Upgrade of an XRF Spectrometer and Acquisition of an Ultrasonic Nebulizer Aerosol Deposition System for Research and Research Training in Environmental Geochemistry and Biogeochemistry

This proposal seeks to support several research projects and research training activities at the Keene State College (KSC) Center for Environmental BioGeoChemistry, through the upgrading of our existing wavelength dispersive x-ray fluorescence spectrometer (XRFS), and the acquisition of an ultrasonic-nebulizer-based aerosol generation and deposition system. The proposed upgrades to the XRFS include equipping it with a primary beam filter and additional analyzing crystals to extend the range of elements which can be successfully analyzed, and acquiring new Fundamental Parameter analytical software, extending the range of sample types which can be successfully analyzed. The aerosol generation and deposition system would be used in conjunction with the XRFS for improved analyses of airborne fine particulate matter and other samples.

The specific research and research training activities that will make us of this instrumentation include: (1) training of undergraduate students in scientific research across courses in Geology, Environmental Studies, Chemistry, Biology, and Safety Studies; (2) studies of the occurrence, transport, and environmental fate of toxic trace elements in river sediments; (3) characterization of ambient airborne fine particulate matter from different source regions; and (4) study of Neotropical migratory bird populations using combined trace element and stable isotope signatures to improve understanding of their ecology and biology. This proposal builds upon the successes of prior NSF support for instrument acquisition at KSC and expands the analytical capabilities of the KSC Center for Environmental BioGeoChemistry.

Results of Prior NSF Support for Instrument Acquisition

Geochemical Analysis across the Geology Curriculum and in Related Courses in Chemistry and Environmental Studies

Award #0087860
$242,223 including matching funds from KSC
June 15, 2001 to January 31, 2005

With this award, we acquired an automated wavelength dispersive XRFS with element mapping and spot analysis capabilities, along with associated sample preparation equipment. We have made extensive use of the XRFS across the Geology curriculum, as well as in courses and student projects in Environmental Studies, Chemistry, Biology, Safety Studies, and Technology Studies (Table 1).

A few examples of undergraduate student research projects that have used the XRFS include:

> Assessment of toxic trace element (As, Pb, Cu, Ni, Cr, and Zn) concentrations in sediments of the Ashuelot River in Keene. Students from classes in Geochemistry, Environmental Geology, Quantitative Analysis, and Environmental Studies Senior Seminar have all contributed to this project. A compilation of our preliminary results were presented at the 2003 KSC Academic Excellence Conference, and published in a peer-reviewed regional publication (Allen et al., 2003). Students continue to work with Professor Allen on this problem, as discussed further in Projects 1 and 2 below.

Characterization of metasomatic alteration of fault breccia at the Wise Mine in Westmoreland, NH, famous for its fluorite mineralization. Samples of altered host-rock clasts and hydrothermal deposits from the breccia, as well as representative un-altered host rocks, were analyzed for comparison with one another. Significant changes in composition were observed between altered and un-altered samples and several possible explanations were explored. The results from this project were presented at the 2003 KSC Academic Excellence Conference.

Investigation of the possibility of using Indian Mustard to "phytoremediate" lead-contaminated soil. Indian Mustard plants were grown from seeds planted in pots of lead-contaminated soil and in a control soil, and then analyzed the different harvests, as well as the soil. The plants grown in the Pb-contaminated soil did take up Pb, and

Semester	**Course**	**Instructor**	**#**	**level**
January 2002	*XRFS first installed*			
Spring 2002	GEOL 412 Geochemistry CHEM 356 Analysis of the Environment CHEM 456 Instrumental Analysis	Tim Allen Steve Stepenuck Steve Stepenuck	8 3 3	Proj Demo Demo
Fall 2002	GEOL 315 Environmental Geology ENST 495 Senior Seminar SAFE 490 Exposure Assessment CHEM 256 Quantitative Analysis	Tim Allen Renate Gebauer Melinda Treadwell Steve Stepenuck	5 1 1 5	Lab Proj Proj Demo
Spring 2003	GEOL 201 Intro Physical Geology BIO 456 Ecological Research Methods GEOL 310 Glacial Geology TDS 253 Materials of Manufacturing ENST 495 Senior Seminar CHEM 456 Instrumental Analysis	Tim Allen Renate Gebuaer Steve Bill Lisa Hix Renate Gebauer Sally Jean	27 1 5 8 2 6	Demo Proj Lab Demo Proj Proj
May 2003	*XRFS moved out of "old" science building*			
Fall 2003 (in temporary quarters)	GEOL 315 Environmental Geology CHEM 255 Quantitative Analysis CHEM 345 Physical Chemistry ENST 495 Senior Seminar	Tim Allen Sally Jean Jerry Jasinski JoBeth Mullens	9 4 3 2	Lab Proj Lab Proj
Spring 2004	GEOL 412 Geochemistry	Tim Allen	5	Proj
August 2004	*XRFS moved into "new" science building*			
Fall 2004	GEOL 315 Environmental Geology ENST 495 Senior Seminar CHEM 255 Quantitative Analysis CHEM 345 Physical Chemistry TDS 253 Materials of Manufacturing	Tim Allen JoBeth Mullens Sally Jean Jerry Jasinski Lisa Hix	9 3 2 6 18	Lab Proj Proj Lab Demo

Table 1: Courses that have used the XRFS since its acquisition, including the name of the course instructor, the number of students from that course that were involved in using the instrument, and their level of involvement —whether it was merely a demonstration, a laboratory session or two, or an extended project requiring more than just one or two laboratory sessions.

accumulated increasing amounts over time, although since they were never fertilized they did not really grow well enough to substantially reduce the Pb content of the soil in the pots. This work was presented at the KSC Academic Excellence Conference in March 2004.

In December 2004, Professor O. Don Hermes of the Department of Geosciences at the University of Rhode Island provided an external review of the project as part of our evaluation plan. He wrote:

> The diversity of projects, topics, and experimental procedures is substantial, and largely reflects upon the considerable talents of the PI, Timothy Allen. The incorporation of the XRF laboratory into a number of interdisciplinary courses has provided a valuable element of experiential learning for the students beyond those previously offered at KSC. Most of the project objectives stated in the original proposal have been initiated. Experimentation has shown that several (e.g., applications toward the introductory Physical Geology offering) have met with less than the hoped for success. However, creative activity has led to the development of new successful initiatives that were not identified in the original proposal. I conclude that most of the overall goals of the proposal have been achieved, and that new experiential learning experiences continue to be evolving and developed. The laboratory is in capable hands.

Integration of Stable Isotopes across the Sciences (ISIS): Instrumentation for BioGeoChemistry and Environmental Studies

Award #0126706
$180,737 including matching funds from KSC
February 1, 2002 to May 31, 2004

With this award we acquired a stable isotope ratio mass spectrometer (IRMS) and constructed two modular multi-purpose high-vacuum sample preparation lines. The goals of this project were to: integrate stable isotope analysis into the science curriculum at KSC, motivate undergraduates to translate scientifically interesting and exciting questions into research projects, and enhance students' integrated understanding of concepts in biology, geology, and environmental studies.

The IRMS and sample preparation lines have been extensively used in courses in Biology, Environmental Studies, and Geology, including:

Biology Research Rotation (sophomore level)
Experimental Ecology and Evolution
Ecological Research Methods
Introduction to Environmental Studies
Junior/Senior Seminar in Environmental Studies
Environmental Geology
Glacial Geology
Geochemistry

Some examples of undergraduate student research projects that have used the IRMS include:

> Measurements of $\delta^{13}C$ in well-watered and water-stressed corn and bean plants (C3 and C4 photosynthetic pathways, respectively) to explore why isotopic composition in plant material varies and how water stress affects the $\delta^{13}C$, a measure of water use efficiency in C3 plants.
>
> Use of $\delta^{18}O$ analyses of different water sources (e.g. precipitation, river water, ground water) to determine the relative contributions of each source to various bodies of water.
>
> Determination of $\delta^{15}N$ and $\delta^{13}C$ in feathers of Canada geese to determine whether stable isotopes can be used to differentiate between populations in Massachusetts and Quebec and to determine the proportion of resident vs. migratory birds in a population. The results of this project were presented at the 2004 KSC Academic Excellence Conference.

Students evaluations showed that students felt that the stable isotope exercises helped them improve general laboratory and technical skills, data analysis skills, ability to think logically through a problem, and that they understood the use of stable isotopes to examine a specific question in the context of that particular class. The assessment of students' learning outcomes generally showed that they did well describing trends and formulating hypotheses and that they were able to interpret patterns of stable isotopes (again within the context of the particular class).

New Science Building

Shortly following receipt of these two awards, KSC also received funding from the State of New Hampshire ($19M), supplemented by a successful capital campaign supported by corporate and private donations ($4M), for a total renovation and major expansion of our science laboratory and classroom building. This construction—which displaced all KSC science faculty, laboratories, and classes into temporary quarters for 14 months—was just completed in August of 2004.

One feature of the project was the creation of a new interdisciplinary research facility consisting of a suite of interconnected laboratories supporting faculty, student, and class projects making use of the NSF-funded XRFS and IRMS instruments, across the disciplines of Geology, Environmental Studies, Chemistry, and Biology. This facility, the "Center for Environmental BioGeoChemistry," is the result of collaboration between a Geologist (Tim Allen) and a Biologist (Renate Gebauer). Both are involved in Environmental Studies and both have expertise in stable isotope and elemental analysis applications within their respective areas.

The facility consists of an instrument room, housing the XRFS and IRMS; a sample preparation lab housing vacuum lines and other equipment, as well as a special acid-digestion fume hood; and a student project laboratory with additional work space and a fume hood accessible to the physically disabled. (It should be noted that the new building is not only fully compliant with ADA requirements, but incorporates many features of universal design, promoting accessibility and inclusion for all students throughout.)

As an example of the type of creative and collaborative interdisciplinary activity promoted by this facility, students in Chemist Sally Jean's sophomore-level Quantitative Analysis class this

Fall worked with both Tim Allen and Renate Gebauer to analyze the C and O stable isotopic composition, as well as the trace element composition, of bone carbonate-apatite from beef cattle bones obtained from local butchers. The "natural" (organic-fed) cow bone showed measurable differences from the regular supermarket cow bones, which we suspect reflect differences in diet between free-range grazing (the "natural" cow) and life in a feedlot (the supermarket cows).

Research and Research Training Activities

Project 1: Research Training for Undergraduate Students

Keene State College is a public four-year liberal arts and science college with a tradition and strength in teacher preparation, focusing primarily on undergraduate education. As part of its mission, KSC promotes strong relationships among students and faculty that emphasize creative and critical thinking, scholarship and research, and a passion for learning, with a commitment to service. Keene State College has a well-established record of involving undergraduate students in research projects and service learning (e.g. Allen et al., 2003; Treadwell and others, 2003, 2002; Burt et al., 2002; Saxon et al., 2001, O'Rourke et al., 1998).

As described in the section on prior NSF support, we have successfully used new instrumentation to make curriculum and laboratory improvements that have increased the involvement of our students in the process of modern scientific investigation, with progressive course-based research experiences preparing students for independent research. Our results are consistent with national trends in science education towards student-centered, inquiry-based, active participatory learning (e.g. Culotta, 1994; Markovics, 1990) and the involvement of undergraduates in authentic scientific process (e.g. Goodwin & Hoagland, 1999; McConnaughay et al., 1999; McGinn & Roth, 1999). Indeed, science-as-inquiry forms the basis of the *National Science Education Standards* (National Research Council, 1996, pages 121, 143, and 173).

With this proposal, we hope to expand our current and on-going research training activities in courses in Geology, Environmental Studies, Chemistry and Biology as well as through student-faculty cooperative research, and to extend research opportunities to students in Safety Studies. Specific courses that will be impacted include:

Geochemistry (Tim Allen, Geology & Environmental Studies)
Environmental Geology (Tim Allen)
Quantitative Analysis (Sally Jean, Chemistry & Science Education)
Instrumental Analysis (Sally Jean)
Biology Research Rotations (Renate Gebauer, Biology & Environmental Studies)
Ecological Research Methods (Renate Gebauer)
Advanced Exposure Assessment (Melinda Treadwell, Safety Studies)
Environmental Studies Junior/Senior Seminars (Tim Allen, Renate Gebauer, and others)
Independent Study

Student research projects in these courses can involve analyzing a wide variety of samples including: fish tissue, animal bones, bird feathers, plants, paint, compost, airborne particulate matter, and treated wood, as well as rocks, sediments and soils. The proposed upgrades to the existing XRFS, along with the additional equipment requested, would facilitate these analyses by extending the range of elements and expanding the types of samples that can be successfully analyzed—including sample types for which calibration standards are not readily available—thus providing opportunity for an increased variety of student research projects.

The next two projects present specific examples of research activities that will be enhanced by the new instrumentation and that will engage undergraduate students in the scientific process, providing them with research training.

Project 2: The occurrence, transport, and environmental fate of toxic trace elements in river sediments

The Ashuelot River is an important hydrologic feature of southwestern New Hampshire, draining the major portion of Cheshire County, a small portion of Sullivan County, and a small portion of north-central Massachusetts. Along its 64-mile course are several population centers and sites of historic and current industrial activity, including the city of Keene.

The release of toxic trace metals to the environment has long been associated with various industrial activities, but toxic metal contamination has also been correlated with population density in areas without significant industrial activity (e.g. Callender & Rice, 2000). Given the history and geography of the Ashuelot River, KSC undergraduate students working with Tim Allen undertook a reconnaissance assessment of the possibility that the river's sediments might be contaminated with toxic trace metals, presumably in and downstream from Keene (Allen et al., 2003).

Lead, Copper, and Nickel were all found at relatively high total concentrations—exceeding toxicological thresholds (Buchman, 1999), in some cases significantly—at one or more sediment sampling sites in Keene (Figure 1). These sediments are presumably toxic to some organisms in the benthic community, which will in turn have an adverse impact on other aspects of the ecosystem (e.g., NH-DES, 2004).

The initial reconnaissance entailed collecting "grab" samples of river-bottom sediment at convenient locations along the course of the river. Additional work is now currently underway to map out the extent and distribution of contamination at selected sites. Initial findings from this work suggest that the occurrence of contaminated sediments is wide-spread (Figure 2), but we do not as yet understand the pattern of distribution in relationship to the pattern of stream flow and

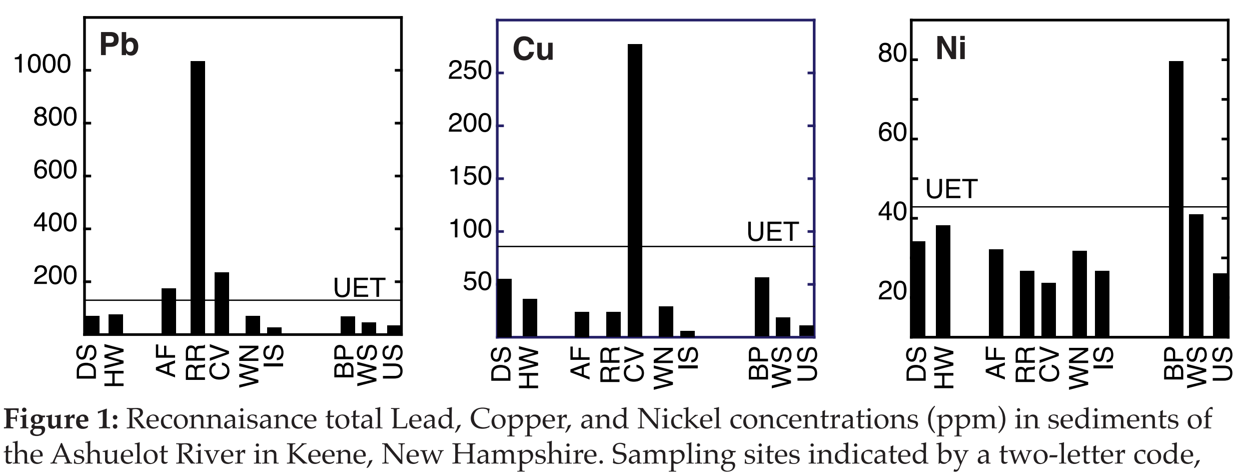

Figure 1: Reconnaisance total Lead, Copper, and Nickel concentrations (ppm) in sediments of the Ashuelot River in Keene, New Hampshire. Sampling sites indicated by a two-letter code, from downstream (DS) to upstream (US). Sites AF and RR shown in detail in Figure 2. The Toxilogical Upper Effects Thresholds (UET) for freshwater sediment are from Buchman (1999).

sediment transport in this meandering river system. For example, the highest Lead concentrations are found on the outsides of the river bends, while sediment deposition would be expected to occur on the insides of the river bends. Additional controlled sampling and analyses will help improve our understanding of the processes controlling the distribution (and redistribution?) of these contaminated sediments, and ultimately help identify their source and predict their fate.

Historical information suggests that Cadmium may also be an element of concern in the Ashuelot River (S. Brackett, personal communication, 2004), but in its current configuration our XRFS is limited in its ability to measure Cadmium concentrations. This proposal seeks to upgrade the existing XRFS so as to enhance our ability to analyze Cadmium and other elements.

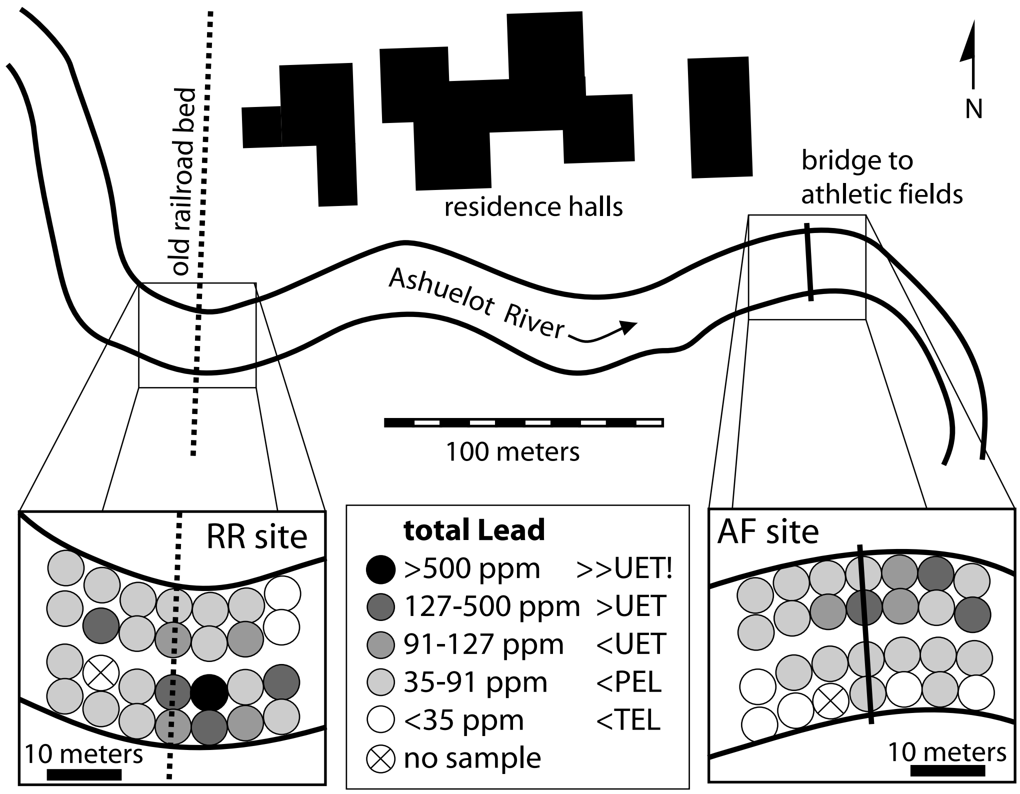

Figure 2: Detailed sampling reveals distribution and extent of Lead contamination in Ashuelot River sediments at the RR (Railroad Trestle) and AF (Athletic Field Foot Bridge) sites (from Figure 1). Toxicological Threshold Effects Level (TEL, 35 ppm), Probable Effects Level (PEL, 91 ppm), and Upper Effects Threshold (UET, 127 ppm) for Lead in freshwater sediments from Buchman (1999).

Project 3: Characterizing the Composition of Airborne Particulate Matter in the Northeast

Recognizing the potential impact of airborne particulate matter on health and public welfare (e.g. Gordon and Reibman. 2000; Laden et al., 2000; Linn et al., 1996; Pearson et al., 2000; and Wong et al., 2002), in 1997 the United States Environmental Protection Agency (EPA) adopted a more stringent mass-based ambient air quality standard for particulate matter with an aerodynamic diameter of <10 um (PM10) and new National Ambient Air Quality Standards (NAAQS) for particulate matter with an aerodynamic diameter of < 2.5 um (PM2.5) (40 CFR Part 50, Federal Register, volume 62 number 138, July 18, 1997).

A mechanistic understanding of the effect of PM10 or PM2.5 has not yet been conclusively determined. In public documents members of the Agency's Science Advisory Board debated the justification of a mass-based standard, with many arguing that particulate matter composition would be a critical consideration in assessing toxicity of a given mass. All members of the panel agreed; however, that it was not practical to establish a composition-based standard, given the limited understanding of fine airborne particulate matter speciation in the nation at the time. In the Criteria Document and Staff Papers supporting the EPA's decision, scientists acknowledged that both the size of the particulate matter and the chemical composition (particularly metallic content) were likely to serve as critical determinants of potential adverse health effects associated with environmental exposures.

Since 1997 significant effort has been expended to characterize the ambient particulate matter mass and composition across the country in support of the most appropriate national standard. Metals leaching from airborne particles pose a highly significant policy concern due to their potential association with the incidence of cardiopulmonary diseases. Primary sources of these metals include both mobile and stationary sources of combustion, such as diesel exhaust and fossil fuel-burning power plants (Laden et al., 2000; Samet et al., 2000). Particles from coal-burning power plants have been shown to contain high levels of nickel and vanadium, with 53% of the measured nickel in emissions being associated with particles <3um in diameter (Samet et al., 2000). Preliminary data in New Hampshire, obtained by Dr. Melinda Treadwell and her students (2002, 2003) indicate variations in nickel concentrations as well. Other researchers have shown that the concentration of nickel is the highest in particulate matter from urban areas (1-328 ng/m3), followed by rural (0.6-78 ng/m3) and remote areas (0.01-60 ng/m3) (Samet et al., 2000).

Ambient air quality monitoring networks exist throughout the northeastern states and long-term average particulate mass values are routinely determined by the states conducting the monitoring as required by the EPA. However, routine characterization of the chemical composition of the particulate matter collected in these monitoring networks is very limited. Thus, although these ambient air quality monitoring networks have been in operation and growing since the early 1970's, questions remain about the variability in ambient particulate matter composition and mass from different urban, rural, and anthropogenic source-specific locations across the region. The proposed research program will begin to address these questions by undertaking compositional analyses of particulate samples collected from monitoring network locations in each setting (urban, rural, and anthropogenic source-specific). Dr. Treadwell and her students will determine metals speciation (in particular, arsenic, cadmium, chromium, lead and nickel) and quantify concentration using the upgraded XRFS at KSC, in collaboration with Tim Allen.

In addition, the project will undertake retrospective characterization of PM2.5 and PM10 samples collected from regional air monitoring stations from the northeast and mid-Atlantic states during defined summer-time pollutions events. Each summer season the northeastern and mid-Atlantic regions of the United States experience high air pollution concentrations across a broad air space for sustained time periods. Such an event occurred during the monitoring period between August 8 and August 20, 2002, where the northeast region experienced extremely high fine particulate matter pollution. Dr. Treadwell will work with state air quality monitoring officials through the Northeast States for Coordinated Air Use Management to obtain archival PM2.5 and PM10 filters collected during this and other defined pollution events, as well as other selected monitoring periods.

Ultimately, with current funding from the National Institutes of Health (Award No. 1P20RR018787-010004), Dr. Treadwell is attempting to assess whether or not exposure to airborne particles of differing composition, such as might be collected at different urban, rural, and source-specific monitoring sites, will produce distinct pathological protein profiles in lung epithelium. Genomic and proteomic techniques will be used to determine the cellular effects of relevant concentrations of particulate matter on human epithelial cells in culture. This work will support the identification of protein biomarkers that can then be taken back into human studies to prove causal relationships between exposure to airborne particulate and pulmonary pathobiology.

However, to fully test this hypothesis, Dr. Treadwell must first characterize particulate matter composition and mass from different urban, rural, and anthropogenic source-specific locations across the region in order to demonstrate that the particulate matter collected from the different sites does vary in total particulate mass and composition. Thus, this proposal seeks to upgrade our existing XRFS, and acquire an aerosol generation and deposition system for generating particulate matter calibration standards (e.g. Haupt et al., 1997; Foster, 2000; Vanhoof et al.,, 2000), to improve our ability to calibrate for and quantitatively analyze the elemental composition of particulate matter filter samples.

Project 4: Unraveling the mysteries of Neotropical migrant birds using new techniques

For decades biologists and conservationists have claimed the importance of incorporating the ecology of Neotropical migrant birds on their wintering grounds into conservation plans. However, wintering-ground ecology of these migrant species has only begun to receive needed attention. Conservation aimed only at breeding grounds is accounting for their needs only one quarter of the year. Despite documented habitat loss and degradation on wintering grounds, conservation is hampered by our lack of knowledge about the threats to migrant bird populations.

Of fundamental importance to conservation of Neotropical migrants is determining the wintering range and habitat, and connectivity between wintering and breeding populations (Webster et al. 2002). All three of these objectives are especially challenging for species such as Bobolinks that are highly mobile during winter. Satellite transmitter technology, while expensive, can provide this type of information for large birds such as waterfowl and raptors, but transmitter size requirements are far too large for use on songbirds.

Given recent population declines of Bobolinks and other migrants (e.g., Renfrew & Sample, 2002), information to guide conservation efforts needs to be collected in a timely manner. Threats to wintering populations of Bobolinks are currently unknown, but may include pesticide exposure and habitat loss and degradation (Basili 1997). Given their range may span hundreds of thousands of square miles in South America, a goal as basic as defining Bobolink winter range via surveys alone would require years of study with many observers.

Fortunately, other emerging technologies provide the potential to assess conservation threats to passerine migrants such as the Bobolink more efficiently. Methods using stable isotopes and elemental markers are being developed and refined to help determine migrant distribution, population connectivity, and habitat use (Smith et al. 2003). Because feathers contain elements present in blood at the time of feather growth, isotopes and elemental markers in feathers can indicate the location, habitat use, and diet of an individual when it grew the feather (e.g., Hebert and Wassenaar 2001, Szép et al. 2003, Wassenaar and Hobson 2000). The feather containing these clues from its place of origin can be collected months later in a different location, after spring or fall migration.

Bobolinks are one of the very few passerine species that molt all their flight feathers twice each year. This provides an excellent opportunity to accumulate clues about the location and habitat use of the bird at the time the feather was grown, from both poles of their life cycle. “Signature” values of isotopes and elemental markers can be obtained for a geographic area by collecting new feathers in their region of origin. Old feathers collected on the summer breeding grounds represent conditions during winter in South America when the feather was grown. In turn, feathers collected in South America, grown before fall migration, can give clues about breeding and staging grounds. Connectivity and habitat use can be assessed simultaneously in both “directions”.

Typically, deuterium isotopes have been used to establish the geographical region of origin of feathers grown in North America (e.g., Hobson and Wassenaar 1997), and more recently, in Europe as well (e.g., Hobson et al. 2004). However, deuterium gradients are minimal in central South America (e.g., Hobson et al., 2003). Application of this technique in North America for migrants that grow their feathers in South America is therefore unlikely to produce meaningful results. Carbon and nitrogen isotopes can give insight into diet and habitat (e.g., Harrington et al. 1998, Smith et al. 2002), although this requires more exploration, especially for species like Bobolinks that potentially feed in N-enriched agricultural environments on both C3 and C4 plants.

Current research recommends using elemental markers to augment stable isotope techniques (T. Donovan, personal communication). The first step it to determine which elements vary among regions and evaluate signature samples to produce basemaps of elemental signatures for a species. These maps will then be used to deduce the location and habitat of the geographic origin of a feather. Further, simultaneously evaluating trace metals together with stable isotopes may be particularly useful in diagnosing an agricultural versus natural-based diet for species like the Bobolink that use agricultural lands. The use of elemental markers on Neotropical migrant feathers is still in the development phase—we have only been able to identify three peer-reviewed papers utilizing this application of elemental markers (Parrish et al. 1983, Vallner et al. 1999, Szép et al. 2003).

In the proposed research, Dr. Rosalind Renfrew, Conservation Biologist with the Vermont Institute of Natural Sciences (Woodstock, Vermont), in collaboration with Tim Allen, would investigate the use of XRFS to obtain trace element analyses from bird feathers, and assess the usefulness of the data so obtained in discriminating between populations of Neotropical migrant birds. XRFS appears to have several advantages over other analytical techniques, in that it may require minimal sample preparation, thus providing cost-effective results with rapid turn-around. In addition, XRFS analysis is non-destructive, so the same feather material could be analyzed both for its elemental composition and its stable isotopic composition. This proposal seeks to upgrade our existing XRFS and acquire new Fundamental Parameter “standardless” software to facilitate improved direct elemental analyses of bird feathers, a sample type for which calibration standards are not readily available. Dr. Renfrew will also be collaborating with Renate Gebauer to carry out stable isotope analyses using the IRMS in the Center for Environmental BioGeoChemistry at KSC.

Senior Personnel and Students Making use of the Instrumentation

In summary, the following Senior Personnel would be involved in the Research and/or Research Training Activities supported by this proposal:

Dr. Timothy Allen (PI), Professor of Geology & Environmental Studies (Projects 1, 2, 3 & 4)
Dr. Melinda Treadwell, Assistant Professor of Safety Studies (Projects 1 & 3)
Dr. Renate Gebauer, Associate Professor of Biology & Environmental Studies (Projs. 1 & 4)
Dr. Sally Jean, Associate Professor of Chemistry & Science Education (Project 1)
Dr. Rosalind Renfrew, Conservation Biologist, Vermont Institute of Natural Sciences Woodstock, Vermont, (Project 4)

In addition, we estimate that each academic year typically about 20 undergraduate students will be explicitly involved in the research and/or research training activities supported by this proposal (e.g., see Table 1). The proposed instrumentation will further support inquiry project-based laboratory exercises in courses in Geology, Environmental Studies, Chemistry and Biology, as well as in Safety Studies, and senior seminar capstone research projects and student-faculty cooperative research.

Beyond KSC, the laboratories of the Center for Environmental BioGeoChemistry have attracted collaborators from other regional institutions, as evidenced by the inclusion of Dr. Rosalind Renfrew of the Vermont Institute of Natural Sciences in this proposal. In addition, graduate students and scientists from the University of New Hampshire, Dartmouth College, Antioch New England Graduate School, and the Saskatchewan Research Council (Canada) have come to KSC to make use of our unique facilities.

Description of Research Instrumentation and Needs

We propose to (1) upgrade our existing Rigaku ZSX 100e automated wavelength dispersive XRFS, acquired in late 2001, and (2) assemble an ultrasonic-nebulizer-based aerosol generation and deposition system.

The Rigaku ZSX 100e XRFS at KSC is well-equipped for traditional whole-rock bulk geochemical analysis, and also has an interactive small spot (0.5 mm) analysis capability, which can be used to analyze individual spots and to map out the spatial distribution of elements. Our XRFS is equipped with a 4 kilowatt Rhodium-anode X-ray tube with an ultra-thin (30 um) Beryllium end-window, optimized for small-spot and light-element analyses. The system includes a 10-position diaphragm changer, standard and fine-resolution primary collimators, a 10-position crystal mill fitted with LiF(200), LiF(220), Ge, PET, and TlAP analyzing crystals, and Flow-Proportional and Scintillation Counter detectors that can be operated independently or in tandem. While most samples are analyzed under vacuum, the instrument is equipped with a helium-flush capability for analyzing liquid samples, or other samples sensitive to being exposed to vacuum (such as some particulate matter samples).

The upgrade of the XRFS will include the following additions: (a) the ZSX-PBF Primary Beam Filter Mechanism, (b) RX45, RX61F, and RX75 synthetic multi-layer analyzing crystals, along with an ultra-coarse primary collimator, (c) a continuous scan count integrator, and (d) Omega Data Systems UniQuant 5 analytical software.

By cutting the characteristic Rh-K lines (produced by the Rhodium anode in our x-ray tube) from the primary x-ray beam used to excite samples being analyzed, the Primary Beam Filter mechanism will enhance analysis of Cadmium and other elements whose characteristic x-ray lines are strongly overlapped by those of Rhodium. Determination of Cadmium concentrations is important to the objectives of Project 2, investigating toxic trace elements in river sediment, and crucial to Project 3, characterizing airborne fine particulate matter. Cadmium could also be a potentially important element of interest in Project 4, developing elemental signatures for migrant bird populations. In addition, the cutting of the Rhodium characteristic x-rays from the primary beam may help extend the life under x-ray of the PTFE membrane filters typically used to collect PM2.5 samples (R. Couture, e-mail communications, 2001, 2003), facilitating analysis of these samples which would be important to Project 3, characterizing airborne fine particulate matter. Finally, the Primary Beam Filter mechanism is required for proper operation of the UniQuant analytical software program, specifically for the measurement of those elements, such as Cadmium, whose characteristic x-ray lines are overlapped by the Rhodium characteristic lines from the x-ray tube.

The RX45, RX61F, and RX75 synthetic multi-layer analyzing crystals, which in turn require an extra-coarse primary collimator and other components, will further expand the range of elements that can be measured on our XRFS, to include Boron, Carbon, and Nitrogen. Including these elements will enhance analyses performed with the UniQuant analytical software program, and will have application to research projects involving a wide variety of environmental samples (Project 1, research training for undergraduate students), including such things as particulate matter filter samples (Project 3) and bird feathers (Project 4, developing elemental signatures for migrant bird populations). In a specific example, with the RX75 crystal students in the Geochemistry class can explore the role of Boron as a flux agent facilitating partial melting in high-grade migmatitic gneisses (e.g., Allen, 1996).

The continuous scan option will allow rapid scanning of the entire x-ray spectrum for quick (<5 minutes) qualitative assessments of the wide variety of samples presented by diverse student research projects (Project 1, research training for undergraduate students). In its current configuration our XRFS is limited to digital-step scanning which takes at least 25 minutes to give a complete qualitative analysis.

UniQuant, developed by Omega Data Systems (http://www.uniquant.com/), is a state-of-the-art analytical x-ray software package using the "fundamental parameters" approach to determining sample composition. It uses discrete line-based intensity measurements instead of spectral scan-based intensity measurements, which compared to fine-step scan-based programs can make the analysis both faster and more precise at the same time. Through its unique approach, this software, in combination with an appropriate XRFS such as ours, can undertake quantitative analyses of up to 79 elements, even at trace levels, in samples of types for which traditional calibration standards are not readily available. This capability would be extremely useful in the analysis of samples such as bird feathers in Project 4 (developing elemental signatures for migrant bird populations) as well as the wide range of samples involved in undergraduate student research projects (Project 1, research training for undergraduate students).

Elemental analysis of fine particulate matter is often done by XRF spectrometry as this technique requires no digestion or other sample preparation, and the filter samples can be placed directly into the spectrometer. The technique does, however, require appropriate reference standards for instrumental calibration. The creation of such calibration materials for particulate matter samples has been problematic, especially for PM10 samples collected on quartz fiber filters. These samples are not "infinitely thin," so elemental thin film standards (e.g. MicroMatter Company, as cited in USEPA, 1999, and Calhoun et al., 2003) cannot be used. Haupt and others (1997) used a cross-flow nebulizer-based aerosol generation and deposition system to generate particulate matter calibration standards from spectrochemical standard solutions. Similarly, Vanhoof and others (2000, 2003) and Foster (2000) reported using ultrasonic nebulizers in their systems for the creation of fine particulate XRF calibration standards. We will acquire a CETAC Technologies U6000+AT ultrasonic nebulizer, along with a peristaltic pump, chiller, vacuum pump, and other components to assemble a system for preparing fine particulate matter XRF calibration standards (Figure 3), modeled after those of Foster (2000) and Vanhoof et al. (2000). This will support the research of Project 3, characterizing airborne particulate matter. While the UniQuant "standard-less" analytical method has been used in the analysis of particulate matter filter samples (Hays et al., 2002; Wasson & Gou, 2002; McGee et al., 2003), the EPA's *Compendium Method IO-3.3* (USEPA, 1999), and Dr. Treadwell's Quality Assurance Project Plan, already submitted to and approved by EPA and NH-DES, both require calibration with certified standards. We anticipate comparing both approaches.

Much effort has been expended over the years to develop sample preparation techniques for concentrating aqueous samples for XRFS analyses (e.g., Potts and others, 1999, 2000, 2001). We anticipate that the ultrasonic-nebulizer-based aerosol generation and deposition system might be useful other applications such as the analysis by XRFS of natural waters, which we intend to explore.

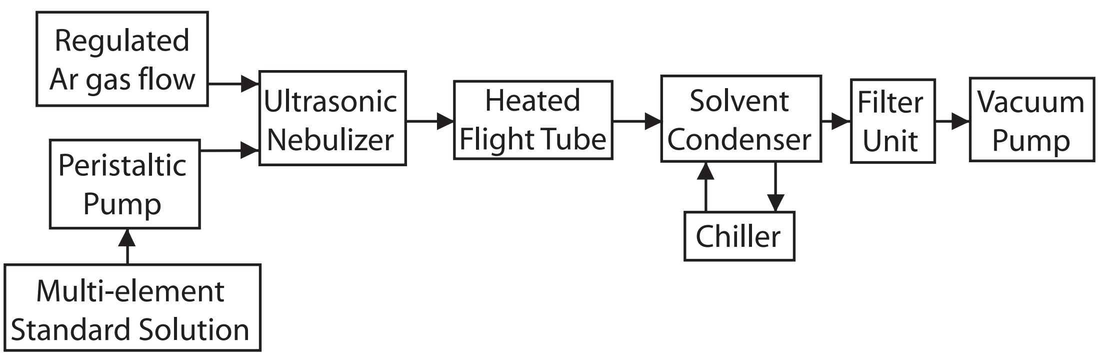

Figure 3: schematic for an ultrasonic-nebulizer-based aerosol generation and deposition system for preparing fine particulate matter XRF calibration standards. Aerosols created by the ultrasonic nebulizer are transported by an Argon carrier gas through a heated flight tube where the solvents evaporate, to be condensed down stream, leaving de-solvated particulates to be deposited on the filter.

Related Instrumentation in the Center for Environmental BioGeoChemistry

Sample preparation equipment for XRFS analysis includes: (1) a Fritsch Pulverisette 6 Planetary Ball Mill with hardened steel, tungsten carbide, and alumina ceramic grinding containers, for pulverizing rock, sediment, soil and other samples; (2) a SPEX X-Press 3620 automated hydraulic lab press with 35mm die assembly for preparing pressed powder specimens; and (3) a Katanax K1 automated fluxer for fusing samples, typically in molten lithium borate glass, and then casting glass discs for XRF analysis or for making solutions for ICP or AA analysis. Related equipment includes a Denver Instruments Analytical Balance, Fisher Isotemp Drying Oven, Thermolyne 48025-80 Programmable Muffle Furnace, and a SPEX 8000 Mixer/Mill.

The KSC Center for Environmental BioGeoChemistry also houses a ThermoFinnigan Delta+ IRMS, configured with both dual-bellows and continuous-flow inlet systems, a universal triple collector, and an H/D dual collector. A Costech CNHS Elemental Analyzer with autosampler is on order, with delivery expected early this spring; it will be interfaced to the continuous-flow inlet system on the IRMS. Supporting equipment for stable isotope analyses includes a Cahn Microbalance, three modular multi-purpose high-vacuum sample preparation lines pumped by Edwards RV3 pumps and equipped with Edwards Active Pirani gauges, and a Neslab RTE-211D constant temperature bath, in addition to the analytical balance, drying oven and muffle furnace described above.

The laboratory facility includes a NuAire NU-156 HEPA-filtered vertical-laminar-flow fume hood for clean acid digestions, exhausted by dedicated acid-proofed ductwork and fan. In addition the lab is supplied with ~13°C recirculating chilled water for process cooling.

Available in the Chemistry Department's Analytical lab within KSC's new Science Center will be a Shimadzu AS68000 combination flame/graphite furnace atomic absorption spectrometer (currently on order), which can be used to augment and validate elemental analysis obtained by XRFS. Pure water supplied by a Millipore Milli-Q Element water purification system is also available in the building.

Infrastructure Impact

Keene State College is a public four-year liberal arts and science college with a tradition and strength in teacher preparation, focusing primarily on undergraduate education. As part of its mission, KSC promotes strong relationships among students and faculty that emphasize creative and critical thinking, scholarship and research, and a passion for learning, with a commitment to service. One of our responsibilities is to provide access and educational opportunity to a broad spectrum of students. We have approximately 4300 full and part-time matriculated undergraduates from across the northeast, as well as about 120 graduate students (in Education) and about 800 non-matriculated students.

While 58% of KSC's undergraduate students are female, only about 34% of the faculty in the Sciences are female. With the exception of the PI (who is a white male), all of the collaborating Senior Personnel involved in the proposed Research and Research Training activities are female. We assume that the availability of active female scientists serving as research mentors will attract female science students, who—having had opportunities to engage in scientific research while undergraduates—are more likely to go on to pursue advanced degrees in science.

In addition, while the KSC student body does not display a great deal of racial or ethnic diversity (about 95% of students are white, non-hispanic), it does have significant socio-economic diversity. About 38% of the students in each KSC entering class are first-generation college students. Keene State College has a well-established ability to involve undergraduate students from all backgrounds in research projects and service learning (e.g. Allen et al., 2003; Treadwell and others, 2002, 2003; Burt et al., 2002; Saxon et al., 2001, O'Rourke et al., 1998).

Many of KSC's students go on to become K-12 teachers—currently 23% of students with declared majors are majoring in Education or other major with Teacher Certification option, including the sciences and mathematics. We feel it is imperative that future science teachers be engaged in authentic scientific research experiences, in agreement with the *National Science*

Education Standards (National Research Council, 1996). We expect that our efforts to promote scientific research activity within the KSC undergraduate college setting will also lead to outreach programs and professional development opportunities for local K-12 teachers, through content-area workshops using inquiry-based research project approaches.

Beyond KSC, the laboratories of the Center for Environmental BioGeoChemistry have attracted collaborators, graduate students, and visiting scientists from other regional (and international) institutions. These collaborations help to further strengthen the sciences and science education at KSC, enhancing the work we do with our students and promoting the role of research in an educational environment.

Management Plan

The XRFS is housed in a purpose-built laboratory in the Center for Environmental BioGeoChemistry in KSC's new Science Center, as described previously. The instrument is used on a regular basis by KSC undergraduate students, faculty, and visiting scientists, all under the supervision of Tim Allen. Dr. Allen performs all routine maintenance, and also assists Dr. Gebauer in the maintenance of the IRMS (Dr. Allen also helped design and build the stable isotope sample preparation vacuum lines, and had previous experience constructing such lines while a graduate student.) Downtime for the XRFS over the three years that we have operated the instrument has essentially been limited to periods surrounding the moving of the instrument necessitated by the construction of our new Science Center. Operational costs, such as for utilities, have been absorbed into KSC operating budgets. In addition, we have been able to recover costs from outside users through per-sample fees. These fees are collected in a dedicated account, which helps augment the operations of the Center for Environmental BioGeoChemistry, as well as offset any expenses we might incur for potential repair of the instrument. We are now about half-way through the expected six-year life of the X-ray tube, and the Dean of Sciences has been preparing for the day when replacing the X-ray tube becomes necessary. Rigaku reports that some users have obtained as many as ten years use from their tubes—we hope we will be one of them.

Dr. Allen has been aggressive in soliciting users for the XRFS across the KSC campus, and has now involved, together with their students, all three faculty from the Geology Department, two faculty members from the Chemistry Department, a faculty member from Biology, one from Safety Studies, one from Technology and Design, with planned future use by a faculty member from Anthropology. Users from other institutions have been attracted to come use the XRFS through word-of-mouth contacts, our website (http://kilburn.keene.edu/GEOL/xrf/), and through the National Association of Geoscience Teachers Analytical Instrument Registry (http://serc.carleton.edu/NAGTWorkshops/petrology/instruments.html).

The upgrades to the XRFS and the additional aerosol generation and deposition system will not necessitate any significant change in the management of the Center for Environmental BioGeoChemistry.

This proposal advances science in several areas of environmental geochemistry and biogeochemistry, and enhances research training by helping KSC better meet its mission of promoting strong relationships among students and faculty that emphasize creative and critical thinking, scholarship and research, and a passion for learning, with a commitment to service.

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