

## Great Smoky Mountains National Park (GRSM) Proposal

### *Application of a Dynamic Watershed Biogeochemical Model (PnET-BGC) to Evaluate the Recovery of Sensitive Aquatic Resources at Great Smoky Mountains National Park from the Effects of Acidic Deposition*

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#### **I. Abstract**

Previous studies have shown that the Great Smoky Mountains National Park (GRSM) has been highly impacted by elevated inputs of acidic deposition resulting in acidification of soil and streams. This proposed research represents an effort to establish total maximum daily loads (TMDLs) and critical loads for sulfur and nitrogen deposition to evaluate the recovery acid-impacted stream-watersheds in the Park. The research will build on long-term biogeochemical data that have been collected, including data for 10 stream-watersheds which the state of Tennessee has listed as impaired under section 303d of the Clean Water Act due to low pH values ( $\text{pH} < 6.0$ ) and other stream-watersheds which are representative of the range of acid-base conditions that occur in the Park. In this study, PnET-BGC will be applied to assess the response of the study stream-watersheds to potential future decreases in atmospheric sulfate, nitrate and ammonium deposition. PnET-BGC is a watershed biogeochemical model that has been widely used to evaluate biogeochemical effects of acidic deposition on high elevation forest and aquatic ecosystems, and project their future response to changes in atmospheric deposition. This proposed research will be organized in two phases. In the first phase, data will be compiled for the GRSM, including data for the stream-watersheds for which critical load calculations will be conducted. These data will be analyzed to provide inputs and parameter values for model application, and data to evaluate model output. In the second phase, PnET-BGC will be applied to the study stream-watersheds in the GRSM. Initially model performance will be compared with soil chemistry and long-term observations of stream chemistry that are available for the study sites. Following satisfactory performance, the model will be run for each site under a series of hypothetical future decreases in sulfate, nitrate and ammonium deposition. Deposition

will be ramped from current values over a period of 10 years to values ranging from current deposition to “background” deposition and the model will be run to the year 2100. These runs will allow for an evaluation of the relative effectiveness of decreases in sulfate and nitrogen deposition in mitigating soil and stream acidification, and the calculation of TMDLs and critical loads. Model runs will provide insight on the time to achieve recovery in the acid-base status of soil and streams. It is envisioned that this research will be a cooperative effort with National Park Service personnel and relevant stakeholders. Initial model calculations will be shared and discussed with Park Service researchers through project conference calls and at a project workshop. Model calculations and project analyses will be revised based on these interactions. A project web site will be established and model results posted and made available to Park Service researchers and relevant stakeholders. The results of this research will be presented at professional meetings and published in peer-reviewed journal articles. The proposed project will be important for the management of GRSM and other national park ecosystems that have been highly impacted by acidic deposition. Results from model calculations will be used to determine the combinations of decreases in sulfate and nitrogen deposition that would result in improvement of critical chemical indicators of acidification stress to values that would restore ecosystem health. Results of this project will also help determine the portions of the GRSM where acidified streams and forest soils can recover, and the long-term sustained deposition loads that would be required to affect such recovery. It will also identify the types of watersheds (if any) for which recovery is unlikely, regardless of the extent of emission reductions. It will provide critical information for Park resource managers to determine which areas might require additional remediation efforts beyond deposition reductions. Finally, this proposed research will be valuable in the national program to develop strategies and experience in the calculation of TMDLs and critical loads for acidic deposition and using these approaches to guide management of impacted resources.

## II. Introduction

### *Problem statement/justification*

The Southern Appalachian Mountain region receives high levels of atmospheric sulfur and nitrogen deposition (Johnson and Lindberg, 1992). Of particular concern are impacts of air pollution on the Great Smoky Mountains National Park (GRSM). The GRSM is a class I area established under the Clean Air Act. The Park receives among the highest levels of acidic deposition in the U.S. (Weathers et al., 2006). Studies have demonstrated that elevated inputs of acidic deposition have resulted in the acidification of soil and streams in the Park (Nodvin et al., 1995; Van Miegroet et al., 2001; Deyton et al., 2008). Streams in portions of the Southern Appalachian Mountain region are highly sensitive to acidic deposition (Elwood et al., 1991). Acid-sensitive streams in the Park show elevated concentrations of sulfate and nitrate, resulting in low values of pH and acid neutralizing capacity and elevated concentrations of aluminum. Elevated inputs of acidic deposition have also apparently affected forest vegetation (Eager et al., 1996) and aquatic biota (Neff et al., 2008) in the Park and the surrounding mountainous region.

In 2006 the state of Tennessee listed 10 streams within the Park as impaired under section 303d of the Clean Water Act due to low pH values ( $\text{pH} < 6.0$ ). The Tennessee Department of Environment and Conservation (TDEC) developed a total maximum daily load (TMDL) to address the impaired waters. The air quality in the Park does not meet air quality standards for ozone and particulate matter. State Implementation Plans are being developed to address air quality violations. However, there is a need for quantitative information to guide and manage decreases in atmospheric sulfur and nitrogen deposition that would facilitate the recovery of the GRSM from elevated acidic deposition.

Two closely related frameworks that could be used to evaluate and manage the recovery of acidic deposition are “total maximum daily loads” (TMDLs) and “critical loads”. A TMDL is a water quality framework which establishes the maximum amount of an impairing substance or stressor that a waterbody can assimilate and still meet water quality standards, and allocates that load among pollution contributors. A critical load is an air quality framework that establishes the level of deposition of an air pollutant below which there is no ecological effects, given current knowledge (Sullivan, 2000; Porter et al., 2005; Burns et al., 2008). Critical loads are used to guide atmospheric emission reduction programs. There are important considerations in determining TMDLs for air pollutants and critical loads. As is the case for the GRSM, atmospheric deposition of sulfur, nitrate and ammonium can all contribute to the acidification of soil and surface waters. As a result, TMDLs and critical loads for a resource can be expressed as combinations of sulfur and nitrogen forms that will result in acceptable critical levels of chemical indicators of acidification stress for soil and water quality. In addition to acceptable levels of deposition, there is a temporal component to ecosystem recovery. Watersheds may respond slowly to decreases in acidic deposition (Driscoll et al., 2001). This delay in recovery is due to: 1) the depletion of soil exchangeable basic cations; and 2) the release of sulfur and nitrogen that has accumulated in soil as a result on an

extended period of elevated acidic deposition. Understanding the time of recovery is an important consideration in the framework of TMDLs and critical loads.

There are three broad approaches that have been used to determine critical loads: empirical relationships, the use of steady-state models and application of dynamic models. All three approaches have advantages and disadvantages. To date empirical approaches and steady state models have largely been used in the determination of critical loads (McNulty et al., 2007). However in this research, I plan to use a dynamic forest watershed element transport model, PnET-BGC, to quantify the response of soil and streams in watersheds of the GRSM to future decreases in atmospheric deposition of nitrogen and sulfur. PnET-BGC has been widely used to evaluate the effects of acidic deposition on forest soil and surface waters (e.g., Gbondo-Tugbawa et al., 2001; Chen and Driscoll, 2004b; Zhai et al., 2008). Unlike many other dynamic watershed biogeochemical models, PnET-BGC has detailed algorithms which depict the cycling of nitrogen in forest ecosystems, so it is capable of predicting the simultaneous effects of atmospheric sulfate, nitrate and ammonium deposition, as well as other major solutes. As a dynamic model, it is also capable of simulating the time of ecosystem recovery following decreases in atmospheric deposition until a critical value of a chemical indicator is attained.

### ***Objectives***

The overarching objective of this proposed study is: *to provide a framework to assess the response of soils and streams in watersheds of the GRSM to decreases in acidic deposition, through analysis of existing data and application of the biogeochemical model PnET-BGC.*

The specific objectives are to:

- 1) *Compile and analyze existing data available for the GRSM on atmospheric deposition, soils, forest vegetation, hydrology, stream chemistry and aquatic biota to provide inputs, parameter values, and ecosystem observations for application of PnET-BGC;*
- 2) *Parameterize, calibrate and test PnET-BGC for a suite of stream-watersheds at the GRSM;*
- 3) *Simulate the response of the study stream-watersheds to a range of decreases in atmospheric deposition of sulfate, nitrate and ammonium, evaluate the TMDLs/critical loads of sulfur and nitrogen for these ecosystems, and determine the time required to reach critical levels of chemical indicators of acidification stress; and*
- 4) *Interact with National Park Service personnel and interested stakeholders on results of model calculations, and conduct outreach activities, including developing a web site for project results, presentation of findings at professional meetings, publication of results in peer-reviewed journals, and translation/communication of results to stakeholders and the general public.*

Although beyond the scope of the RFP, if time and resources permit I hope to address two additional objectives:

- 1) *Evaluate fish response model algorithms used in PnET-BGC with regard to fisheries data available for the Park; and*
- 2) *Evaluate the sensitivity of critical load calculations to scenarios of climate change for the Park.*

### **III. Background**

The Great Smoky Mountains National Park stretches over more than 494,000 acres in North Carolina and Tennessee. World renowned for the diversity of its plant and animal life, the beauty of its ancient mountains and its remnants of Southern Appalachian mountain culture, it is one of America's most visited national parks (over nine million visitors each year). One of the most impressive features of the Park is the great variety of plant and animal life. A recent inventory shows that the Park has 125 species of trees, 200 species of birds, 60 species of mammals and a total of 1500 species of flowering plants. Five different forest types can be found within the Park; Spruce-Fir, Northern Hardwood, Pine Oak, Cove Hardwood Forest and Hemlock Forest.

There is considerable variation in atmospheric deposition in high elevation areas in the Southern Appalachian Mountain region. This variation is due to elevation, aspect and vegetation, and proximity to major emission sources. At Clingmans Dome in the GRSM, total sulfur deposition was estimated to be 36 kg S/ha-yr and total nitrogen deposition 27 kg N /ha-yr (Lindberg, 1992; Lindberg and Lovett, 1992; Lovett and Lindberg, 1993). A large fraction of these inputs occur by dry (25% for sulfur, 50% for nitrogen) and cloud (50% for sulfur, 30% for nitrogen) deposition. Cloud deposition is thought to be proportional to cloud immersion times (Eager et al., 1996), so high elevation forest sites which experience elevated dry and cloud deposition receive particularly high total sulfur and nitrogen deposition.

More detailed spatial modeling often reveals complex patterns of atmospheric deposition, particularly in mountainous terrain. Weathers et al. (2006) developed a spatial model of atmospheric nitrogen and sulfur deposition for the GRSM. Their maps showed six-fold variations in nitrogen and sulfur deposition across the Park. For total nitrogen deposition the area weighted mean for the year 2000 was 10 kg N/ha-yr, with values ranging from 5 to 31 kg N/ha-yr. For total sulfur deposition the area weighted mean for 2000 was 14 kg S/ha-yr, with values ranging from 7 to 42 kg S/ha-yr. This spatial variability is largely due to variation in elevation and vegetation type, and results in “hotspots” of atmospheric deposition across the complex landscape.

Research has shown that acidic deposition has chemically altered soils with consequences for acid-sensitive ecosystems. Soils impacted by long-term inputs of acidic deposition lose their ability to neutralize continuing inputs of strong acids, provide poorer growing conditions for plants, and extend the time needed for ecosystems to recover from

acidic deposition. Acidic deposition has altered and continues to alter soils in sensitive regions of the southeastern U.S. in three important ways: acidic deposition depletes available calcium, magnesium and other nutrient cations from exchange sites in soil; mobilizes dissolved inorganic aluminum into soil-water; and increases the accumulation of sulfur and nitrogen in soil.

Southeastern soils are heterogenous, with variations in their physical, chemical and biological characteristics. An important controlling factor of forest ecosystem sensitivity to acidic deposition is elevation. Soils in the high elevation spruce-fir zone of the Southern Appalachians are generally shallow, and characterized by high concentrations of soil organic matter and highly acidic conditions (Joslin et al., 1992; Eager et al., 1996). High elevation zones are mostly underlain by unreactive bedrock (e.g., sandstone) which limits the ability of soils to replenish nutrient cations through weathering (Elwood et al., 1991).

Studies suggest that net calcium and magnesium loss from soil is a critical environmental issue for forest ecosystems in the Southeast (Huntington et al., 2000). Joslin et al. (1992) summarized mass balance studies of high elevation spruce-fir ecosystems in the Southeast and generally found that net loss of calcium and magnesium was associated with elevated leaching of sulfate and nitrate. Nodvin et al. (1995) observed marked net leaching of calcium associated with elevated leaching of nitrate and sulfate at Noland Divide Watershed at the GRSM. There have been direct measurements of changes in soil cation pools in Southeastern forests. Johnson and co-workers (Johnson et al., 1988; Johnson and Todd, 1990) reported declines in exchangeable calcium and magnesium for a mixed deciduous forest in Tennessee. They attributed the soil depletion of calcium to the accumulation of forest biomass, while magnesium losses were attributed to sulfate leaching. Knoepp and Swank (1994) studied changes in soil exchangeable cations over a 20-year period in a mixed hardwood watershed and a pine plantation in Coweeta, North Carolina. They observed marked decreases in exchangeable calcium, magnesium and potassium over the 20-year period. These changes were attributed to accumulation of forest biomass and elevated leaching losses.

Joslin et al. (1988) reported very high concentrations of aluminum in upper soil horizons (15-35  $\mu\text{mol/L}$ ) with concentrations increasing with greater soil depth (35-50  $\mu\text{mol/L}$ ) in spruce-birch forests in Raven Fork watershed of the GRSM. Other studies have reported similar high concentrations of aluminum in the Smokies, Mount Mitchell, North Carolina and Whitetop Mountain in Virginia (Joslin and Wolfe, 1992; Eager et al., 1996). There are seasonal variations in aluminum concentrations in soil solutions, with the highest concentrations coinciding with variations in concentrations of nitrate during the summer and the period of greatest root activity (Johnson, 1995; Eager et al., 1996).

Studies of effects of acidic deposition on trees in the Southeast have focused on red spruce. Red spruce in the southeastern U.S. is generally confined to elevations exceeding 1300 m, which largely occur in the states of North Carolina and Tennessee. 74% of the spruce fir forests in the southern Appalachian region occur in the GRSM (Eager et al., 1996).

Some investigations have noted poor crown condition of red spruce in some areas (Bruck et al., 1989; Peart et al., 1992). Long term mortality rates for the region appeared stable in the 1990s (Nicholas, 1992; Eager et al., 1996; Smith and Nicholas, 1999). Nevertheless, there is ample evidence suggesting that acidic deposition has contributed to stress and poor health of red spruce in the southeastern U.S. Available evidence includes (Eager et al., 1996; Sullivan et al., 2002):

- Acidic deposition and exposure to cloud water results in loss of foliar calcium and in particular membrane-bound calcium (Joslin et al., 1988; Nodvin et al., 1995; DeHayes et al., 1999). Elevated aluminum in soil solutions has also been shown to decrease foliar concentrations of calcium and magnesium (Raynal et al., 1990; Thornton et al., 1994; Eager et al., 1996). Two fertilization studies have indicated that calcium addition stimulated needle growth of red spruce sampling (Van Miegroet et al., 1993) and growth of foliage in mature trees (Joslin and Wolfe, 1994). The loss of calcium renders the needles of red spruce more susceptible to freezing damage, thereby reducing the tolerance of trees to low temperatures and increasing the occurrence of winter injury and subsequent tree damage or death (Thornton et al., 1994; DeHayes et al., 1999). In addition, elevated aluminum concentrations in soil solutions may limit the ability of red spruce to take up water and nutrients through its roots. Water and nutrient deficiencies can lower the tolerance of trees to other environmental stresses and potentially cause decline.
- Radial growth of spruce trees above 1520 m has declined in the Southern Appalachian Mountains. This decline started around 1960 and cannot be explained by unusual climate or stand competition (McLaughlin et al., 1987; Cook and Zedaker, 1992). Starting in the 1950s there has been a coincident change in wood chemistry with increases in aluminum relative to calcium (Bondietti et al., 1989).
- Saplings have experienced reduced photosynthesis relative to respiration coincident with decreases in foliar calcium, increases in foliar aluminum and low calcium to aluminum ratios in soil solutions (McLaughlin et al., 1993). Joslin et al. (1992) reported decreases in root growth in deep mineral soils relative to organic soils with more favorable aluminum chemistry.

In addition to forest effects, there have been studies of streams in the GRSM. Cook et al. (1994) examined longitudinal and temporal variations in water chemistry of several low-order, high elevation streams. During base flow the acid neutralizing capacity (ANC) of the streams studied ranged from -30 to 28  $\mu\text{eq/L}$  and pH values ranged from 4.54 to 6.40. Nitrate and sulfate were the dominant anions in these streams. Cook et al. (1994) also used stable sulfur isotopes to determine that most of the sulfate in stream water was derived from atmospheric deposition. Streams showed low ANC and pH values, and high aluminum concentrations at high elevations. Values of ANC and pH increased and aluminum concentrations decreased with increasing drainage area. Nodvin et al. (1995) studied two streams in Noland Divide Watershed of the Great Smoky Mountains National Park. Values of ANC were very low in these streams (-10 to 20

$\mu\text{eq/L}$ ), with nitrate occurring as the dominant anion and elevated concentrations of sulfate. High export of nitrate and sulfate facilitated leaching losses of nutrient cations from these watersheds. Episodic acidification has also been shown to be an important component of acidification stress in streams of the GRSM, with decreases in ANC associated with increases in concentrations of sulfate and nitrate, dilution of basic cations and increases in concentrations of organic acids (Deyton et al., 2008).

Atmospheric emissions of sulfur dioxide in the eastern U.S. peaked in the early 1970s, and have been declining since in response to emissions controls mandated by the 1970, 1977 and 1990 Amendments to the Clean Air Act. Trends indicate that recovery of sensitive lakes and streams throughout acid-sensitive areas of the East is slow (Stoddard et al., 1999; Driscoll et al., 2003; Stoddard et al., 2003). Lakes and streams in the Adirondack and Catskill Mountains of New York, northern New England, the Upper Midwest and western Virginia have been intensively monitored since the early 1980s. A recent analysis shows that these lakes and streams have shown decreases in concentrations of sulfate at all sites except western Virginia (Stoddard et al., 2003). This pattern is consistent with decreases in emissions of sulfur dioxide and atmospheric deposition of sulfate. However, these lakes and streams exhibit limited recovery in pH and acid neutralizing capacity, as well as continued acid episodes (Stoddard et al., 1999; Stoddard et al., 2003). In contrast, most streams that have been monitored in the southeastern U.S. have not yet shown signs of regional chemical recovery in response to decreases in sulfur emissions and deposition (Webb, 2004). This lack of recovery is consistent with trends reported for streams of the GRSM (Robinson et al., 2008). This analysis showed a general lack of long-term trends in pH, ANC, sulfate and nitrate, with elevation and discharge influencing water chemistry patterns.

Several factors account for the slow chemical recovery of the acid impacted surface waters in the Southeast, despite the decreased deposition of sulfur associated with the Clean Air Act. First, sulfate has accumulated in Southeastern soils in response to elevated emissions of sulfur dioxide and sulfate deposition. With time, the rate of sulfate accumulation has decreased as soil adsorption sites become more saturated with sulfate. As a result, sulfate is increasingly transported to surface water, even though sulfate deposition has decreased in recent years. Concentrations of acid-neutralizing base cations have decreased markedly from the soil exchange complex due to elevated leaching losses. Finally some high elevation spruce-fir watersheds exhibit elevated leaching losses of nitrate which are influenced by vegetation and climatic conditions and disturbance events (Van Miegroet et al., 2001).

Model calculations (Sullivan et al., 2002) also have shown that streams within the Southern Appalachian Mountain region that are most likely to improve their acid-base status in response to emissions reductions occur in West Virginia, Virginia, and at higher elevations in western North Carolina and eastern Tennessee.

#### **IV. Procedures/Methods**

This proposed study will be divided into two research phases. The first phase will involve the compilation of environmental data from the GRSM and analysis of these data

for model application. Data analysis will include developing of files for model inputs and parameter values, and data observations and summaries for model comparison and testing. It will be necessary to complete this phase prior to model application. The second phase will involve testing and application of the PnET-BGC. Initial model calculations will be conducted following completion of the analysis of field data. These calculations will be shared with Park Service personnel and other stakeholders cooperating on the project. I envision that a workshop would be organized at the GRSM with Park Service personnel within the first nine to 12 months of the project to discuss initial model results, model testing, scenario calculations and estimates of critical loads. The results of this workshop will be used to guide the analysis conducted prior to the completion of the research.

### ***Site data analysis***

During the first phase of the study, relevant biogeochemical data will be compiled for the GRSM. Based on the data set compiled by Pardo and Duarte (2007), it appears that most, if not all, of the data needed to establish input files, and parameter values for PnET-BGC simulations, and for model testing are available. Key data for input files include: meteorological data (air temperature, precipitation and solar radiation), and wet, dry and cloud deposition data. Data needed for model parameterization include: soil bulk density, soil cation exchange capacity, soil exchangeable cations, soil extractable sulfate, soil organic matter, soil water chemistry and vegetation element composition. Soil chemistry data and long-term stream hydrology and water chemistry will largely be used for model evaluation.

Key data analysis activities will include the calculation parameter values for model application, including soil cation selectivity coefficients, sulfate adsorption binding constants and vegetation stoichiometric coefficients. An important activity of this phase of the study will be the establishment of historical atmospheric deposition and meteorology time series data for the study watersheds. I envision working with researchers who have previously worked at the GRSM to develop these input values. In past studies, I have used long-term measurements of atmospheric deposition for the site coupled with historical emission inventories for sulfur dioxide and nitrogen oxides to reconstruct the historical deposition record (Driscoll et al., 2001; Chen and Driscoll, 2004a). These data will be used for model input to simulate historical deposition, and simulate soil and water quality conditions prior to the advent of acidic deposition. Hydrology and stream chemistry data will be used to calculate stream element fluxes and volume-weighted concentrations. The stream values will be compared with the results of model output to test the results of model simulations, including time series comparisons and element mass balances (Chen et al., 2004).

### ***Model description and application***

#### **Model description**

PnET-BGC is a comprehensive forest-soil-water model that links a C, N and water balance model, PnET-CN (Aber et al., 1997), with a biogeochemical model, BGC

(Gbondo-Tugbawa et al., 2001). While PnET-BGC has largely been applied in the northeastern U.S., it has also been tested in other regions of the U.S. (Backx, 2004). The model performs well in small, high-elevation watersheds where detailed site data are available to constrain inputs and parameter values, such as those that will be used in this study, but regional scale applications have also been conducted (Chen and Driscoll, 2004b; Chen and Driscoll, 2005; Zhai et al., 2008).

PnET-BGC extends the simulations of PnET-CN to include the cycling of all major elements (i.e., C, N, P, S, Ca, Mg, K, Na, Al, Cl, Si). Both major biotic and abiotic processes are represented in PnET-BGC, including atmospheric deposition, canopy interaction, CO<sub>2</sub> fertilization, litterfall, forest growth, root uptake, snowpack accumulation and loss, routing of water along hydrologic flowpaths, soil organic matter dynamics, nitrogen mineralization and nitrification, mineral weathering, wetland biogeochemical processes, chemical reactions involving solid and solution phases, and surface water processes. PnET-BGC can be run on a time step specified by the user; at this time, I plan to use a monthly time step for this study.

PnET-BGC requires input parameters related to the site: meteorological conditions, atmospheric deposition, element weathering, soils and vegetation and land-disturbance history. Basic soil parameters needed for PnET-BGC include properties such as soil mass, cation exchange capacity, cation exchange constants and anion adsorption constants. Vegetation is characterized in PnET-BGC using the major forest cover types represented at the study site and the element stoichiometry associated with these cover types.

A thorough description of the model including the processes depicted and a detailed sensitivity analysis of parameter values is provided in Gbondo-Tugbawa et al. (2001). While other models (e.g., MAGIC, ILWAS, NuCM, CHUM, ETD, Birkenes) have been used to simulate effects of atmospheric deposition on forest nutrient cycling and loss, these models either ignore biotic processes or have large input requirements. PnET-BGC requires a modest number of inputs, making it an excellent candidate for the calculations outlined in this proposal.

#### Model calibration and application

Following our previous research (Zhai et al., 2008), model runs will be started for the GRSM sites in 1000 AD, and run under constant background deposition and no land disturbance until 1850 to achieve steady-state and evaluate “background” (i.e., pre-1850) conditions. Changes in atmospheric deposition and land disturbance events will be initiated after 1850. The model will be run from 1850 through today based on measured values of atmospheric deposition and reconstructions of historical deposition from emission records that will be obtained from the first phase of the study. Model simulations will continue through the year 2100 with a series of forecasts which will include a range of deposition scenarios from current to “background” deposition for sulfate, nitrate and ammonium individually and in combination. Future scenarios will involve a 10 year ramp from current values to the level of deposition of interest and

continued simulation at this deposition level through 2100. This range of values will enable evaluation of tradeoffs associated with reductions in sulfur dioxide, nitrogen oxides or ammonia emissions to achieve ecosystem recovery from acidic deposition.

For this study PnET-BGC will be applied to the 10 impaired stream-watersheds and other sites that are representative of acid-base conditions of watersheds in the Park where detailed time-series data of meteorology, atmospheric deposition, hydrology and surface water chemistry and site characterization data are available. These time-series data will provide a good opportunity to evaluate model performance. I anticipate for applications at the proposed GRSM sites, that most, if not all, model inputs, and vegetation, soil and hydrologic parameters are either directly available for model application or can be derived or estimated from field data or values in the literature, with the exception of element mineral weathering rates. Element mineral weathering rates will be determined for each site through model calibration and held constant for model simulations.

### Model output

The large number of processes depicted in PnET-BGC provides an opportunity to comprehensively examine how the flux and cycling of ecologically relevant elements (C, N, P, S, Ca, Mg, K, Na, Al, Cl, Si) are altered by decreases in atmospheric deposition of sulfate, nitrate and ammonium. It is necessary to examine fluxes and concentrations of all major solutes to assess the response of ecosystems to changes in acid-base status. However, I will particularly focus analysis on critical chemical indicators of stream acidification stress, including pH, acid neutralizing capacity (ANC), sulfate, nitrate and aluminum speciation (Driscoll et al. 2001). Solute and metrics that are indicative of the nutrient status of the soil and vegetation of watershed ecosystem will also be evaluated, including nitrate, calcium, magnesium, potassium and soil percent base saturation. From model output, predicted changes in the nutrient status of the soil exchange complex and vegetation will also be evaluated. Of additional interest is acidification induced changes in dissolved organic carbon (DOC; Monteith et al., 2007). DOC is a critical model output as it strongly influences water quality by facilitating the transport of trace metals and altering the acid-base status of surface water (Thurman, 1985).

An important feature of model output and model evaluation is metrics of model performance. There are many metrics of performance that are used in model evaluation and testing (Janssen and Heuberger, 1995). Normalized mean error, and normalized mean absolute error will be used to test and validate the model results in this proposed study.

By examining the suite of simulation results for a given site, it will be possible to quantify the combinations of decreases in sulfate and nitrogen deposition that would result in improvement of critical chemical indicators to values that would restore ecosystem health, and determine TMDLs and critical loads. Simulations will also provide insight on the time to achieve recovery in the acid-base status of soil and streams. Results of this project will also help determine the portions of the GRSM where acidified streams

and forest soils can recover, and the long-term sustained deposition loads that would be required to affect such recovery. It will also identify the types of watersheds (if any) for which recovery is unlikely, regardless of the extent of emission reductions.

#### Additional activities

If time and resources permit, I would like to conduct two additional activities which are related to the proposed study but beyond the scope of the RFP. An algorithm of fish species richness has been developed which can be used in PnET-BGC to examine fish response to changes in acidic deposition (Sullivan et al., 2006). This algorithm was developed using data from the Adirondack region of New York and has been preliminarily tested in streams in the Shenandoah National Park. If the appropriate fisheries data are available, I would like to evaluate the usefulness of this algorithm to streams of the GRSM and in TMDL/critical load calculations.

Our recent research has shown that critical load calculations are highly influenced by climatic changes (Wu and Driscoll, in review). If time and resources permit, I would like to apply PnET-BGC to evaluate the effects of climate change on the chemistry of streamwater of the GRSM and these interactions with changes in acidic deposition. Climate input data for this work will be generated using a new statistical technique that downscales atmosphere-ocean general circulation model (AOGCM) simulations to a finer temporal and spatial resolution. The advent of this downscaling technique has made it possible to run PnET-BGC with higher resolution climate data developed for individual sites (Campbell et al., in press). Future climate simulations will be generated using monthly output from three of the latest AOGCMs available from the Intergovernmental Panel on Climate Change, Data Distribution Centre (<http://www.ipcc-data.org/>). The models selected for this analysis are the Hadley Centre Coupled Model, version 3 (HadCM3), Parallel Climate Model (PCM), and Geophysical Fluid Dynamics Laboratory (GFDL) model. Two future greenhouse gas emission scenarios will also be used, for a total of six climate simulations. These scenarios approximate potential lower and upper bounds (respectively, 550 and 970 ppm by 2100) of projected atmospheric CO<sub>2</sub>. The monthly ensemble AOGCM forecasts will be bias corrected, downscaled to 1/8° horizontal resolution, and disaggregated to a daily time step following the convention of Hayhoe et al. (2006). In this application, PnET-BGC output examined will span the period from 1950 through the end of the 21<sup>st</sup> century (150 years total). For this work the interactions of changing climate and changing acidic deposition will be examined.

#### **V. Expected Outcomes/Products/Deliverables**

From this study I anticipate there will be improved quantitative understanding of how watersheds of the GRSM will respond to anticipated decreases in acidic deposition, both in terms of the magnitude of chemical inputs required and the time frame for recovery. This information will be used in the development of critical loads of atmospheric sulfur and nitrogen deposition for the Park. This work should also inform the TMDL process being conducted by the TDEC for the impaired streams of the Park. This research will also provide valuable insight to the National Park Service and the other

agencies (USDA Forest Service, EPA) and states (North Carolina, Tennessee) that are interested in using TMDLs and critical loads as tools to guide and inform the levels of emission reductions that are needed to achieve recovery of ecosystems that have been impacted by acidic deposition.

An important outcome of this proposed study will be a calibration of PnET-BGC and associated input and parameter files for the 10 impaired stream-watersheds and additional watersheds that are representative of the range of acid-base conditions that occur at the GRSM. The model and files will be available for use in future assessments of effects of air pollution on watersheds in the Park. The calibrated model could also be used to evaluate scenarios of climate change on the hydrology and water quality of the Park.

I anticipate that the model calculations from this study will be published in pertinent peer-reviewed journal articles. Results will also be presented as oral presentations and posters at national professional meetings. An annual and final report summarizing the results of this study will be written.

## **VI. Technology/Information Transfer**

The interaction of National Park Service personnel and the research community working in the Park will be critical to the success of this study. It is envisioned that there will be periodic conference calls and meetings to discuss progress and problems during the study period. As part of this research, I plan to organize a workshop at the GRSM within the first nine to 12 months of the project to share information on initial model results with Park Service personnel and other relevant stakeholders. The information and feedback from the workshop will be used to guide the completion of the study. The workshop will also be used to discuss plans for publications and professional presentations.

In addition to the above outputs, a major product of the proposed work will be to continue to make PnET-BGC freely accessible so that it can be adopted more widely by researchers and the broader hydrologic, hydrochemistry and ecological communities. The model will be further developed and the graphic user interface will be refined, thereby improving usability. A description of the model and instructions on how to run the model will be updated, particularly with respect to acidic deposition assessments, and made available on the project web site. A CD containing the model, source code and sample scenarios will be distributed to interested personnel along with the model description. The PnET-BGC website (<http://www.ecs.syr.edu/faculty/driscoll/personal/PnET%20BGC.asp>) will be further developed as an avenue for distributing the model and for providing information about the model so that it can be easily downloaded and run on personal computers.

For this project, a password protected section of the PnET-BGC web site will be established to provide model results and project information exchange. This section of the website will only be available to project participants, Park Service personnel and

relevant stakeholders. The website will also contain input data and modeled output with accompanying metadata for the atmospheric deposition scenarios outlined in this proposal. The project web site will be the primary mechanism by which day-to-day progress and results of the project will be communicated with the site cooperators.

## VII. Work Schedule

The proposed study will occur over a period of two years (Figure 1). The initial phase of the project will involve a compilation of relevant data from the GRSM and an analysis of

these data for use in PnET-BGC simulations. Data analysis will include the calculation of input and parameter values for model simulations, and summaries of field data to compare with and

	Year							
	2009			2010				2011
	Qtr			Qtr				Qtr
	2	3	4	1	2	3	4	1
Compile and analyze field data (objective 1)	■	■	■					
Model parameterization, calibration and testing (objective 2)				■	■	■	■	■
Model simulations, critical load calculations (objective 3)				■	■	■	■	■
Project workshop (objective 4)					■	■	■	■
Project website, outreach publications (objective 4)	■	■	■	■	■	■	■	■
Annual and final reports (objective 4)				■	■	■	■	■

Figure 1. Timeline for project activities shown by objectives. The timeline is shown for quarters over the two year study period.

test model output. This initial phase of the study will also involve the design of a web page for the posting of data base summaries, model inputs and parameters and results of model simulations as well as the associated metadata. Application of PnET-BGC will occur shortly after the GRSM data have been obtained, and model inputs and parameters developed. Initial calculations will involve model testing in comparison with measured site data. Once model simulations are adequate, future sulfate, nitrate and ammonium deposition scenarios will be conducted and TMDLs and critical loads determined. A workshop will be planned after the first nine to 12 months of the project to discuss the initial results of the models and plan for making additional model simulations. During the workshop plans for final products and publications will be discussed and developed.

## VIII. Personnel

*Personnel* – Charles T. Driscoll is currently University Professor of Environmental Systems Engineering and Director of the Center for Environmental Systems Engineering at Syracuse University (see CV, section X). His teaching and research interests are in the area of environmental chemistry, biogeochemistry and environmental quality modeling. His principal research focus has been the response of forest and aquatic ecosystems to disturbance, including air pollution, climate change and land use change. Dr. Driscoll uses a variety of research approaches to study the effects of disturbance, including field investigations, laboratory studies, long-term field

measurements, whole-ecosystem manipulation studies, and the development and application of models.

In the proposed research project, Charles Driscoll will serve as the principal investigator, and will be responsible for all aspects of project management and study implementation. He will also serve as the primary advisor of a graduate student assigned to the project and will assist the student with methodology and analysis. Lastly, Charles Driscoll will coordinate collaboration among U.S. National Park Service personnel and other cooperators who are involved and interested in the project and will ensure timely accomplishment of project objectives and products.

## **IX. Budget**

The project budget is summarized by year in Table 1 and by project objective in Table 2.

*Salary:* 0.5 months of salary is requested during the summer and 0.17 months during the academic year for Dr. Charles T. Driscoll is the principal investigator for the proposed study. Dr. Driscoll will oversee the entire project and work with the Park Service cooperators and the student on all phases of the study. Dr. Driscoll will write annual and the final reports and supervise outreach activities. Salary is also requested for the summer and academic year for a graduate research assistant (GRA) during the two-year study period. The GRA will help establish the input files for the study sites, establish parameter and input files for model application to the study sites, application and testing of the model to the study sites, scenario analysis and analysis and writing results. The GRA will be supervised by Dr. Driscoll.

*Fringe Benefits:* Fringe benefits are requested. The fringe benefit rate for the PI during the summer is 16.8% and during the academic year is 31.1%. The fringe benefit rate for GRA at Syracuse University is 15.4% of salaries.

*Supplies:* Funds are requested for supplies. Supplies to be used in this project include printer and printer cartridges, the maintenance of computing equipment and data storage and backup devices.

*Travel:* Funds are requested for travel. Travel would include travel to the GRSM to initiate the project, travel for Dr. Driscoll and the GRA to the GRSM for a project workshop, and travel to participate in professional meetings.

*Tuition:* Funds are requested for tuition for the GRA.

*Indirect Costs:* Indirect costs are 46% of total direct costs less tuition.

*Cost –sharing:* Syracuse University will cost-share credit hours for GRA tuition as needed.

The estimated project cost by objective is shown in Table 2. It is estimated that: 16.6 % (\$24,888) of the budget will be used to accomplish objective 1, data compilation and analysis; 17.3 % (\$25,955) of the budget will be used parameterization and testing PnET-BGC (objective 2); 34.0 % (\$51,054) of budget will be used for simulation of response of study watersheds to decreases in atmospheric deposition and the evaluation of TMDLs/critical loads (objective 3); and 32.1 % (\$48,101) of the budget will be expended to accomplish objective 4, interaction with Park Service personnel, outreach activities, development and maintenance of the project web site, publication and presentation of results, and developing reports.

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