

## **Seasonal Synchrony of Nitrogen: LTER Cross Site Comparison Working Group Report**

**PI: Jon Duncan, UNC Chapel Hill (BES), Co-PIs: Larry Band, UNC Chapel Hill (BES, CWT) and Peter Groffman, Cary Institute of Ecosystem Studies (BES, HBD)**

### **Summary:**

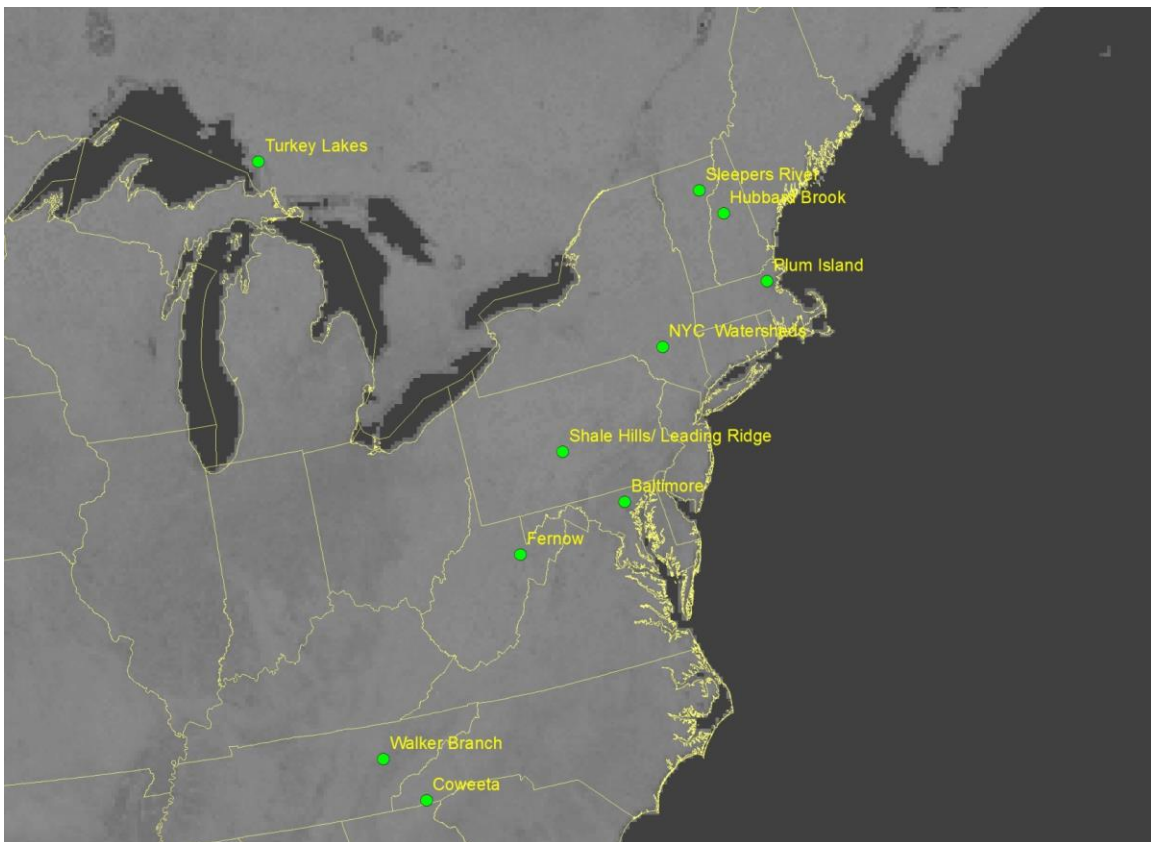
Time series of nitrogen (N) export from long-term experimental watersheds across a latitudinal gradient from Canada through the southeastern USA reveal marked differences in the seasonal timing and magnitude of export. Our group is interested in comparing N export patterns across sites and through time. Activities included: 1) collecting discharge and stream nitrogen concentration data from sites 2) calculating N loads for sites that don't have them 3) examining seasonal trends 4) examining long-term trends and 5) examining other datasets that can explain temporal/spatial trends.

Our working group has held several conference calls, submitted a proposal to NSF Macrosystems Biology, and convened a very productive in-person workshop May 28-May 30, 2013 in Chapel Hill, NC. The agenda (**Appendix A**) and participant list (**Appendix B**) reflect the breadth and depth of our approach. As a result of this grant, two manuscripts are in preparation and are discussed below.

We hypothesize that the controls on seasonal patterns of stream N concentrations and loads exported from watersheds emerge from a cascade of sources and sinks at multiple spatial and temporal scales that accumulate along converging flowpaths. This cascade integrates atmospheric, geologic, geomorphic, land use/land cover, water infrastructure and plant, soil and microbial responses. In order to synthesize controls from patch (10-100 m<sup>2</sup>) to continental scales, we must: (1) understand how N is coupled to water and carbon cycling within reference forest ecosystems, broadly defined to include surface water drainage networks, across current climatic, atmospheric N deposition, geologic, geomorphic and vegetation gradients; and (2) develop a mechanistic understanding of how human activity alters the timing, magnitude and pattern of these coupled processes. De-convolving the controls requires an interdisciplinary approach that captures the progressive coupling of ecosystems and (a) atmosphere, (b) hydrology, and (c) human activity, from small watersheds to continental scales. Doing so will enable a mechanistic understanding and modeling framework connecting N cycling and export across a continuum of terrestrial through aquatic ecosystems.

Sites include LTER, USGS, USFS, and Environment Canada and Ontario Ministry of Natural Resources:

1. Turkey Lakes Watersheds (Ontario, CA)
2. Hubbard Brook, NH
3. Sleepers River, VT
4. Plum Island, MA
5. Biscuit Brook, NY (part of the New York City, drinking watersheds)
6. Fernow, WV
7. Leading Ridge, PA
8. Baltimore Ecosystem Study, MD
9. Coweeta, NC
10. Walker Branch, TN



**Figure 1. Map of our initial 10 watershed studies**

At the workshop, each of the sites were asked to present:

- Brief site description- size, forest type, stand age, etc.
- The seasonal pattern of N export (at least  $\text{NO}_3^-$ ) as a function of seasonal inputs and internal cycling
- What combination of site factors and processes control the seasonal pattern? Factors affecting inter-annual variability and/or annual maxima are also of interest

#### Sharpened Initial Focus:

Early into our working group we decided to place our initial focus on forested watersheds, although we maintained an element dedicated to land use effects, which is indeed low hanging fruit and included in future steps (see below). Total nitrogen, ammonium, and dissolved organic nitrogen data were not consistently collected in a comparable manner at enough sites, so we restricted our initial analysis to nitrate.

#### The seasonality of nitrate export:

Early watershed studies revealed a consistent seasonal pattern in nitrate export from snow dominated watersheds with peaks occurring in late winter/early spring (Stoddard, 1994). However, additional watershed studies have shown a growing number of sites exhibit peak concentrations and mass flux during the growing season (Mullholland, 1992, Mulholland and Hill, 1997, Swank and Vose, 1997, Band et al., 2001, Goodale et al., 2009). Following Bormann and Likens (1967), we recognize the importance of accounting for in-stream *and* terrestrial processes in determining the suite of factors that control seasonal patterns of N export at each site. We note that some watersheds have highly detailed studies of in-stream processes such as Coweeta and Walker Branch, where others have focused exclusively on terrestrial ecological and/or hydrological processes, making the quantification of all processes at all sites difficult. The current focus is placed on small headwater catchments and we note that seasonal patterns may change or disappear at larger spatial scales. Processes that control the seasonal pattern of N export from forested headwaters can be grouped into legacy and boundary conditions, ecological, hydrological, edaphic/geological factors.

#### Legacy and Input Factors:

The initial conditions of a watershed at which point the long-term observational record begins are critically important. The physical structure of the watershed including the morphology of riparian zones and streams are typically considered as stationary for nitrogen studies but are critical parameters to determine landscape-aquatic connectivity as well as variable redox zones that are critical for nitrogen transformation and transport. Results from a previous LTER working group show that major structural changes occurred in most LTER sites prior to the instrumental and observational record (Bain et al., 2012).

In addition to the legacy conditions, the fluxes into a watershed via wet and dry atmospheric N deposition are critically important to determine N export (Aber et al., 1989). There have been dramatic changes in atmospheric N deposition over the course of the observational record. Understanding the lag and lead times between deposition and export are important considerations and require additional research.

#### Edaphic Factors:

Soils and parent material can determine if any geogenic sources can contribute N to aboveground and stream ecosystems via geochemical weathering (Holloway et al., 1998). The geomorphic characteristics of a watershed can also serve as an important determinant for N removal via denitrification (McClain et al., 2003,

Duncan et al., 2013). Catchment topography and drainage patterns vary dramatically across the 10 sites, and even within sites, especially at Turkey Lakes. We hypothesize that a fuller consideration of the spatial arrangement of landscapes and the connectivity of terrestrial and aquatic components using terrain indices will better predict N export across all sites than a patch-based approach.

#### Ecological Factors:

Aspects of the terrestrial ecosystem such as species composition (Lovett et al., 2004), forest age (Vitousek and Reiners, 1975) are important in determining the amount of N that can be processed. In-stream processes are proximal controls and can process, retain, and alter the form of N received from terrestrial ecosystems (Peterson et al., 2001), often through related processes including coarse woody debris (Bernhardt et al., 2005). In watersheds with more autochthonous streams such as Walker Branch, in-stream processes are the dominant control on seasonal N export (Roberts et al., 2007).

#### Hydrological Factors:

The hydrologic conditions (baseflow vs. high flow) have been shown to be important controls for stream nitrate concentrations. Underlying the baseflow/stormflow pattern in many catchments are seasonal patterns that relate to coupled streamflow and groundwater which provide higher proportions of groundwater during the growing season. In general, watersheds that have annual hydrographs dominated by snowmelt peaks exhibit higher magnitudes of N export and concentrations, although we note that the location of snow dominated catchments with higher N concentrations co-varies spatially with increased levels of atmospheric N deposition and an increased abundance of species with higher foliar N content. Antecedent conditions (duration since last rainfall) have been shown to be an important control on stream nitrate concentrations (Biron et al., 1999) because it sets the temporal limit on the amount of nitrate produced via mineralization and nitrification.

#### Preliminary data analysis:

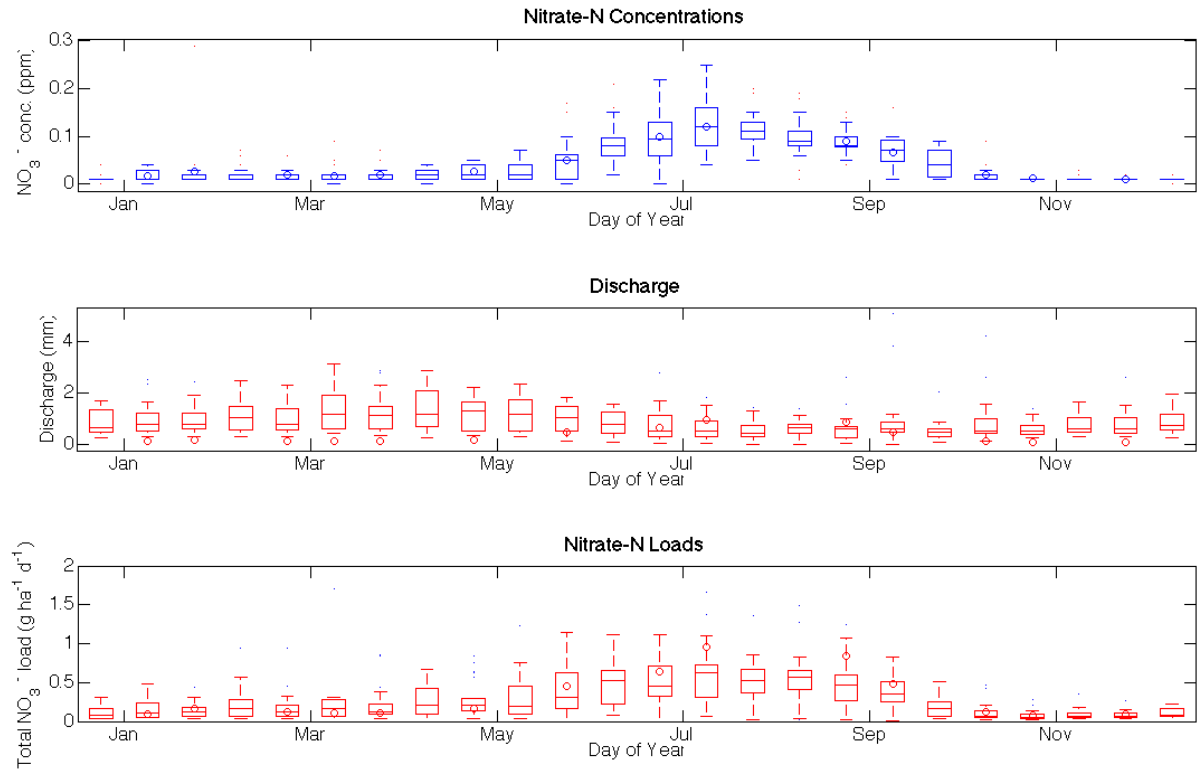
We have conducted preliminary analysis for 9/10 sites. The remaining site is currently digitizing discharge data from strip charts on a largely unfunded basis and will contribute more data following QA/QC.

#### Work in Progress:

- Proposal Submitted to NSF Macrosystems Biology- PI: Lawrence E. Band.
- We also have two manuscripts in preparation as a result of our ongoing synthesis.

1) Manuscript 1 has three components: a) it describes general patterns of mean annual export across the continental transect, b) it characterizes the seasonality of N export, and c) it assesses changes over temporal and spatial dimensions. Changes in seasonal pattern and annual export over the continental scale gradient has profound implications for transferring knowledge from one site to another and for the impacts of global change on nitrogen biogeochemistry.

The first method for exploring the seasonality of nitrate concentrations, discharge, and flux was to construct boxplots for each site. Here, flux is calculated by multiplying the concentration on a given day times the discharge for that day. Those fluxes across all years were then binned into half month (bi-weekly) intervals for plotting. This helps to show how changes in concentration and discharge manifest themselves to show seasonality in flux calculations. An example from Pond Branch, MD (BES) (Figure 2) shows that changes in nitrate concentration compensate for a seasonal decrease in discharge, so that nitrate flux is maximal during the growing season.



**Figure 2. Bi-weekly variation in nitrate, discharge, and loads from Pond Branch, MD.**

One issue we encountered is how to deal with load calculation. Nitrate load can be calculated as:

$$N_{\tau} = \int_0^{\tau} QC \, dt$$

where:

$N_{\tau}$  = total load of  $\text{NO}_3^-$  (mass per time)

$C$  = concentration (mass/volume)

$Q$  = discharge (volume/time)

$t$  = time

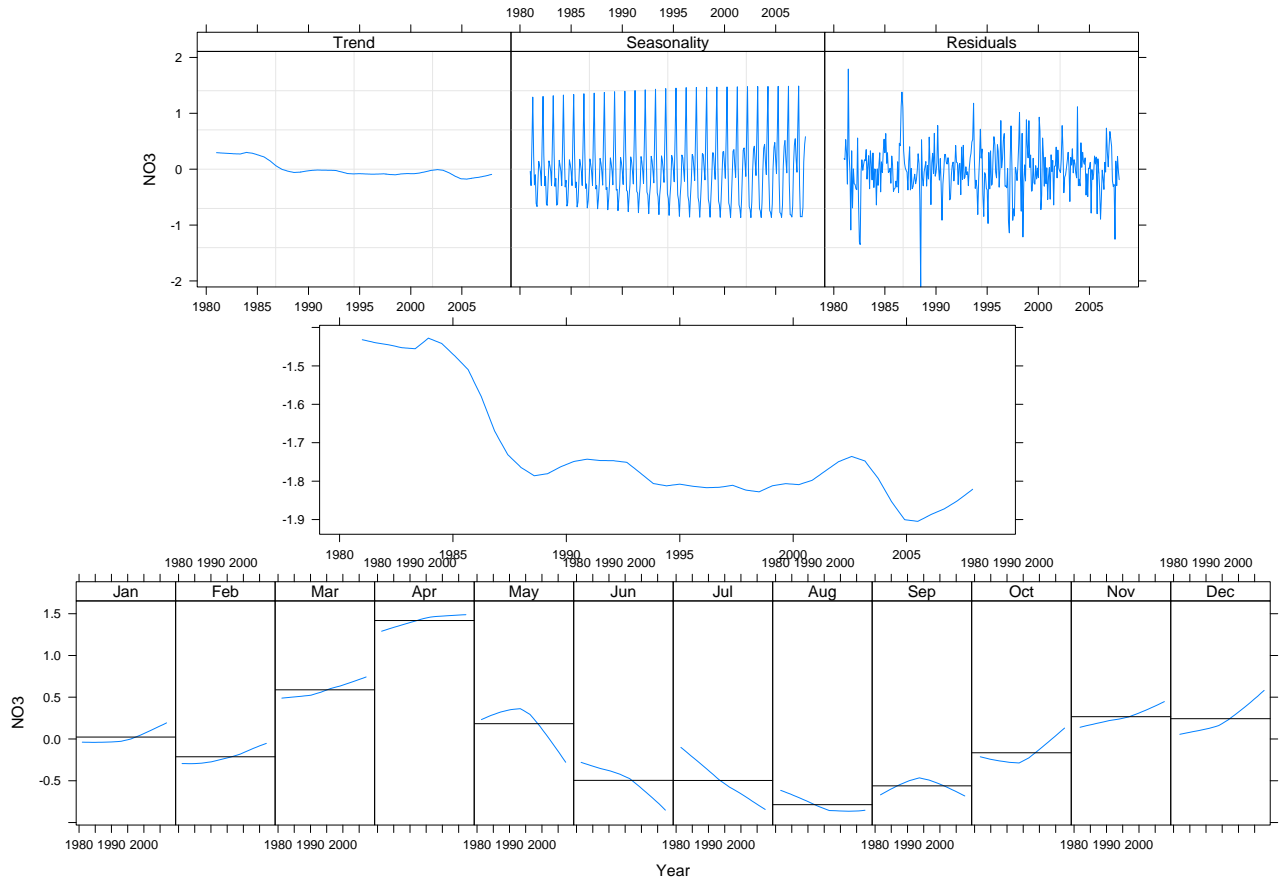
There are a variety of approaches to estimate total loads based on periodic water quality measurements. One of the most widely used is the USGS LOADEST approach (Cohn, 1992, Runkel et al., 2004). The multiple regression based approach can use the most parsimonious of nine different models that follow the form of:

$$a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi dtime) + a_4 \cos(2\pi dtime)$$

where sin and cos terms can capture seasonal trends.

Determining a uniform method to calculate nitrate loads across these sites is difficult. For some locations, particularly those dominated by occasional storm event, the seasonal terms are not helpful. In others, like Pond Branch, discharge is not a significant term because nitrate export is so strongly seasonal. Therefore, we decided to use site specific daily loads where available. If loads had not been calculated for a site we used a LOADEST type approach based on daily discharge and long-term weekly samples to account for discharge conditions and seasonal components. Future work and other related efforts including QUEST and a STREAM-DB could explore determining the most parsimonious model for each site and how to deal with the autoregressive nature of weekly samples. Rather than delving into the specifics of flux calculations, we maintained focus on examining the seasonality of N export.

Seasonal Trend decomposition using Loess (STL) has been successfully applied to river flux data (Qian et al., 2000) and was suggested and used by B. Lutz as a primary exploratory data analysis method. The methodology determines the long-term trend using loess fitting as well as monthly trends over the course of the record. It does this by fitting a seasonal component to the data. An example from Turkey Lakes Watershed 38 (Figure 3) shows a composite graph with the upper panel has the long-term trend (top left), seasonal cycle (top center) and the residual not explained by time (top right). The top panel centers the long-term, seasonal, and residual components at 0 for easy visual comparison. Centering the long-term trend is accomplished by subtracting the long-term mean from the trend. The middle panel shows the long-term trend without normalization. The bottom panel is long-term trends for each month shown in blue, with the long-term mean for each month represented by the black bars.



**Figure 3. STL analysis for nitrate flux at TLW watershed 38. Courtesy B. Lutz.**

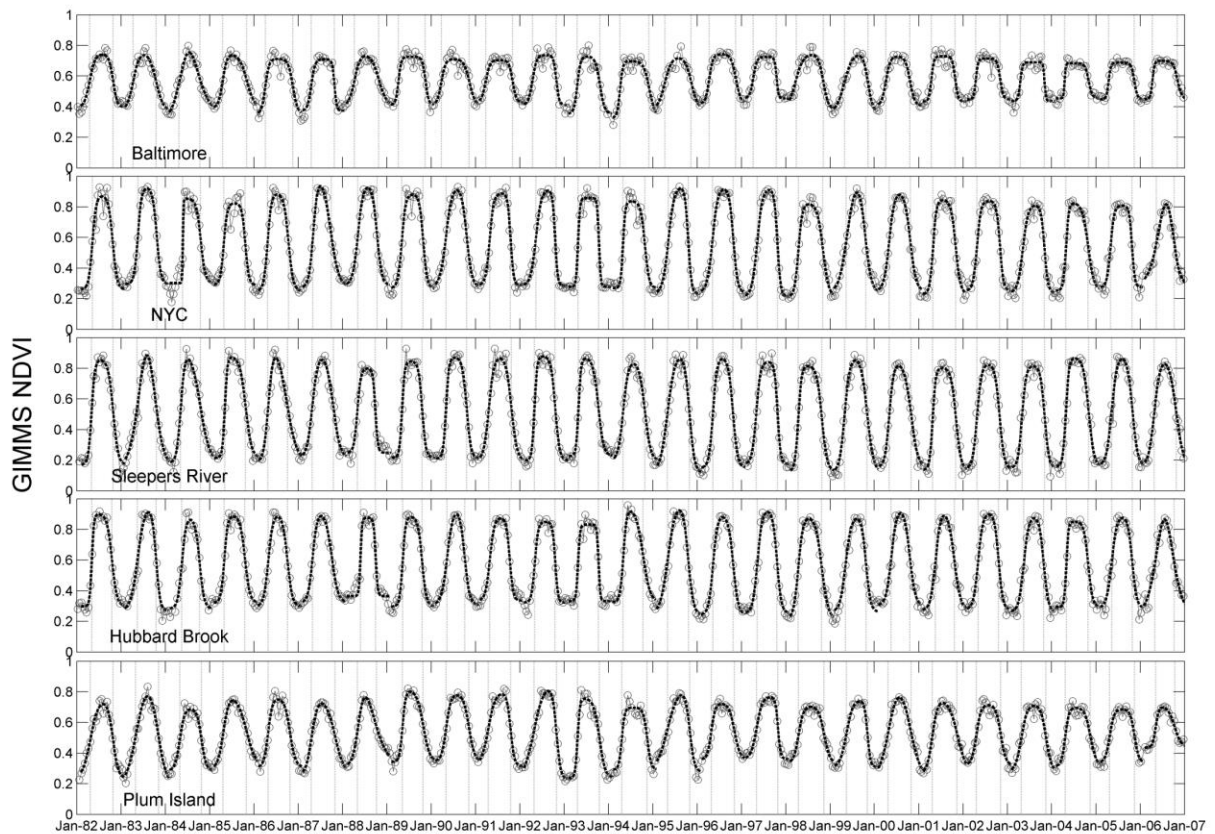
Preliminary results suggest that multiple sites are experiencing long-term trends in flux and the patterns are divergent across sites. This implies that nitrate flux patterns are similar in that regard to divergent long-term patterns in concentration that were recently reported (Argerich, et al., 2013).

2) Manuscript 2 will be led by Kyle Whittinghill (a post-doc at UNH). It examines the effects of climate change on N cycling and export by examining changes in the vernal and autumnal windows over time. It has been observed that snow is melting earlier and growing seasons are prolonged for some watersheds in some years. With earlier snow melt and increased growing season, there is a difference in soil microbial and canopy growing seasons. This has profound implications for climate change on nitrogen biogeochemistry. One method to scale up understanding from the site level to a continental area spanning multiple sites is to use remote sensing data for vegetation phenology and snowpack duration.

Growing season:

Preliminary results show that growing season length calculated on a normalized difference vegetation index (NDVI) (Hwang 2011a, Hwang 2011b) (Figure 4) is

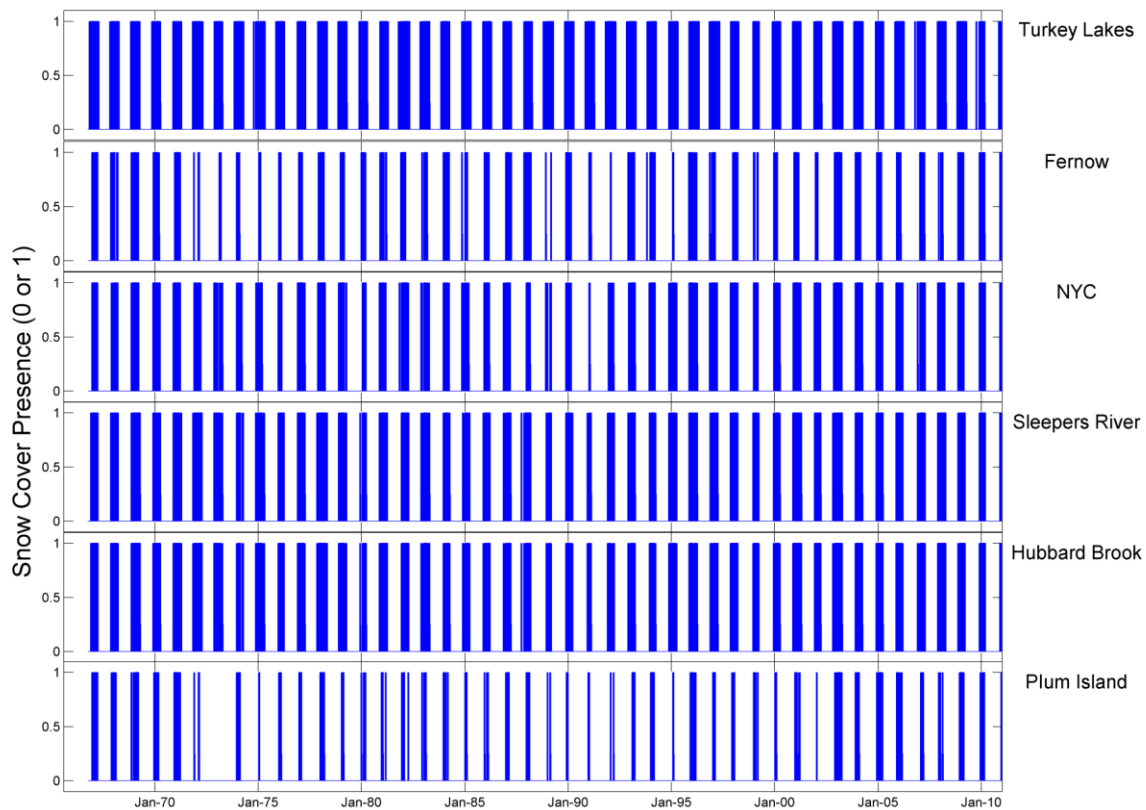
increasing over time at multiple sites. Thus far, the growing season length calculations are comparing quite closely with available site observations.



**Figure 4. NDVI GIMMS datasets upon which, growing season length can be calculated. Courtesy of T. Hwang.**

#### Snowpack:

Specifically, we are interested in the window between final snowmelt and leaf out. That window will help quantify the amount of time microbial activity can increase prior to leaf out. To quantify if winters are getting shorter, we hypothesized we should be able to calculate winter length by measuring snowpack duration using EASE-2 snow cover product (Figure 5). Preliminary results suggest our initial attempts to quantify a change in snowpack duration length show no statistical trend. Our next steps entail validating remotely sensed data with site-specific observations.



**Figure 5. Temporal Patterns of snow cover using the EASE2-Gridded Snow Cover Dataset. Courtesy of T. Hwang.**

### **Future Plans:**

I also want to note that there is great interest and potential for additional syntheses to emerge. Future endeavors would also include expanding the number of sites and collaborators. Three additional products generated considerable interest and will be pursued if we can find a mechanism to have more interaction and data synthesis.

These projects include:

- 1) Examining watershed nitrogen export in the context of land use change.
- 2) Examining site factors that explain residuals from the overall transect trend.
- 3) Examining storm dynamics- hysteresis characteristics across sites

In general, there was considerable excitement and cooperation. The team is currently examining options for further funding. Now that communication lines are open and we have started compiling a formatted database we realize how productive this synthesis could be with more time.

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## **Appendix A**

### **Seasonal Synchrony of Nitrogen:**

### **LTER Cross Site Comparison Workshop Agenda**

Location: Joslin Classroom (C106) North Carolina Botanical Gardens (NCBG), Chapel Hill, NC

#### **Day 0: Monday May 27<sup>th</sup>, 2013**

6:00pm- Dinner for those who are in town and interested

#### **Day 1: Tuesday May 28<sup>th</sup>, 2013- Project Context and Goals and Site Descriptions**

The goal today is to learn about each site's conceptual model for what controls the magnitude and timing of N export. We will also discuss issues of data comparability/compatibility and begin discussing how different our current conceptual models are.

**12:00pm** Sign in and Lunch

Welcome, Introductions, and Ground Rules

**1:00pm** Objectives: Proposal of two manuscripts:

- 1) One paper to examine the mean annual and seasonal synchronicity of N input and output. This will be a function of the timing and magnitude of:  
a) precipitation and nitrogen inputs, b) outputs, and c) internal cycling and stores across and within the continental transect. To achieve this goal, we need to compile long-term data sets of precipitation, discharge, nitrogen concentrations, and calculated loads. We will look at temporal trends in annual and seasonal export patterns.
- 2) A potential second paper that examines aspects of climate change on nutrient cycling and transport. Openings of the vernal and autumnal windows are of greatest interest.

Review of Macrosystems- full gradient and some site-specific data.

**1:30pm-** Brief introductions (~ 3 slides) of site conceptual models. What combination of site characteristics and processes control the seasonality and magnitude of stream N export at your site? (10 minutes per site.) To whatever extent possible, show us the seasonal patterns in input, export, and internal cycling (decomposition, mineralization, denitrification, nitrification).

1. Turkey Lakes- Irena Creed
2. Hubbard Brook- Peter Groffman
3. Sleepers River- Jamie Shanley
4. Plum Island- Kyle Whittinghill

5. Biscuit Brook- Doug Burns
6. Leading Ridge- Beth Boyer
7. Fernow- Mary Beth Adams

**3:15-3:30pm-** Break

**3:30pm**

8. Pond Branch- Jon Duncan
9. Coweeta- Jennifer Knoepp
10. Walker Branch- Brian Lutz
11. In-stream controls- Jack Webster

**5:15pm-** Group Discussion: Aspects of integrated conceptual model.

- What factors and metrics are emerging for such a model?
- Hydrologic and Biogeochemical Controls
- What is the hierarchy of controls?
- What hypotheses can we test with existing data to test the relative importance of controls?
- What are the unifying concepts?
- Homework: Think about an integrated conceptual model and metrics

**5:45pm-** Effects of load calculation

What methods are required? There are multiple groups assessing this very topic (including the LTER QUEST project). Capturing the co-variance between discharge and concentration is important, but the point here is not to get bogged down in the details but to try for consistency in order to examine seasonal patterns. The first step is to confirm that methods are comparable.

**6:00pm-** Sign out. Dinner on-site at NCBG. Catered by Mediterranean Deli

**8:00pm-** Shuttle back to hotel.

## **Day 2: Wednesday, May 29<sup>th</sup>, 2013: Conceptual Models of Inter-annual and Seasonal N Export**

The goal today is to develop a unified conceptual model that accounts for seasonal and annual differences in N export across sites

**7:45am-** Van from hotel to NCBG

**8:00am-** Sign in and Continental Breakfast at NCBG. Discussion from Day 1

**8:30am-** Characterizing and quantifying export patterns- **Jon Duncan and Brian Lutz**

Typologies of Seasonal N Export

- Winter peaks
- Summer peaks
- Primary winter peaks, secondary summer peaks

Metrics of Seasonal Patterns and discussion

- Timing of rise, Timing of descent
- Day of maximum concentration/load
- Length of winter peaks
- Amplitude

Discussion: Others?

**9:00am-** Toward an integrated conceptual model- **Larry Band**

Is there an overarching conceptual model to explain the trend (and residuals) from the continental pattern? Are some factors more important than others? Are there thresholds or non-linearity to consider? Can different landscapes provide similar functions?

**9:15am-** Group Discussion- Conceptual models as a function of geography/climate?

How to quantify the relative importance across sites?

North to South- snow to rain dominated catchments.

**10:00am-** Brainstorm an integrated conceptual model

Consider both annual and seasonal export patterns:

How related are the controls on N export at difference space and time scales?

**12:00pm-** Lunch

**1:00pm -** Breakout Groups- to brainstorm a unified conceptual model of seasonal export.

Do we have enough data to systematically identify/quantify drivers in export?

How consistent are the seasonal patterns at each site? Do they change from year to year or have they evolved over time?

- What about secondary peaks?
- Are there inter-annual variations?
- Are there trends in timing?

Causes for inter-annual variation in N export

- Climate- droughts/floods and memory during recovery
- Forest changes
- Other?

**3:00-3:15pm-** Break

**3:15pm-** Coupled cycles and considering an integrated approach- **Emily Bernhardt**

**3:30pm-** Group Discussion:

How do our overarching conceptual model(s) explain seasonality across sites? How well can they resolve residuals from the continental pattern in mean annual export? Are some factors more important than others? Are there thresholds or non-linearity to consider? Are there trends in any of these patterns?

- Homework: Consider where our emerging conceptual model doesn't work

**5:30pm-** Sign out and depart for dinner at Crooks Corner in Chapel Hill

**8:00pm-** Van back to hotel

## **Day 3: Thursday, May 30<sup>th</sup>, 2013: Examining the residuals**

The goal today is to refine questions, approaches, and analyses for the papers.

**7:45am-** Van from hotel to NCBG

**8:00am-** Sign in and Continental Breakfast at NCBG

**8:30am-** Summary from Days 1 and 2

Questions/Epiphanies

**8:45am-** Toward Validating our Conceptual Models- **Irena Creed**

Constructing data analysis and approaches to see how robust they are. What about residuals? Quantifying geomorphic features for residuals.

**9:00am-** Group Discussion: What specific processes do we need to account for and quantify at each site to examine residuals? How well do these data conform to our themes?

**10:00am-Developing Analyses to Test Conceptual Models**

The goal of this session is to confront our conceptual models with data from all of our sites. How well can our conceptual models explain residuals across sites?

**Ecological** – Forest type, C/N ratio, in-stream auto vs hetero trophy, auto vs. allochthonous systems.

**Physical-** Hydrology and flowpath dynamics, geomorphology

**12:00pm-** Working Lunch

**1:00pm-** Beyond the forest: The role of land use- **Peter Groffman**

How does land use change alter the timing and magnitude of N export? At what thresholds? Would this change across a continental gradient? Is it as simple as: As N inputs increase so do N outputs?

**1:15pm-** Group discussion on land use.

Using Baltimore, Plum Island, and now Coweeta- what can we reliably say about land use influences?

What factors need we account for?

- Impervious cover
- % Fertilized
- Infrastructure- potable water and wastewater 'streams'
- Detention area- relict wetlands and Best Management Practices

**2:15pm-** Outlining manuscripts, identifying figures and analyses

Group 1: Full continental gradient and inter-annual trends

Group 2: Seasonal/End member sites not accounted for integrated conceptual model

**3:00-3:15pm-** Working Break

**4:00pm-** Known Unknowns and Unknown Unknowns

What don't we know and are there steps to move towards a broader theoretical understanding? Develop a priority list for additional analyses. What else is needed and where do we go from here?

**4:30pm-** Wrap-up-

Writing assignments

**5:00pm- Adjourn-** sign out and van(s) to airport

**6:30pm- Dinner for those still in town**

## **Appendix B**

### **LTER Cross Site Nitrogen Workshop and Working Group Members**

#### **Workshop Attendee List**

1. Mary Beth Adams, Research Soil Scientist  
U.S. Forest Service  
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Institute for the Environment  
University of North Carolina at Chapel Hill  
Chapel Hill, NC 27599
3. Emily Bernhardt, Associate Professor  
Duke University  
Department of Biology  
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Durham, NC 27708
4. Beth Boyer, Associate Professor of Water Resources and Director,  
Pennsylvania Water Resources Research Center  
Penn State University  
304 Forest Resources Building  
University Park, PA 16802
5. Doug Burns, Research Hydrologist  
U.S. Geological Survey  
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Troy, New York 12180-8349
6. Irena Creed, Professor, Canada Research Chair, Watershed Sciences  
University of Western Ontario  
Department of Biology  
University of Western Ontario  
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7. Jon Duncan, Organizer  
University of North Carolina at Chapel Hill  
Department of Geography/Institute for the Environment  
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8. Peter Groffman, Senior Scientist  
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10. Jennifer Knoepp, Research Soil Scientist  
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12. Charles Scaife, Graduate Student  
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