulations in place as of 2003), and a gain of 0.9 and 1.5 species under the Moderate and Aggressive Additional Emissions Control scenarios, respectively.

#### **EFFECTS OF ACID RAIN ON THE CHEMISTRY OF WESTERN ADIRONDACK STREAMS IN 2003-2005**

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Relatively little information is available on streams in the Adirondack region of New York, although they are more prone to acidification than the more studied lakes of this region. A chemical assessment of streams was therefore undertaken in the Oswegatchie and Black River drainages; an area of 4585 km<sup>2</sup> in the western part of the Adirondack region of New York. Acidification was assessed with the newly developed base-cation surplus (BCS) and acid-neutralizing capacity by Gran titration (ANC<sub>G</sub>). During the survey when stream water was most acidic (March 2004), 105 of 188 sampled streams (56 percent) were acidified based on the criterion of BCS < 0 µeq L<sup>-1</sup>, whereas 29 percent were acidified based on an ANC<sub>G</sub> value < 0 µeq L<sup>-1</sup>. During the survey when stream water was least acidic (August 2003), 15 of 129 streams (12 percent) were acidified based on the criterion of BCS < 0 µeq L<sup>-1</sup>, whereas 5 percent were acidified based on ANC<sub>G</sub> value < 0 µeq L<sup>-1</sup>. The contribution of acidic deposition to stream acidification was greater than that of natural acidity in each of the surveys by factors ranging from approximately 2 to 5 but was greatest during spring snowmelt and least during elevated base flow in August. During snowmelt, the percentage attributable to acidic deposition was highest, reaching 81%, whereas during the October 2003 survey, when dissolved organic carbon (DOC) concentrations were highest, this percentage was 66%. The total length of stream reaches estimated to be prone to acidification within the study area was 718 km, although a remaining 3085 km were not assessed because of inaccessibility.

## ASSESSMENT OF NITROGEN AND ACIDIC DEPOSITION IMPACTS TO TERRESTRIAL AND AQUATIC ECOSYSTEMS OF TUG HILL

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The Tug Hill region of New York encompasses ~291,000 ha and is the third largest, intact forested landscape in the state. The region contains 6400 km of streams, supports world-class fisheries, serves as a drinking water supply for several municipalities and sustains an \$80-million wood products and paper manufacturing industry. Atmospheric nitrogen (N) and acid deposition rates on the Tug Hill are consistently among the highest in the eastern United States and, compared to other regions of New York that are impacted by atmospheric deposition, the Tug Hill receives the highest long-term (1980-2002) average annual deposition rates for total inorganic N,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$ . Therefore, great potential exists for the Tug Hill to display symptoms of N saturation and acidification. Our research objective was to conduct the first region-wide assessment of N and acid deposition to the aquatic and terrestrial systems of the Tug Hill. At 57 randomly selected first-order streams we collected water samples during spring snowmelt events in 2005-2007, and during summer baseflow periods of 2005 and 2006. Soils and foliage of canopy dominant trees were collected at upland sites immediately adjacent to stream sampling locations. Foliar N content, foliar N:Mg and Ca:Al ratios, and forest floor C:N ratios for the region were beyond empirical thresholds established by high chronic N dosing experiments in New England. Ninety-four percent of streams exhibited seasonal high  $\text{NO}_3^-$  concentrations during spring snowmelt periods, and 20% of streams exhibited high summertime  $\text{NO}_3^-$  concentrations ( $>20 \mu\text{eq/L}$ ). Average stream pH is 7.2 during summer baseflow and 6.4 during spring snowmelt events. All streams exhibited total alkalinity  $<100 \text{ mg CaCO}_3/\text{L}$ , and 3-7% of streams were acidified during spring snowmelt events. Our data indicate that the region's forests may be entering early stages of N-saturation and its surface waters are sensitive to future acidification.

### BIOGEOCHEMISTRY AND HYDROLOGY OF AN ADIRONDACK WATERSHED: A COMPARATIVE APPROACH

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The current study examined the role of sampling interval (weekly versus monthly) on the chemistry of a long-term monitoring site that is part of two independent Adirondack programs evaluating lake/watershed responses. The Arbutus Lake watershed is the site of intensive investigations on the effects of atmospheric pollutants and climate change on watershed processes conducted by the Biogeochemical Laboratory at State University of New York College of Environmental Science and Forestry (SUNY-ESF). Arbutus Lake outlet is also monitored as part of the Adirondack Long Term Monitoring (ALTM) program of 52 lakes conducted by the Adirondack Lakes Survey Corporation (ALSC). Two independent chemistry datasets were evaluated with one set of lake discharge measurements from 1 January 1995 through 31 December 2002. Solute concentrations at the Arbutus lake outlet measured by SUNY ESF weekly measurements and ALTM monthly measurements had the greatest percentage differences for mean solute concentrations for  $\text{H}^+$  (15%),  $\text{NH}_4^+$  (7%),  $\text{NO}_3^-$  (6%) and total Al (6%) with all other solutes showing mean differences of  $<3\%$ . Total Al and  $\text{NH}_4^+$  concentrations were near their respective detection limits. Average monthly solute fluxes calculated for ALTM and SUNY-ESF chemistry measurements were similar, but varied for maxima and minima values. The most notable differences occurred from January and May (with the exception of February) corresponding to those months with the highest discharge. Annual discharge weighted concentrations from the two data sets were generally strongly correlated ( $r>0.85$ ) for most solutes with the weakest correlations ( $r<0.80$ ) for  $\text{H}^+$ ,  $\text{K}^+$ , and  $\text{NO}_3^-$ . Because climate change will have a marked influence on both the amount and timing of flows across watersheds in the Northeastern US future sampling strategies in the Adirondack region need to accommodate these expected changes. These results confirm, however, that monthly sampling is adequate for examining long-term effects on the chemistry of Adirondack lakes associated with changes in atmospheric inputs. This comparison demonstrates how an intensive study site within a regional monitoring response program compliments the coarser temporal records and how a single lake type responds within the greater regional context.

## REAL-TIME ACCESS OF REMOTE DATA IN THE ADIRONDACK MOUNTAINS

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The Arbutus Watershed at the Huntington Forest has been the focal point for analyzing the effects of atmospheric pollutants and climate change in the Adirondack Mountains of New York. Atmospheric deposition measurements and biogeochemical responses have been continuously measured for over two decades. The Biogeochemistry Group at SUNY-ESF has been continuously collecting data hydrological and biogeochemical data from the inlet and outlet of Arbutus Lake. Data collection has been time and labor intensive, requiring site visits by HWF personnel in order to download the data. Data were then emailed to SUNY-ESF as attached files. Any programming or site configuration modifications also require site visits from qualified technicians at SUNY-ESF, traveling about 175 miles to the site. These conditions have also limited the number of study sites we can maintain.

In 2005, we were awarded a National Science Foundation, Major Research Instrumentation grant to instrument additional study sites, as well as a wireless radio network. In addition to continuous measurements at the Arbutus Lake inlet and outlet, we have added a meteorological tower, two upper watershed stream gauges and five groundwater wells to the monitoring network. The increase in study sites, coupled with near real-time data from the wireless network now allows a more sensitive and comprehensive examination of critical environmental parameters within a forested Adirondack watershed in response to atmospheric deposition and climate change. Both archived data and realtime data are available at the following web site:

<http://www.esf.edu/hss/huntington/index.htm>

This system is also designed to allow for additional watershed measurements to be incorporated into the network. These results are also being integrated into other measurements taking place at the Huntington Forest including those from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN), Clean Air Status and Trends Network (CASTNET) and the Mercury Deposition Network (MDN). The information is also being made available for undergraduate and graduate instruction as well as outreach programs.

## EVALUATING CHANGES IN WATER QUALITY IN ADIRONDACK LAKES FROM ADIRONDACK LONG-TERM MONITORING (ALTM) PROGRAM

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Long-term changes in the chemistry of wet deposition and lake water were investigated in the Adirondack region. Marked decreases in concentrations of  $\text{SO}_4^{2-}$  and  $\text{H}^+$  have occurred in wet deposition since the late 1970s. These decreases are consistent with long-term declines in emissions of  $\text{SO}_2$  in the eastern US. Changes in wet  $\text{NO}_3^-$  deposition and  $\text{NO}_x$  emissions have been minor over the same interval. Virtually all Adirondack lakes have exhibited large decreases in concentrations of  $\text{SO}_4^{2-}$ , which coincide with decrease in atmospheric S deposition. Since 1992, concentrations of  $\text{NO}_3^-$  have also decreased in many (27 of 48) Adirondack lakes. As atmospheric N deposition has not changed appreciably over this period (1992-2004), the mechanism contributing to this apparent increase in lake/watershed N retention is not evident. Decrease in concentrations of  $\text{SO}_4^{2-} + \text{NO}_3^-$  have resulted in increases in acid neutralizing capacity (ANC; 37 of 48 lakes), and decreases in concentrations of inorganic monomeric Al, particularly in acid sensitive lakes. Concentrations of dissolved organic C (DOC) have also increased in some (15 of 48) lakes coinciding with decreases in acid deposition. Examination of changes in lake chemistry by hydrologic classes showed that drainage lakes in watersheds with thin deposits of glacial till and mounded seepage lakes have generally been the most responsive to decreases in acidic deposition.

Fish populations from 45 Adirondack Long Term Monitoring (ALTM) lakes were resurveyed during 1994-2005 following the 1984-1987 Adirondack Lakes Survey (ALS) methods. The mean number of fish populations in each lake was 3.27 in the ALS survey and 3.91 in the ALTM resurvey. There have been improvements in the intervening 14 years between surveys, but results have been mixed and moderate.

Additional components of the ALTM program include: bi-weekly and event-based chemistry monitoring of Buck Creek and its tributaries; weekly snowmelt monitoring at twelve ALTM lake outlets; hydrologic gaging at select ALTM lake outlets; an investigation of eight original ALTM sampling points data records with up-stream lake sampling data records; and a comparative evaluation of chemistry and discharge from two independent sampling programs at Arbutus Lake outlet.

### **UNEXPECTED RESPONSES OF AN OAK FOREST TO NITROGEN AMENDMENT**

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Institute of Ecosystem Studies

Excess nitrogen deposition can have multiple effects on forests, including alteration of growth, nutrition and carbon allocation by trees and increased leaching of nitrate through the ecosystem. Nitrate leaching can cause depletion of base cations in the soil such as calcium (Ca), magnesium, potassium, and sodium and lead to soil acidification and increased aluminum (Al) concentration and mobility. Experimental addition of nitrogen (N) to an upland oak-hickory forest near Millbrook, New York has revealed several unexpected results. First, nitrate leaching began to increase within a year after the start of N fertilization, before there was evidence of increased nitrification. Control plots showed little N leaching. Second, the fertilized plots experienced significant tree mortality, especially after two summers of moderate drought. The mortality appears to be associated with soil acidification. Third, surviving trees in the fertilized plots had higher relative growth rates than those in the control plots, indicating that the fertilization and N saturation effects of excess N deposition can occur simultaneously in the same forest stand.

### **MINERAL SOURCES OF CALCIUM AND PHOSPHORUS IN SOILS OF THE NORTHEASTERN USA**

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State University of New York, College of Environmental Science and Forestry

Apatite is ubiquitous in igneous, metamorphic and sedimentary rocks although often present only in trace amounts. Apatite is a primary source of P and, due to its relatively rapid dissolution rate, can be an important Ca source in non-carbonate soils. We investigated the distribution of apatite in glacial-till soils across the northeastern USA derived from different rock types: crystalline silicate, clastic sedimentary and carbonate bedrock. Soils were extracted with 1M HNO<sub>3</sub> to quantify the amount of easily weathered minerals such as apatite and calcite. Soils underlain by crystalline silicate and clastic sedimentary rocks contained 1M HNO<sub>3</sub>-extractable Ca (0.05-41 mmol/g soil) and P (0.05-27 mmol/g soil); at most of these sites, the P:Ca ratio was 3:5 indicating the dominance of apatite. Soils underlain by carbonate rocks had P concentrations (3-17 mmol/g soil) similar to the latter groups suggesting similar concentrations of apatite. Not surprisingly, these sites had large concentrations of easily weathered Ca (50-1950 mmol/g soil) indicating the extraction of carbonates. We also examined exchangeable Ca in surface soil horizons as a function of local bedrock. Exchangeable Ca concentrations in soils underlain by carbonate bedrock were an order of magnitude higher than in soils underlain by crystalline silicate and clastic sedimentary rocks. Furthermore, the exchangeable Ca concentration in the upper soil was correlated to the concentration of 1M HNO<sub>3</sub>-extractable Ca in the underlying soil parent material. These results suggest that, to a first order, bedrock controls the spatial distribution of apatite and carbonate in the glacial till in the northeastern USA, as well as the concentration of exchangeable Ca in overlying horizons.

### **THE INFLUENCE OF CALCIUM ADDITION UPON FOREST FLOOR AND MINERAL SOIL HORIZONS IN A WATERSHED IMPACTED BY ACIDIC DEPOSITION**

Youngil Cho, Civil Engineering, Syracuse University

A mitigation technique for acidification in watershed 1 (WS-1: 11.8 ha) of the Hubbard Brook Experimental Forest (HBEF) in New Hampshire (NH), USA was applied in October of 1999 by the addition of calcium silicate mineral (CaSiO<sub>3</sub>), wollastonite. In the summer of 1996, 1998, 2000, and 2002, soil samples from Oie, Oa, and mineral horizons were collected in a treated watershed to evaluate the effects of the wollastonite treatment on the soil chemistry. Exchangeable Ca<sup>2+</sup> (Exch. Ca<sup>2+</sup>), cation exchange capacity (CEC<sub>e</sub>), base saturation (BS<sub>e</sub>), pH<sub>s</sub> increased, and exchangeable acidity (EA<sub>pH8.2</sub>) decreased in forest soil horizons after the manipulation due to the increased Ca<sup>2+</sup> concentration associated with the dissolution of added wollastonite. There were either little increases in Exch. Ca<sup>2+</sup>,

CEC<sub>e</sub>, BS<sub>e</sub>, and pH<sub>s</sub> and decreases in EA<sub>pH8.2</sub> or no changes in mineral horizons. The experimental addition of wollastonite on soil in WS-1 decreased the magnitude of changes in soil chemistry with decreasing soil depth. There were a north-south pattern (an elevational pattern), since higher elevations (north areas) have shallow soil depth and are more susceptible to the deposition of strong acid anions (before the treatment) or calcium added (after the treatment).

### **COMPARISON OF CLOUD AND RAIN CHEMISTRY OBSERVATIONS AT WHITEFACE MOUNTAIN**

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High terrain or mountain locations are often affected by deposition arising from both non-precipitating and precipitating clouds. One such station is the summit of Whiteface Mountain, NY (elevation 1497 m) where sampling of non-precipitating cloud water in summer season has been on-going along with the precipitation measurements at a nearby lower elevation (599 m). In this study we examined the trends and relationships based on a decade-long (1996 to 2006) record of ion chemistry at these two locations, and evaluated the potential linkage in estimated deposition between them.

We find that both rain and cloud water has four dominant ions: sulfate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), hydrogen (H<sup>+</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>). On the seasonal level, major ions have the same relative contributions in both rain and cloudwater. However, concentrations are considerably higher in the cloud samples than in rain. Because of this, and the large frequency of cloud occurrence at the summit during the summer season, deposition from non-precipitating clouds is much higher than that occurring from precipitation. This observation appears to be in concert with the preliminary result that high elevation lakes in the Adirondack region, those which occur above 600 m, exhibit higher sulfate and nitrate levels than those at lower elevations.

An assessment of linear trends in the deposition ions generally indicates downward trends. However, inter-annual oscillations are sizable and application of Sen's trend test did not demonstrate significance of these downward trends.

Further analysis of these data is on-going to understand effects of ion concentration deposition on high terrain landscapes between non-precipitating and precipitating clouds.

### **REGIONAL FOREST HEALTH AND STREAM AND SOIL CHEMISTRY USING A MULTI-SCALE APPROACH AND NEW METHODS OF REMOTE SENSING INTERPRETATION, CATSKILL MOUNTAINS, NY**

Richard Hallett, USDA Forest Service, Northern Research Station, Durham, NH

Collaboration between the US Geological Survey and the US Forest Service will link field and remote sensing data to produce the most detailed maps to date of forest, soil, and surface-water condition. The resulting GIS database will highlight forest stands and watersheds sensitive to changes in atmospheric deposition and logging in the Catskill Mountain region. During this collaboration, we will further develop existing remote-sensing methods for forest condition mapping that will make it possible to assess regional changes in forest health (foliar calcium and nitrogen, and tree decline) at a fine scale across the landscape. The result will be an integrated picture of landscape sensitivity to disturbance, as well as the spatial variability in potential forest and surface water response to decreased or increased levels of acidic deposition. Data products derived from state-of-the-art hyperspectral imagery will be validated by regional surveys of foliar, soil, and stream chemistry, and the combined datasets used to map areas most susceptible to calcium depletion due to nitrogen (N) and sulfur (S) deposition and harvesting in the watersheds of the New York City water supply. The methods proposed follow the Federal Collaborative Environmental Monitoring and Research Initiative (CEMRI), in which data from intensive research areas, regional surveys, regional gradient studies, and remote sensing instruments are systematically integrated to generate a comprehensive research and monitoring strategy.

**THE ADIRONDACK EFFECTS ASSESSMENT PROGRAM: LAKE WATER CHEMISTRY  
COMPARISONS BETWEEN 1994 AND 2006**

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<sup>2</sup>NYS Department of Environmental Conservation

<sup>3</sup>Department of Natural Resource Sciences and LA., University of Maryland

<sup>4</sup>US Geological Survey

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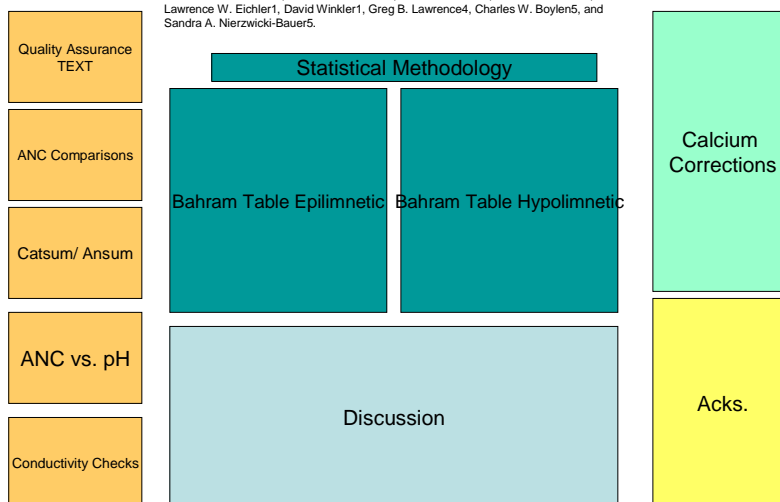
The Adirondack Effects Assessment Program (AEAP) was established with funding from the US EPA to conduct a synoptic chemical and biological sampling program on 30 lakes and ponds in the Adirondacks. These were selected to represent hydrologic categories that 1) are the most impacted by acidification and 2) may be most likely to demonstrate the effects of recovery. These waters are a subset of those included in the Adirondack Lakes Survey Corporation's Long-Term Monitoring (LTM) program of water chemistry. Data presented here include results from 30 AEAP lakes monitored from 1994 through 2006 reveals distinct trends. Results include comparisons of 2006 and 1994 values, for both epilimnetic and hypolimnetic samplings, along with statistical verification of significant changes and associated yearly rate changes. In addition, results of quality assurance tests are provided along specific analyte trends for a single case study lake, Brooktrout Lake.

Comparison results revealed that the majority of lakes showed increases in pH, ANC, and Sodium, and decreases in Sulfate, Nitrate, dissolved organic carbon, labile monomeric Aluminum, Calcium, Magnesium, Chloride and Potassium. For epilimnetic samples, pH increased in 26 of the 30 surveyed lakes, with 17 of these lakes showing significant yearly increases. 19 lakes showed increased ANC with 13 of these being significant. Sulfate decreased in all 30 lakes with 22 lakes showing significant declines. Nitrate decreased in all but 1 lake, with 20 lakes revealing significant decreases. Labile monomeric Aluminum values decreased in 20 study lakes, with 8 showing significant reductions. With respect to base cations, all lakes showed decreased levels of magnesium, with 14 lakes reporting significant yearly decreases. 28 lakes showed decreased levels of Calcium, with 8 showing significant yearly decrease rates. Sodium increased in 28 lakes, and Potassium decreased in 22 lakes, but neither revealed a high percentage of significant change.

Hypolimnetic sample comparisons revealed overall trends similar to those found for epilimnetic samples. However, some differences included a lower percentage of lakes showing decreases in Calcium (65%) and Magnesium (83%), a higher percentage of lakes showing a decrease in labile monomeric Aluminum (96%), and a higher number of lakes showing an increase in ANC (80%).

**THE ADIRONDACK EFFECTS ASSESSMENT PROGRAM: LAKE WATER CHEMISTRY  
COMPARISONS BETWEEN 1994 AND 2006.**

James W. Sutherland<sup>2</sup>, James P. Harrison<sup>1</sup>, Bahram Momen<sup>3</sup>, Robert Bombard<sup>1</sup>, Lawrence W. Eichler<sup>1</sup>, David Winkler<sup>1</sup>, Greg B. Lawrence<sup>4</sup>, Charles W. Boylen<sup>5</sup>, and Sandra A. Nierzwicki-Bauer<sup>5</sup>.



## AMPHIBIAN COMMUNITIES OF BROOKTROUT LAKE, A “RECOVERING” ACIDIFIED LAKE IN THE ADIRONDACKS

Kolozsvary, Mary Beth. NYS Biodiversity Research Institute, New York State Museum

Brooktrout Lake is a high elevation, clear water lake located in the southwestern Adirondack mountains, which underwent an extended period of increased acidification during the latter half of the last century. Over the last decade, long term monitoring of water chemistry indicated signs of recovery from acidified conditions. In 2005 - 2007, amphibian communities were sampled using minnow traps, activity traps, and dip net sweeps to assess amphibian species composition, relative abundance, and reproductive success. Seven amphibian species were documented at the site, with 6 of these species showing successful reproduction. The most abundant amphibians at the site were eastern newts (*Notophthalmus viridescens*) and green frogs (*Rana clamitans*). In November 2005, brook trout (*Salvelinus fontinalis*) were stocked into the fishless lake (which contained brook trout prior to acidification). Subsequent to the restocking, stomach contents of eastern newts and brook trout have been sampled to determine degree of dietary overlap and to monitor any changes in relation to the fish introduction. Activity traps are also being used to monitor invertebrate community changes over time, in response to changes in water chemistry and biological communities, including brook trout populations.

## ATMOSPHERIC DEPOSITION AND STREAM WATER MONITORING IN BISCUIT BROOK WATERSHED, CATSKILL MOUNTAINS, N.Y.

Michael R. McHale, Benjamin Snyder  
U.S. Geological Survey

The Biscuit Brook watershed has been a focus of environmental research in the Catskill Mountains for nearly 25 years. Streamflow monitoring and stream water-quality sampling began in 1983 at Biscuit Brook and during that same year a National Trends Network (NTN) station was established to monitor atmospheric deposition. Since then data from Biscuit Brook have been used to measure stream chemical and biological responses to decreased acid deposition in the Catskills. Atmospheric deposition is measured every week at Biscuit Brook while stream water-quality samples are collected bi-weekly and during storms. This detailed record of streamflow, stream water-quality, and atmospheric deposition has been used in over 40 scientific journal articles from Biscuit Brook and the Neversink River basin to which Biscuit Brook contributes.

In 2004 Biscuit Brook was added to the nationwide Mercury Deposition Network (MDN) when an MDN collector was co-located with the existing NTN collector thanks to funding provided by the New York State Energy Research and Development Authority (NYSERDA). NYSERDA has continued to fund the Biscuit Brook MDN gage through 2007 and as a result the Neversink River basin has become a focus of mercury research in the Catskill Mountains. The BioDiversity Research Institute, the New York State Department of Environmental Conservation (NYS-DEC), and the U.S. Geological Survey have all conducted Hg research within the Neversink River basin. The long record of water-quality and atmospheric deposition data and the support of NYSERDA promise to keep Biscuit Brook a focus of environmental research in the Catskills for years to come.

## RECOVERY OF AN ACID LAKE, BROOKTROUT LAKE. III. BIOLOGICAL AND CHEMICAL INTERACTIONS

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C. W. Boylen<sup>3</sup> and S. A. Nierzwicki-Bauer<sup>3</sup>

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<sup>3</sup>Darrin Freshwater Institute

Brooktrout Lake is a deep (max. depth, 24 m), moderate sized (30 ha.) high elevation (722 m) lake in the southwest quadrant of the Adirondack Park, New York State. The lake was characterized since the 1970's as a typical clear-water acid lake but has demonstrated a remarkable recovery from acidification following the implementation of the 1990 Clean Air Act Amendments. The rapid recovery, chemical and biological, was not predicted by most models because they did not consider biological interactions as a mechanism in chemical recovery. Biological interactions appear to be key processes accelerating acidification recovery.

Brooktrout Lake secchi disk transparency decreased while chlorophyll concentrations increased over the study period. Prior to 1996 the lowest transparency recorded during open water seasons was 6.8 m in July of 1987 – all

other measurements were greater than 7 m. After 1996 it was unusual to see transparencies greater than 5 m. Chlorophyll concentrations were generally less than 1 ug/l until 1997 and have been above 2 - 4 ug/l on almost all dates since 1997. The annual pattern of transparency in 1987 was marked by lowest values in the spring, steadily increasing throughout the summer, reaching a maximum of 13 m in September. Transparency was generally between 4 m and 6 m throughout 2005 and 2006, reaching maximums of 6.2 m in July 2005, and 7.25 m in August 2006. Transparency was somewhat higher in 2007.

Brooktrout Lake waters were very clear in the 1980's – true color did not exceed 4 Pt/Co. Color increased throughout the study period and was generally greater than 16 Pt/Co after 2000. Dissolved organic carbon also increased significantly over the study period, the increase averaging about 6 umol./l/yr. DOC concentrations were generally less than 150 umol./l in 1993 through 1997 except for brief late winter-spring spikes in concentration. A second annual spike in DOC concentration was evident from 1998 through 2003. In addition to the late winter-spring peak there was also a late summer increase which was generally of the same magnitude as the initial peak.

Total phosphorus concentrations did not exhibit significant trends over the course of the study yet chlorophyll levels increased significantly. The higher chlorophyll per unit phosphorus, i.e., greater productivity, suggests nutrient enrichment in Brooktrout Lake. Increased productivity dramatically changed the dynamics of nitrogen. Nitrate concentrations were high throughout the year prior to 1998 but were below detection levels for much of the growing season in the years subsequent to 1998. The decrease to levels below detection is the result of biological uptake which spurred greater productivity. The uptake of nitrates also accelerated the chemical recovery of the lake by removing acid ions. The increased productivity was responsible for pH increases of about 0.5 pH units.

#### **RESPONSE OF PHYTOPLANKTON ASSEMBLAGES TO DECREASING ACIDIC DEPOSITION IN ADIRONDACK MOUNTAIN LAKES**

Don F. Charles<sup>1</sup>, Frank A. Acker<sup>1</sup>, Paul A. Bukaveckas<sup>2</sup>, William H. Shaw<sup>3</sup>,  
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We analyzed changes in phytoplankton assemblages in 30 lakes in the southwestern Adirondack Park from 1994 through 2006. This research is part of the Adirondack Effects Assessment Program (AEAP), a multi-disciplinary study assessing biological recovery from acidification. At the start of the monitoring program, the lakes ranged in pH from 4.5 to 7.1; 13 lakes had pH < 5.2. Integrated samples of the epilimnion were collected two times each summer (late June – early September). The Utermöhl settling chamber technique was used to determine species composition and abundance (cell and biovolume densities). The strongest relationship was an increase in number of algae species with increasing pH. Indicator metrics based on this relationship were the most sensitive phytoplankton indicators found for indicating change in acidity status. There are no clear trends towards increasing number of taxa, or other assemblage changes, that would indicate other than weak biological recovery from acidification during the study period. There have been, however, some marked inter-annual changes in species composition in several lakes. As in other studies of acidic lakes, dinoflagellates and coccoid cyanobacteria were abundant in lakes with pH < 5.2; chlorophytes and chrysophytes were more common at higher pH values.

#### **SUBMERSED MACROPHYTE COMMUNITIES OF ADIRONDACK LAKES: RELATIONSHIPS BETWEEN COMMUNITY STRUCTURE AND pH**

Lawrence W. Eichler and Charles W. Boylen

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Aquatic plant communities play a major role in the structure of lake habitats and ecosystems. As part of the Adirondack Effects Assessment Program, submersed aquatic plant communities in a diversity of lake types are being evaluated. In addition to their position as primary producers where they serve as the base of numerous aquatic food chains, aquatic plants provide habitat for algae and zooplankton, invertebrates and numerous fish species. A total of 763 macrophyte specimens including 64 species have been identified and archived from 31 lakes as part of the database for the AEAP. The lakes range in pH from 4.71 to 7.80. The lakes surveyed contained an average of

14.3 ( $\pm 1.3$ ) species per lake, which is comparable to low elevation, moderately productive lakes in New York State (15 species). Drainage lakes produced a substantially greater number of species per lake ( $15.5 \pm 1.5$ ) than seepage lakes ( $6.5 \pm 1.8$ ). In general, aquatic plants were distributed from the lakeshore (emergent species) to a maximum depth of about 7 meters. In several lakes, specimens of the bladderwort, *Utricularia purpurea*, were found as deep as 12 meters. Deep-water range extension is commonly observed in weakly rooted species such as the bladderworts; however, these specimens rarely survive to the next growing season. Aquatic plant species range from highly tolerant species, which are present over a wide range of pH, to species which are distinctly circumneutral or acidophilic. Overall, lakes having decreased pH will have a characteristic littoral zone where aquatic plant species are represented largely by nymphaeids, isoetids, *Sphagnum* spp., and *Utricularia* spp. Lakes with less acid pH levels typically support larger pondweeds (*Potamogeton* spp.) with greater habitat complexity and species richness. Aquatic plant community structure in Adirondack lakes has important implications for recovery assessment, given their importance in structuring littoral zones and their associated communities.

## **ACIDIFICATION EFFECTS AND RECOVERY OF ZOOPLANKTON IN SELECTED ADIRONDACK LAKES**

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James W. Sutherland, NYSDEC, Senior Scientist - Retired  
Charles W. Boylen, Darrin Freshwater Institute, Associate Director  
Sandra A. Nierzwicki-Bauer, Darrin Freshwater Institute, Director

Microcrustaceans and rotifers were examined from 30 Adirondack lakes 1994-2006 as part of the Adirondack Effects Assessment Project to generate baseline data by which to measure biotic recovery should pH rise, which was expected from the Clean Air Act and Amendments. The 28 species of microcrustaceans and 53 species of rotifers displayed differential sensitivity to acidic conditions and showed direct correlations of species richness, diversity and evenness with pH that was readily apparent during 1994-1996, the most acidic period during the study. Biotic recovery is expected to follow chemical recovery at some point in time. Since there was considerable variation in pH between collections and collection years, pH change was evaluated by comparing the average pH of lakes from the first 3 years (1994-1996) and the last 3 years (2004-2006). Only 10 lakes have shown  $> \text{pH } 0.4$  units rise during the 13 years of study and only 5 lakes exceeded pH 6.0, a critical level where community changes are believed to have already begun. Acid sensitive species were identified by detrended correspondence analysis and by the lowest pH of occurrence in the 30 lakes. Changes in densities of acid sensitive species and species richness was used to evaluate biotic recovery in lakes displaying pH improvement. Regression analysis revealed only minor changes in species number or density relative to pH or elapsed time in only 4 of the 10 lakes for microcrustaceans and 4 different lakes for rotifers. It appears that very little chemical or biotic recovery has occurred in these lakes to date. Furthermore, there is evidence that the trajectory of chemical improvement may have stalled during the last 3 years. The average summer pH of all 30 study lakes was the lowest in 2004 and 2006 since 2000 and 6 of the 10 lakes showing pH improvement lost an average 0.23 pH units since 2003. Since it is important to know if the trajectory of improvement has changed, continued monitoring of these lakes is of critical.

## **RECOVERY OF AN ACID LAKE, BROOKTROUT LAKE**

### **I. CHEMICAL RECOVERY**

Quinn, Scott O.<sup>1</sup>, J. A. Bloomfield<sup>1</sup>, C. A. Siegfried<sup>2</sup>, R. Bombard<sup>1</sup>, K. Roy<sup>1</sup>,  
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<sup>1</sup>New York State Department of Environmental Conservation, <sup>2</sup>New York State Museum

<sup>3</sup>Darrin Freshwater Institute

Brooktrout Lake is a deep (max. depth, 24 m), moderate sized (30 ha.) high elevation (722 m) lake in the southwest quadrant of the Adirondack Park, New York State. The lake was characterized since the 1970's as a typical clear-water acid lake but has demonstrated a remarkable recovery from acidification following the implementation of the 1990 Clean Air Act Amendments. Sulfate concentrations have declined steadily during the period of record, from 120 - 140 uequiv./l in the 1980's to less than 80 uequiv./l by 2004, a decrease of nearly 3 uequiv./l per year. Nitrate concentrations have also declined by a third, from an average of about 15 - 20 uequiv./l to less than 10 uequiv./l; a decrease of about 0.4 uequiv./l per year. Nitrate concentrations exhibited a dramatic spring peak during snowmelt (usually March - April) but then declined to seasonal lows during mid-summer to early fall (August - November). Prior to 1996 nitrate seasonal minimum concentrations occurred between December and May and were about 20 uequiv./l. From 1998 through 2003 the seasonal lows occurred between June and November and were less than 1

equiv./l. . ANC and pH have risen with the declines in sulfate and nitrate. Mean annual pH increased from less than 5.00 in the 1980's to a mean of 6.12 in 2000. Until late 1996, pH did not exceed 5.5 on any sample date, but after 1997 pH was below 5.5 only during periods of snowmelt. ANC was generally negative throughout the year until 1996. From 1996 through 1998 ANC was negative through April each year but positive for the remainder of each year. Since 1998 ANC has remained positive except for a few periods of snowmelt, peaking at an annual mean of 13.3 in 1999.

The concentration of base cations also decreased but at a much slower rate than sulfate, 1.88 uequiv./l per year over the study interval, and also exhibit steep declines during periods of intense runoff. The relative composition of the cation pool was marked by decreased importance of hydrogen accompanying the increase in pH. Anion composition was marked by decreases in the importance of nitrate to the anion pool and increases in DOC and bicarbonate anions.

Total monomeric aluminum concentrations averaged about 9 umol./l in the early 1990's but declined by more than 50% by the 2000's, an annual rate of about 0.4 umol./l per year. Spring peaks exceeding 8-10 umol./l were evident for most years of record. Mean total monomeric aluminum concentration has not exceeded 4.0 since 1997.

## **RECOVERY OF AN ACID LAKE, BROOKTROUT LAKE II. BIOLOGICAL RECOVERY**

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<sup>1</sup>New York State Department of Environmental Conservation, <sup>2</sup>New York State Museum  
<sup>3</sup>Darrin Freshwater Institute

Brooktrout Lake is a deep (max. depth, 24 m), moderate sized (30 ha.) high elevation (722 m) lake in the southwest quadrant of the Adirondack Park, New York State. The lake was characterized since the 1970's as a typical clear-water acid lake but has demonstrated a remarkable recovery from acidification following the implementation of the 1990 Clean Air Act Amendments. Chemical recovery has been dramatic but the rapid biological recovery was unexpected. The biology of Brooktrout Lake was studied intensively in 1987 and 1988, making Brooktrout Lake one of the few lakes with extensive biological data prior to the implementation of the 1990 Clear Air Act Amendments.

The biological communities of Brooktrout Lake in the 1980's were typical of those of clear water acid lakes. The plankton communities were characterized by low species richness and diversity and the dominant predator was the phantom midge. Fish had not been present in the lake since the mid-1970's. The benthos community was also characterized by low diversity and species richness. The AEAP monitoring program documented increasing plankton species richness through the 1990's and into the 21<sup>st</sup> century. The most dramatic biological change was the increase in productivity – reflected in decreasing transparency and increased chlorophyll concentrations. More intensive study of the plankton communities (2005-2007) confirms greater diversity and greater productivity. However, comparisons to data sets for another clear water acid lake suggests that the productivity change may be within the range of normal inter-annual variability. Consistently higher diversity and productivity support the conclusion that biological recovery is occurring. Recovery is further suggested by the presence of mayflies, amphipods and fingernail clams in the littoral benthos – all of which were absent in the 1980's.

Brook trout were re-introduced to the lake in 2005, and additional stocking has taken place in 2006 and 2007. The fish have survived and growth has been typical of heritage strains in the Adirondacks. The diet of Brook trout is largely phantom midges. We are continuing to monitor the communities of the lake to document recovery and the impacts of the re-introduction.

## **INVESTIGATING INTERACTIONS BETWEEN CARBON, NITROGEN, AND CALCIUM CYCLES IN THE WOODS LAKE WATERSHED, ADIRONDACK PARK**

April Melvin and Christine Goodale  
Department of Ecology & Evolutionary Biology, Cornell University

We are investigating long-term changes in C, N, and Ca cycling following an experimental Ca addition in the Woods Lake Watershed, Adirondack Park, NY. In 1989, calcium carbonate (lime) was added to half of this

watershed to assess whether forest liming could be an effective strategy to reduce acidification of surface waters. Now, nearly 20 years later, the Woods Lake experiment provides a unique opportunity to study the long-term effects of increased Ca on forest health, as well as C and N pools and fluxes. We are currently quantifying stocks of C, N, and Ca in the soils and vegetation within control and Ca-amended plots. In addition, we are studying processes which may influence soil C and N stocks, including rates of leaf litter input and decomposition, Ca-organic matter binding, and gross N mineralization and nitrification rates. Preliminary results suggest that the forest floor mass in limed plots is greater than that in the controls.

#### **SEASONAL VARIATION IN NITROGEN RETENTION PROCESSES IN A COUPLED TERRESTRIAL-AQUATIC ECOSYSTEM: A TRACER EXPERIMENT**

Christine Goodale<sup>1</sup>, Jed P. Sparks<sup>1</sup>, Guinn Fredriksen, Steven A. Thomas<sup>2</sup>

<sup>1</sup>Department of Ecology & Evolutionary Biology, Cornell University

<sup>2</sup>School of Natural Resources, University of Nebraska

This project follows the fate of NO<sub>3</sub><sup>-</sup> entering in Upper Susquehanna forests in different seasons through a field study of coupled terrestrial and aquatic N retention. Pulse applications of 15N-NO<sub>3</sub><sup>-</sup> were applied as simulated throughfall in late April (post snowmelt, pre-leafout), late July (mid growing-season), and late October (end of leaf fall), to allow comparison of N retention processes. The fate of these tracer additions is being followed as losses of N gases, assimilate into upland forest ecosystem pools (roots, foliage, wood, soil), down through the soil profile, through the near-stream zone, and into and down the stream reach. The experiment integrates terrestrial and aquatic perspectives and will assess the relative contribution of watershed subsystems in N retention, providing a far more comprehensive understanding of the fate and control on N retention in northeastern forests than exists to date.

#### **EXPECTED CHANGES IN DEPOSITION OF SULFUR AND NITROGEN OVER NEW YORK STATE FOLLOWING CLEAN AIR INTERSTATE RULE (CAIR)**

Kevin Civerolo, Christian Hogrefe, Mike Ku, Winston Hao, Eric Zalewsky, and Gopal Sistla  
New York State Department of Environmental Conservation, Division of Air Resources

As part of its obligations to the state implementation process for ozone, fine particulate matter, and regional haze, the New York State Department of Environmental Conservation participated in modeling exercises of baseline and future years using the Community Multiscale Air Quality (CMAQ) modeling system. The baseline year simulation incorporated the best available emissions information for 2002, whereas the simulations for future years through 2018 used projections that accounted for emissions decreases resulting from Clean Air Interstate Rule (CAIR) legislation and other planned reduction programs. While reductions in emissions of SO<sub>2</sub> and NO<sub>x</sub> are needed for improvement in O<sub>3</sub>, PM<sub>2.5</sub>, and visibility, they would also have benefits in terms of sulfur and nitrogen deposition to important ecosystems such as the Adirondack and Catskill regions and the Long Island Sound estuary. In this study, we compare the model predictions of wet and dry deposition of sulfur and nitrogen in the baseline and future years. These results provide useful information to address a variety of issues such as critical loads and water quality that affect New York, and aid in the development of total maximum daily loading (TMDLs).

#### **ORGANIC CONTAMINANT SOURCES TO THE LOWER HUDSON BASIN**

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<sup>1</sup>Lamont-Doherty Earth Observatory of Columbia University

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<sup>3</sup>Pratt Institute – Dept of Math and Science

Fine-grained sediment samples were collected from the Lower Hudson River basin and dated via radionuclides. An objective source appointment method has been established based on several source-sensitive molecular indicators we found. An over 100 year historical record of energy usage in New York City has been reconstructed in one core from Central Park Lake. The reconstructed history is consistent with historical energy consumption data of NYS compiled by the US Department of Energy. Wood combustion was dominant one century ago in Manhattan, followed by coal combustion dominance from the 1900s to the 1940s. Petroleum combustion, mainly from motor

vehicles in Manhattan, increased gradually from the 1920s, and became the dominant PAH input after 1940s. In most samples collected from elsewhere in the lower Hudson River Basin, petroleum combustion was the dominant PAH input in the last half century. Petroleum spills were considerable sources of PAHs in some harbor samples and the dominant sources in the Arthur Kill during most of the last century. Coal combustion became important in the past several decades in some areas in the mainstem Hudson, presumably due to a major fuel shift from oil to coal in some power stations along the river. Wood combustion and Natural diagenetic sources of PAHs were insignificant in urban waters, but were found to dominate in historical sections of cores from more rural areas of the Hudson basin.

### **FISH ASSEMBLAGES OF THIRTY-ONE (31) ADIRONDACK LAKES, 1995-2006**

Robert A. Daniels, New York State Museum

As part of the fisheries component of the Adirondack Effects Assessment Program, 31 Adirondack lakes were sampled between 1995 and 2006. Twenty-two (22) lakes were sampled using Adirondack trap nets and nine (9) lakes were assessed by snorkeling. Two lakes were both snorkeled and netted. A subset of three lakes was sampled twice yearly throughout the 12-year study.

Twenty-five (25) species and two (2) hybrids were present in lakes sampled between 1995 and 2006 Brown bullhead was present in nineteen (19) lakes. Golden shiner, creek chub, white sucker, pumpkinseed, yellow perch and brook trout were present in ten (10) or more lakes. Nine (9) taxa were taken in only one (1) of the lakes and another four (4) taxa were found in three (3) or fewer lakes. The most abundant species in the catches were yellow perch, brown bullhead and white sucker, respectively. Although species richness is positively correlated to pH (Fig. 5), other factors, such as introductions of exotic species, limit the usefulness of this metric in assessing the role of pH in fish distribution and abundance. Lakes undergo seasonal and annual change in fish abundance. Most lakes sampled are dominated by exotic fish species, although many are long-term residents. Native species are most abundant in the high-elevation lakes where fish persist. Exotic species affect the presence-absence and abundance of native species and are more important in determining assemblage composition than physico-chemical characteristics.

### **USE OF 16S rDNA SEQUENCING TO ELUCIDATE MICROBIAL COMMUNITIES IN ADIRONDACK LAKES OF NEW YORK STATE**

Sascha F. Percent<sup>1</sup>, Vincent Milano<sup>1</sup>, Margaret McLellan<sup>1</sup>, Marc E. Frischer<sup>2</sup>, Christie Stagnar<sup>1</sup>, Michael P. Schaaff<sup>1</sup>, Sandra A. Nierzwicki-Bauer<sup>1</sup>, Charles W. Boylen<sup>1</sup>

<sup>1</sup>Darrin Fresh Water Institute and Department of Biology, Rensselaer Polytechnic Institute

<sup>2</sup>Skidaway Institute of Oceanography

In recent years the use of nucleotide sequencing has done much to redefine how microbial ecologists view taxonomic phylogeny of microbial components of freshwater food chains. Not only has our knowledge of bacterial community structure of freshwaters progressed from the limitations of pure cultures to phylogenetic characterization using 16S rDNA amplification, but recent studies based on a limited number of nucleic acid sequence data worldwide suggest that there exists a unique global freshwater prokaryotic flora. As of 2005, combined diversity studies using random cloning have produced less than 5,341 freshwater bacterial 16S rDNA sequences deposited to the databank. Earlier studies on a suite of six Adirondack lakes had shown that the bacterial sequences from the Adirondacks were closely related to other freshwater clones, illustrating species or groups of species indigenous to freshwater. Although over 2,800 lakes exist in the Adirondack region of upstate NY, they are extremely varied in their pH, alkalinity, and nutrient chemistry. Over half of the high elevation lakes in the Adirondacks have surface waters below pH 5.0. We have selected 34 lakes for long term study and characterization that represent a range of limnological characteristics. As of January 2006, we have obtained over 1200 16S rDNA gene sequences from 31 of these Adirondack lakes. Because these lakes vary considerably in their limnology, results are more intriguing amongst these lakes than previously thought. In both the upper epilimnetic layer and the hypolimnetic layer beneath the summer thermocline, our data supports the conclusion that species diversity increases with pH. The Actinobacteria, alpha-proteobacteria, beta-proteobacteria, and Cytophaga-Flexibacter-Bacteriodes dominated throughout all the lakes; whereas, delta-proteobacteria were found in 19 of 31 lakes and gamma-proteobacteria in 22 lakes.

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## AIR QUALITY AND RELATED HEALTH RESEARCH

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### **MONITORING THE IMPACT OF TITLE IV (EPA ACID RAIN PROGRAM) AT WHITEFACE MOUNTAIN: AN EXERCISE IN “ACCOUNTABILITY” IN AIR QUALITY MANAGEMENT**

Kenneth L. Demerjian and Utpal Roychowdhury  
Atmospheric Sciences Research Center University at Albany, SUNY

Air quality measurements in the Northeast U.S. and associated relationships with source emissions have made important contributions to our understanding of regional air quality and the role played by long range transport. The air we breathe today is significantly cleaner than that which was present thirty years ago. Regulatory actions past and present have managed to improve air quality in the region in the midst of sustained growth and increasing consumption. Title IV of the 1990 Clean Air Act amendments has resulted in significant reductions in SO<sub>2</sub> and to a lesser extent NO<sub>x</sub> emissions. A retrospective analysis of trends in air quality and deposition in the downwind regions is presented and compared with estimated emission trends and evaluated for consistency with regulatory actions. The case provides an excellent demonstration of the importance of long term air quality measurements in selected regions of the country in support of an “accountable” air quality management system.

### **TRAFFIC IMPACTS ON AIR QUALITY: THE MISSING LINK IN POLLUTION EXPOSURE?**

Kenneth L. Demerjian, James J. Schwab, Yongquan Li, Qi Zhang and Ga Lala,  
Atmospheric Sciences Research Center University at Albany

Urban monitor networks are deployed with the intent of measuring spatially representative air quality within domains most likely for estimating representative population exposures. The classification of monitors as urban versus traffic is based on EPA site monitoring guidance which basically distinguishes their differences in terms of the monitor’s distance from the road/highway. We report on measurements that show that urban sites can be significantly influenced by local traffic and that traffic monitors may be far more important in assessing population exposures than previously thought. A case study of the Long Island Expressway plume transport across the Queens College urban monitoring site in New York City shows high pollutant levels from primary mobile source emissions and suggests high levels of population exposure within intervening neighborhoods. These results have significant implications to concentration exposure estimates to criteria pollutants, and more importantly to exposures to air toxics and nano particles.

### **FAST TIME RESPONSE MEASUREMENTS OF GASEOUS NITROUS ACID USING A TUNABLE DIODE LASER ABSORPTION SPECTROMETER: HONO EMISSION SOURCE FROM VEHICLE EXHAUSTS**

Yongquan Li, James J. Schwab, Kenneth L. Demerjian  
Atmospheric Sciences Research Center, University at Albany, State University of New York

We present the measurement of gaseous nitrous acid (HONO) using a tunable diode laser absorption spectrometer. This method utilizes one strong absorption feature at 1713.511cm<sup>-1</sup>, which is free of interference and suitable for ambient HONO measurements. The detection limit for a 1-second integration time is determined to be better than 200 pptv. The measurement method has been demonstrated by sampling room air over an 11-day period. HONO mixing ratios ranged from below the detection limit ( $\leq 200$  pptv) to 4.8 ppbv, with a mean value of 0.73 ppbv. A number of elevated HONO events lasting from several seconds up to hours were observed and have been associated with roadway traffic adjacent to the building where the measurements were performed. The variation in the ratio of HONO/NO<sub>x</sub> and its anti-correlation with ambient NO<sub>x</sub> measurements indicate that the source of HONO in this measurement study is mainly from the direct emission of traffic exhausts and local heterogeneous reactions. The demonstrated application of TDLAS fast response measurement technology is capable of providing new information on the sources and sinks of HONO in the environment.

## **HONO EMISSIONS FROM VEHICLE EXHAUST AS A FUNCTION OF VEHICLE OPERATING CONDITIONS**

Yongquan Li<sup>1</sup>, Shida Tang<sup>2</sup> and Kenneth L. Demerjian<sup>1</sup>

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This presentation describes the results of HONO emission measurements from light duty vehicles as a function of vehicle operation conditions. To better understand HONO emissions, the measurements of total hydrocarbon (THC), carbon monoxide (CO), nitrogen dioxide (NO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), as well as carbon dioxide (CO<sub>2</sub>) have also been performed in the study. Two gasoline passenger cars and three light duty diesel vehicles were tested over a unified driving cycle LA92, a highway fuel economy cycle (HWFE), a New York City cycle (NYCC), and a US06cycle. HONO and NO<sub>2</sub> emissions were measured by a tunable diode laser absorption spectrometer (TDLAS), and other regulated species were simultaneously monitored by bench devices: non-dispersive infrared detection systems, heated chemiluminescence analyzer and heated flame ionization detection system. The study was performed using a light duty dynamometer at NYSDEC's automotive emission laboratory (AEL) located in Albany, NY. The results show that HONO emissions depended on driving mode and were primarily generated during acceleration and deceleration events. Diesel vehicles produced more HONO than gasoline vehicles, and more emissions were generated by aged vehicles. In each driving cycle, HONO emissions showed a good correlation with NO<sub>2</sub> emissions, and less correlation with NO<sub>x</sub>. Higher correlation between HONO/NO<sub>x</sub> ratios and CO/NO<sub>x</sub> ratios may imply that most of HONO emissions could be resulted from engine combustion.

## **PHOTOELECTRIC CHARGING CHARACTERISTICS OF PARTICLES FROM MOBILE EMISSIONS: APPLICATIONS TO SOURCE-SELECTIVE MEASUREMENTS**

Michael Hill, Suresh Dhaniyala, Clarkson University

Brian Frank, and Thomas Lanni, New York State Department of Environmental Conservation

Aerosol particles composed of photoemissive substances such as carbon can be selectively detected and distinguished from background concentrations using the technique of photoelectric charging (Matter et al., 1995). Here, we present measurements using a photoelectric tandem differential mobility analyzer (P-TDMA) which uses the combination of photoemissive response and mobility measurement to obtain real-time compositional information about combustion particles. In the P-TDMA, two differential mobility analyzers are operated in tandem with a photoelectric charger (222 nm KrCl excimer lamp) in between. Laboratory experiments with a range of intermixed aerosols confirm that carbon particles can be quantitatively identified from the mixture. For deployment of the P-TDMA for ambient source-selective measurements, the photoelectric charging profiles of different emission sources are required. Towards that end, emission measurements of a diesel generator, and SI and diesel vehicles, were made at the New York State Department of Environmental Conservation's mobile sources test facility. The engine loads were varied and the photoelectric profiles of the emissions were obtained as a function of particle size. Preliminary analysis suggests that the photoelectric response of particles in the 100 nm size range can be used to identify different mobile source contributions to urban ambient particle populations.

## **MINIATURE INSTRUMENTS FOR PARTICLE SIZING AND COMPOSITIONAL ANALYSIS**

Manish Ranjan and Suresh Dhaniyala, Clarkson University

Real time size distribution and size-resolved chemical composition measurement is essential for effective characterization of ambient aerosol. Towards development of a compact instrument for size-resolved submicron particle composition studies, a new instrument called the compositional Miniature Electrical Aerosol Spectrometer (c-MEAS) is presented. This instrument is built on the design of Miniature Electrical Aerosol Spectrometer (MEAS). In MEAS, charged aerosol particles are size-segregated based on their response to applied electrical and drag forces. Ultrafine particles over a narrow size range are collected on metallic plates in c-MEAS. Underneath the collection plates, ultraminiature heaters and heat sensors (Minco Inc.) are located to heat the plates to selected temperatures to volatilize the collected particles. Numerical results suggest that heating under appropriate conditions of Grashof and Reynolds numbers will enable extraction of volatile species without loss to the walls. Gas detectors downstream of c-MEAS will provide quantitative information on the volatilized species. A CO<sub>2</sub> NDIR sensor is currently being integrated for measurement of organic carbon volatilized from the size-segregated samples. A comparison of cMEAS performance against that of the Sunset EC/OC will be presented. Also, measurements of the size-dependent high-volatile OC in ultrafine diesel emissions will be presented.

## A NEW CONCEPTION FOR ENVIRONMENTAL MEASUREMENT OF ULTRAFINE PARTICLES

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It is well known that ultrafine particles have an impact on human health. Consequently it is necessary to monitor the exposure in cities and urban areas. There are some instruments commercially available for this task like SMPS, DMPS or FMPS but their original field of application is contradictory to the utilization in air pollution monitoring networks.

These sensitive devices had been developed primarily for scientific purposes in the lab environment, they are servicing-intensive and delicate to handle. The use of radioactive sources in the charger complicates the transport of the devices. Furthermore a compromise has to be found between the necessary accuracy in the field of air monitoring and the costs of the devices. The high accuracy of these devices is not needed within the scope of air pollution monitoring and lead to too high costs.

Based on the requirements of monitoring networks a new concept was developed and tested in the project UFIPOLNET – using of a diffusion charger instead of a radioactive source and an electrometer instead a CPC

Additional components are a long DMA (TSI 3081) with sheath air circuit, a complete control unit (PCB) and a single board computer for data processing and a database driven data storage.

The data inversion delivers the particle number concentration in the following size classes:

<b>CH1 (nm)</b>	<b>CH2 (nm)</b>	<b>CH3 (nm)</b>	<b>CH4 (nm)</b>	<b>CH5 (nm)</b>	<b>CH6 (nm)</b>
20...30	30...50	50...70	70...100	100...200	>200

In the field of environmental aerosols particular attention has to be paid to the sampling system. Basically it consists of a PM1-inlet, a membrane dryer and an equalizing tank. The membrane dryer requires no maintenance and induces only minimal particle losses. In comparison measurements between the new spectrometer and a DMPS at a street canyon site in Leipzig a good correlation was found

Within the project UFIPOLNET at four measurement stations in Europe prototypes were installed with identical sampling systems. The instruments are running over a longer period and experiences of the users will also be presented.

UFIPOLNET ([www.ufipolnet.eu](http://www.ufipolnet.eu)) is financed by the LIFE financial instrument of the European Community under No. LIFE04 ENV/DE/000054.

## MODELING FORMATION AND EVOLUTION OF SIZE-RESOLVED SOOT PARTICLES IN DIESEL ENGINE

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Study of soot particle formation in the combustion engine becomes one of the important research fields because of the harmful effects of soot on human health and on climate. Controlling soot emission is one of the important goals in engine design to improve air quality. A clear understanding of the key processes and parameters controlling soot formation and size distribution evolution is important and remains to be achieved. A simple seven steps chemical kinetic model for soot formation was included in a sectional aerosol dynamics model to simulate the size distribution evolution of soot inside a diesel engine. Typical fuel, O<sub>2</sub>, temperature and pressure profiles predicted by KIVA code for a diesel engine were used as input to study the soot formation and evolution. In the simple soot formation scheme, a 2-carbon-atom soot nucleus is assumed to form from an intermediate radical specie which is formed from the fuel molecules. Then soot grows by surface reaction, oxidation and coagulation. The size-resolved model results were compared with those based on a simple mono-disperse soot model as well as some observations. Significant

difference was found between our sectional model and simple mono-disperse model. Our simulations show that in the earlier stage of particle formation, soot number concentration was dominated by nucleation and then it was limited by coagulation. The effects of temperature, nucleation rates, and surface reaction rates on soot size distribution were studied.

### **CHARACTERIZATION OF ULTRAFINE PARTICLE EMISSIONS FROM A GASOLINE VEHICLE**

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Atmospheric Sciences Research Center, State University of New York at Albany

Emissions from a gasoline vehicle were measured at steady state speeds of 30, 45, 60 and 70 mph, with particle size distributions determined using an Engine Exhaust Particulate Spectrometer (EEPS) and total concentration measured using a Condensation Particle Counter (CPC). Samples were taken after ambient dilution, with a SEMTECH-D Portable Emissions Monitoring System (PEMS) used to calculate instantaneous dilution ratios based on carbon dioxide which ranged from 10:1 to 450:1.

For both the 30-45 mph speeds and the 60-75 mph speeds, some bi-modality was observed in the particle size distributions with modes at ca. 11 and 34 nm. For the 30-45 mph speeds, the 11 nm mode was dominant and dilution-corrected number concentrations for the particle size distributions were as high as 105 particles/cubic centimeter. For the 60-75 mph speeds, the 34 nm mode was dominant and dilution-corrected number concentrations for the particle size distributions exceeded  $1E7$  particles/cubic centimeter.

In addition, mass concentrations were observed of up to 9 micrograms/cubic meter for the 30-45 mph steady states and up to 1165 micrograms /cubic meter for the 60-75 mph steady states. These high number and mass concentrations suggest that gasoline emissions can be a significant contribution to mobile source emissions in the fine and ultrafine range and warrant further investigation. Our measurements also indicate that high concentrations of chemiions were present in the exhaust only when the vehicle was undergoing acceleration.

### **NANOPARTICLE FORMATION IN THE EXHAUST OF VEHICLES RUNNING ON ULTRA-LOW SULFUR FUEL**

Hua Du and Fangqun Yu  
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The concern of potential adverse health impacts from exposure to nanoparticles (NPs) has been escalating over the past few years. Vehicle emissions are known to be a major source of NPs in urban areas. How to minimize their environmental and health impacts demands a clear understanding of NP formation mechanisms. Laboratory and field studies revealed that sulfur to sulfuric acid conversion efficiency ( $\mathcal{E}$ ), sulfur storage/release effect, and presence of nanometer-sized non-volatile cores/particles have significant impacts on vehicular NP emissions. In this study, a detailed size- and composition- resolved aerosol microphysical model with a recently improved  $H_2SO_4$ - $H_2O$  homogeneous nucleation (BHN) module is employed to study in detail the influences of all the above-noted effects.

We show that the model predicts particle size distributions that are in good agreement with measurements carried out with different dilution setups. Our previous study conclude that BHN is incapable of producing NPs if fuel sulfur content (FSC) is reduced below 100 ppm assuming  $\mathcal{E} = \sim 1\%$ . However, we show in this study that the potential to form NPs are higher for vehicles running on ultra-low sulfur fuel than on high sulfur fuel due to the employment of diesel particulate filters. Old diesel vehicles equipped with either diesel particulate filters or oxidation catalysts are likely to emit more NPs than new ones due to higher lube oil consumption rate. In addition, we show that main evolution mechanisms of NPs near the roadway are different, depending on exhaust aftertreatment setups. For vehicles equipped with diesel particulate filters, dilution is the main evolution process; however, for those without diesel particulate filters, organic condensation and evaporation are the main processes.

## **APPLICATIONS OF PASSIVE AND ACTIVE REMOTE SENSING FOR MONITORING OF AEROSOLS**

Min Min Oo, Barry Gross, and Sam Ahmed  
Remote Sensing Laboratory, City College of the City University of New York

Monitoring and forecasting aerosol and other pollutants in the atmosphere requires detailed knowledge of the state of the atmosphere distributed over space (horizontal and vertical) as well as time. A combination of atmospheric modeling using coupled meteorology and atmospheric chemistry (such as the CMAQ) and ground sampling together with remote sensing data offers a powerful approach for air quality forecasting and management. This presentation describes

algorithms and techniques to optimize aerosol remote sensing for regional applications using a combination of ground based radiometers, multispectral polar orbiting satellite measurements, and geostationary satellite imaging data. In addition, we describe the use of lidar measurements both as a validation tool for air-transport models as well as a way of connecting total column measurements to surface PM<sub>2.5</sub> levels.

### **ULTRAFINE PARTICLES AND CARDIAC RESPONSES: EVALUATION IN A CARDIAC REHABILITATION CENTER**

David Chalupa<sup>1</sup>, William Beckett<sup>1</sup>, Karen Stulpin<sup>2</sup>, Laurie Kopin<sup>2</sup>, John Kasumba<sup>3</sup>, Mark Frampton<sup>1</sup>, Phillip Hopke<sup>3</sup>, and Mark J. Utell<sup>1</sup>

<sup>1</sup>University of Rochester Medical Center, <sup>2</sup>University of Rochester Cardiac Rehab Center  
<sup>3</sup>Clarkson University

This study examines the effects of ultrafine particles (UFP) on cardiovascular responses in patients undergoing medically monitored exercise rehabilitation in Rochester, NY following hospitalization for acute coronary events, such as myocardial infarctions (heart attacks) or unstable angina. Seventy-five (75) patients will be participating and are closely monitored during their rehabilitation 12-week protocol; to date, 30 patients have been enrolled and 22 have completed the entire protocol. The patients undergo electrophysical monitoring (Holter monitor) as well as blood sampling; complete medical histories and diaries are also recorded. The program involves supervised, graded twice or thrice weekly exercise sessions for a total of 12 weeks.

Ultrafine particle number and size (Wide range Particle Spectrometer, MSP Corp.) are being measured continuously outdoors ( $3.8 \pm 2.1$  (SD)  $\times 10^3$  p/cm<sup>3</sup> from Sept. 06 to Sept. 07) and indoors ( $1.3 \pm 0.8$  (SD)  $\times 10^3$  p/cm<sup>3</sup>) at the rehab site. Particle number, size (TSI SMPS model 3071), and mass (TEOM) are also measured continuously at a central measuring site in eastern Rochester. Other EPA criteria pollutants are measured at the eastern Rochester DEC site. In addition, one-third of the patients (n = 25) will have personal particle count monitoring in their cars to and from the rehab facility (n = 7 completed, particle count concentration =  $14.1 \pm 8.5$  (SD)  $\times 10^3$  p/cm<sup>3</sup>) and in their homes (n = 10 completed, particle count concentration =  $8.1 \pm 2.8$  (SD)  $\times 10^3$  p/cm<sup>3</sup>) for 48 hours using a portable nuclei counter (TSI model 3781).

With completion of enrollment, levels of ambient ultrafine and fine particles will be linked with cardiac performance outcomes. A unique strength of the design is the availability of longitudinal measurements on each subject, enabling each subject to be used as their own control.

### **NEW YORK STATE AIR POLLUTION AND HEALTH STUDIES INVENTORY DATA BASE**

Ronald H. White, Department of Epidemiology, Risk Sciences and Public Policy Institute  
Johns Hopkins Bloomberg School of Public Health

Under a contract with the New York State Energy Research and Development Authority (NYSERDA), the Johns Hopkins Risk Sciences and Public Policy Institute has developed an inventory of air pollution and health studies that utilize New York State air pollution data. Thirty studies conducted between June 2002 and June 2005 were identified utilizing a questionnaire and literature review. The inventory includes the following information where available: study name, study location(s), principal investigator, co-investigator(s), total funding amount and source(s), air pollutant analytes and data source(s), health outcomes examined and data source(s), and key study findings (for completed studies). For studies involving the collection of air pollutant samples, the following

information was collected where available: sampling location(s), sampling frequency, time period of sample collection, sampling technologies and filter media employed, whether sample filters were archived and, if so, method of storage. These data have been captured in a Microsoft Access database format. Narrative summaries of the key information available have been developed for each of the air pollution and health studies included in the inventory. NYSERDA will be providing public access to the data base and study summaries through its website.

### **SEASONAL ABUNDANCE OF WOOD SMOKE MARKERS AND CHOLESTEROL IN FINE PARTICLES FROM THE NEW YORK METROPOLITAN AREA**

Harmonie Hawley, Min Li, and Monica A. Mazurek  
Civil & Environmental Engineering Department, Rutgers University

Polar organic compounds are not well documented in U.S. urban airsheds. This study investigates the atmospheric abundance of wood smoke markers and cholesterol in the New York City (NYC) metropolitan area. Wood smoke originates from many sources including biomass burning due to human activities (home heating, campfires, agricultural burning, structural fires) and to wildfires. Cholesterol is a molecular marker for meat charbroiling, grilling and frying. The influence of wood smoke and cooking emissions on the PM<sub>2.5</sub> mass in this high-population area is not well understood and, therefore may be important sources of fine particulate matter (PM) in the NYC area. This information is also valuable for source apportionment models such as the EPA CMB 8.2.

### **ORGANIC SPECIATION OF VEHICLE EXHAUST PARTICULATES: GASOLINE AND DIESEL LIGHT DUTY VEHICLES**

Min Li<sup>1</sup>, Shida Tang<sup>3</sup>, Robert Whitby<sup>3</sup>, Monica A. Mazurek<sup>1\*</sup>, Claire Belisle<sup>1</sup>, and Majad Ullah<sup>2</sup>

<sup>1</sup>Civil & Environmental Engineering Department, Rutgers University

<sup>2</sup>Chemical Engineering, Rutgers University

<sup>3</sup>New York Department of Environmental Conservation

On road vehicle emissions is a major source of particulate matter pollution, especially in urban areas. In this study, organic speciation of fine particulate matter (PM<sub>2.5</sub>, d<sub>p</sub> ≤ 2.5 μm) was carried out on 18 light-duty vehicles tested from July, 2005 to May, 2006 on a chassis dynamometer over different driving cycles. Twelve gasoline vehicles were evaluated including a gasoline-electric hybrid. Two of the vehicles operated on compressed natural gas (CNG), and four were diesel vehicles. Three gasoline vehicles were tested with both summer and winter fuels.

A detailed chemical profile was constructed for the vehicle exhaust particulates collected from each vehicle and fuel type. More than 100 organic molecular marker compounds quantified by gas chromatograph/mass spectrometry (GC/MS). The major organic components identified were n-alkanes, PAH (polycyclic aromatic hydrocarbons), hopane, sterane, n-alkanoic acids and benzoic acids. These chemical profiles will update current vehicle emission profiles for motor vehicles operating in the NY City metropolitan area. The detailed chemical profiles corresponding to the fine organic PM will provide new apportionment and modeling tools to distinguish organic particulate pollution from gasoline and diesel powered vehicles.

### **A QUANTITATIVE PROTOCOL FOR HIGHLY POLAR ORGANIC COMPOUNDS IN PM<sub>2.5</sub> FROM THE NEW YORK CITY AIRSHED**

Harmonie Hawley, Min Li, and Monica A. Mazurek  
Civil & Environmental Engineering Department, Rutgers University.

This project focuses on the quantitation of highly polar organic compounds extracted from PM<sub>2.5</sub> samples collected as part of the Speciation of Organics for Apportionment of PM<sub>2.5</sub> in the New York City Area (SOAP). The SOAP network operated from May 2002 to May 2003 at four sites: Queens, NYC (high density urban residential); Elizabeth, NJ (adjacent to the NJ Turnpike); Westport, CT (downwind NYC); and a regional background site in Chester, NJ (upwind NYC).

A key science question was how much of the carbonaceous PM<sub>2.5</sub> is primary versus secondary. To address this question, a group of highly polar, low molecular weight organic acids were selected as secondary species and do not appear as significant species in the chemical profiles of known primary sources such as motor vehicle exhaust and

cooking emissions. The target compounds selected were diacids (oxalic acid and malonic acid) and oxo-carboxylic acids (glyoxylic acid, pyruvic acid, 2-oxobutanoic acid, levulinic acid, 5-oxohexanoic acid and oxobutanedioic acid). A quantitative extraction and gas chromatographic/mass spectrometric (GC/MS) chemical analysis procedure was developed and evaluated. Trimethylsilyl (TMS) derivatives were prepared prior to GC/MS analysis and 5-point calibrations and multiple replicates were evaluated to determine method precision. Good precision and sensitivity was seen based on the statistical analysis of the standard compounds evaluated and in the ambient PM<sub>2.5</sub> samples. This procedure establishes a new identification and quantitation method for determining highly polar and oxidized secondary molecular markers in regional fine aerosols samples.

#### **CHARACTERIZATION OF OXYGENATED ORGANIC COMPOUNDS USING A HIGH RESOLUTION TIME-OF-FLIGHT AEROSOL MASS SPECTROMETER**

Olga Hogrefe, Brian P. Frank\*, Yele Sun, Qi Zhang, Min-Suk Bae,  
James J. Schwab, G. Garland Lala and Kenneth L. Demerjian  
University at Albany, Atmospheric Sciences Research Center,  
\* New York State Department of Environmental Conservation

A suite of oxygenated organic compounds was characterized in the laboratory using an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). The compounds included levoglucosan and adipic, glutaric, glyoxylic, malonic, malic, oleic, oxalic, palmitic, pinonic, phthalic, and succinic acids. This work was undertaken to study the physical and chemical properties of atmospherically relevant oxygenated organic aerosol (OOA) components and characterize their mass spectral signatures for potential applications in OOA source identification and apportionment.

Polydisperse aerosols were generated by spray-atomization of solutions of pure organic compounds in the ASRC aerosol research facility and were equilibrated in a slow-flow chamber, where relative humidity was maintained at approximately 30%. The aerosols were sampled and analyzed with an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS), an R&P Differential TEOM, a TSI Scanning Mobility Particle Sizer and on many occasions by a Sunset Labs OCEC monitor.

Characteristic high-resolution “fingerprint” mass spectra of various organic compounds obtained in this study can be applied to ambient databases of ambient aerosol mass spectrometric measurements to better identify and quantify the AMS organic mass fraction of PM and to provide better estimates of the attribution of anthropogenic and biogenic sources to these measurements.

#### **CHARACTERIZATION OF LABORATORY-GENERATED SECONDARY ORGANIC AEROSOLS USING A HIGH RESOLUTION TIME-OF-FLIGHT AEROSOL MASS SPECTROMETER**

Olga Hogrefe, Brian P. Frank\*, Yongquan Li, Yele Sun, Qi Zhang, Min-Suk Bae,  
James J. Schwab and Kenneth L. Demerjian  
University at Albany, Atmospheric Sciences Research Center,  
\*New York State Department of Environmental Conservation

The physical and chemical properties of laboratory generated secondary organic aerosols (SOAs) were studied using a suite of measurement techniques. The aerosols were generated via reactions of various VOCs (pinene, toluene, xylene and limonene) and OH radicals in the ASRC slow-flow reaction chamber. Measurements were performed with an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS), an R&P Differential TEOM, a TSI Scanning Mobility Particle Sizer, and a Condensation Particle Counter. In this poster we will present information about optimal conditions for the SOA generation in the slow-flow chamber. The results of a detailed High Resolution mass spectrometric analysis of laboratory-generated SOA will be presented as well.

## **EMISSIONS CHARACTERISTICS OF RESIDENTIAL GAS, OIL AND WOOD PELLET FUELED HEATING SYSTEMS**

Roger J. McDonald, Brookhaven National Laboratory

The goal of the Emissions Characteristics of Heating Systems project is to develop an up-to-date evaluation of emissions from typical residential, gas-fired, oil-fired, and wood-fired heating equipment. The project seeks to accurately analyze heating equipment performance with natural gas, heating oil of different sulfur contents, varied blends of biofuels, and wood pellets, by measuring emissions of carbon monoxide, sulfur oxides, nitrogen oxides, unburned hydrocarbons, and fine particulate matter (PM<sub>2.5</sub>). Phase I of the project measured emissions from a representative sample of typical gas-fired, oil-fired, and wood pellet-fired, residential heating systems that are found in homes and small businesses in New York State. Oil-fired heating systems were tested with conventional, 0.2% sulfur heating oil, low sulfur (500 ppm S) diesel fuel, and ultra-low sulfur (15 ppm S) diesel fuel. Wood pellet-fired heating systems shall be tested with both standard and premium (low ash content) quality pellet fuel. Phase II of the project will measure emissions from advanced heating technologies including: low NOX burners, condensing boilers and furnaces. Phase II shall also include the testing of both conventional and advanced, oil-fired, heating technologies with B20 and B100 biofuels.

## **CHARACTERIZATION OF NITROGEN CONTAINING ORGANIC SPECIES IN FOG/CLOUD WATERS USING A HIGH RESOLUTION TIME-OF-FLIGHT AEROSOL MASS SPECTROMETER**

Yele Sun and Qi Zhang

Atmospheric Sciences Research Center, University at Albany, State University of New York

Despite the fact that nitrogen-containing organic species are ubiquitous in atmospheric particles and water droplets and likely play important roles in atmospheric chemistry and ecosystem health, very little is known about the concentration or composition of this class of compounds. Here we present the development of a new method that allows the quantification and bulk-characterization of water-soluble organic nitrogen (WSON) species in atmospheric fog and cloud waters using an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). The success of this method relies on the facts that 1) the AMS mass spectra can be deconvolved to quantify and chemically characterize organic material in complex mixtures such as atmospheric aerosol particles and 2) the high resolution capability of the HR-ToF-AMS can distinguish nitrogen containing organic fragments (e.g., C<sub>x</sub>H<sub>y</sub>N<sub>p</sub><sup>+</sup> and C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>N<sub>p</sub><sup>+</sup>) from ion fragments lack of N atom (e.g., C<sub>x</sub>H<sub>y</sub><sup>+</sup> and C<sub>x</sub>H<sub>y</sub>O<sub>z</sub><sup>+</sup>). We have evaluated this method through HR-ToF-AMS analyses of a suite of WSON standard compounds, including 19 amino acids, urea, peptides and proteins. The elemental ratios of C:H:O:N were determined in the spectrum of each compound and compared to the theoretical values. In addition, we will present the application of this technique in analyses of atmospheric fog and cloud water samples and aerosol extracts. Attempts will also be made to characterize different classes of WSON species (e.g., amino compounds vs. amides) in atmospheric samples based on mass spectral signature identified in standard compounds.

## **IMPACTS OF CLEAN DIESEL STRATEGIES/TECHNOLOGIES ON AIR QUALITY AND EXPOSURE IN NEW YORK**

H. Oliver Gao and K. Max Zhang, Cornell University

New York State and the New York Metropolitan Area have both been ranked highest in the nation in terms of health impacts from diesel fine particles. Implementation of Clean diesel strategies/technologies and switching to ultra-low-sulfur diesel fuel are likely to improve ambient air quality in New York Metro and across the State. Given the diversity of applications and engines, as well as significant technical, institutional, and funding issues, however, the magnitudes and the scope of the improvements are uncertain. This study employs an integrated emission-air quality-exposure modeling system to assess the impact of diesel emission technologies/strategies on air quality and human exposure in the State of New York focusing on the New York Metropolitan Area. The modeling system is created by combining advanced mobile emission models, state-of-science chemical transport models and Geographic Information Systems (GIS) tools. More specifically, for emission modeling, non-road mobile source and stationary source emissions inventories for the NYC Metro will be projected from the base-year emissions inventories in combination with pertinent non-road diesel cleaning strategies. On-road mobile source emissions will be estimated by applying a grid-based on-road emissions model to New York Metropolitan Transportation Consortium's (NYMTC) travel demand forecasts. In air quality modeling, we adopt the Community Multiscale Air Quality Model (CMAQ) and its advanced variation, CMAQ-UCD, to simulate the ambient air quality corresponding to each future scenario. The study will quantify the changes in ambient O<sub>3</sub> and PM<sub>2.5</sub> (primary and secondary components)

concentrations associated with the emissions updates. The modeling results will provide important information for exposure assessments at both ambient level and near-source level.

### **A COMPREHENSIVE STUDY OF THE NYS CLEAN SCHOOL BUS PROGRAM: DEMONSTRATION, OPERATION, AND POTENTIAL IMPROVEMENT FOR EFFECTIVE DIESEL EXPOSURE REDUCTION**

H. Oliver Gao, School of Civil and Environmental Engineering, Cornell University

Cleaning up the existing school bus fleet to reduce diesel emissions and children's exposure risk remains a challenge and opportunity in New York State (NYS) and across the country. State Clean Air School Bus Programs play a critical role in achieving cost-effective school bus clean-up. Retrofit devices need to be used in the right application. Even with good certified technologies, unwise decisions in operations and deployment of a retrofit program could significantly limit the benefit. To provide NY State and local school bus cleaning programs with the most useful scientific and empirical information for cost-effective emissions reduction and children exposure mitigation, this study conducts comprehensive and systematic assessment of the NYS Clean School Bus Program by coherently integrating assessments of the State-wide program with a demonstrative school bus retrofit project. It consists of a phased approach involving two parallel but interrelated flows of tasks at both the State Program level and a specific project level. At the level of State Program assessment, the objectives are to 1) analyze and evaluate the NYS Clean Air School Bus Program and its associated emissions reductions; 2) examine the programmatic details regarding the methodology and implementation of this state-wide initiative; 3) develop school bus retrofit decision supporting database and analysis tools, and; 4) provide suggestions to program managers for program improvement and recommend bus retrofit maintenance guidelines to bus managers. Parallel to assessing the State Program, Cornell University and the NY Greece Central School District (GCSD) have teamed up to implement and study a demonstrative case of GCSD's school bus retrofit project. This demonstrative case will retrofit 244 school buses with EPA verified diesel oxidation catalyst (DOC) and closed crankcase filtration system using funds from the EPA Clean School Bus USA program.

### **PREDICTING NEAR REAL-TIME PM<sub>2.5</sub> FRM CONCENTRATIONS FROM CONTINUOUS MASS AND SPECIES MEASUREMENTS IN NEW YORK CITY**

Dirk H. Felton, Oliver V. Rattigan, New York State Department of Environmental Conservation  
James J. Schwab, and Kenneth L. Demerjian, University at Albany, Atmospheric Sciences Research Center

Near real-time PM<sub>2.5</sub> mass data is used routinely by air monitoring agencies to provide air quality information and health warnings related to pollutant concentrations to the public. This data is presented in concentrations, which are as similar as possible to FRM filter data.

Since the FRM data is not available for several months following sampling agencies generally use statistical correlations to produce "FRM-like" data from continuous mass instruments. Measurements from collocated semi-continuous sulfate, nitrate, elemental carbon (EC) and organic carbon (OC) instruments can be used in conjunction with TEOM mass and meteorological data to produce PM<sub>2.5</sub> data that is more reflective of actual FRM measurements.

For cities in the Northeastern United States, the data from TEOM instruments that operate at 50 deg C is not adequate to produce data for public reporting purposes. The heated TEOM sampling inlet causes a negative bias in relation to the FRM, which varies seasonally. This work demonstrates one method to calculate hourly PM<sub>2.5</sub> mass that includes estimates of the fractions of individual PM<sub>2.5</sub> species retained on the FRM filter. This allows the technique to account for the seasonal bias between the FRM and TEOM continuous mass measurements.

The continuous species data used in this study are correlated to 24-hr integrated 1 in 3 day filter measurements from the Speciation Trends Network.

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### **CHARACTERISTICS OF AEROSOL GROWTH EVENTS AT URBAN AND RURAL LOCATIONS IN NEW YORK**

Min-Suk Bae<sup>1</sup>, James J. Schwab<sup>1</sup>, Qi Zhang<sup>1</sup>, Olga Hogrefe<sup>1</sup>, Kenneth L. Demerjian<sup>1</sup>, Silke Weimer<sup>2</sup>, Kevin Rhoads<sup>3</sup>, Doug Orsini<sup>3</sup>, Prasanna Venkatachari<sup>4</sup>, Philip K. Hopke<sup>4</sup>

<sup>1</sup>Atmospheric Sciences Research Center, University at Albany, State University of New York

<sup>2</sup>EMPA, CH-8600 Dübendorf, Switzerland, and Paul Scherrer Institute, CH-5232 Villigen, Switzerland

<sup>3</sup>Department of Chemistry, Siena College

<sup>4</sup>Center for Air Resources Engineering and Science, Clarkson University

Measurements of particle number concentrations and size distributions were obtained using both nano- and long-tube scanning mobility particle sizers (SMPS) at the rural site of Pinnacle State Park (PSP) in upstate New York from July 18 through August 8 in 2004 and the urban site of Queens College (QC) in New York City from January 9 through February 6 in 2004. Due to the relatively high background levels of aerosols (and the associated condensation sink for new particles), condensation and growth events are much less common in these locations than reported by other groups for lower background sites.

With co-located measurements (such as ionic species from PILS-IC, oxygenated/hydrocarbon-like organic aerosol (OOA / HOA) from an Aerodyne Aerosol Mass Spectrometer, organic & elemental carbon from a SUNSET (NIOSH5040) real time carbon aerosol analyzer, gaseous pollutants, PM<sub>2.5</sub> using a tapered element oscillating microbalance (TEOM), and meteorological data), diurnal variation and correlation between particle number size distributions and ambient pollutants at two monitoring sites present a rich data set for exploration of particle growth events at high average background sites. Analysis of the characteristics of particle growth in comparison to other observations allow classification of the events and illustrate that particle growth contains different physical behavior related to different compounds for these sites. The growth rate associated with each event will be discussed in relation to physical, chemical, and meteorological conditions.

## A METHOD FOR EXTRACTING ADDITIONAL INFORMATION ON THE ORGANIC, ELEMENTAL AND PYROLYZED CARBON FROM REAL TIME MEASUREMENTS WITH THE SUNSET CARBON AEROSOL ANALYZER

Min-Suk Bae<sup>1</sup>, James J. Schwab<sup>1</sup>, Kenneth L. Demerjian<sup>1</sup>, Oliver Rattigan<sup>2</sup>, Dirk Felton<sup>2</sup>

<sup>1</sup>Atmospheric Sciences Research Center, University at Albany, State University of New York

<sup>2</sup>Division of Air Resources, Bureau of Air Quality Surveillance, NYS Department of Environmental Conservation

Semi-continuous Organic Carbon and Elemental Carbon (OCEC) instruments are becoming more widely employed to measure the carbonaceous fraction of atmospheric particulate matter. Determining accurate concentrations of atmospheric OC and EC is necessary for identifying their sources and predicting their effects on various atmospheric processes, but lacks the detail required to fully elucidate sources. We have obtained hourly time-resolved measurements of OC and EC at Pinnacle State Park (PSP) in upstate New York and the South Bronx, New York City. OC and EC were determined using a NIOSH-like protocol and a Sunset Real Time ECOC Analyzer - that is, using four temperature steps to a final temperature of 840 °C for OC and two steps to 850 °C for EC.

There is currently no standard procedure for determining concentrations of the empirical parameters OC and EC in the atmosphere, and there is considerable controversy over measurement methods and parameter designations. In this study, we examine contour plots of the time series carbonaceous concentrations associated with the analysis temperature steps in the hope of providing additional information and details into the carbonaceous nature of sources.

## INVESTIGATION OF SECONDARY ORGANIC SIGNALS IN NITRATE MEASUREMENTS BY AEROSOL MASS SPECTROMETER

Min-Suk Bae<sup>1</sup>, James J. Schwab<sup>1</sup>, Qi Zhang<sup>1</sup>, Olga Hogrefe<sup>1</sup>, Kenneth L. Demerjian<sup>1</sup>, Silke Weimer<sup>2</sup>, Kevin Rhoads<sup>3</sup>, Doug Orsini<sup>3</sup>, Prasanna Venkatachari<sup>4</sup>, Philip K. Hopke<sup>4</sup>

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<sup>3</sup>Department of Chemistry, Siena College

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Highly time-resolved measurements of nitrate in ambient aerosols were conducted by an Aerodyne Quadrupole Aerosol Mass Spectrometer (Q-AMS or simply AMS) and a Particle-into-Liquid Sampler with Ion Chromatography (PILS) from field intensives at two sites; an urban site in New York City (Queens College; QC) for wintertime (January 22 to February 5, 2004) and a rural site in southwestern New York state (Pinnacle State Park; PSP) for summertime (July 20 to August 4, 2004).

In this study, the inorganic nitrate signal from Q-AMS may contain significant interferences from organic signals, especially in rural atmospheres. Analysis of the QC data indicates a good agreement between the PILS-nitrate and AMS-nitrate measurements ( $R^2 = 0.94$ ; linear regression slope = 1.05). In addition, the  $m/z$  30 and  $m/z$  46 (two dominant ion fragments in nitrate mass spectrum) signals tightly correlate at QC ( $R^2 = 0.98$ ) and have an average ratio similar to that determined in the laboratory for  $\text{NH}_4\text{NO}_3$  ( $m/z$  30 /  $m/z$  46 = 2.4). In contrast, at the PSP site the correlation between PILS- and AMS-nitrate was poor ( $R^2 = 0.34$ ), the AMS reported nitrate values were substantially higher, and the  $m/z$  30 to  $m/z$  46 ratios were generally much larger than 2.4. These observations, together with evaluations by aerosol phase ion balance, indicate that the AMS  $m/z$  30 signals at PSP have been strongly influenced by organic compounds that also produce signals at  $m/z$  30, including organic nitrates ( $\text{NO}^+$ ), oxygenated organics ( $\text{CH}_2\text{O}^+$ ), hydrocarbon-like organics ( $\text{C}_2\text{H}_6^+$ ), and nitrogen-containing organic compounds ( $\text{CH}_4\text{N}^+$ ).

## A CASE STUDY OF URBAN PARTICLE ACIDITY AND ITS INFLUENCE ON SECONDARY ORGANIC AEROSOL

Qi Zhang, Jose-Luis Jimenez, Douglas R. Worsnop, and Manjula R. Canagaratna

Atmospheric Sciences Research Center, University at Albany, State University of New York, Albany, New York

The mass concentrations and size distributions of non-refractory (NR) chemical species (including  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ , and organics) in submicron particles (approx.  $\text{PM}_{10}$ ) were characterized using an Aerodyne Aerosol Mass Spectrometer (AMS) in Pittsburgh from September 6 to 22, 2002. Since Pittsburgh particles generally contain very low levels of the metal ions, such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$ , we estimated particle acidity based on ion balance between  $\text{NH}_4^+$  and the anions –  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ . Particles are considered “more acidic” if the measured  $\text{NH}_4^+$  concentration is significantly lower than the amount needed to fully neutralize measured anions (e.g., with the predicted stoichiometric ratio of bisulfate to sulfate  $> 1$ ) and as “bulk neutralized” if the two values are within 10%. The rest of the periods are excluded from the analysis. Changes of particle acidity as function of particle size and on a highly resolved time grid (5-10 min.) were investigated. Acidic particles were frequently detected, most often during the high-mass-loading periods, when the size distribution of particles is dominated by the accumulation mode. In order to examine the influence of particle acidity on SOA formation we examined the mass concentrations and size distributions of oxygenated organic aerosol (OOA) vs. particle acidity. OOA concentration and size distribution were estimated using a recently developed custom principal component analysis (CPCA) method [Zhang *et al.*, 2005a]. There is strong evidence that the majority of OOA in Pittsburgh is SOA [Zhang *et al.*, 2005b]. The average mass concentrations and size distributions of OOA were compared between acidic and neutralized periods (Figure 1a & 1b). The average size distribution during acidic periods is significantly narrower than that during neutralized periods. The average concentrations of OOA during acidic and neutralized periods were  $3.28 \pm 1.86$  and  $2.77 \pm 1.46 \mu\text{g m}^{-3}$ , respectively (Figure 1c). The much larger average hydrocarbon-like organic aerosol (HOA, closely related with combustion emissions in Pittsburgh) concentrations in neutralized periods is likely due to neutralized periods being more frequent in the morning and at night while acidic periods typically occur in the afternoon, when photochemistry is more active and HOA has been diluted by the rise of the boundary layer. The average OOA concentration during acidic periods is  $\sim 0.5 \mu\text{g m}^{-3}$  higher than that during neutralized ones. This enhancement is likely the outcome of SOA photochemical production followed by condensation and/or acid-catalyzed SOA formation. Nevertheless, if we attribute the entire difference to acid-catalyzed formation, we can estimate an upper bound of  $\sim 18\%$  increase of SOA mass in the ambient aerosol due to acid catalyzed SOA formation. This is the first dataset for which such an estimate has been made using ambient data. While this analysis has significant uncertainty due to the comparison of different time periods during a relatively short study, an important result is the lack of very large enhancements of SOA (e.g. several fold, [Jang *et al.*, 2002]) due to acid-catalyzed formation.

## A HIGH-RESOLUTION TIME-OF-FLIGHT AEROSOL MASS SPECTROMETER STUDY ON SIZE RESOLVED AEROSOL COMPOSITION AT THE PEAK OF WHISTLER MOUNTAIN DURING INTEX-B

Qi Zhang, Yele Sun, Richard Leitch, Anne Marie Macdonald, Kathy Hayden, Shao-Meng Li, John Liggio, Aaron van Donkelaar, Randall Martin, Douglas Worsnop, and Mike Cubison

Atmospheric Sciences Research Center, University at Albany, State University of New York

A new Time-of-Flight Aerosol Mass Spectrometer with a high mass resolution of  $\sim 5000$  (HR-ToF-AMS; DeCarlo *et al.*, *Anal. Chem.*, 2006) was deployed at the summit of the Whistler Mountain, British Columbia, from April 20 to May 17, 2006. With this instrument, we determined the concentration, composition, and chemically speciated size distributions of submicron particles (approximately  $\text{PM}_{10}$ ) every 5 minutes. We also obtained the highly  $m/z$ -resolved mass spectra, based on which the elemental composition of most small ion fragments ( $m/z < 100$  amu) was quantitatively determined. This improved chemical characterization of organic aerosol mass spectra significantly enhances our ability to address the sources and processes of organic aerosol. Organic aerosol (OA) prevailed at the Whistler summit (elev.  $\sim 2200$  m), accounting for  $\sim 50\%$  of the total  $\text{PM}_{10}$  mass. The OA appeared to be highly aged and was composed almost completely of oxygenated organic aerosol (OOA). Sulfate aerosol was usually less abundant than the OA but episodes of strongly enhanced sulfate aerosol were observed. A major sulfate episode occurred on May 15, 2006, during which ammonium sulfate contributed  $> 90\%$  of the total  $\text{PM}_{10}$  mass. This episode lasted for  $\sim 0.5$  day and was followed by a high organic aerosol episode. The mass spectra reveal that the organic aerosol is more highly oxidized during the sulfate period. Also, the high resolution mass spectra indicate significant structure difference in organic species between these two episodes. Simulations from a global model of oxidant-aerosol chemistry (GEOS-Chem), backtrajectory analysis, evolution of the size distribution of aerosol species, and

correlation of the Whistler aerosol spectrum with previous AMS measurements in rural British Columbia, and in Asia provide supporting evidence of Asian influence during the high sulfate period, in contrast with regional influence during the high organic period.

### **COMPONENT ANALYSIS OF ORGANIC AEROSOLS IN URBAN, RURAL, AND REMOTE ATMOSPHERES BASED ON AEROSOL MASS SPECTROMETRY**

Qi Zhang, Jose-Luis Jimenez, Katja Dzepina, Edward Dunlea, Ken Docherty, James Allan, M. Rami Alfarra, Paul Williams, Hugh Coe, Keith Bower, Manjula Canagaratna, Timothy Onasch, John Jayne, Douglas Worsnop, Akinori Takami, Takao Miyoshi, Akio Shimono, Shiro Hatakeyama, Silke Weimer, Ken Demerjian, Frank Drewnick, Nobu Takegawa, Yukata Kondo, Ann Middlebrook, and Roya Bahreini  
Atmospheric Sciences Research Center, University at Albany, State University of New York

More than 30 highly time-resolved organic aerosol datasets from the Aerodyne Aerosol Mass Spectrometer (AMS) were analyzed to gain insights into the characteristics, sources and processes of atmospheric organic aerosols. These datasets were sampled from 12 urban locations and 11 rural and remote sites representative of high elevation, forested, and pristine or continentally-influenced-marine atmospheres. Most of the sites are located in the Northern Hemisphere's mid-latitudes. The mass concentrations, size distributions, mass spectra, temporal, spatial, and seasonal variations of hydrocarbon-like and oxygenated organic aerosols (HOA and OOA, respectively) will be presented and compared among various locations. HOA and OOA are determined using a recently developed custom principal component analysis technique based on AMS mass spectral data [Zhang et al., 2005a]. In urban areas the extracted spectra of HOA are remarkably similar to those of directly sampled vehicle exhaust, while those of OOA are qualitatively similar across locations, and also show similarity with the spectra of humic and fulvic acids—humic-like substances representative of highly processed and oxidized organic compounds that are ubiquitous in the environment. There is strong evidence linking OOA with SOA and water-soluble organic aerosol in some studies [Dzepina et al., 2006; Kondo et al., 2006; Zhang et al., 2005b]. HOA represent a significant fraction of the organic aerosol in cities, although OOA are present in similar and even larger concentrations (Figure 1). Freshly-emitted combustion HOA appear as a distinct mode at small vacuum aerodynamic diameters at all urban locations due to their fractal morphology, which is confirmed by AMS "chase" sampling behind individual vehicles. HOA diurnal profiles are to a first order determined by the interplay of emissions and boundary layer height. OOA is generally concentrated in the accumulation mode, even in cities, suggesting that most SOA condensation occurs on regional rather than urban scales. At times OOA appears in the ultrafine mode, likely due to condensation of gas phase oxygenated organics on traffic particles or on growing sulfate particles. Organic aerosols at rural and remote locations are almost always dominated by oxygenated compounds with HOA typically accounting for 10% or less of the total OA mass (Figure 1). In one remote study where this analysis is possible, the HOA mass concentrations estimated from the AMS mass spectra are comparable to the POA concentrations estimated based on urban primary emission ratios of POA/BC or POA/CO, and the observed BC and CO enhancements. This observation suggests that urban combustion-related POA makes a small contribution to atmospheric OA mass loading on a regional-to-global scale, and that oxidation of POA is not a major source of OOA. Rural and remote OOA appear to be a mixture of a highly oxidized organic component with mass spectrum similar to fulvic acid and a less oxidized component that appears to be associated with biogenic sources. Correlations between the concentrations of less oxygenated OA and biogenic SOA tracers from GC-MS analysis will be presented. In addition, comparison of the degree of oxidation of atmospheric OOA to chamber SOA will be made based on AMS mass spectra.

### **OZONE, TRACE GAS, AND PARTICULATE MATTER, AND KEY INDICATOR MEASUREMENTS AT ASRC'S RURAL FIELD SITE IN ADDISON, NY: 1995 – 2005**

James J. Schwab, John B. Spicer, and Kenneth L. Demerjian  
Atmospheric Sciences Research Center, University at Albany

A research site for atmospheric chemistry and air pollution measurements was established at Pinnacle State Park in Addison, NY in 1995. This poster presents an overview of the site characteristics and measurement program, as well as monthly average concentrations for many of the trace gas and aerosol pollutants over the full measurement period. Monthly averaged ozone concentrations range from values as low as 15 ppb during cold season months, to values approaching 50 ppb during some spring and summer months. SO<sub>2</sub>, NO<sub>x</sub>, and NO<sub>y</sub> all show distinct seasonal variation, with summertime monthly averages as low as 1-3 ppb, and wintertime monthly averages from 6-12 ppb. The variation in CO is much smaller, with minimums of roughly 150 ppb, and maximums only rarely exceeding 250 ppb. Data for three hydrocarbon species, propane, benzene, and isoprene are presented. Propane and benzene show

higher monthly averaged concentrations in the winter, and lower values in the summer – with values ranging over a factor of 4 to 5. Isoprene, on the other hand has much higher values during the summer season, sometimes a factor of 10 or more greater than concentrations measured in the winter. Monthly averaged plots for PM<sub>2.5</sub> beginning in 1999 show a robust summer maximum and winter minimum, and a roughly factor of two difference between the two. An empirical measure of ozone production using the correlation of hour averaged ozone and nitrogen oxide data illustrates relatively robust ozone production during some, but not all, summer time months over the time period. Finally, the hour averaged ozone data are analyzed to determine the hour-of-day of the maximum ozone concentration. A frequency distribution of these maximum ozone hours shows a strong mid-afternoon peak, as expected, but also a prominent secondary maximum centered around midnight. The secondary peak is interpreted as ozone transported from ozone producing areas to the west, including Buffalo, Cleveland, Pittsburgh, and the Ohio Valley.

#### **CONTINUOUS MEASUREMENTS OF NITRIC ACID AND AMMONIA AT A RURAL NEW YORK SITE**

James J. Schwab, Min-Suk Bae, John Spicer, Kenneth L. Demerjian  
Atmospheric Sciences Research Center, University at Albany

Nitric acid and ammonia are trace gases that are not routinely monitored at atmospheric chemistry and air quality measurements site, but are of great interest to scientists and policy makers as they try to understand the air quality problems of oxidant and particulate matter formation. The EPA NCORE program strategy lists both nitric acid and ammonia as target species for continuous measurement, but there are not yet recommended continuous methods for either species. We have measured both of these species using continuous monitors at our research and monitoring site at Pinnacle State Park (PSP) in Addison, NY. The nitric acid method utilizes a denuder difference technique, specifically, the difference between a standard NO<sub>y</sub> channel and an NO<sub>y</sub> channel preceded by an annular denuder that removes HNO<sub>3</sub>. After a period of testing, we have settled on sodium chloride (NaCl) coated denuders to quantitatively remove HNO<sub>3</sub> without affecting other NO<sub>y</sub> species. We have about three years of HNO<sub>3</sub> data using the NaCl denuder at this site. Early in 2006 we deployed a continuous ammonia analyzer at the site – an AirSentry Ion Mobility Spectrometer (IMS). The technique utilizes ionization of the NH<sub>3</sub> molecule followed by electrostatic extraction of its ions into a drift chamber and detection at a collector plate. The ammonia molecule is identified by its unique time-of-flight in the drift chamber. The detection limit for the analyzer is on the order of 0.3 ppb. Results from a three month (March – May, 2006) field evaluation of this instrument at the PSP site are presented. Comparisons of the HNO<sub>3</sub> and NH<sub>3</sub> data sets for the overlap period are analyzed and presented.

#### **RELATIONSHIPS BETWEEN AEROSOL SCATTERING AND FINE PARTICULATES AT WHITEFACE MOUNTAIN IN UPSTATE NEW YORK**

Utpal K. Roychowdhury, Atmospheric Sciences Research Center  
University at Albany, SUNY

Although visibility is well correlated with fine particulate loading in the atmosphere, significant variations in relationship between these two parameters are often observed. Relationships between visibility and the fine particles in the Adirondack region of Upstate New York are explored for selected ‘events’. The dependence, if any, of B<sub>Scattering</sub> on the chemical compositions of PM<sub>2.5</sub> are investigated. The measurements were carried out at Whiteface Lodge (44° 23.597' N, 73° 51.531' W, 634 m above msl) as part of PMTACS-NY “Supersite” program.

#### **USE OF CMAQ MODELING SYSTEM IN FORECASTING PM<sub>2.5</sub> AIR QUALITY OVER NEW YORK STATE**

Prakash Doraiswamy\*, Atmospheric Sciences Research Center, University at Albany, State University of New York

Christian Hogrefe, Winston Hao, Kevin Civerolo, J.-Y. Ku and Gopal Sistla,  
Division of Air Resources, New York State Department of Environmental Conservation

\* On assignment to Bureau of Air Quality Analysis and Research, NYSDEC

In this study we report on the results of a pilot study in the application of a photochemical modeling system as a tool for forecasting air quality over New York State. The modeling system comprised of the use of ETA/CMAQ system up to June 2006 which was replaced with a WRF/CMAQ system subsequently, with a 12-km horizontal grid

resolution. Model simulations were conducted on a daily basis since June 2005, and the results reported here address the ability of the model in predicting PM<sub>2.5</sub> concentrations and thus its capability as a forecast tool.

Model based 24-hr average total PM<sub>2.5</sub> concentrations show better correlation (*r*) with measured concentrations during winter (1.3 to 2.5 times higher) than summer. Total PM<sub>2.5</sub> predictions for sites within the New York City area were often found to be in poor agreement with measurements. Median root mean squared errors [RMSE] were >15 µg/m<sup>3</sup>, and median normalized mean bias (NMB) >50% at sites within New York City compared to that at other sites in New York State that yielded median RMSE typically 5 µg/m<sup>3</sup> and median NMB within ±25%. The model is found to over-predict PM<sub>2.5</sub> concentrations for the New York City region, irrespective of the season, while it under-predicted during summer and over-predicted during other seasons for other sites in New York State. Comparisons with 24-hr average species concentrations suggest that the consistent over-prediction for New York City is related to overestimation of emissions utilized in the modeling system. Results also indicate under-prediction of secondary organic aerosol concentrations during summer. A comparison of diurnal predicted concentrations of PM<sub>2.5</sub> and constituent species with observed concentrations from continuous measurements at Bronx, NY shows inconsistencies in diurnal profiles during summer. These results suggest that there is an urgent need for improving the modeling system ability in estimating PM<sub>2.5</sub> levels and thus the forecasting capability over New York State.

### **LONG-TERM AIR QUALITY SIMULATIONS OVER THE NORTHEAST: MODEL PERFORMANCE AND POTENTIAL APPLICATIONS FOR HEALTH IMPACT ANALYSES**

C. Hogrefe<sup>1,2</sup>, B. Lynn<sup>3</sup>, K. Knowlton<sup>3</sup>, R. Goldberg<sup>4</sup>, C. Rosenzweig<sup>4</sup>, and P.L. Kinney<sup>3</sup>

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<sup>3</sup>Columbia University

<sup>4</sup>NASA-Goddard Institute for Space Studies

This study describes the use of long-term regional scale meteorological and air quality simulations for tracking changes in air quality and for supporting public health assessments. For this purpose, year-round simulations with the MM5/CMAQ modeling system have been performed over the northeastern United States for 1988 – 2002. Emission inputs for the CMAQ simulations were prepared with the SMOKE processing system and were based on available 1990 and 1996 – 2002 inventories. Model evaluation results show best performance for ozone and sulfate concentrations while model errors generally are larger for nitrate and organic carbon. During the analysis period, significant reductions in anthropogenic emissions of VOC, NO<sub>x</sub>, and SO<sub>2</sub> have occurred in the point source and mobile source sectors. For the purpose of dynamic model evaluation, simulated changes in long-term average acid deposition and atmospheric sulfate concentrations are compared against measurements obtained at National Acid Deposition Program (NADP) and Clean Air Status and Trends Network (CASTNet) monitors before and after the implementation of significant reductions in SO<sub>2</sub> emissions from power plants. Results show good quantitative agreement between observed and simulated changes. Furthermore, we describe how CMAQ model simulations can be integrated with available observations to characterize ambient air quality by generating daily gridded fields of O<sub>3</sub> and PM<sub>2.5</sub>. These fields can subsequently be used to study links between climate variability, air quality, and health by measuring the independent and joint effects of air quality and weather on acute mortality and hospitalization risks in New York.

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## **ALTERNATIVE ENERGY AND EMERGING TECHNOLOGIES**

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### **MITIGATION OF ECOSYSTEM DEGRADATION BY BIO-ENERGY USING BIOCHAR**

John Gaunt, Kelly Hanley, Johannes Lehmann  
Cornell University

Pyrolysis for bioenergy production combined with biochar application to land represents an exciting opportunity to off-set fossil fuel use, to support economic development whilst addressing the immediate and pressing problems of soil degradation resulting from biomass production and climate change resulting from the release of greenhouse gasses to the atmosphere.

Pyrolysis combined with biochar production and application to land offers an energy technology that delivers negative greenhouse gas emissions in combination with soil improvement. This preliminary feasibility assessment identifies that the technology can be applied in a number of situations relevant to New York State and we propose three models for further evaluation:

Model 1. Yard Waste - a municipal facility processing yard waste,

Model 2. Institutional Facility - to process compostable organic wastes in large institutional settings, and

Model 3. Green Business Park - to process animal wastes, co-located with other waste streams.

Our analysis of Model 1, suggests that a plant using yard waste as a feedstock will be financially viable based on estimates of revenues derived from a combination of tipping fees, biochar sales, carbon trading revenues and electricity production.

New York State represents an ideal situation to apply the technology. Our initial analysis suggests a hypothetical potential for the sequestration of at least 11.7 Million Metric Tons per Carbon Equivalent (MMTCE), representing 29,481 operating years of the slow pyrolysis technology.

Our preliminary analysis suggests that there is significant commercial potential within the turfgrass and wetland construction sectors as well as potential application in high value agricultural applications, suggesting that biochar application to land could be achieved under a commercial model. Further research is required to demonstrate and quantify the benefits of biochar in these settings to enable detailed product specification and market analysis.

In the next phase of this project, we will test the biophysical suitability of the various feedstocks identified to be of potential significance for New York State for their longevity in soil and their ability to improve soil productivity and to reduce off-site pollution by runoff, leaching and gaseous emissions.

### **ETHANOL/BIODIESEL – CHALLENGES AND OPPORTUNITIES**

Carl Mas, New York State Energy Research and Development Authority

The ethanol and biodiesel industries have seen unprecedented growth over the past ten years, fueled in part by State and National initiatives and growing public concern over energy security and climate change. In response, the New York State Energy Research and Development Authority (NYSERDA) has sponsored work by the Pace Energy Project that is developing a better understanding of the energy and environmental impacts associated with the use of these fuels. Find presented here the preliminary results of a literature review that examines total fuel cycle analyses for ethanol and biodiesel, focusing on: net-energy-ratio, greenhouse gas emissions, air pollutants, and land-use impacts.

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## CLIMATE CHANGE

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### PERMANENT CARBON DIOXIDE STORAGE IN DEEP OCEAN SEDIMENTS ALONG THE U.S. NE COAST

David Goldberg and Juerg Matter  
Lamont-Doherty Earth Observatory, Columbia University

Onshore deep saline aquifers, which could be used as potential large volume carbon dioxide storage sites, are not widespread along the NY coastline. This results in a mismatch between emission sources and sinks. Deep ocean sediments along the U.S. NE coast could provide the necessary storage capacity for permanent and safe carbon dioxide sequestration. At high pressures and low temperatures common in deep ocean sediments a few hundred meters below seafloor, carbon dioxide will be in its liquid phase and denser than the overlying pore fluid and seawater. The lower density of the pore fluid provides a cap to the denser liquid carbon dioxide and ensures gravitational stability.

The majority of tectonically stable ocean floor at necessary depths is composed of calcareous sediments. This study evaluates the feasibility of carbon dioxide injection in deep ocean sediments and estimates the potential storage capacity. Storage capacity varies with permeability and porosity of sediments, seafloor depth, geothermal gradient and pore water salinity. Using field data from deep ocean sediments we show how in-situ conditions may affect permanent storage of carbon dioxide.

### MODELING THE POTENTIAL IMPACTS OF CLIMATE CHANGE ON AIR QUALITY AND DEPOSITION OVER THE NORTHEASTERN U.S.

C. Hogrefe<sup>1,2</sup>, K. Civerolo<sup>2</sup>, J.-Y. Ku<sup>2</sup>, B. Lynn<sup>3</sup>, J. Rosenthal<sup>3</sup>, K. Knowlton<sup>3</sup>, B. Solecki<sup>4</sup>, C. Small<sup>3</sup>, S. Gaffin<sup>3</sup>, R. Goldberg<sup>5</sup>, C. Rosenzweig<sup>5</sup>, and P.L. Kinney<sup>3</sup>

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In recent years, there has been growing interest in estimating the potential impacts of climate change on air quality at regional and urban scales. To estimate the possible impacts of climate change on air quality and deposition over the Northeastern U.S., a suite of modeling tools was coupled over a wide range of scales. Global and regional climate change was simulated by the NASA-GISS Global Atmosphere-Ocean Model and the MM5 mesoscale model. Processing of anthropogenic and biogenic emissions was performed using SMOKE. Finally, CMAQ was utilized to simulate air quality for various future climate scenarios. Results indicate that climate change under the IPCC A2 emissions scenario is expected to cause an increase in summertime average daily maximum 8-hr ozone concentrations as well as an increase in the frequency and duration of extreme ozone events compared to the 1990s, with the number of ozone exceedance days almost doubling by the 2080s. Over a number of eastern US watersheds, the modeling system also estimates 3-14% increases in Nitrogen deposition as a result of climate change by the 2050s. Through additional sensitivity analyses, it is further shown that potential increases in urban land use for the New York City metropolitan area could result in a local rise in temperatures, altered flow patterns, local decreases in biogenic emissions and shifts in the spatial patterns of extreme air pollution events.

## **CARBON SEQUESTRATION UTILIZING THE WOLLASTONITE RESOURCES OF NEW YORK STATE**

Sam Krevor, Klaus S. Lackner, Columbia University

Several mineral types have been identified as candidates for use in a mineral carbonation process. Due to its high reactivity relative to other minerals, the process has already been successfully demonstrated with the calcium silicate mineral wollastonite. Despite this early success, research on mineral carbonation has focused on magnesium silicate minerals such as olivine and serpentine because wollastonite is relatively rare. The largest deposits of wollastonite in the United States, however, exist in Essex and Lewis counties of New York State. The deposits are currently being mined by the NYCO and R.T. Vanderbilt mining companies. It is estimated that there remain 7-14 Mt of wollastonite that would be sufficient for the permanent sequestration of 2-5 million tons of carbon dioxide. This project seeks to demonstrate the feasibility of utilizing this resource for the permanent disposal of carbon dioxide.

## **CARBON SEQUESTRATION IN NEW YORK**

Langhorne (Taury) Smith, Richard Nyahay, Alexa Stolorow  
Reservoir Characterization Group, New York State Museum Institute

## **PLANYC 2030**

Carter Strickland, Jr.  
Mayor's Office of Long Term Planning and Sustainability

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## **ENVIRONMENTAL TECHNOLOGY: POWER GENERATION**

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### **MODELING ADVANCED DESIGNS FOR ZERO EMISSION POWER PLANT TECHNOLOGIES**

Xinxin Li, Columbia University

The study proposes to develop a computational model that will analyze power plant components and will enable a modeling exercise to combine existing technology components into innovative thermal power plant designs. By defining the criteria performance of each module and identifying performance-limiting steps in each module, we are able to compare the advantages and disadvantages of the modules with similar functions, and further compare different plant designs we produce.

The study will be conducted in three stages as follows:

- Development of a computational model to assess emissions and energy efficiencies of a wide range of combinations of power plant components.
- Assessment of a wide range of power plant designs based on overall emissions and energy efficiency criteria and creation of a technology roadmap to demonstrate how components of existing designs might be combined in next generation power plants.
- Dissemination of results to industrial and energy policy groups including ongoing programs established at Columbia University.

### **USING LIBS MEASUREMENTS FOR COAL QUALITY MONITORING AND UPGRADE POWER PLANT CONTROL**

Carlos Romero and Ricardo Moreno, Energy Research Center; Lehigh University  
Arel Weisberg, Joseph Craparo, Larry Mulligan and Robert De Saro; Energy Research Company

Laser-induced breakdown spectroscopy (LIBS) has been applied to measure key inorganic components in coal ash – such as Si, Al, Fe, Na, Ca, Mg, and K - which contribute to the slagging and fouling behavior of pulverized coal. A coal inventory was assembled from fuels used at utility boilers, with a range of slagging/fouling characteristics. These coals included Eastern US bituminous and sub-bituminous coals, and some foreign fuels. These coals were tested in a custom-built LIBS analyzer for ash metal composition and major element concentration (i.e. C and S). The elemental analyses will be used in concert with an artificial intelligence algorithm to estimate a slagging index and the ash fusion temperature for the prediction of ash deposition behavior. The preliminary resulting values of the predicted indices are very similar to the resulting indices from standardized coal analysis procedure. The integrated approach will be tested at a 650 MW coal-fired unit to demonstrate the real-time capabilities of this technology to monitor coal ash composition, slagging prediction and recommend actions to the operators for boiler operation modifications for slagging mitigation.

### **CASE STUDY: USING MILLING TECHNOLOGY AND CFD MODELING TO IMPROVE TRONA UTILIZATION FOR SO<sub>3</sub> CONTROL AT AES SOMERSET.**

### **CASE STUDY: USING TRONA INJECTION TO CONTROL SO<sub>3</sub> AND IMPROVE EFFICIENCY AT A COAL-FIRED POWER PLANT**

Jonathon Norman, P.E., O'Brien & Gere

O'Brien & Gere has successfully used trona injection at the AES Somerset power plant to control SO<sub>3</sub> emissions. SO<sub>3</sub> emissions result in a visible blue or brown plume and also cause corrosion of flue gas systems at coal-fired power plants. Although trona injection is proven to be effective for SO<sub>3</sub> control, this NYSERDA-funded study

looked at using O'Brien & Gere's milling technology, as well as using computational fluid dynamics (CFD) modeling for injection grid design, to improve the utilization of trona. The study concluded that using in-line milling and CFD modeling of the injection grid substantially increased trona utilization and therefore improved the economics of using trona injection for SO<sub>3</sub> control.

In addition, this study used SO<sub>3</sub> measurements at several locations in the flue gas system to determine the trona injection rate that would be needed to safely and effectively remove SO<sub>3</sub> at the air pre-heater inlet. Trona injection at the air pre-heater inlet would lower the acid dew point in the flue gas duct, therefore allowing a coal-fired power plant to lower the flue gas temperature. Lowering the flue gas temperature would reduce fuel use and therefore emissions, including CO<sub>2</sub> emissions.

### **SUBSTRATUM INTAKE SYSTEM: AN ALTERNATE POWER PLANT COOLING TECHNOLOGY**

Roy R. Stoecker, PhD, James E. McAleer, BA, and Michelle K. Nannen, MS  
EEA: Energy & Environmental Analysts, Inc.

An alternate form of power plant cooling has been developed by a team of hydrogeologists, engineers, and biologists at EEA, Inc. This cooling technology, the Substratum Intake System (SIS), is novel because it utilizes the natural sandy substrate that exists under many large bodies of water as a pre-filtering agent to eliminate all of the environmental drawbacks (impingement & entrainment) cited under EPA 316 (b).

Traditionally power plants use surface water intakes to supply the enormous demands of their once-through-cooling systems. Because SIS intake laterals are installed below the seafloor pulling water through stainless steel screens only sterile water is taken into the internal workings of the plant's cooling system.

SIS introduces a concept EEA engineers call cold geothermal cooling by providing cooling water at colder temperatures during summer. The result enables much greater operating efficiencies in energy production meaning a reduction in the amount of fuel required to produce the same amount of energy and likewise a reduction in stack emissions. Just a small temperature change can have a significant impact on fuel consumption but the benefit is extended further because exiting cooling water is returned to the environment at lower temperatures mitigating thermal discharge concerns cited under EPA 316 (a).

Reductions in O&M are another byproduct of SIS. Because incoming water is sterile no biocides are required and unit shutdown for condenser cleaning is no longer necessary during peak load periods. Directional drilling is utilized for installation and well fields are custom designed to meet the requirements of each plant. No plant shutdowns or alterations are required during installation and no impacts on marine environment are encountered. The ability to revert to surface water intake is retained providing a fail-safe system of operation.

EEA is also considering the financially promising installation of the system in fractured bedrock given the cost efficiencies SIS has over the construction, operation and maintenance of cooling towers.

The SIS idea was conceived in March of 2003 by Roy Stoecker, a principal scientist at EEA, and then submitted for a patent in September of that year. This system has developed rapidly and expanded in the past few years. The SIS caught the attention of the Electric Power Research Institute (EPRI) and NY State Department of Environmental Conservation (NYSDEC) both of which invited the SIS team to make formal presentations. KeySpan then awarded EEA with a feasibility contract to determine if the Northport Power Station would be a suitable location to pilot the SIS. By 2005, the EPA and water industry engineers had taken favorably to the SIS concept. Also, a new SAS (Scattered Array System - desalinization concept using SIS technology) and STS (Substratum Tandem System – a co-located SIS and SAS) were developed, both of which are patent pending.

SIS was awarded a patent in October of 2006. Construction of a pilot will begin in early 2008 through a NYSERDA grant and additional funding through the Long Island Power Authority and KeySpan Energy, a division of National Grid. It should be noted that SIS retains all the advantages of once-through-cooling while addressing the environmental concerns associated with it. The cost of installation is more than offset by the operating efficiencies it provides which cannot be said of any other product intended to meet NPDES (National) or SPDES (State) regulations.