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Chlorophyll a and Total Phosphorus: New to the Complement of Chemical Parameters Analyzed by the Adirondack Long-Term Monitoring Program.

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Reductions in emissions may change the biological activity and production within lakes and ponds in the Adirondack Mountains of Upstate New York. Baseline monthly data are necessary to capture the seasonal changes in water chemistry associated with biological production. Long-term biological data collection, based on a review of the monthly data, is necessary to evaluate potential acidic deposition recovery in Adirondack lakes and ponds. In October 2008 the Adirondack Lakes Survey Corporation (ALSC) began collecting and analyzing total phosphorus and chlorophyll a for inclusion in the Adirondack Long-Term Monitoring program (ALTM) suite of water chemistry parameters. Total phosphorous and chlorophyll a data will assist analysis and evaluation discussions of acid deposition recovery in Adirondack waters.

A Comparison of Contemporary Cloudwater pH to Pre-Industrial Values at Whiteface Mountain

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Fossil fuel combustion, the oxidation of sulfur and nitrogen compounds to sulfuric (H₂SO₄) and nitric acids (HNO₃), produces elevated acidity concentrations in non-precipitating clouds in the atmosphere. High elevation forested areas in the Adirondack Mountains have been impacted by the acidity levels of cloud water. Recent acidity levels of cloudwater exhibited values of SO₄²⁻ more than 6 times the level that produced baseline pre-industrial pH values that ranged from 4.5 to 5.6. The researchers found that the wind direction of clouds that pass over Whiteface Mountain varied from summer to summer. The research team analyzed three major ions (SO₄²⁻, NO₃⁻, & H⁺) found in cloud chemistry during several summers. The researchers determined that cloud water acidity levels are related to wind direction and have identified 15 wind octants since 1994 that are associated with baseline pre-industrial pH values. The researchers conclude that the pH of clouds will approach the lower limit of pre-industrial pH when SO₄²⁻ and NO₃⁻ are consistently below the target values of 35 µeq/L and 22 µeq/L, respectively.

The TERRA Mercury Network: Understanding Mercury in Terrestrial Ecosystems

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The TERRA (Terrestrial Ecosystem Research and Assessment) Mercury Network, which currently includes 221 locations around the globe, focuses on using songbirds and bats to determine the potential negative impact of pollutants on terrestrial ecosystems. Mercury (Hg), a toxin long thought to affect only aquatic systems, also has the ability to move into terrestrial systems and bioaccumulate in upper trophic level terrestrial organisms. TERRA examines mercury exposure in multiple aspects of ecosystems, including atmospheric deposition, soil, litterfall, several invertebrate compartments, songbirds, and bats. The breadth of this inquiry allows us to track how inorganic mercury moves into ecosystems, becomes bioavailable to organisms, accumulates in invertebrates, and then biomagnifies up the food chain in several TERRA sites in New York State.

Assessing the Impact of Long-term Mercury Contamination on Wildlife Health in New York, Using the Common Loon as a Sentinel Species

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Exposure of wildlife to mercury through atmospheric deposition and biomagnification is a concern throughout the upper Midwestern and Northeastern U.S. and Canada due to depositional, geological, and pedological characteristics of the area. The common loon (*Gavia immer*) is employed in this study as a sentinel species for aquatic ecosystems to assess the effect of long-term mercury accumulation on wildlife health in New York's Adirondack Park. Mercury suppresses immune function in young loons in the laboratory, but the impact on the immune system of wild loons is unknown. By evaluating the immune function of loons in relation to their mercury burden, this project will provide an increased scientific understanding of the (possibly synergistic) interactions between multiple stressors on wildlife health. In 2008 and 2009, a total of 37 loons (25 adults and 12 juveniles) were captured using nightlighting and playback techniques on 19 lakes in the Adirondack Park. Blood samples were collected for evaluation of mercury levels, health parameters, and immune function. Birds were banded with USFWS bands and a unique color combination of plastic bands to facilitate subsequent observations to determine reproductive success and long-term survival and site fidelity. Loon immune function was measured by adapting in-vitro methods using cryopreserved lymphocytes. Proliferation was assessed by an ELISA measuring the incorporation of bromodeoxyuridine into newly synthesized DNA. Thrombocyte and heterophil contamination was higher in loons than in other species. This research addresses a primary data gap of how mercury interacts with other stressors by suppressing the immune system and increasing the susceptibility of birds, thus contributing to an improved understanding of potential causes of population changes; contributes to the management of wildlife populations and regulation of environmental pollutants by evaluating the risks contaminants pose to wildlife health; and provides policy-makers with essential scientific information for making informed decisions about critical environmental protection.

Assessment of Methylmercury Availability to Bats in New York – 2006-2009

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More than half the species of bats in the U.S. can be characterized as occasionally foraging over water and on emergent insects. There have been very few investigations of bat exposure to metals. For a variety of reasons relating to their natural history and vulnerability to some human impacts, an alarming 56% of the U.S. bat species were either listed as endangered or were under consideration for listing as of 2001. Bats have the highest percentage of endangered or candidate species among all the mammals in the United States. This research presents findings from an effort to evaluate mercury (Hg) exposure in various species of bats from New York State. Fur was sampled from 196 bats at 14 different sites around New York. The samples were analyzed for total Hg (60-90% Hg fur is MeHg). The researchers found 22% of the bats sampled had Hg concentrations in their fur above lowest observed effects levels in dosed mice. This study indicates that bats can be used as bioindicators for atmospheric and point-source contaminated areas.

**Long-term Effects of Liming on Carbon and Nitrogen Cycling in the Woods Lake Watershed,
Adirondack Park (Recipient of EMEP Student Fellowship)**

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Nutrient availability in Northeastern U.S. forests has been dramatically altered by anthropogenic activities. Acid deposition has increased nitrogen (N) availability, but has also been linked to soil acidification and a loss of base cations, largely calcium (Ca). The research team is studying the long-term effects of a Ca addition on carbon (C) and nitrogen (N) cycling. In 1989, calcium carbonate (lime) was added to two subcatchments within the Woods Lake Watershed, Adirondack Park New York, while two additional subcatchments were left as controls.

Nineteen years after the Ca addition, soil exchangeable Ca and pH remain elevated in the limed plots relative to the controls. The mass of the forest floor at Woods Lake is very large (100-200 tons/ha), and measurements show that the forest floor in the limed plots is significantly larger than that in controls. This pattern appears to be driven by differences in the mass of the Oa soil horizon and leads to increased total soil C and N stocks in the limed plots relative to one of the control subcatchments. Percent C and N of the forest floor and mineral soils appear to be less affected by the Ca addition. Findings suggest decreased rates of decomposition, increased rates of litter or root production in the limed subcatchments, or stabilization of organic matter resulting from the increased Ca availability. Trees growing in limed plots show a small but significant growth enhancement relative to controls. Ongoing research includes further investigation of these processes.

Critical Loads of Sulfur and Nitrogen Deposition to Protect and Restore Acid-Sensitive Resources in the Adirondack Mountains: Progress to Date

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A multi-disciplinary and multi-institutional effort to establish critical loads (CL) for sulfur (S) and nitrogen (N) deposition continues in the Adirondack region of New York. This research builds upon a project recently completed for NYSERDA in which the same research team modeled the acid-base response of 70 Adirondack lakes in response to historic acidic deposition and several scenarios of future emissions controls using the model of acidification of groundwater in catchments (MAGIC) and the integrated biogeochemical model PnET-BGC. The lakes studied include a group of statistically selected lake-watersheds that can be directly extrapolated to the full population of acid-sensitive Adirondack lakes, and a group of lakes for which chemical and biological long-term monitoring data are available. This project provides data that will inform management of New York ecosystems that have been highly impacted by acidic deposition.

Acidic Deposition Effects on Sugar Maple in the Adirondacks: Linkages Among Streams, Soils, and Vegetation Health – Background, Objectives, and Field Sampling

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The research team studied the health and regeneration of sugar maple trees in association with chemical characteristics of watershed soils in the Oswegatchie and Black River basins in the western Adirondack Mountains. This region receives relatively high levels of atmospheric sulfur (S) and nitrogen (N) deposition that has lowered the acid-buffering capacity of soils by depleting calcium (Ca) reserves at some locations. The research team measured the relative abundance, growth, regeneration, and/or health of sugar maples in particular areas of the study sites along with the base cation supply and other soil characteristics. The research team identified relationships among sugar maple growth and health, soil chemistry, and stream chemistry. These data will contribute to the development of an integrated ecosystem assessment of acidic deposition effects in the Adirondack region.

Comparison of the New York State Atmospheric Deposition Monitoring Program with Nearby NADP Sites

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The New York State Department of Environmental Conservation (NYSDEC) has been monitoring acidic deposition across the state since the mid-1980s. In contrast to the mostly rural National Atmospheric Deposition Program (NADP)/National Trends Network (NTN), the 20 NYSDEC monitors are located in urban, suburban, and rural settings. These two networks measure a number of common parameters and have a similar weekly sampling schedule, but some of the operating procedures are different. In an effort to quantify potential differences or biases between the two networks, the researchers focus on four pairs of nearby (<10 miles apart) sites across NY. The NADP/NTN and NYSDEC monitors at Whiteface Mountain are less than 10 miles apart. The researchers compared trends and average levels of precipitation chemistry over the past two decades by performing ion and conductance percent difference (IPD and CPD) checks on the datasets. The research team found that there are fewer samples in recent years that do not meet the IPD criteria established by the NADP/NTN than in earlier years. The preliminary results presented here suggest that the NYSDEC network can supplement the spatial coverage of the NADP/NTN monitoring efforts in New York State to provide valuable data for ecosystems research and management.

Baseline Measurements of Ambient Concentrations of Elemental, Reactive Gaseous and Particle-bound Mercury at Two Urban Locations in New York

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Since 2008 the New York State Department of Environmental Conservation has been monitoring wet deposition of total mercury with Mercury Deposition Network (MDN) samplers and ambient levels of elemental mercury (Hg^0), reactive gaseous mercury (RGM), and particle-bound mercury (PBM) in Rochester and New York City using full speciation Tekran systems. These data will be used to monitor baseline concentrations and deposition of mercury prior to planned state and national emission reduction programs, and eventually will be included in the national Atmospheric Mercury Initiative. Preliminary findings of this monitoring effort are presented here, including spatial, diurnal and seasonal variations, analysis of co-pollutants, and lessons learned. Also, several high pollution episodes and high RGM events over this period are examined, using wind roses and back trajectory analysis.

Mercury and Selenium in Fish in Important Recreational Waters of New York State

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During the last century, atmospheric deposition has caused increased mercury (Hg) levels in freshwater ecosystems in the northeastern United States. In many areas of this region, mercury levels have risen to levels high enough to threaten aquatic ecosystem health and pose potential health risks to people that consume fish. Atmospheric mercury emissions have been significantly reduced in the Northeast, and there is interest in further reducing mercury emissions from the utility sector. There is a need to quantify the resulting changes in mercury deposition and the impacts on the aquatic resource. The research is in the second year of a mercury monitoring program for fish. Data obtained in the Strategic Monitoring of Mercury in New York State Fish study have been compared with data from an earlier mercury study for 12 Adirondack lakes. A small but statistically significant decrease was found in mercury in yellow perch in these lakes. There was a large amount of variability from lake to lake. Five of the 12 lakes had a significant decrease in mercury, five lakes showed no significant change, and only two lakes had a significant increase in mercury in yellow perch. In the current study, these lakes will be re-sampled to determine if these trends continue.

A Fifteen Year Dataset on Chemistry and Biota in Adirondack Lakes: Trends and Future Directions

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In 1994, the Adirondack Effects Assessment Program (AEAP) began synoptic sampling on 30 ponded waters investigating physical, chemical, and biotic parameters: bacterioplankton, phytoplankton, zooplankton, macrophytes, and fish. The AEAP was designed to assess various trophic levels to estimate ecosystem health while gathering baseline data to evaluate long-term changes of lake communities as indicators of ecosystem recovery. Midsummer epilimnetic and hypolimnetic chemistries from 1994-2008 revealed that the majority of lakes increased in pH and acid neutralizing capacity (ANC). In both the epilimnion and hypolimnion bacterioplankton species diversity increased with pH. Phytoplankton species richness also increased with increasing pH. No clear trends towards increasing number of taxa, however; or other assemblage changes, were evident. Twenty-eight species of microcrustaceans and 53 species of rotifers displayed differential sensitivity to acidity and showed direct correlations of species richness and diversity with pH that were readily apparent during 1994-1996. Macrophyte diversity increased with increasing pH. Fish species richness ranged from 0 to 18 species. Species composition differed both among lakes and within lakes over time. Establishment of exotic fish probably masked any assemblage changes caused solely by physico-chemical changes. The researchers concluded that the chemical recovery from acidification is occurring more quickly than the biological recovery. While some biotic recovery is occurring, it is insufficient to overcome individual lake variability in zooplankton species richness and community composition and annual variation in weather and local ecological conditions.

Role of Residence Time in an Oligotrophic Lake on Increased Export of Dissolved Organic Carbon

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Dissolved organic carbon (DOC) plays an important role in terrestrial and aquatic ecosystems including the production, decomposition, sedimentation and transport of organic matter. The dynamics of DOC are affected by the deposition of atmospheric pollutants and alteration of climate. The researchers studied DOC at inlet and outlet of Arbutus Lake located in the central Adirondack Mountains of New York from 2000 to 2007. In outlet DOC concentration, a linearly decreasing pattern was shown from 2000 to 2003 ($\text{Conc.} = -0.06 \cdot \text{day} + 2527$, $R^2 = 0.08$, $p < 0.001$), but from 2004 to 2007, a sine curve pattern was indicated ($\text{Conc.} = 72 \cdot \sin(2\pi \cdot \text{day} / 365 + 6.3) + 437$, $R^2 = 0.30$, $p < 0.001$), even though no distinct difference of inlet DOC patterns occurred between the two periods shown. In 2007, stable carbon isotopic ($\delta^{13}\text{C}$) analysis of DOC was used to determine whether the carbon was derived from terrestrial (allochthonous) or aquatic sources (autochthonous). Isotopic values were compared by season (dormant versus growing) and between the lake outlet and major inlet. There was no significant difference ($p > 0.05$) between sampling periods and sites ($\delta^{13}\text{C}$ value: -26.5 ± 0.7 ‰). These results suggest that for 2007 there were no marked changes in DOC due to autochthonous processes as DOC passes through the Lake. Future work will refine these analyses and determine the sources of DOC and how DOC concentration varies as a function of water source and season.

The Importance of Soil Mineralogy to Calcium Availability in Forests

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Calcium depletion in northern hardwoods has been implicated in sugar maple decline, increased winter frost injury to trees, and other environmental problems. Apatite is a trace mineral that is widely appreciated as the primary source of phosphorus (P), but has been only recently recognized as an important source of calcium (Ca). Soil samples were collected from 21 sites across the northeastern US and subjected to a 3-step sequential extraction that distinguished exchangeable Ca from readily weathered (apatite and calcite) and less readily weatherable mineral forms. Leaf litter was also analyzed from the dominant tree species to assess which species were most likely to reflect weathering of Ca from apatite pools. The research team found that birch species, red maple, and sugar maple showed the most response to soil variation in Ca. Spruce and fir showed the least response, having low Ca across all sites. It is not yet clear from this analysis that any soil horizon or extract is a better predictor of leaf Ca.

Atmospheric Deposition and Cycling of Mercury in Adirondack Forest Ecosystems

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The western-central Adirondack region is considered to be a biological mercury hotspot. The majority of mercury contamination in the Adirondacks is due to atmospheric deposition. This study investigated atmospheric deposition and cycling of mercury across the Adirondack region using both intensively sampled plots and extensive regional survey methods at two locations: Huntington Forest and Whiteface Mountain. The goal of the Huntington Forest project was to compare and contrast mercury cycling between hardwood and coniferous forest plots, while the goal of the Whiteface Mountain project was to examine mercury deposition across an elevation gradient and among different forest community types. At each site, canopy vegetation, litterfall, throughfall, and soil were collected regularly from May-October 2009. In addition, a cloudwater collector was installed at the summit of Whiteface Mountain to quantify mercury inputs from cloud deposition and an extensive survey was conducted at 50 sites across the Adirondack Park. Each site was visited once during the 2009 season, and canopy vegetation, forest floor and mineral soil samples were collected from each site. Canopy vegetation was used as an indicator of atmospheric deposition with the goal of characterizing spatial patterns of mercury deposition based on latitude, longitude, elevation, precipitation, and forest type. This combination of intensive and extensive research will provide significant insight into mercury deposition and cycling within the Adirondack Park.

The Production and Transfer of Methylmercury within Terrestrial Foodwebs across the Northeastern Land (Recipient of EMEP Student Fellowship)

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Mercury (Hg), a potent neurotoxin, has been shown to impact the behavior, growth, and reproductive success of wildlife through bioaccumulation within food webs. The detrimental effects of Hg contamination have been extensively documented in aquatic ecosystems, but it is equally important to understand the impacts that Hg deposition, methylation, and bioaccumulation may have on biota within the adjacent, surrounding landscape. Unfortunately, relatively few studies have focused on the mechanisms of Hg bioaccumulation in terrestrial ecosystems.

From 2005-2009, soils, litterfall, Sphagnum moss, fresh vegetation, invertebrates, and songbird blood and feather samples were collected at over 60 study sites within the northeastern United States. Samples were analyzed for total mercury, methylmercury (MeHg), and $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ stable isotopes as a means to better define the connections between mercury deposition and the ecological health of forested landscapes across the Northern Forest region.

Regional Forest Health and Stream and Soil Chemistry Using a Multi-Scale Approach and New Methods of Remote Sensing Interpretation, Catskill Mountains, NY

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Collaboration between the US Geological Survey and the US Forest Service has linked field and remote sensing data to produce the most detailed maps to date of forest, soil, and surface-water condition. The resulting GIS database highlights forest stands and watersheds sensitive to changes in atmospheric deposition and logging in the Catskill Mountain region. During this collaboration, the researchers have further developed existing remote-sensing methods for forest condition mapping that makes 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 is 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 have been 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 used 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.

Impacts of Acidification on Macroinvertebrate Communities in Streams of the Adirondack Mountains, New York, USA

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Decreased acidity of precipitation and small increases in acid neutralization capacity (ANC) have occurred in lakes of the southwestern Adirondack Mountains since the 1980's. However, little is known about the effects that acid deposition has had on chemistry and macroinvertebrate assemblages in local streams. Water chemistry in 200 headwater streams of the region was assessed during 2002-04 to characterize current effects of acidification. Macroinvertebrates were sampled at 35 of these streams where median ANC ranged from -36 to 309 $\mu\text{eq L}^{-1}$, pH ranged from 4.37 to 7.68, and inorganic monomeric aluminum (Al_{im}) concentrations ranged from 0.1 to 11.2 $\mu\text{mol L}^{-1}$. Inorganic monomeric aluminum periodically reached concentrations toxic to acid-tolerant brook trout in as many as 45% of the 200 streams. A new macroinvertebrate Acid Biological Assessment Profile index (acidBAP), derived from percent mayfly richness and percent acid-tolerant taxa, was strongly correlated with pH, ANC, and Al_{im} concentrations. A combination of pH, sulfate, nitrate, DOC, and Al_{im} accounted for 58 to 76% of variability in the index. AcidBAP data indicate that macroinvertebrate communities in 56% of the 35 streams were negatively affected by acidification. If these streams are representative of all streams in the region, acidification may be seriously disrupting ecosystems in many other Adirondack Mountain streams.

Mercury in Wet-Only Precipitation in the Catskill Mountains, New York, 2004-2008

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In March 2004, the U.S. Geological Survey, in cooperation with the New York State Energy Research and Development Authority, installed a Mercury Deposition Network (MDN) collector in the Biscuit Brook watershed (USGS gaging station number 01434025) in Ulster County, NY. The MDN collector was co-located with the existing National Atmospheric Deposition Program National Trends Network (NADP/NTN) collector on land owned by the Frost Valley YMCA. Weekly wet-only precipitation samples have been collected at the site through the 2008 calendar year. Total mercury concentrations in wet-only precipitation were generally low (median of 6.6 ng/L for the study period) at Biscuit Brook compared to other areas of the country. In contrast, annual total mercury deposition (the product of precipitation amount and Hg concentration) was high (mean of 9.6 ug/m² from 2005 through 2007) relative to the rest of the northeastern US and comparable to deposition in Pennsylvania. This difference between concentrations and deposition resulted from higher annual precipitation at the Biscuit Brook site than at other sites throughout the Northeast. Biscuit Brook receives higher annual precipitation because of the orographic effect caused by the Catskill Mountains and moisture that moves northwest from the Atlantic Ocean. Surface-water mercury concentrations are low in the Catskills compared to other areas of New York, such as the Adirondack Mountains. However, high concentrations of methylmercury have been measured in fish and other aquatic biota in another Catskill stream, the Neversink River and its reservoir.

**Mercury Deposition through Litterfall and Subsequent Accumulation in Soils:
Influence of Forest Community Type**

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The researchers investigated the influence of forest community type on mercury deposition to forest soils, more precisely to the Oi, Oe, Oa, and A soil horizons. Studies have estimated that roughly half the mercury deposition in forests occurs through litterfall. Because of the importance of litterfall in the mercury deposition process, the presence or absence of forest and the type of forest may have a large impact on the magnitude of the deposition fluxes and the accumulation in soils. Also, the concentration of mercury in soils is related to the retention of organic carbon. Eighteen sites were sampled throughout Vermont in 2008 and 2009. The sites were located in three distinct Northern Forest community types: Northern Hardwoods, Enriched Northern Hardwoods, and Lowland Spruce-Fir. The researchers sampled total mercury (THg) concentration in the upper soil horizons at nine sites in 2008 (THg: 59-300 ng/g, n=100), as well as mercury concentration in leaves at five of these sites, for each major tree species present (THg: 23-104 ng/g, n=25). Results were consistent within soil horizons and within tree species. The researchers measured total leaf mass at senescence at these five sites and estimated total mercury mass per hectare deposited yearly through litterfall for each site. The researchers calculated mercury to carbon ratios for each soil horizon and compared ratios. In addition to the role of soil chemistry, the researchers also considered the role of the earthworm and its potential impact on soil retention of mercury.

Gravitational Trapping of Carbon Dioxide in Deep Ocean Sediments

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At the high pressures and cold temperatures of the deep (>2 miles) marine sediments off the coast of New York State liquid carbon dioxide is denser than the surrounding pore water and will sink under gravity. Deep ocean sediments off the New York State coast therefore offer a very large stable reservoir for disposal of New York State's carbon dioxide emissions. Unfortunately, the low permeabilities of most deep ocean sediments will require injection enhancement to achieve economically viable CO₂ injection rates. Two options for injection enhancement are fracturing or chemically altering the sediments. The researchers propose to test several procedures for chemically altering sediments. A high-pressure flow-through system has been built at Schlumberger-Doll Research Center in Cambridge, Massachusetts to measure permeability changes of rock cores from geochemical reactions (dissolution/precipitation and hydrates) and geomechanical stresses. Among the more reactive rocks, the researchers plan to include Indiana limestone, Baker dolomite, and, if possible, a turbidite. The planned measurements include pressure, porosity, phase saturation, and effluent elemental content in order to analyze the effect of dissolution and precipitation on permeability. Permeabilities are not expected to change dramatically in sandstones from either salt precipitation or mineral dissolution, while carbonates are expected to show changes in permeability. The role of confining stress is unknown. Hydrate formation is expected to shut down all permeability, acting as a seal, and reducing leakage potential.

CO₂ Capture using NIMS and Ex-Situ Carbon Mineralization using Wollastonite

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Carbon mineralization is one of the safest methods of sequestering anthropogenic carbon dioxide. It is based on the reaction of carbon dioxide with the metal ions present in silicate minerals to form geologically and thermodynamically stable mineral carbonates. For large-scale carbon mineral sequestration processes, magnesium silicate is the most suitable mineral due to its abundance in nature. Thus, research on CO₂ mineralization has been focused on magnesium silicate minerals such as olivine (Mg₂SiO₄) and serpentine (Mg₃Si₂O₅(OH)₄). However, calcium silicates including wollastonite (CaSiO₃) have not been investigated for carbon sequestration. Although relatively rare, the largest deposits of wollastonite in the United States exist in New York State. CO₂ mineralization using wollastonite could be one of the best sequestration options for New York State, which has relatively few options for carbon storage. To this end, the researchers developed a carbon mineralization process using wollastonite procured in New York State. The research team evaluated both technical and economical feasibilities based on the two step dissolution-carbonation process, which is based on the pH swing technology. For the dissolution step, a differential bed reactor was used instead of a batch reactor in order to capture the fast reaction kinetics during the first few minutes of the dissolution process. The research team investigated the effects of pH and reaction temperature on the wollastonite dissolution, and evaluated various chelating agents as the chemical enhancers for the mineral dissolution. For the carbonation step, carbonic anhydrase was used to improve the carbonation rate at near neutral pH conditions. Finally, the researchers evaluated the chemical and morphological properties of precipitated calcium carbonates for their industrial applications as value-added products.

Urban Climate Change Mitigation Strategies

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The City University of New York (CUNY) is dedicated to minimizing its ecological impact and promoting a culture of sustainability throughout its community. The Sustainable CUNY initiatives are in response to the goals of PlaNYC 2030 and span CUNY instructional, research and operational activities. The strategic location of 19 CUNY campuses within the five Boroughs of New York City enables us to identify the impacts of strategic investments in building energy efficiency on neighborhood-level air quality and public health metrics, as well as the reliability of the electric grid at the electrical substation level. This method, which is evolving from a partnership between (Environmental Protection Agency (EPA) Region II, The CUNY Graduate Center, Brookhaven National Laboratory (BNL) and New York State Energy Research and Development Authority (NYSERDA), has the potential to be applied throughout New York State. The researchers will conduct an exploratory spatial data analysis (ESDA) of energy and environmental impacts of CUNY campuses at the neighborhood level. The researchers will explore concerns of neighborhood groups connecting energy use, environmental sustainability, and environmental justice. The researchers will discuss the obstacles to successful student-CUNY-community communication and outline strategies to ease the process of collaboration by bringing together local stakeholders in a relationship to foster communication and collaboration. Based on data collected, the research team will develop a comprehensive energy data base at the building and campus level for selected CUNY campuses; adapt the EPA-BNL New York City MARKAL (MARKet ALlocation -- an integrated energy, environment and economic model used to examine market potential for energy technologies over a short-, medium- and long-term horizon under alternative policy scenarios within the entire energy system) model, [with linkages to the EPA Portfolio Manager tool of the Energy Star Buildings Program and Energy Plus Department of Energy (DOE) building simulation model] to project the impact of energy supply and demand management choices on CUNY's emissions of carbon dioxide and criteria pollutants; and develop a conceptual framework for addressing the effect of CUNY operations on urban air quality, the reliability of the electric grid, and on neighborhood health.

A Field Laboratory for Evaluating the Effects of Climate Change and Atmospheric Pollutants in the Adirondack Mountains: the Huntington Forest and the Arbutus Watershed

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The Huntington Forest (HF), located in the central Adirondack Mountains of New York, has an extensive infrastructure for evaluating the effects of atmospheric pollutants and climate change on forest ecosystems and associated surface waters. Meteorological data has been collected for more than 60 years. This field laboratory is part of three national air pollution monitoring networks: NADP/NTN (National Atmospheric Deposition Program/National Trends Network), CASTNET (Clean Air Status and Trends Network) and MDN (Mercury Deposition Network). Arbutus Lake has been part of the Adirondack Long Term Monitoring (ALTM) project since its inception in June 1984.

The Arbutus Lake watershed has had discharge measured from 1991 and has a “state of the art” system for measuring hydrological and biogeochemical responses including chemical and isotopic measurements at four surface water-gauging stations as well as in ground water wells and soil lysimeters. A web site is available for live cameras as well as real time and archived data. Several different types of data are collected at these sites. The researchers report physical measurements taken during the winter including snow depth, aboveground temperature, soil temperature, well water height, and discharge that were combined with chemical analyses of soil, ground water and surface water solutes. These measurements were used to evaluate how changing climatic components (including snow depth) affected the mobilization and transport of important solutes including nitrate, sulfate, and dissolved organic carbon (DOC). The researchers also examined these measurements to discern the contribution of atmospheric pollutants (e.g., sulfur and nitrogen) to these climate change responses. Such results are used for comparing not only responses of climate change and atmospheric pollutants within the Adirondacks, but also responses at sites throughout the world.

An Integrated Analytical Tool for Electric Load Management, Local Energy Planning, and Greenhouse Gas Emission Mitigation

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The research team is in the process of developing a methodology for strategic investments in building energy efficiency focused around improvements in the electrical substation load patterns in New York City, which has the potential to be applied throughout New York State. The US Environmental Protection Agency (EPA) Region II, New York State Energy Research and Development Authority (NYSERDA), Brookhaven National Laboratory (BNL), and the City University of New York (CUNY) are working together on integrating strengths of complementary energy system tools like the US Department of Energy (DOE) -developed EnergyPlus, the USEPA-developed Portfolio Manager and MARKAL (MARKet ALlocation -- an integrated energy, environment and economic model used to examine market potential for energy technologies over a short-, medium- and long-term horizon under alternative policy scenarios within the entire energy system) to evaluate energy and emissions savings potential in CUNY campuses, hospitals, hotels and housing projects, as anchors within Community Planning Boards (CPBs) in Manhattan-New York City and to propose alternative strategies using advanced green technologies. Improved building performance and demand management are reflected in reduced load at the local substation modeled in the New York City MARKAL energy system model, which will help to decrease the peak and emissions for New York City. The method serves as a stimulus for further improvements in buildings surrounding the case studies, where as the local CPBs serve as the interface for a university-city relationship that will assure that the energy and environmental policies of these buildings reflect community needs. With an extension of this framework, the MARKAL model can be applied to evaluate the impact of demand response and management on the region's system peak load, generation costs, air and emissions. The integrated nature of the model could facilitate the restructuring of the electricity distribution network through alternative supply strategies such as the integration of energy efficiency, demand-side management, clean distributed generation and renewable resources.

Determining Sustainable Forest Harvest and Regeneration for Biofuels and Bioproducts in the Adirondacks: A Research Needs Agenda

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The demand for biofuels and other bioproducts from low-grade wood fiber is likely to grow rapidly in the next decade, posing new opportunities for and challenges to management of Adirondack forests. Sustainable forest management on private lands has the potential to provide the feedstock for these bioproducts, generate a variety of new jobs, and provide revenue for landowners to reduce land subdivision pressures. Environmentally, this has the potential to reduce climate change impacts by increasing carbon sequestration, enhance wildlife habitat, promote biological diversity, and reduce or preclude forest destruction from invasive species. Managing private timberlands on a sustainable economic, environmental, and ecological basis requires an understanding of the key variables that together define forest sustainability. While much is known, gaps exist and information specific to the Adirondacks is needed in five primary areas: (1) initial protocols for sustainable management (2) biotic integrity and ecological resilience of the Adirondack ecosystem (3) carbon balance and climate change (4) quantification of harvestable quantities of mixed timber and impacts on the economy and (5) environmental regulations of Adirondack Park and green certification programs. The project team highlights several research needs in these five areas as identified by members of the Adirondack Research Consortium and discuss the link between demand for low grade wood and a successful sustainable forestry industry in the Adirondacks. Ideas for additional research needs are welcome.

Carbon Storage vs. Biofuel Production in the Northern Forest: Implications of Changes in Harvest Regimes for Net Carbon Benefits over Time

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The researchers used data from the U.S. Forest Service Forest Inventory and Analysis (FIA) network of plots from the states of Maine, New Hampshire, and the 13 northern-most counties of New York for an analysis of (1) the landscape-scale frequency distribution of current C stocks in aboveground tree biomass, (2) the annual rates of C increment within plots as a function of current C stocks, and (3) the frequency and intensity of harvesting (logging), again as a function of current C stocks. Results of these analyses were then used in a simple simulation model to project landscape-scale changes in rates of carbon storage and C in harvested biomass, as a function of different harvest scenarios. For northern hardwood forests, carbon increment is a quadratic function of current carbon stocks, with a predicted mean of approximately 1.1 mt/ha for a stand with approximately 50 mt/ha aboveground C. Mean C increment becomes negative for northern hardwood stands with > 115 mt/ha. The results indicate that under the current rate of C increment and the current pattern of harvest in the region, total C stocks in live, aboveground tree biomass in these forests can be expected to roughly double over the next 100 years, from approximately 55 metric tons/hectare (as a landscape-scale average) to roughly 105 mt/ha. Average annual harvest in northern hardwood forests during the period covered by the data (2001 – 2005) was less than a third of the landscape-average rate of C increment in aboveground biomass (~ 0.25 mt/ha/yr harvested vs. ~ 0.75 mt/ha/yr C net increment). As the frequency distribution of plot-level C changes over time, simulations indicate that annual rates of carbon increment in aboveground tree biomass at the landscape will increase slightly over the next 25 years, and then decrease gradually to equilibrate with the current average rate of harvest (~0.25 mt/ha/yr). The researchers have explored various scenarios of changes in landscape-scale harvest regimes, including alternatives with no harvesting and with significant increases in harvest rates. While there are clear economic and silvicultural benefits from increasing markets for low-grade wood in the northern forests, all of the scenarios that have been examined that increase overall harvest levels are less beneficial, in terms of the net reduction in atmospheric C through the combination of C sequestration and displacement of fossil fuels by biomass, than either the current relatively low rates of harvest or no harvest at all.

Assessing the Economic Viability of Anaerobic Digesters on Dairy Farms in New York State Through the Use of Mathematical Models

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Anaerobic digestion (AD) is a biological process that is used to treat farm manure and other organic wastes. It assists compliance with regulations that require CAFOs (Concentrated Animal Feeding Operations) to manage and store manure in an appropriate manner and has the added benefits of reducing unpleasant odors, reducing greenhouse gases, and producing biogas. Biogas, composed of approximately 60% methane and 40% carbon dioxide, is a biofuel that can replace natural gas in electricity and heat production. By burning biogas, methane that would otherwise be released to the atmosphere is converted to carbon dioxide, which has approximately 1/25 of the climate change impact of methane. However, implementation of anaerobic digesters is hampered by high capital costs and the need to maintain digesters at a constant temperature of approximately 37 °C.

The USDA AgSTAR program generally considers anaerobic digestion to be an economically viable method of manure treatment for farms with more than 500 cows. However, approximately 77% of New York State dairy farms have fewer than 500 cows. This does not mean that one should discount the use of AD systems on the majority of NYS farms because many factors contribute to the complex economic picture surrounding anaerobic digesters including type of bedding used, availability of net-metering, and government support and incentives. A more detailed analysis of the economic viability of anaerobic digesters needs to be considered.

The Clarkson Biomass Group has been working on two mathematical models that will aid farmers and policymakers in their decisions regarding anaerobic digesters. The first model is an extensive spreadsheet that may be manipulated to assess the viability of digesters in different situations. This model allows for estimated projections of income and expenditures for digesters fed by farms of different herd size, using different beddings, and receiving different levels of government support. The researchers are currently developing a second model, created in MATLAB® & SIMULINK® to more accurately model an actual AD system with combined heat and power (CHP).

Pathogen Reduction and Correlation to Factors Responsible for Pathogen Reduction in Dairy Farm Operations Treating Agricultural Waste

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Three hundred fifty million tons of manure are produced every year by agriculture in the United States. Manure disposal at large concentrated animal feeding operations (CAFO) represents a significant challenge. Anaerobic digestion (AD) of livestock manures reduces odors and produces biogas for energy generation. AD has proven to be a beneficial technology for the treatment of municipal waste; digesters have been successfully constructed and operated at waste water treatment facilities for decades. However, AD use on farms has generally been less successful. Biogas production from digesters may offset heating and electrical costs on dairies and for larger dairies may yield profits from net metering of electricity to the national grid. For operations that seek to reuse dry digested solids as bedding materials, reduction of the causative agents of mastitis, including *Klebsiella pneumoniae*, is an additional benefit of anaerobic digestion. Although pathogen reduction is not required for manure application to land as is the case for wastewater biosolids, the reduction of populations of zoonotic pathogens such as *Salmonella spp.* and *Campylobacter spp.* may also reduce public health risks following runoff events when digested solids replace raw manures as soil amendments. Pathogen reduction is likely correlated to operational parameters on the farm including storage, treatment processes (solid separation, composting etc.) temperature, pH, influent substrate composition, e.g. manure, various co-digestates, and solid bedding materials. Identification process and operational parameters during AD that yield greater pathogen reduction and thus allow for better recycling of farm waste solid residuals will increase economic benefits of AD to U.S. dairy farms. Given the simplicity and scale of farm operations, AD influent feed compositions vary which, in turn, affects pathogen reduction. The research team's hypothesis is that pathogen content in bedding samples are dependent on moisture content, volatile solids content, and chemical oxygen demand. Preliminary results show that pathogen concentration was correlated to moisture content with maximum pathogens observed in samples with 70-80% moisture. Also, main effects plots for volatile solids content, chemical oxygen demand and acetic acid concentration show the affect of these variables on pathogen concentrations.

Life Cycle Assessment of Alternative Energy Sources: A Case Study of Anaerobic Digestion

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Considering a broad range of potential environmental impacts during development and wide-scale implementation of technologies for energy production or recovery, is vitally important to prevent pollution “trade-offs.” Life cycle assessment (LCA) is a systems approach to modeling environmental impacts related to a product or process. LCA was used as a tool in the design of a renewable energy system involving anaerobic digestion to ensure a full understanding of environmentally-related impacts and benefits. Anaerobic digestion (AD) is a biological process for treating organic wastes including manure or municipal waste. Energy contained in organic material in the waste can be recovered as biogas, produced through bacterial digestion, and displace natural gas for the production of electricity and/or heat. Concentrated animal feeding operations (CAFO) have the capacity to recover significant energy from animal waste through AD, due to the quantity of energy-rich wastes being produced in a particular facility. Manure is typically applied to land as a fertilizer supplement to displace mineral fertilizer use. AD can be implemented into existing operations to recover energy from the waste before it is land applied without destroying the nutrient value of the manure, thus giving the waste stream an added value.

The research team explored the impacts and benefits of implementing an AD system with combined heat and power generation (CHP) capacity through the use of a life-cycle approach. The researchers focused on North Harbor Dairy (NHD), a farm in northern New York State considering implementation of an AD/CHP facility to recover energy from the waste of its 600 dairy cows. The energy recovered through AD/CHP displaces fossil fuel-based sources of electricity and heat, reducing impacts in related environmental categories such as resource depletion and human toxicity. However, when a broader perspective is taken, impacts such as eutrophication and particulate formation, which are related to nitrogen and phosphorous nutrients, dominate the assessment. Desirability of implementing AD technology depends on the importance placed on different impact categories. Additionally, a broad assessment may open the discussion to other impact-mitigating approaches such as manure application methods. This knowledge can inform decisions about technology implementation or policy development.

Increasing the Efficiency of Wood Heating Through Public Education

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Wood can be an excellent fuel source, but, like all fuel sources, it carries inherent problems. Foremost are environmental and health concerns related to inefficient wood-fired heaters and improper burn practices. This project enlists a variety of methods to educate a broad spectrum of the public on how to reduce the negative impacts of heating with wood. There are three basic types of wood-fired heaters: outdoor wood boilers (OWBs), woodstoves, and wood boilers with forced draft. This project deals with the first two types because they are the most common. The project team will conduct a multifaceted education campaign to 1) increase awareness of air quality concerns related to wood burning, 2) increase purchasing of high-efficiency units, and 3) decrease air pollution through improved operation and maintenance of wood-fired heaters. The project team will develop a variety of media, such as creating a web site that addresses the issues involved in heating with wood. Major topics developed will include the environmental and health concerns related to burning wood, comparisons of the efficiencies and creation of particulate matter associated with various types of heaters, outdoor wood boilers, how to properly size a woodstove for a given space, detailed information on the importance of proper woodstove operation and maintenance, how high-efficiency woodstoves differ from less efficient models, and how to buy and store firewood. Links on the web site will direct visitors to a list of resources for further information. Key points selected from the information compiled for the web site and a CD-ROM will be made available in brochures, radio public service announcements and articles and press releases for local newspapers, as well as through public events. The project team is working with local, state, and federal partners on these materials: retailers, departments of health and planning, the New York State Department of Environmental Conservation, the Environmental Protection Agency, and the American Lung Association.

Avian Risk Assessment for a Community Wind Project in Albany County: Empowering "Citizen Scientists"

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Wind energy permitting often requires intensive monitoring of bird and bat activity in conjunction with meteorological conditions. A community wind project in rural Albany County, New York State, conducted studies of bird and bat activity using on-site X-band marine radar for tracking avian passage rates, Doppler SoDAR (Sonic Detection and Ranging) profiling, a 50-m meteorological tower, acoustic monitoring for bats, and NexRad data, a network of 159 high-resolution Doppler weather radars operated by the National Weather Service. The SoDAR, a meteorological instrument that measures the scattering of sound waves by atmospheric turbulence, allowed the project team to determine wind speed and direction as well as turbulence intensity to a height of 200 m. More than 25 community members and students were trained in the use of the marine radar for making avian counts. Student interns also acquired and worked with the NexRad data. The project team tracked migratory bird activity with X-band marine radar at site as well as with (regional) NexRad. NexRad data were collected over three migration seasons, two of them concurrent with onsite X-band marine radar. The X-band marine radar screens were captured so that a digital record of each night's "voyage" was kept. The marine radar was operated in a "vertical" mode so that bird migration could be related to particular heights above the ground. The movement of individual birds was tracked, allowing correlation between the meteorological conditions and rate of movement of the birds. Night-migrating birds took flight within a short period of time after sunset, and returned to ground shortly before sunrise. The bulk of night-migrating birds were found to be at least 300 m above the ground, well above the top of the rotor sweep of utility-scale wind turbines. This study presents an unusual integration of multiple sources and scales of meteorological and biological data for environmental permitting of wind energy. In addition, citizen scientists were an essential part of this project, which facilitated community education about wind energy and avian behavior.

Alternate Source of Energy in the Forms of Liquid Fuel from Solid Waste Plastic

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A great deal of research and development of alternate energy sources has focused on biomass, solar, wind, and turbines, but these alternate sources have limitations, e.g., biomass energy requires large amounts of arable land to be devoted to the cultivation of plants. However, alternative energy derived from solid municipal waste such as waste plastic has the potential to overcome many economic and environmental problems. Plastics are macromolecules, formed by polymerization of hydrocarbon materials. They do not biodegrade in landfills and are not easily recycled. The United States produces approximately 30 million tons of waste plastics per year. Natural State Research, Inc. (NSR) has developed a means to make use of this resource: a new alternative and economically viable energy source derived from converting waste plastic into a hydrocarbon fuel that can power any internal combustion engine. This fuel burns more efficiently than commercial gasoline and diesel and would be produced at a lower cost. Preliminary tests performed at NSR labs reveal that this fuel has an average octane rating of 76 and offers approximately 17% higher mileage per gallon in a low-fuel-efficiency automobile relative to commercial gasoline with an octane rating of 87.

NYSERDA's High Efficiency Biomass Heating Research and Development (R&D) Program

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Historically, increased burning of wood for heat has been associated with high prices for home heating oil. The last few years have also seen a return to using dormant wood stoves and new purchases of wood burning equipment as oil prices have risen. These technologies have only 45-65% energy efficiency and are gross pollution emitters when compared with the oil-fired heating systems they displace. The outdoor wood boiler has also emerged as a popular heating technology and its very low efficiency of 43% and very high emissions have resulted in numerous complaints to the New York State Department of Environmental Conservation (NYSDEC), NYS Department of Health (DOH), and the NYS Office of the Attorney General. The recent "Assessment of Carbonaceous PM_{2.5} for New York and the Region," funded through NYSERDA's Environmental Monitoring, Evaluation, and Protection (EMEP) program indicated residential wood combustion to be the source of one-third of primary fine particles in New York State. In great contrast to what is described above, high-efficiency biomass heating technologies are possible and commonplace in Europe. Gasification, or two-stage combustion allows efficiency performance in the range of oil-fired systems (>80%).

In an effort to encourage a market for high-efficiency biomass heating technologies with acceptable emissions performance in New York State, New York State Energy Research and Development Authority's Environmental Research and Development and Building Research and Development Programs jointly developed the Biomass Heating Research and Development Program. The program will 1) evaluate the energy efficiency and emissions performance of a wide-range of conventional and advanced biomass-fired heating technologies, 2) evaluate the energy, moisture, and chemical composition of biomass fuel feed stocks, 3) develop advanced boiler technologies by supporting R&D and commercialization efforts with New York manufacturers, 4) demonstrate advanced technologies in representative applications, and 5) provide objective scientific information for the development of high-efficiency and low-emissions biomass heating initiatives in New York State. This effort has resulted in \$3 million of support for approximately 20 projects that are partnerships with universities, a Resource Conservation and Development (RC&D) district, New York State manufacturers, and other federal, state, and regional air and energy agencies.

Spectrothermography of Carbon Containing Compounds Using the SUNSET Real Time ECOC Instrument

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Spectrothermography, the evaluation of thermograms of carbon evolved from heated aerosol samples, is an established technique for evaluating differences in particle characteristics associated with their chemical compositions. In this study, the researchers present patterns of carbon evolution as a function of temperature for 18 carbon-containing compounds (glyoxylic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, DL-malic acid, adipic acid, levoglucosan, phthalic acid, *cis*-pinonic acid, palmitic acid, oleic acid, 5 α -cholestane, fluoranthene, and benzo[*a*]pyrene) generated from an aerosol chamber in the Atmospheric Sciences Research Center- PM (ASRC PM) laboratory and then collected and analyzed by a real time elemental and organic carbon analyzer (SUNSET ECOC) instrument.

The researchers used four different temperature protocols to collect thermograms for the 18 carbon-containing compounds listed above. Three methods have been widely used for thermal optical measurement of carbonaceous aerosol: the NIOSH 5040 method (elemental carbon/diesel particulate) issued by the EPA Speciation Trends Network; the IMPROVE method; and a simplified version of the NIOSH method used for the real time Sunset ECOC instrument. The researchers also developed an ASRC method (8 temperature steps in helium (He) and 3 temperature steps in He/O₂) which showed a greater separation of the thermographical peaks compared to the other three methods. The researchers believe that this ASRC method can more fully identify the spectrothermography patterns related to the different carbon containing compounds. The researchers have observed that temperature of the peak signal depends on the number of rings, i.e., the three ring aromatic, fluoranthene, has the first maxima at 150°C whereas the first maxima of the five-ring aromatic, benzo[*a*]pyrene, is at 300°C for the ASRC method. Additional work planned for this study includes measurement of combustion aerosols; analysis of selected organic compounds incorporated into mixed aerosols to evaluate matrix effects; and the evaluation of the effects of aerosol loading.

Use of Conditional Probability Function and Other Analysis Tools to Understand the Aerosol and Gas Pollutant Source Contributions to a Rural New York State Sampling Site

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To identify directionality of sources contributing to observed air pollutant concentrations the researchers use the conditional probability function (CPF), which estimates the probability that a given source contribution from a given wind direction will exceed a predetermined threshold value. Hourly averaged particles in the air with a diameter of less than or equal to 2.5 micrometers (PM_{2.5}) mass, Organic Mass (OM) calculated from Organic Carbon (OC), optical Elemental Carbon (EC), and trace gas (SO₂, CO, NO_y, O₃) concentrations were measured at the Pinnacle State Park (PSP) site in rural New York State. PM_{2.5} was measured using a tapered element oscillating microbalance (TEOM), OC and EC using a SUNSET carbon aerosol analyzer, gaseous pollutants with various analyzers, and metrological data with standard equipment. The period considered for this study is Dec 2004 to Nov 2007. These measured pollutants were coupled with on-site wind data to identify the directionality of the sources; which were then compared to known stationary source locations from the US Environmental Protection Agency (EPA) Air Data web site. There were numerous emission facilities of PM_{2.5} mass, SO₂, CO, NO_y, and volatile organic compounds (VOC) in New York, New Jersey, and Pennsylvania to the south and south-southeast, but fewer stationary emission sources to west, north, and northeast. Preliminary results indicate that the vector-averaged wind direction exhibited a strong seasonal variation (summer, fall, and winter indicated SW, and spring indicated NW). Although the CPF plot of the O₃ showed no distinct directionality areas, the Pinnacle State Park site was frequently impacted by plumes of relatively high PM_{2.5} mass, SO₂, CO, NO_y, EC and OM concentrations which closely correspond to the directions of emission facilities listed in the 2002 National Emissions Inventory. The researchers believe that most of these plumes arose from pollutants that were transported several hundred miles (mid range transport) rather than from local pollutant emissions.

Relationship between Particle Size Distributions and Elemental Carbon Measured by Different Methods in New York City

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The researchers chose to investigate the composition and correlations of carbonaceous aerosol with potential gaseous surrogates and measurements of particle number and size distributions. In particular, the researchers explored the association of the ultrafine (sub-100nm in diameter) particles in high traffic dominated exhaust plumes. The researchers compared carbon particulate matter (PM) and particle number and size distributions from a variety of collocated measurement systems deployed from the ASRC Mobile Measurement Van and the New York State Department Environmental Conservation (NYSDEC) permanent monitoring station at Queens College. The researchers monitored air during a three week-long period (Jul 13th – Aug 3rd in 2009) at two sites within the urban location of Queens College (QC) in New York City. The main site was located at parking lot 6 adjacent to an athletic field and site of the 2001 PM_{2.5} Technology Assessment and Characterization Study – NY (PMTACS-NY) summer intensive field study. The second site, sampled during the last week of the study, was located approximately 30 meters from the Long Island Expressway. The latter was selected to assess mobile source plumes from traffic exposure.

High Resolution Mass Spectrometry Analysis of Laboratory-Generated Secondary Organic Aerosols

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Secondary organic aerosols (SOAs) generated in the Atmospheric Sciences Research Center (ASRC) aerosol facility from the reaction of volatile organic carbons (VOCs) (pinene, toluene, xylene and limonene) with OH radicals have been monitored via their evolving particle size distribution and composition via mass spectrometry. The SOAs have also been generated and conditioned in the slow-flow chamber under different seed aerosol conditions and, in some experiments, exposed to factors (heat and light) contributing to aerosol aging. The research team reports on the resulting aerosol mass spectra of these SOAs as measured with an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and present analyses of the composition of the SOAs in terms of the relative contribution of hydrogen-like (HOA) and oxygenated-like (OOA-1 and OOA-2) organic aerosol fragments.

NO₂ and Trace Gas Measurements by QC Laser and Other Methods: The Summer 2009 Queens College Special Study

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Understanding and quantifying the impacts of energy related pollution on air quality and health effects remains an important and challenging task. Combustion sources, both stationary and mobile, emit precursors to both ozone and particulate matter with a diameter less than or equal to 2.5 micrometers (PM_{2.5}) pollution. Directly emitted pollutant gases such as nitrogen dioxide (NO₂) and formaldehyde (HCHO) have been identified as species that have significant impacts on health outcomes in addition to their very central roles in oxidant production in the atmosphere. The research team measured these and other trace gases of interest as part of the summer 2009 Queens College special study. The dual quantum cascade laser system from Aerodyne Research is a high precision instrument for fast time response measurement of atmospheric trace species. The researchers describe the deployment of the system as configured for the measurement of NO₂ and HCHO and show comparisons of the QCL measurements of NO₂ with less specific photolytic and catalytic converter based NO/NO₂/NO_x measurements made simultaneously at the Queens College site during the period July 15-August 2, 2009. The research team highlights the NO₂ and/or HCHO measurements made during pollution events, as well as measurements of ozone and other gaseous pollutants made at the Queens College measurement locations. Finally, the researchers show results from the roadside deployment at a location approximately 30 meters from the Long Island Expressway. Periods of elevated NO₂ and HCHO at this site are combined with ambient CO₂ measurements to explore near-roadway sources of these pollutants.

**Size-Resolved Aerosol Chemistry with High-Resolution Aerosol Mass Spectrometry during QC
Summer 2009 Field Intensive Study**

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The research team revisited the Environmental Protection Agency (EPA) particulate matter (PM) Supersite (PMTACS-NY) on the campus of Queens College (QC) during the summer of 2009. The research team compared AMS (Aerosol Mass Spectrometer) analyses to analyses performed during the 2001 campaign, when a substantial bimodal distribution in organic particle matter was observed, to determine if this bimodal distribution in organic PM persists in the summer of 2009 and if its size and compositional attributes have changed. Drawing on HR-ToF-AMS (High Resolution Time-of-Flight Aerosol Mass Spectrometer) spectra the research team reports on the composition and attribution of the small mean mode organic particles and observed changes in the composition of organic aerosol (OA) as a result of the introduction of low sulfur (15 ppm) diesel fuel. The research team applied multivariate analysis techniques to AMS spectra, which provide unambiguous mass spectra interpretation and determination of elemental ratios (e.g., O/C and N/C). In addition, the research team measured concentration gradients downwind of the Long Island Expressway (in the vicinity of QC) to assess exposures from mobile source emissions in intervening neighborhoods and determine the ability of central urban monitors to characterize emissions exposures to mobile sources.

Emissions Characteristics of Residential, Gas Oil and Wood Pellet Heating Systems

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The researchers measured emissions from a sample of common natural gas, wood pellet and oil-fired, residential heating systems as found in homes and small businesses in New York State. The researchers also measured the emissions from more advanced heating technologies including low NO_x burners and condensing heating appliances (boilers and furnaces) and both conventional and advanced, oil-fired, heating technologies with liquid biofuels (biodiesel). The researchers measured fine particles (PM_{2.5}) with a dilution tunnel following the protocol found in US EPA CTM-039 (PM_{2.5} stack sampling method) and developed emissions profiles for units with conventional design as well as more advanced designs (CO, CO₂, NO_x, SO₂ and PM_{2.5}). Given existing EPA emission factors for gas, oil and wood combustion there was the expectation that emissions would be lowest for gas, slightly higher for oil and higher yet for wood combustion. A significant effort was placed on oil heating technology due the nature of the fuel and the perceived possibilities for improvement based on changing fuel characteristics and equipment designs. A strong almost linear correlation was found between the reduction of sulfur content in the fuel and reductions in the level of fine particulates emitted from oil-fired systems. The fine particles from fuel oil heating units using ultra low sulfur (ULS) fuel were found to compare very favorably to those measured for natural gas heating systems. The larger portion of the particulate emissions of the three wood pellet stoves were categorized as PM_{2.5}, but they did have measurable amounts of particles sized over 2.5 microns in diameter.

Dispersion of Highway Generated Pollutants in Urban Areas (Recipient of EMEP Student Fellowship)

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Aerosol particles play an important role in the local environment, human health, and global climate change. In particular, particles smaller than 100nm, i.e., ultrafine particles, are speculated to have a particularly adverse effect on human health. In urban environments, a major source of these particles is traffic exhaust from highways. There have been several studies on the concentration decay of the highway generated particles as a function of distance from the road. The particle dispersion characteristics in the vertical direction, are, however, not completely known and this mechanism may critically control particle concentration field in urban area. For measurements of particle concentration profiles in both the vertical and horizontal directions, field measurements were recently conducted near the I-90 freeway in Liverpool, NY (near Syracuse, NY). A 10m-high tower was used to sample particles from the ground to the top of the tower. Four condensation particle counters (CPCs), including one TSI 3025 and three TSI 3786, were used to simultaneously measure the particle concentrations in the different heights. The four CPCs were used in different combinations to sample from seven different heights. A fast mobility particle sizer (FMPS; TSI 3091) was used to obtain the particle size distribution at the different heights. In addition to the particle measurements, gas-phase pollutants – carbon monoxide and carbon dioxide - were also measured. Real-time measurements of particulate polycyclic aromatic hydrocarbon (PAH) were also obtained as a function of sampling height. Horizontally, the tower was placed at locations of 20m, 50m, and 100m from the edge of the highway.

Integrated Unipolar Charger with Tailored Electrode Concentration Sensor (TECS) For Ambient Ultrafine Particle Measurements.

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Accurate estimation of the human health effects of ultrafine particles requires size distribution measurements incorporating particle spatial and temporal variability. Such measurements involve the deployment of instruments over a large number of sites or on a mobile platform; but the large cost, size, and power requirements of the existing instruments make such deployments difficult. The Tailored Electrode number-Concentration Sensor (TECS) is a new novel electrical-mobility-based technique that can measure total particle number concentration over a selected size range. The salient features of the TECS include: compact size, fast response, single flow operation, and a design that will enable eventual miniaturization. In the TECS, charged particles are condensed out onto an electrode that is shaped such that the product of its transfer function and the particle charging efficiency is a constant. The resulting total current is then proportional to the number concentration of the sampled particles over the collected size range. While the original TECS instrument used a bipolar charger, in the modified instrument, a corona-discharge-based unipolar mini-charger is integrated with the TECS instrument to improve its concentration detection limit.

Gaseous, Particulate, and Semi-volatile Emission Rates from a High Efficiency Wood Pellet Boiler

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Residential combustion of wood for space heating has found renewed interest due to the rising cost of natural gas and oil. Several studies have indicated that emissions from wood combustion pose a potential environmental problem. However, newer designs of fully automated, high efficiency wood boiler systems are a good alternative due to their low emissions of some of the criteria pollutants. In this study, a high efficiency commercial wood boiler was tested using wood pellets at a nominal heat input rate of 3.9×10^5 BTU hr⁻¹. Stack gas was drawn through an in-stack PM_{2.5} (particulate matter with a diameter less than or equal to 2.5 microns) cyclone into a dilution sampling system conforming to the Environmental Protection Agency's (EPA's) conditional test method (CTM) 039. The stack gas was diluted between 20 to 40 times with HEPA filtered ambient air. Sampling ports located at the end of the dilution tunnel allowed for continuous measurements of CO, NO_x, SO₂, CO₂, PM_{2.5} mass concentration, and particle size distribution. The research team collected quartz fiber filters and polyurethane foam (PUF) samples to determine particulate organic and elemental carbon content as well as the gaseous and particulate organic chemical speciation of organic compounds including polycyclic aromatic carbon (PAHs) compounds, n-alkanes, alkanolic acids, dicarboxylic acids, certain bio-markers and levoglucosan. Teflon filters were collected for particulate elemental analysis. The average concentrations emitted during steady state operation were 25.1, 115, 18.4, and 0.26 mg/MJ for PM_{2.5}, CO, NO_x and SO₂ mg/MJ respectively. The average particulate elemental and organic carbon emissions were 2.15 and 0.07 mg/MJ, corresponding to total carbon making up 8.85 % of PM_{2.5}. The average particle number concentration was 1.50×10^{13} ; the number mean ultrafine particle diameter during steady state operation was 88.5 nm. The research team profiled gas particle partitioning behavior and speciation of organic compounds present in gas and particle phase, as well as elemental analysis of PM_{2.5}.

Development and Field Test of an Automated Sampling System for Particle-Bound Reactive Oxygen Species in Rochester, NY

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Reactive oxygen species (ROS) include families of oxygen-centered or related free radicals, ions, and molecules. Prior studies found ROS associated with particulate matter especially ambient particles with diameters less than 1 μm . Thus, particle-bound ROS can penetrate deeper into the lungs to deliver oxidative damage to the tissue. Manual measurements in the summer (Rubidoux, CA) and winter (Flushing, NY) have found the presence of significant quantities of particle-bound ROS. However, it is not practical to use manual methods to make long term, time resolved ROS measurements. The sample processing and analysis must be done immediately because of the short lifetimes (high reactivity) of ROS. This study will lead to the first practical system to measure this vital particle compound in a way that would permit exposure studies and generate data that could be used in epidemiological studies. The researchers have developed a laboratory version of a monitor for particle-bound ROS was developed by automating dichlorofluorescin (DCFH) oxidation as a non-specific indicator of the oxidative capacity of particle surfaces. The measured fluorescent intensities were converted into equivalent hydrogen peroxide (H_2O_2) concentrations using calibration curves obtained from H_2O_2 assay. A 5 μM DCFH working solution was found to be adequate because ROS ambient concentrations were not expected to exceed 1×10^{-6} M H_2O_2 . Following initial field tests in Potsdam, NY, the system was deployed at the New York State Department of Environmental Conservation (NYSDEC) site in Rochester beginning in August 2009. The researchers report results of these measurements.

Application of Integrating Sphere Method to Apportion Ambient Particle Sources

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According to the World Health Organization, approximately two millions early deaths per year are due to the effects of ambient air pollution. In many areas in New York State, emissions from traffic, power plants, and residence heating can substantially affect local indoor and outdoor air quality in fall and winter. PM_{2.5} (fine particulate matter with diameter less than 2.5 microns) can pass through to the lungs and cause acute and chronic respiratory diseases; it also has particular radiative forcings and plays an important role in climate change. Current methods for detecting PM_{2.5} include optical devices with four wavelengths that estimate black carbon levels and environment tobacco smoke somewhat successfully, but this method may misclassify components when additional colored particle sources are significant. For this reason the researchers are developing an end-member optimization method to apportion light-absorbing particles collected on Teflon filters. End-member standards explored to date are: kerosene soot (for BC), side stream cigarette smoke for environmental tobacco smoke (ETS), ammonium sulfate, and three iron oxides (goethite, hematite, and magnetite). In its application, the algorithm shows that fitting data at four wavelengths (as has been previously studied) proves to be sufficient beyond two end-member standards, but these four wavelengths must be chosen carefully. In processing clinical data, the method shows preliminary success, finding statistically significant different mean ETS filter loadings in households with and without smokers. The researchers also found that the iron oxide end-members explored generally exist below this method's possible detection levels in U.S. urban environments. Future improvement to this method includes incorporating more end-members into this model, such as particles from cooking and biomass combustion.

Do Peaking Units Emissions Form Local Air Pollution Hotspots?

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In urban centers, meeting the peak electricity demand, typically occurring on hot summer days in metropolitan areas often requires power systems operators to turn on electric generating or peaking units that are otherwise rarely used. The peaking units usually have lower stack heights than the baseload units, therefore their emissions are more readily distributed in the lower portion of the atmosphere, affecting human exposure to air pollution. In this study, the researchers aim to explore whether the emissions from peaking units will cause the formation of local air pollution hotspots where people are exposed to elevated pollutant concentrations. The researchers analyzed the impact of peaking unit emissions on local air quality in the environmental justice communities in the New York Metropolitan Area from 2006 through 2007 using the United States Environmental Protection Agency's air pollution model for environmental managers (USEPA AERMOD).

On the most polluted days of 2006 and 2007, emissions from multiple peaking units could cause 24-hour averaged PM_{2.5} (particulate matter with diameters of less than or equal to 2.5 microns) concentrations up to 60 $\mu\text{g m}^{-3}$ 200 meters away from the emission point, and 18 $\mu\text{g m}^{-3}$ 400 meters away from the emission point. These emissions, when combined with other sources of particulate matter, could place the nearby communities in danger of non-attainment with the USEPA's National Ambient Air Quality Standards (NAAQS). Modeling results strongly indicate that the emissions from the peaking facilities with low stack heights could form local air pollution hotspots, which warrant further investigations into the human exposure to peaking unit emissions. Conducting continuous air quality monitoring during High Electric Demand Days (HEDDs) near the vicinities of peaking units is needed. In conclusion, reducing peaking emissions would achieve several benefits: mitigating human exposure to local particulate matter air pollution, reducing regional ozone pollution and global greenhouse gas emissions. The researchers suggest several mitigation strategies.

Air Quality and Exposure Impacts of Clean Diesel Strategies in New York—Progress in Emissions Estimation and Air Quality Modeling

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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 the New York Metropolitan Area and across the State. Given the diversity of applications and engines, as well as significant technical, institutional, and funding issues, 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 and strategies on air quality and human exposure in 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. The researchers report the progress in modeling truck traffic activities that are essential for on-road mobile source emissions estimation and results from testing runs of the Community Multiscale Air Quality modeling system (CMAQ) and its advanced variation, CMAQ-UCD (University of California at Davis).

Comparison of Particle Mass and Number Emissions across Temporal and Spatial Scales from a Diesel Transit Bus (Recipient of EMEP Student Fellowship)

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Single metrics are often used to represent the entire distribution of aerosol particles emitted from vehicles. Two of the most common metrics evaluate the total number of particles (particle number) and the total mass of the particles (particle mass). This work analyzed particle number and mass emission rates measured on-board a 2002 diesel transit bus under real driving conditions using an Electrical Low Pressure Impactor (ELPI) together with a mini-dilution system. Mass emission rates derived from the ELPI are verified to be consistent with concurrent gravimetric filter measurements. The behavior of the number and mass emission rates were examined at resolved temporal and spatial scales across three facility types: urban arterial, rural arterial and divided freeway. The number and mass metrics were compared to the particle-size distribution at select locations on the road-network. The time-based particle emission rates were highest on the freeway, but the largest episodes of distance-based particle emission rates (i.e., “hot-spots” for exposure assessment), for both particle number and mass emissions, occurred at intersections when the bus was accelerating from stopping. Generally, the number and mass emissions were highly correlated both temporally and spatially. However, some deviations did occur because particle mass emissions were highly elevated during sustained fueling events, such as traveling up high grade, while particle number emissions were more sensitive to short fuel fluctuations. The observations were validated using statistical models across two days of testing. The data provided by this study will enable transportation and other regulatory agencies to understand better the effect of bus route conditions on the public exposure of diesel particle emissions.

Modeling Microenvironment Air Quality in Rochester, NY

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Human exposure assessments are strongly affected by the level of detail provided in resolving the temporal and spatial variation of airborne pollutant concentration values. Exposure studies have indicated significant spatial variability of airborne pollutants at scales smaller than 1 km. However, there is no appropriate modeling tool to address this issue. While Eulerian grid-based chemical transport models like the Community Multi-scale Air Quality modeling system (CMAQ) are able to simulate the physical/chemical processes in the atmosphere, they are not capable of resolving spatial variability at such local scales. On the other hand, source-based dispersion models are able to simulate the transport of pollutants within a few hundred meters from the source, but they are not able to treat the transformation of reactive or volatile pollutants. The project team will integrate a multi-component (including organic compounds) aerosol dynamics model into atmospheric dispersion models to create a microenvironment model. This model is able to simulate transport and transformation of airborne pollutants from emission sources to urban backgrounds at spatial scales <1-10 km. The unique feature of this microenvironment modeling approach is its ability to simulate particle size distributions at meter scale from sources. The project team validated this model by field measurement data collected in Rochester, NY, and used the model to elucidate the contributions of the electricity generation and transportation sectors to local air quality and human exposure in Rochester. As part of this project, a micro emission inventory for the City of Rochester was developed using a “bottom-up” approach. This emission inventory contained highly time-resolved and size resolved particulate emission rates for point, mobile, and major area sources in the region.

CMAQ Validation of Optical Parameters and PM_{2.5} Based on Lidar and Sky Radiometer

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With the increasing importance of climate change, atmospheric monitoring has become critical. Several atmospheric monitoring instruments are used for measuring atmospheric composition, optical coefficients, PM_{2.5} (particulate matter with a diameter less than or equal to 2.5 microns), aerosol optical depth, size distribution, Planetary Boundary Layer (PBL) height and many other parameters. However, modeling is an inexpensive method of determining these parameters and one model in particular that depicts the aerosol dynamics in the atmosphere is the Community Multi-scale Air Quality (CMAQ) model. The research team converted CMAQ retrieval outputs into optical coefficients that can be compared to the LIDAR, AERONET and TEOM measurements performed at City College of the City University of New York. Differences between the full approach and parameterized methods such as the MALM formula used in AIR-NOW were observed and comparisons with AERONET showed that full modeling is in general superior to the MALM formula.

Dynamic PM_{2.5} Estimators Based on PBL Height and Aerosol Climatology

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To provide reasonable forecasts of near surface PM_{2.5} (particulate matter with a diameter less than or equal to 2.5 microns) levels, it is necessary to couple satellite estimates of PM_{2.5} to a transport model.

Unfortunately this requires that the aerosol be homogeneously mixed and the extent of the Planetary Boundary Layer (PBL) be sufficiently accurate. For example, the IDEA product (Infusing Satellite Data into Environmental Applications) used by the Environmental Protection Agency (EPA) relies on a static relationship connecting PM_{2.5} to Moderate Resolution Imaging Spectroradiometer (MODIS) aerosol optical depth (AOD) which, in turn, relies on a static model of the PBL aerosol height. The research team showed that the PBL height is far from static. By taking the variable PBL into account, a better prediction of PM_{2.5} from the MODIS (AOD) measurements was obtained. In addition, seasonal variations in the microphysical properties were also demonstrated and accounting for the additional variability further improved the PM_{2.5}/AOD slope predictor.

**Federal Equivalent Method Testing, Results, and Approval for the BAM-1020
Continuous Particulate Matter Mass Monitor**

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The United States Environmental Protection Agency (USEPA) first promulgated fine particulate matter (PM_{2.5}) as one of the criteria pollutants of the National Ambient Air Quality Standards (NAAQS) revisions in 1997. The concept of the “Class III” Federal Equivalent Method (FEM) was also introduced as part of the 1997 rules. This FEM category opened the door for continuous and semi-continuous particulate matter (PM) mass monitors to gain USEPA method designation for use in the national PM_{2.5} air monitoring network. It was not until 2006, however, that Class III FEM test criteria would be established. These test criteria were issued as part of the USEPA’s September 2006 action to amend its national air quality monitoring requirements. Although not promulgated as one of the criteria pollutants, test criteria were also established for coarse particulate matter mass concentration (PM_c) methods. Prior to this, in 1987, rules for PM₁₀ methods were published. Clear and concise test procedures now exist that allow the manufacturers of continuous PM₁₀, PM_{2.5}, and PM_c monitors to apply for and receive USEPA FEM designation. A beta attenuation monitor (Met One Instruments, Inc., Grants Pass, Oregon) became the first continuous measurement method to receive the PM_{2.5} and PM_c FEM regulatory approval. The researchers present a brief overview of the BAM-1020 monitor, the field test logistics, test results, and designation approvals for the BAM-1020 monitor. It is likely that PM measurement instruments with such designations will continue to supplement, and gradually replace, manual gravimetric samplers for enforcement and compliance purposes.

An Initial Assessment of Trace Elements in Fuel Oil Used in New York State

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Trace elements, including mercury, lead, and arsenic, pose significant public health risks due to inhalation toxicity or the carcinogenicity of certain compounds containing these elements. Nickel and vanadium concentrations in fine particulate matter may be associated with average daily mortality coefficients. Recent emission studies of crude oil in North American markets have shown mercury levels to be substantially lower than those used in emission factors for distillate and residual oils. This work was undertaken to determine whether or not available emission factors for oil are appropriate for use to develop trace elemental emissions inventories in New York State. The substantial market for both oils in the Northeast, particularly in the New York City area, supports a measurement campaign to better understand the emissions potential for mercury and other trace elements that may be of concern. The research team created profiles of trace elements from in-use oils in an effort to aid scientists performing source apportionment analysis of fine particulates (PM_{2.5}). The research team worked with major oil distributors in the New York market and collected samples of various oil grades, including home heating oil, biodiesel, on-road diesel, and residual oil. The research team analyzed samples for sulfur content and trace elements. The elemental analysis (V, Mn, Co, Ni, Zn, As, Se, Pb, Hg), with a subset of samples analyzed for mercury using cold vapor atomic absorption, relied on Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In general, the trace elemental composition of light distillates appears to be somewhat lower than reported profiles from AP-42 (EPA's Compilation of Air Pollutant Emission Factors). As expected, the trace elemental composition of residual oil far exceeds that of lighter distillates. These current elemental measurements can be used along with existing fuel use in New York State to better understand the relative importance of different sources of trace elements in the overall emissions inventory.

Evidence for the Oxidation of Hydrocarbons by Atomic Chlorine

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Quantitative analysis of PAMS (EPA's Photochemical Assessment Monitoring Stations program) data indicates inconsistencies with the widely accepted idea that the oxidation of hydrocarbons can be accounted for almost exclusively by hydroxyl. If hydroxyl radical alone could account for hydrocarbon oxidation, then a log-log plot of the ratios of hydrocarbon concentrations χ_4/χ_3 and χ_2/χ_1 should yield a straight line with a slope given by

$$m = \frac{(k_4^{OH} - k_3^{OH})}{(k_2^{OH} - k_1^{OH})}$$

where the k's are the respective reaction rate coefficients with hydroxyl radical. While the plots do result in straight lines, the slopes of fitted lines are quite different than the slopes predicted by the equation above; in some cases, the fitted line is essentially perpendicular to the predicted line.

If the above equation is modified to include the reaction with atomic chlorine, it becomes

$$m = \frac{(k_4^{OH} - k_3^{OH})[OH] + (k_4^{Cl} - k_3^{Cl})[Cl]}{(k_2^{OH} - k_1^{OH})[OH] + (k_2^{Cl} - k_1^{Cl})[Cl]}$$

where [OH] and [Cl] are the hydroxyl radical and atomic chlorine concentrations respectively. While the slope cannot be determined because it depends on the unknown concentrations [OH] and [Cl], the ratio of [Cl] to [OH] can be estimated. It is found to be on the order of 10^{-2} , consistent with previous estimates reported in the literature. This would imply that 30-50% of the oxidation of many hydrocarbons may be due to atomic chlorine. For ethane, almost 70% of the oxidation may be due to atomic chlorine. This quantitative analysis suggests that the role of chlorine and other oxidants may play a more important role in photochemistry than previously thought.

A Multi-Model Air Quality Forecast Guidance System for New York State

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In recent years, the application of comprehensive grid-based one-atmosphere modeling systems to provide numerical guidance has become an integral part of air quality forecasting for both federal and state agencies. For example, since 2005 the New York State Department of Environmental Conservation (NYSDEC) has been utilizing the Community Multiscale Air Quality (CMAQ) model driven by operational National Centers for Environmental Prediction (NCEP) weather forecasts to provide guidance to state air quality forecasters. In an attempt to better quantify uncertainties associated with these ozone and PM_{2.5} forecasts, in 2008 NYSDEC, in collaboration with the University at Albany and Stony Brook University, embarked on a research project to apply multiple modeling systems for daily air quality simulations. The concept of ensemble forecasting, a technique that is widely used in the meteorological community to provide for a more robust and accurate weather forecast, is only beginning to be explored in air quality forecasting applications. Building upon various ongoing meteorological and air quality modeling efforts at federal, state, and academic institutions, the project is implementing this concept for New York State. The forecasts for New York State differ in terms of the meteorological forecasts, the emission inventories, and the air quality models that drive the simulations. The researchers analyzed the ozone and total PM_{2.5} forecasts generated by the multi-model system during its first year of operation by comparing the model predictions with observations from the AIRNOW database. Results indicate better performance for ozone than PM_{2.5} and a pronounced seasonal variation in PM_{2.5} model performance with frequent overpredictions during winter and underpredictions during summer. The researchers also analyzed the mean and variability predicted by the multi-model system to assess the benefits of utilizing a multi-model system for air quality forecast guidance.

Simultaneous Hourly Measurements of EC, OC and SO₄ at two sites in New York City

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Determining the contribution of local versus regional sources in urban centers is important in the development of effective emission control strategies. In general, pollutant species which are dominated by primary emissions show high spatial intraurban heterogeneity whereas species controlled by secondary formation are homogeneous across an urban area. The researchers examined simultaneous hourly measurements of elemental carbon, organic carbon and sulfate at a site in the South Bronx and Queens, New York. Both sites are impacted by traffic emissions from nearby roadways. The distance between the sites is approximately 10km. The researchers used the hourly measurements to examine the spatial and temporal variability of the particle species. The researchers also analyzed the correlation coefficients, diurnal patterns, and day of week differences; and used the temporally resolved measurements to investigate the relationship between variation in pollutant species and meteorology.

Spatial and Temporal Trends of Wood Smoke Markers in Rural and Urban NY, NJ, and CT

Airsheds from 2002 to 2007

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Levoglucosan, dehydroabietic acid, and retene were used to assess the contribution of biomass combustion emissions to fine particle concentrations in the regional New York City area from 2002 to 2007. Six receptor locations were collocated at state-operated Speciation Trends Network (STN) sites at two rural and four urban sites during two separate sampling phases of the Speciation of Organics for Apportionment of PM_{2.5} (particulate matter with a diameter less than or equal to 2.5 microns) in the New York City (NYC) Area (SOAP) project: SOAP 2002-2003 (13 months, one-in-three day collection frequency) and SOAP 2005-2007 (18-month, one-in-six day collection frequency). Twenty-four hour PM_{2.5} filter samples were collected for both field sampling phases. The two campaigns provided a data set for smoke biomarker concentrations in which comparisons could be made between two rural upwind sites (Chester, NJ and Pinnacle State Park, Addison, NY) and four urban/suburban sites (Elizabeth, NJ, Flushing Queens, NY, Westport, CT and Bronx, NY). Separately, the July 2, 2002 fine PM samples from Elizabeth, NJ, Chester, NJ and Flushing Queens, NY, were examined to assess the impact of 85 wildfires in central Quebec, Canada on July 2-3, 2002 during which large amounts of smoke were produced that extended across parts of the eastern US, including NY, NJ, and CT.

Seasonal smoke concentrations were greatest during the cooler periods for rural and urban sites. However, year-round concentrations of levoglucosan in the highly urbanized sites suggested emission sources more closely connected to localized urban sources such as commercial cooking, outdoor wood stoves and boilers, structural fires, outdoor cooking, yard waste removal, and municipal solid waste combustion for energy production. Finally, smoke from large natural wildfires advected from upwind sources had a significant impact on detection of regional background PM measures in the NYC metropolitan area. Higher regional smoke concentrations were found during the SOAP 2002-2003 due to persistent wildfires in the western US and Canada. Therefore, a single annual sampling period does not capture the regional background of fine PM due to smoke from large-scale wildfires.

Chemical Profiles of PAH Marker Compounds in PM_{2.5} from Gasoline, Diesel and Hybrid Vehicles

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Polynuclear aromatic hydrocarbons (PAHs) are common components in urban fine particles (PM_{2.5}, d_p < 2.5 μm). Incomplete combustion of carbonaceous fuels is the main formation mechanism for PAH and in urban airsheds motor vehicles are the dominant emission sources. PAH compounds also are considered air toxics. On a broader scale, the PAHs are active chemical coatings on fine particles that may play a less well-understood role in atmospheric chemistry and climate processes. The research team focused on the chemical profiles of PAH marker compounds collected as PM_{2.5} from the exhaust of 17 on-road test vehicles from individual dynamometer test runs conducted at the New York State Department of Environmental Conservation Automotive Emissions Laboratory (NYDEC AEL) facility. The research team screened 22 PAH compounds ranging in molecular weight (MW) from 142 to 300 atomic mass units (amu) using Gas Chromatography-Mass Spectrometry (GCMS) analysis in extracts from the filtered exhaust PM_{2.5} samples. The research team calculated emission rates for individual PAH marker compounds per distance traveled (ng/km) and chemical profiles were constructed for gasoline (7), gasoline-hybrid (1), diesel (4), and compress natural gas (CNG) (1) vehicles. The research team found no unique single PAH compounds emitted from the 4 vehicle types. This has important consequences for Chemical Mass Balance-Molecular Marker (CMB-MM) source apportionment models which typically have used single PAH compounds from a vehicle's PAH chemical profile to estimate diesel versus gasoline PM_{2.5} emissions in urban locations. A second key finding was the rate of emission of total PAH compounds (22) which varied significantly between fuel sources and model year. For gasoline vehicles and model year <2000, the average total PAH emitted was 22,900 ng/km (n=5), while gasoline vehicles > 2000 emitted 322 ng/km (n=2). Average total PAH from the diesel vehicles with model year <2000 emitted 10,600 ng/km (n=2) and those >2000 emitted 2,720 ng/km (n=2).

These PAH emissions rates and PAH chemical profiles demonstrate the importance of continued improvement in PM_{2.5} control technologies for motor vehicles. Significant reduction of PAH-laden fine PM from motor vehicles will reduce urban population exposure levels and atmospheric concentrations of climate-forcing carbonaceous aerosols at the regional scale.

On Board Evaluation of Real-time PM Sensors to Determine DPF Failures for Retrofits on Heavy Duty Vehicles

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During the summer of 2008, TSI Incorporated participated in a test program at Environment Canada, Ottawa funded by New York State Energy Research and Development Authority (NYSERDA) and California Air Resources Board (CARB) to demonstrate and evaluate the performance of in-use particulate matter (PM) portable emission measurement systems (PEMS). The goal for this program was to identify measurement techniques which would be applicable to real-world measurement of PM and ultrafine particle emissions from diesel and other mobile emission sources and to detect diesel particulate filter (DPF) failures with an acceptable degree of confidence. Other criteria on evaluation were size, power, reputability and reproducibility of the measurement techniques. The program included two phases. In Phase I the researchers performed the candidate techniques in the laboratory under controlled conditions and challenged the PM measurement systems over a variety of engine operating conditions, i.e. steady state and transient (FTP). The researchers also controlled the amount of PM-laden exhaust through the after-treatment system to develop a robust data set over a range of PM levels and compared results to the reference systems (47mm and 70mm filters). In Phase II the same candidate systems were performed on a vehicle with and without a DPF to see if they were able to determine not only DPF removal efficiencies but also to provide second-by-second PM emissions data on a gram/ sec and g/gallon and g/BHp-hr basis. At 24% engine load the electrical aerosol detector (EAD) measured 98.8% over all the runs, and 44.6% removal efficiency at 100% and 50% DPF levels respectively. At 70% engine load the EAD measured 98.5% and 65% removal efficiency (35% penetration) at 100% and 30% DPF levels respectively. For the transient federal test procedure (FTP) cycles, the EAD measured 98.2% and 49.6% DPF efficiency at 100% and 50% DPF conditions respectively. For the engine exhaust particle sizer (EEPS) the values were similar at 95.9 and 45.9%. The EAD and Dust Trak DRX both predicted the level of emissions with the DPF on at 96.5 and 99%, respectively.

Production of Sustainable Hydrocarbon Fuels via Electrolysis of CO₂ and H₂O with Renewable/Nuclear Energy

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To improve the sustainability of transportation, a major goal is the replacement of conventional petroleum-based fuels with more sustainable fuels that can be used in the existing infrastructure (fuel distribution and vehicles). As an alternative to hydrocarbon fuels produced from biomass and fossil fuel feedstocks, synthetic hydrocarbon fuels can be produced in a potentially more sustainable manner from CO₂, H₂O, and renewable and nuclear energy. Production of these fuels involves CO₂ capture, storage of renewable/nuclear energy as chemical energy by dissociation of CO and/or H₂O, and fuel synthesis using dissociation products. The research have focuses on the storage of renewable/nuclear energy, using a promising means of efficient dissociation by high temperature electrolysis of CO₂ and/or H₂O in solid oxide cells to yield synthesis gas (syngas, a gas mixture rich in CO and H₂). The researchers used solid oxide cells for co-electrolysis of CO₂ and H₂O simultaneously. The cells are produced by Risø and designed for use as fuel cells. The performance and durability were characterized using electrochemical impedance spectroscopy. High performance for co-electrolysis was observed, and the durability might be sufficient for an economically viable synthetic fuel production process. The researchers discuss possible routes to improving the cell durability based on an analysis of the feasibility and sustainability of a fuel cycle involving co-electrolysis. Opportunities are discussed for fuel production using inexpensive, intermittent renewable energy (e.g. excess wind power supply or solar arrays built in remote, sunny locations) and constant-supply nuclear power. The energy balance and economics of the process are estimated. With a high cost of oil and inexpensive non-fossil energy sources, it will be possible to produce clean synthetic fuels at a lower cost than to produce equally clean fossil fuels.

A Numerical Method for Optimizing Advanced Coal-fired Power Plants

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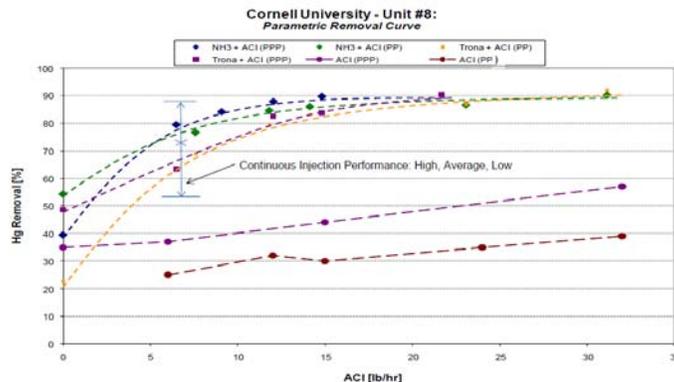
This poster presents a computational methodology for optimization of different technologies for advanced coal-fire powered plants based on user-supplied evaluation criteria. The resulting software tool allows for comparisons of different plant modules, different power plants, and different technological pathways leading from current power plants to future power plants. Technology development is path dependent, and choosing an optimal set of intermediate stepping stones is important. The novel methodology used makes such assessments by introducing penalty functions that are applied to modules, plants, and sequences of plants. During optimization one varies design parameters to minimize the penalty function, which would be zero for some perfect, usually unattainable state. The penalty is a sum of penalties for specific aspects of the plant such as efficiency, cost or environmental impact. Individual modules may have component penalties, but some penalties can only be defined for the entire plant, or even for a sequence of plants. The user chooses the relative weights of these penalties. A novel object-oriented computer code is being developed, with structures and modules to assemble flow sheets comprising power plant modules, like furnaces and turbines, into complete power plants. An iterative process (the Reconcile operation) is used to make inter-module material flows internally consistent. The program then assigns penalties and changes design parameters in order to minimize the penalty. Version 1.0 is working, and it includes libraries of modules and successfully reconciles the flows between modules. The program starts from a user-supplied initial guess of internal material and energy flows, and through iteration arrives at a consistent set of flows. This, in turn, allows the user to calculate properties of the plant, like overall efficiency. The program assigns costs and will optimize the design parameters.

Mercury and Sulfur Trioxide Control at Cornell University Boiler #8

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Cornell University Central Heating Plant (CHP) has been working for several years to quantify and control mercury emissions from its two coal fired stoker boilers. The New York State Energy Research and Development Authority (NYSERDA) has provided the CHP with an agreement to continue testing sorbent technologies for mercury emissions control. As part of that agreement, NYSERDA formed a project advisory group and ADA was chosen as the testing company for the project. A PAG meeting was held at the CHP on August 29, 2008 and testing occurred in February 2009. In preparation for the testing program, ADA installed a temporary trona and aqueous ammonia injection system at the Cornell Heating Plant. The powdered activated carbon (AC) injection grid was owned and operated by Cornell University Continuous mercury measurements were made throughout testing using two Thermo Fisher mercury Continuous Emission Monitoring Systems: one temporarily installed two feet upstream of the trona/aqueous ammonia injection lance and the other at the outlet of the fabric filter. Sorbent Trap Measurements based on EPA Method 30B were used for quality assurance purposes. SO₃ flue gas levels were monitored by two in-situ monitor probes, one operated by ADA and the other by Thermo Fisher. Unit operating data were also monitored and recorded using the plant distributed control system. The test consisted of injecting various combinations and concentrations of either trona or aqueous ammonia (for SO₃ capture) and activated carbon (AC) or brominated AC (for mercury capture). SO₃ and mercury were trapped on the AC, then captured in the plant's fabric filter and disposed of with the fly ash. Analysis of the mercury removal data revealed a significant beneficial improvement in mercury removal when either ammonia or trona was used to reduce flue gas SO₃ levels while injecting PAC.



Long Island MARKAL Electricity Generation Optimization and the Impacts of Policy Change

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Recently, there has been a growing movement towards increasing sustainability. Corporations, universities, towns, and cities have established long-term sustainability plans. For example, Levittown, New York (Nassau County) has recently established the Citizens Campaign for the Environment. This initiative strives to improve the environment by increasing efficiency and creating economic, ecological, and social sustainability. The goal of this research is to develop a plan for improving air quality by creating a plan for optimizing use of electric generating facilities, which are a source of air pollution. The research team will use the MARKAL model (MARKet ALlocation -- an integrated energy, environment and economic model used to examine market potential for energy technologies over a short-, medium- and long-term horizon under alternative policy scenarios within the entire energy system) to determine an optimal mix of multiple energy sources for generating electricity on Long Island. The research will examine possible future outcomes of multiple scenarios using this model, e.g. minimum renewable energy portfolios and carbon taxes. The data will be made available to policy makers and other sustainability organizations for planning purposes.

Oxygen Transport Membrane Based Oxy-fuel Combustion for CO₂ Capture

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Praxair is developing an oxygen transport membrane (OTM) technology that could revolutionize the way oxy-combustion is carried out. Oxy-combustion technology has emerged as a viable option for carbon dioxide (CO₂) capture from power plants and industrial processes. In a conventional oxy-combustion process, a cryogenic air separation unit (ASU) separates oxygen from nitrogen. By keeping nitrogen out of the combustion process, this technology generates CO₂-rich flue gas. The flue gas is then compressed and purified to remove trace impurities, non-CO₂ gases, and moisture to produce a purified compressed CO₂ stream for pipeline transportation to a sequestration site. Instead of separating a pure stream of oxygen in a separate air separation unit and then delivering it to a boiler for combustion, the OTM technology integrates oxygen separation and combustion in one unit. In the novel OTM boiler concept, a ceramic membrane separates the air and fuel streams. Oxygen from the air side is transported to the fuel side in the form of an oxygen ion using a chemical potential difference as the driving force and oxygen reacts with the fuel on the membrane surface itself. Building on this concept, Praxair has defined a power cycle concept comprised of OTM-based oxidation units and other well-known unit operations. This power cycle will significantly improve the efficiency of a power plant with CO₂ capture. The main objectives of the current phase of work are to develop membrane technology that meets commercial targets for oxygen flux, strength and reliability; to down-select an optimum process integration cycle for the OTM membranes with CO₂ capture; and to provide a full system and economic analysis of that cycle.

ENrG, Inc. is developing an Advanced Substrate Technology for Praxair's Oxygen Transport Membranes. The Advanced Substrate has high porosity and low tortuosity and significantly reduces the mass transport resistance associated with diffusion of reactant and products in the membrane support structure. As a result, a step change in membrane performance has been realized. The step change is required in order to move forward with pilot demonstration of OTM oxy-fuel combustion technology.

Optimization of Low-NO_x Operation at Cayuga Unit 1

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AES Cayuga Unit is a 160 mega watt (MW) unit, equipped with a low-NO_x firing system and an anhydrous ammonia Selective Catalytic Reduction (SCR) system for additional NO_x emissions control. An optimization was performed over the unit load range to achieve upgrades to the combined boiler/SCR/air preheater operation and control scheme for enhanced low-NO_x constrained operation. A fouling probe was installed at the air preheater inlet for on-line ammonium bisulfate (ABS) formation monitoring, and as a constraint to the SCR optimization. Boiler and low-NO_x system control settings, soot blowing, and the SCR and air preheater operating conditions were included in a parametric field test program. The optimization was performed using an approach that included a support vector machine, genetic algorithms and tuned proportional-integral-derivative (PID) control gains. The test data generated in this project with unit operating data have made it possible to estimate total annual savings of approximately \$750,000. This includes savings of \$69,000 due to a 22% reduction in ammonia usage, an estimated \$45,000 savings due to projected increased catalyst lifetime, an annual fuel savings of \$151,000 due to a 0.6 % heat rate improvement, and a \$483,000 reduction in air preheater cleaning costs.

Use of Waste and CO₂ Compression Heat to Reduce Penalty Due to Post-Combustion CO₂ Capture

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Coal combustion emits the largest amount of carbon dioxide (CO₂) per unit energy from fossil fuel sources. In the U.S. coal-fired utility boilers generate more than 50% of the electricity. CO₂ concentration in the atmosphere has increased over the last 150 years from 180 to 380 ppm, and is considered a likely cause of a global temperature increase, resulting in regulations restricting CO₂ emissions from emitting sources. The required level of reduction in CO₂ emissions and the development status of affordable CO₂ abatement technologies will have a major impact on the commercial options and economics of new coal-fired power plants.

Existing coal-fired power plants will also need to reduce their carbon footprints. While oxy-fuel, Integrated Gasification, Combine Cycle (IGCC), and post-combustion carbon capture and sequestration (CCS) technologies are viable options for the new power plants, it is likely that most of the existing power plants will be retrofitted with post-combustion CCS technology. The major barriers to this technology are high cost, significant reduction in power plant output, and high performance penalty.

The project team will assess the efficiency improvements that can be achieved at existing power plants by recovering heat from the flue gas leaving the plant, use of recovered heat in the CO₂ scrubbing process to offset performance and capacity penalties, and use of compression heat associated with post-combustion CO₂ capture for efficiency improvement. The Researchers will determine the efficiency improvement achieved by integrating CCS with the power plant waste and other heat sources to reduce overall energy requirements for the CO₂ capture and to allow use of CO₂ compression heat to improve performance of the steam turbine cycle. Recovered heat from flue gas and compression heat will be used for feedwater (FW) heating, air preheating, and CO₂ scrubbing. The achieved efficiency improvement will offset, in part, the performance penalty incurred by implementation of CCS. The results will provide information about innovative strategies for superior plant performance and CO₂ emissions reduction and support implementation of CO₂ reduction regulations and technologies at coal-fired power plants. These strategies will help improve ambient air quality and foster business and technology development in New York State.