NH WRRC Annual Project Report - 2008

Title: The role of landscape controls on stream chemistry variability and inorganic aluminum mobilization in the White Mountains of New Hampshire.

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Problem Statement:

Surface waters in the White Mountain region of New Hampshire largely emanate from headwaters dominated by shallow soils and short water residence time. Aluminum mobilization associated with these conditions has been a concern due to impacts on aquatic organisms and habitat. Even though some reduction in aluminum concentrations have been observed for surface waters in a few well-studied experimental watersheds, the extent of impacted systems in the White Mountain region remains unknown, especially with regards to aluminum species considered to be most toxic (e.g., inorganic monomeric aluminum, Al_i).

The spatial distribution of headwaters catchments that experience high Al_i stream concentrations is controlled by numerous factors including catchment characteristics such as topography, vegetation, soil depth, and bedrock and till composition. In addition to spatial variability, stream water chemistry in headwaters has been shown to vary among flow regimes from snowmelt in the spring to low flow in the summer. There are very few studies that address controls on stream chemistry, especially aluminum concentrations, at the landscape level (e.g., Palmer et al., 2005) or compare water quality across flow regimes at large scales (Cory et al., 2006). Understanding stream chemistry variation in headwaters in the White Mountain region is essential because headwaters account for a large proportion of New Hampshire's river basins where first-order headwater streams comprise >40% of the river basin area (Nadeau and Rains, 2007). Even though headwaters have been responding to reductions in acidic deposition, including declines in Al_i concentrations (Kahl et al., 2004; Palmer and Driscoll, 2002); many these headwaters may still be vulnerable to chronic or episodic Al_i mobilization. Additionally, data only exists for a small number of streams in the region. Thus, it is important to assess the variability of Al_i concentrations across the White Mountain region and to understand the controls on spatial patterns in headwaters. This information will be useful for policymakers as new water quality standards for surface waters in the state are considered.

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Objectives:

The main goal of this study was to understand which landscape features affect stream chemistry across catchments of various scales and under different flow conditions during the year (i.e., snowmelt high flow and late summer low flow). The significance of comparing these two flow conditions stems from the fact that snowmelt is typically when the most acidic conditions occur, along with the maximum extent of episodic Al_i pulses. In contrast, summer low flows are when groundwater inputs are greatest; Al_i mobilization during this period characterizes chronically impacted systems with minimal groundwater input.

The following objectives were used to achieve our overall goal:

1. Develop a set of metrics easily derived from GIS data that can be used to characterize catchments.
2. Select sample sites representing a range of catchment characteristics within the White Mountain region.
3. Collect and analyze samples for stream chemistry.
4. Identify spatial patterns and relationships between stream chemistry and catchment characteristics.
5. Predict which headwater regions are susceptible to Al_i mobilization.

Methods:

Watershed GIS Terrain Analysis (Objective 1):

Digital Elevation Models (DEMs) from the National Elevation Dataset (http://ned.usgs.gov/) were downloaded at 1/3 arc second resolution for the project region. Watersheds for each sampling location were delineated automatically using these DEMs and pre-processing tools available in spatial analyst toolbox of ArcView. A series of topographic distributions for each watershed was computed based on flow accumulation algorithms computed from the DEMs (Seibert and McGlynn, 2007). Quantiles from the topographic distributions were used as indices for characterizing the watersheds.

A common topographic index used in hydrology is $\ln(a/\tan\beta)$, which describes the upslope drainage area (a) and slope ($\tan\beta$) of each DEM grid cell as a wetness index (Beven and Kirkby, 1979; Sørensen and Seibert, 2007). This topographic wetness index (TWI) was shown by Wolock et al. (1997) to be related to subsurface contact time of water in soils affecting stream chemistry. The amount of time water spends in contact with soils and bedrock is related to the concentrations of ions available as weathering products, and thus, can have significant impacts on acid buffering. Another related index is the downslope index (DSI) that characterizes site drainability due to the influence of down gradient topography such as benches (Hjerdt et al., 2004). Percent riparian area was also determined topographically by setting a threshold elevation (3 m) above the stream channel that was projected laterally onto the topslope forming a buffer around each stream. Riparian zones have been shown to accumulate and release Al and DOC (McGlynn et al., 1999; Pellerin et al., 2002).

Other topographic metrics that index potential subsurface flow paths were computed as well. Simple flow path distributions (distance to creek-DFC, gradient to creek-GTC, and a DFC/GTC ratio) determined from surface topography were shown to be well correlated to isotopically estimated water residence time in catchments that spanned 4 orders of basin size (McGuire et al., 2005). Likewise, McGlynn et al. (2003) found that the median area of sub-catchments (MSA) that drain to stream channels was correlated to water residence time. The relationships found in these studies suggest topographic organization may play an important role in stream chemistry patterns.

All of the topographic indices were computed using a set of computer codes called Geasy developed by Jan Seibert. These codes were used in McGlynn and Seibert (2003), McGlynn et al. (2003), and McGuire at al. (2005).

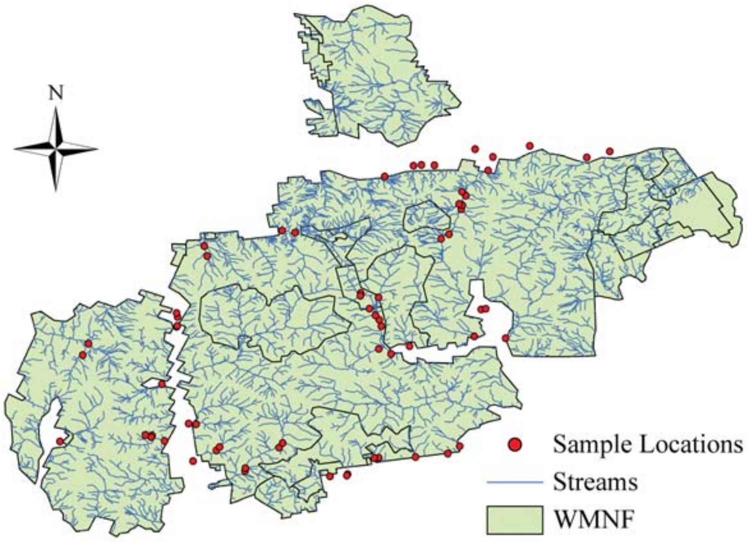

Figure 1. Map of sample sites within the White Mountain National Forest (WMNF) region.

Watershed vegetation cover was analyzed using the 2001 New Hampshire Land Cover Assessment (NHLCA) raster dataset available through the state GIS clearinghouse GRANIT. The NHLCA raster was clipped to the White Mountain region and then further clipped to each watershed boundary. The percent of watershed cover in Spruce-Fir type was combined with the Mixed Forest type to assess the major coniferous component in each watershed.

A weighted average of the percent calcium content in till for the watershed was calculated using 1 km^2 raster of till calcium concentrations generated by a till source envelope model (Bailey and Hornbeck, 1992). Till calcium concentrations were weighted using the percent of watershed area occupied by each raster grid cell.

Comprehensive Regional Stream Chemistry Dataset (Objectives 2 and 3):

A sampling design of 73 sites was developed in and near the White Mountain National Forest (WMNF) based on previous sampling in the region (Hornbeck et al., 2001) and by stratifying sites to represent a broad range of the topographic variables (Figure 1). Sites were also stratified over geology, vegetation type, and a range of watershed sizes to enable statistical characterization. Since there were only a few large watersheds (e.g., Saco River, Swift River, Ammonoosuc River, E. Branch of Pemigewasset River, Mad River, and Wild River) in the

WMNF, they were included in our sample set. Sites were also chosen based on road accessibility.

Laboratory Analysis of Stream Water (Objective 3):

Samples were collected on April 24-25, 2008 (immediately after snowmelt) and September 19-20, 2008 for the high and low flow period, respectively. These 2 sampling periods were selected to provide a snapshot of a relatively high and a relatively low flow condition. Samples were run for major ion concentrations in the Center for the Environment's water quality lab at Plymouth State University. The chemical analysis involved major ion concentrations, ANC, electrical conductivity, and pH. Major ions (F, Na, K, Mg, Ca, NH_4, Cl, Br, NO_3, SO_4) were run on a dual channel Dionex ICS-2000. ANC and pH were run on a Radiometer TIM860 titration manager (w/Ross Orion 8104BN combination rugged pH electrode). Electrical conductivity (the sum of all charged species in a water body) was analyzed on an Accument AB 30 benchtop conductivity meter with automatic temperature compensation and Accument glass body conductivity cell. Samples were analyzed for DOC and monomeric aluminum speciation at the Forest Service lab in Durham, NH. Total monomeric and organic monomeric aluminum were measured (Al_i was calculated by difference) by the automated, colorimetric pyro-chatecol-violet (PVC) technique on a Latchet continuous flow system (Lawrence et al., 1995).

Stream Chemistry Variability to Evaluate Al_i Mobilization (Objectives 4 and 5):

Relationships between stream chemistry (Al_i, total monomeric aluminum $Al_{t,}$ DOC, ANC, pH, and sum of base cations) and topographic variables (Area, Coniferous Cover, DFC/GTC, DSI, Elevation, MSA, Riparian%, TWI, and Till Ca%) were analyzed to examine the landscape control on stream chemistry between high and low flow conditions. Each of the stream chemistry dependent variables was compared to independent topographic variables using stepwise regression (p-value to enter = 0.05 and p-value to remove = 0.10) to find the best possible set of independent variables for a predictive model. The stepwise regression also allowed us to evaluate which predictive variables were more important in explaining the variability of different chemistry data. Several quantiles of the topographic distributions were tested and since no consistent differences were found, only median values were used in final regression models. Complementary to the stepwise regression was graphical exploration of the data using scatter plots and LOWESS smoothing. Both chemistry and topographic variables were compared between flow regimes to see if predictive indices were different between flow conditions. Chemistry was also analyzed in notched boxplots grouped by topographic variables into three equal-sample size bins. Groups where analyzed using the non-parametric Kruskal-Wallis test and Tukey multiple comparison analysis to determine which groups were different.

Major Findings to Date:

The variability of stream chemistry and topographic features captured in this study is vital information in addressing inorganic aluminum mobilization in the White Mountain region. We consider this project a pilot scale effort since we sampled stream chemistry on two occasions and over a large regional scale with only 73 sites. Nevertheless, we found that simple topographically derived indices and till source information can explain a significant portion of the stream water chemical variance across our sites. Concentrations of Al_i and DOC were generally higher with a lower pH during the spring period compared to the summer period.

However, despite the differences in concentrations between the two flow regimes, relationships between the chemistry and topographic indices were generally similar during both flows.

Univariate regression analysis generally showed that little variation in stream chemistry could be explained by any one topographic index or catchment variable. For example, the best single variable model, percent till calcium concentration, could only explain 12% of the spring Al_i variability ($R^2 = 0.122$, p-value = 0.004). The addition of median sub-catchment area (MSA) and median topographic wetness index (TWI) as variables in a stepwise regression increased the explained variance of Al_i to 36% and other indices were not significant (p-value<0.000) (Figure 2). The same three topographic indices could explain 18% of the variance in the summer low flow Al_i concentrations ($R^2 = 0.175$, p-value = 0.009). The percent till calcium concentration was also the most important predictive variable in the stepwise regression analysis for spring DOC and pH as well. The geographic distribution of calcium concentration in till is important in providing buffering to acid deposition and appears to be especially important during spring high flows that are characteristic of episodic acidification events with the highest inorganic aluminum mobilization. Generally, the stepwise regression analysis of other chemistry (DOC, pH, ANC, and sum of base cations) showed that other topographic indices besides till calcium such as MSA, TWI, and the DSI were important, but the amount of variance in stream chemistry explained remained below 50%. The simple flow path distribution surrogate, DFC/GTC, was not seen as an important factor in the stepwise regression analysis contrary to our hypothesis.

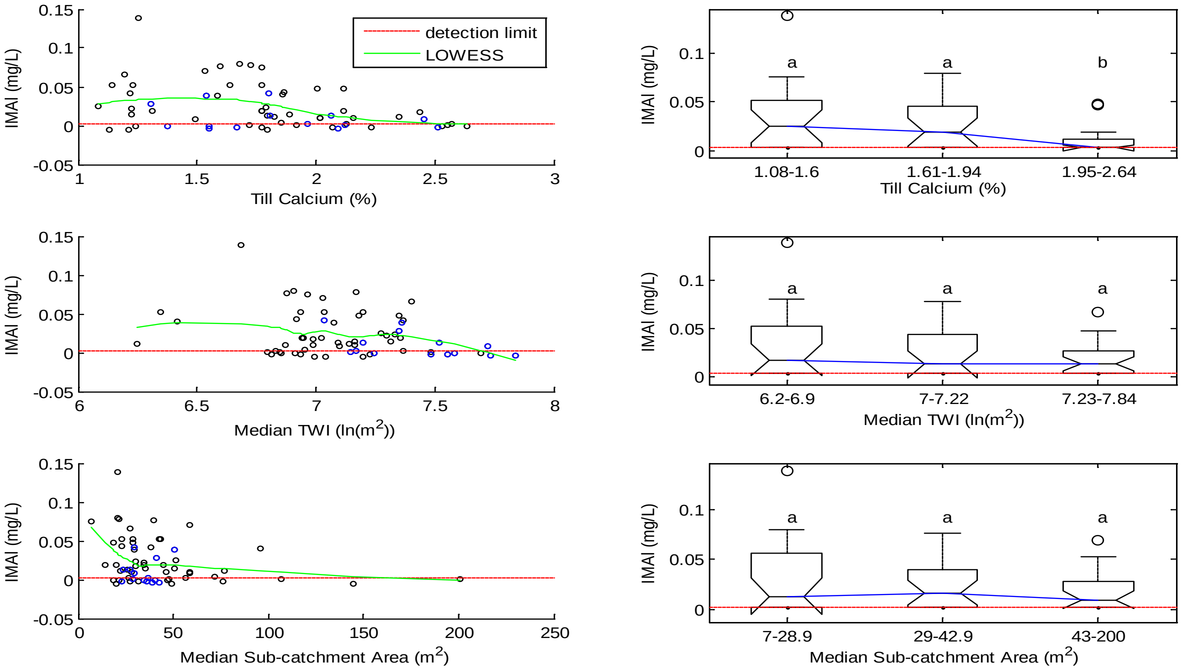

Figure 2. Scatter plots on the left show the relationship between spring inorganic aluminum concentrations with topographic indices. The blue circles represent sites with watershed area >50 km^2 and the black circles sites less than that. Boxplots on the right represent spring inorganic aluminum concentrations equally binned by topographic indices with corresponding letters representing which groups are statistically similar.

With the exception a few watersheds with basin areas >50 km² (i.e., Saco, Sawyer, and Mad Rivers) which had higher Al_i concentrations, it appears that regardless of the till calcium concentration which spanned the entire range for >50 km² watersheds, larger watersheds had lower Al_i concentrations during spring high flows suggesting episodic acidification. It is important to note that the three larger watersheds with high Al_i, the Saco, Sawyer, and Mad Rivers all fell into the lower third in terms of ranking of till calcium concentration.

Significance and Future work:

Results thus far suggest the topographic indices individually have poor predictive capability for stream chemistry. Both the median subcatchment area (an index of contributing hillslope size) and the topographic wetness index were the strongest terrain variables in explaining inorganic monomeric Al chemistry. It is clear that till calcium concentration is also important and could play a role in regional planning and management. Although the predictive ability of the topographic indices is weak ($R^2 < 0.10$) for inorganic aluminum, they may provide better results for total or organic aluminum concentrations, which is currently being evaluated. In addition, we are testing the same variables at the Hubbard Brook Experimental Forest (HBEF) where a much higher density dataset exists (Likens and Buso, 2006). The Likens and Buso (2006) dataset contains sample locations along the main Hubbard Brook and every 100 meters along each tributary. The data from the Hubbard Brook study provides an opportunity to test these methods and topographic indices at finer spatial scale and much larger sample size (roughly 700 sites). Analysis currently underway includes looking at a principle component analysis of the topographic indices to reduce dimensionality and using alternative methods to linear regression analysis since many of the data appear to be non-linear. The results from this study to date provide insight to the relationship between stream chemistry and the landscape, but continued work is needed. Further work including better resolution digital elevation models from LiDAR and soil classification data, which are both being developed in the WMNF and at HBEF, could lead to increased predictive capabilities for stream chemical patterns in headwater catchments.

Publications, presentations and awards:

1. Doogan, C.B., in preparation. Using terrain indices to explore controls on stream chemistry variation and inorganic aluminum mobilization in the Hubbard Brook Experimental Forest and White Mountains of New Hampshire, M.S. Thesis, Plymouth State University.
2. Doogan, C.B., McGuire, K.J., Bailey, S.W., Kahl, J.S., Estabrook, R.H., 2008. The role of landscape controls on stream chemistry variability and inorganic aluminum mobilization in the White Mountains of New Hampshire. Northeastern Ecosystem Research Cooperative Conference, November 12-13, Durham, NH.
3. Joe and Gail White Graduate Fellowship, an environmental education fellowship for C. Doogan to assist in the completion of his program. http://www.plymouth.edu/development/difference/white.html

Number of students supported:

1 MS student – Christian Doogan, expected completion – June 2009
1 undergraduate assistant – Mandy Hook

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