TITLE: Investigating inorganic and organic-mediated cation transport from soils to streams

Investigator: Elizabeth Herndon, Kent State University

BACKGROUND

Water mediates the movement of elements between rock and life in the Critical Zone. For example, biota exude organic acids that accelerate mineral dissolution and enhance soil formation. Elements that are released into soil pore waters subsequently precipitate as secondary minerals, are taken up by vegetation, or are transported downslope during periods of saturated flow. The chemical speciation of an element in water dictates its mobility and reactivity in the environment; however, little is known about chemical speciation in stream and soil waters at SSHO. It has been inferred that cations are transported through the catchment as a combination of free ions, organic complexes, and particulates, but direct evidence for these forms is still needed. The purpose of this research is to evaluate chemical speciation in soil waters and the stream in order to evaluate controls on element transport from soils into the stream under changing flow conditions.

Previous research at SSHO identified that concentrations of certain elements (iron, manganese, calcium, aluminum) are correlated with DOC in organic-rich pore waters along the swale transect, and these soils may serve as prime sources of DOC and metal cations to the stream during summer and fall flushing events (Andrews, 2011; Andrews et al., 2011; Herndon, 2012). Subsequently, Herndon et al. (*to be submitted*) proposed that the solutes associated with DOC are “bioactive” either due to intense biotic cycling and storage in plant biomass (Ca, Mn) or complexation by DOC released during organic matter decomposition (Fe, Al). As a result, concentrations of bioactive solutes in the stream are controlled by changing hydrologic connectivity of the stream to organic-rich soil waters under different flow regimes. In contrast, solutes that are not correlated with DOC (Na, Mg, Si) are spatially homogeneous in catchment soils and “chemostatic” in the streams, i.e. stream concentrations vary little with stream discharge.

However, the mechanisms underlying these observations remain unclear. For example, correlations between bioactive solutes and DOC may be due to 1) release of both DOC and metal cations from decomposing organic matter, or 2) enhanced release of metal cations from soil minerals by DOC chelation. Furthermore, evidence is needed to support the hypothesis that cation exchange on mineral surfaces regulates the mobility of chemostatic solutes. In order to better model soil weathering rates, nutrient bioavailability, and downstream hydrochemistry, it is necessary to and elucidate the processes that mobilize and transport these elements.

PROPOSED WORK

We will examine mechanisms driving the water-mediated transport of elements from soils to streams and investigate the hypothesis that bioactive elements are transported as complexes with organic compounds. Many studies examine element concentrations in catchment reservoirs and streams, but few investigate their chemical speciation. The initial project will measure a suite of cations with a focus on four “bioactive” elements: Al, Fe, Mn, and Ca. Specifically, the aims of this work are to:

1) measure concentrations of dissolved (< 10 kDa) and colloidal (10 kDa – 0.45 µm) cation species in soil pore water, stream water, and water-soluble soil extracts
2) characterize the chemical properties of water-soluble organic C and cation species in various size fractions using spectroscopy
3) quantify concentrations of common metal-chelating organic acids and siderophores in water samples and soil extracts
4) evaluate organic-metal complexes and cation exchange properties of bulk soils obtained from SSHO, shale transect sites, and possibly other CZOs

The proposed work will build on previous hydrochemical analyses in the catchment and will address mechanisms linking H2 [*The distribution of weathering reactions across a landscape can be described as a function of biotic and abiotic production and consumption of acids*(CO_2 *and DOC) and* O_2] and H6 [*Ions that are released quickly from ion exchange sites (Mg, Na, K) throughout the catchment demonstrate chemostatic behavior (~constant concentration in the stream) whereas Fe, Mn and DOC concentrations vary with changes in watershed-stream connectivity*]. Furthermore, evaluating DOC compounds will yield information on available metal chelators, and more broadly, products of organic matter decomposition. Finally, the work will address the hypothesis, as proposed by Jin et al. (2010) and Yesavage et al. (2012), that loss of Fe and Al from hillslope soils may occur via downslope transport of particulates. These results can be compared to larger-scale estimates of dissolved and particulate fluxes of metals in riverine systems (e.g. Shaver's Creek watershed) in order evaluate the contribution of headwater streams to downstream river fluxes. Understanding how organic compounds mobilize metals will enable better predictions of metal transport as climate forcing shifts C and water dynamics.

METHODS

The majority of the proposed work will be completed in the Aqueous Geochemistry laboratory at Kent State University. Analytical equipment at Kent State includes a UV-Visible spectrophotometer, Dionex chromatography system, Shimadzu Total Organic Carbon analyzer, freeze-drier, and anaerobic glove box. Field equipment, including pH probes, are available for class use. A fluorescence spectrometer is available in Biological Sciences. As a new faculty member, Herndon will also be upgrading laboratory equipment to include a Fourier transform infrared (FTIR) spectrometer for analysis of mineral and organic functional groups. X-Ray Absorption Spectroscopy (XAS) will be used to differentiate between organic-complexes and oxide colloids of Fe and Mn. XAS will be completed at synchrotron user facilities, similar to previous work conducted at the Advanced Photon Source and Stanford Synchrotron Radiation Lightsource.

Sample collection will occur once between mid-August to mid-September and once in mid-October. Soil pore waters will be collected from all depths from suction lysimeters installed in valley floor soils (sites SPVF, SSVF, and NPVF). To obtain pore water near the soil surface (< 10 cm), suction macrorhizons (Eijkelkamp) will be installed between 0 – 10 cm depth. Additional water samples will be collected from the stream at various points between the stream headwaters and catchment outlet. Shallow soil cores and stream sediments (< 30 cm) will be collected from near the water sampling sites. Since these soils are generally well-drained, no special precautions to maintain anoxic conditions will be taken during sampling; however, samples for redox sensitive analyses will be stored in the absence of oxygen. Stream and soil water will be filtered in the field (< 0.45 µm) and split into subsamples for cation and DOC analyses. Additional water will be stored "unfiltered" (< 1.3 µm) at 4°C for later processing in the lab, including ultrafiltration to obtain the dissolved fraction (< 10 kDa). Electrical conductivity and pH will be measured in the field.

Concentrations of cations in filtered and dissolved water fractions will be quantified on ICP-MS at Penn State following established protocols. Quantification and characterization of organic C will occur at KSU, including DOC quantification, nondestructive characterization with spectroscopic techniques (UV/VIS, fluorescence), and organic acid and siderophore measurements. Soil and sediment samples will be used to obtain water extractable organic C (WEOC) and to measure the cation exchange pool. Subsamples of WEOC will be filtered to determine water-soluble concentrations of colloidal and dissolved cations. Remaining WEOC will be freeze-dried to preserve metal and organic C chemistry for spectroscopic analysis and long-term storage. Detailed spectroscopic techniques (FTIR, XAS, SEM/EDS) will be conducted on freeze-dried WEOC and bulk soils, since pore water and stream waters may not contain enough material for these analyses.

PROPOSED SSHO INTERACTIONS

PI Herndon currently collaborates in a non-funded capacity with SSHCZO and SSHO Shale transect researchers (P. Sullivan, A. Dere, S. Brantley) to compare concentration-discharge behaviors across two transect sites (SSHO and Plynlimon, Wales, UK). With this proposal, Herndon seeks to continue collaboration with P. Sullivan to optimize sampling protocols and integrate chemical data into reactive-transport models, and with A. Dere to evaluate WEOC and cation exchange properties of soils from shale transect sites. Cation concentrations will be measured at PSU facilities for continuity with previous samples. Lysimeter sampling will be conducted by PI Herndon and coordinated with PSU researchers (J. Kaye). Additional analyses may include scanning electron microscopy imaging of colloids and particulates at the Smithsonian Institute (courtesy C. Rosenfeld) and XAS at a synchrotron.

A portion of the funds will be used to finance a field trip to SSHO for Hydrogeochemistry students at KSU (Fall 2014). This trip would be used to train upper-level undergraduate and graduate students in environmental research and water quality methods. Additionally, the trip would be incorporated into the class curriculum as a learning tool to examine water-rock interaction and water quality. Kent State is a research-oriented university with a majority female undergraduate population (59%) and a third of undergraduates pursuing STEM degrees. An undergraduate, potentially from the Hydrogeochemistry course, will be recruited to pursue independent research using sample collection at SSHO as a launching point. This project will also support career development for PI Herndon, a female junior faculty member in the Geology department at KSU, and allow continued CZO collaboration between Herndon and two additional new faculty members at research-oriented (P. Sullivan) and primarily undergraduate (A. Dere) institutions.

Results of the proposed work are expected to yield at least one peer-reviewed publication related to DOC and metal cation chemistry and transport. Additionally, results will be presented at one or more scientific conferences. Co-authorship will be sought with all SH collaborators who provide fundamental data and/or intellectual input. These findings will serve as the basis for a larger NSF-funded grant to support cross-CZO research investigating mechanisms of inorganic versus organic-mediated elemental transport across environmental gradients established by the CZO network. Chemical data, including spectroscopic characterization, will be made available in the CZChem database and on the CZO website following publication. Freeze-dried samples will be catalogued, archived, and made available for future investigators.

PRIOR SSHO SUPPORT

PI Herndon previously researched the biogeochemistry of manganese contamination at Shale Hills. This work resulted in one PhD dissertation, three manuscripts and one additional pending manuscript, and seven abstracts at international conferences (Goldschmidt, American Geophysical Union, Geochemistry of the Earth's Surface). Portions of Herndon's work were supported by NSF grant EAR-1052614 (Soils and Vegetation as a Record of Anthropogenic Pollutants: Mn in the Shale Hills CZO), which was co-written as part of her dissertation.

Herndon EM, Martínez CE, and Brantley SL (2014, *in review*) Spectroscopic (XANES/XRF) characterization of contaminant manganese cycling in a temperate watershed. *Biogeochemistry*.

Herndon EM, Jin L, Andrews DM, Eissenstat DM, and Brantley SL (2014, *in review*) Vegetation acts as a capacitor for manganese contamination at the Susquehanna/Shale Hills Critical Zone Observatory. *Global Biogeochemical Cycles.*

Herndon EM (2012) Biogeochemistry of manganese contamination in a temperate forested watershed. PhD Dissertation, The Pennsylvania State University.

Herndon, EM, Jin, L, and Brantley SL (2011) Soils reveal widespread manganese enrichment from industrial inputs. *Environ. Sci. Technol.* 45(1), 241-247.

BUDGET SUMMARY

Category	Item	Description	Total Cost
Travel	Transportation	Travel to SSHO for sampling trip #1 (412 mi)	$231
	Transportation	Field trip minivan rental + gas	$225
	Transportation	Travel to Argonne National Lab	$424
	Lodging	Field trip cabin rental for 12 people	$150
	Lodging	Argonne National Lab Guest House ($75/nt)	$300
Supplies	Sampling	Rhizon soil moisture samplers (pack of 10)	$200
	Sampling	Syringe filters (0.45 µm; 4 packs of 50)	$556
	Analysis	Amicon Ultra-15 Centrifugal Filter Units (3 packs of 24)	$753
	Analysis	Dionex AS11 organic acid column	$1,150
	Analysis	Dionex guard column	$100
Analyses	ICP-MS	Analysis of < 100 samples (~8 hrs)	$1,138
Salary	Work	Undergraduate salary, intermediate level	$1,500
Indirect Cost (47.2%)			$3,175
Total			$9,902

BUDGET JUSTIFICATION

Field trips expenses include two minivan rentals for two days, gas, and rustic cabin lodging for 12 people. The field trip will be incorporated into an upper-level undergraduate Hydrogeochemistry curriculum. The Kent State Geology department will support field trip costs. Additional mileage compensation (412 mi roundtrip Kent to State College at $0.56/mi) is requested for a preliminary sampling trip to SSHO by the PI. Mileage (758 mi roundtrip at $0.56/mi) and lodging at the Guest House ($75/nt for 4 nights) are also requested to fund travel for the PI to the Advanced Photon Source to analyze metal speciation using X-ray Absorption Spectroscopy.

Rhizon soil moisture samplers (Eijkelkamp Agrisearch Equipment) will be used to collect soil pore water from the upper 10 cm of soils which are not sampled by lysimeters. Syringe filters and centrifugal filter units are required to partition water samples into filtered and dissolved fractions. A Dionex AS11 column is needed to analyze low-molecular weight organic acids on the Ion Chromatography system at Kent State. Other basic sampling equipment (syringes, tubing, plastic bottles, glass vials, pH probes, auger, etc.) are already available to the PI or will be purchased using department startup funds.

ICP-MS is required to measure the low concentrations of metal cations in filtered and dissolved solutions. No ICP-MS is available at Kent State; therefore, funds are requested to analyze these samples at the Penn State Laboratory for Isotopes and Metals in the Environment at the external academic rate of $142.22/hr (8 hours). Other analyses (DOC quantification, UV-VIS spectroscopy, Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy, X-ray absorption spectroscopy) will be conducted at no additional cost.

Salary will be used to compensate an undergraduate at the KSU intermediate pay level ($10.08/hr + fringe benefits at 14.5%) for 130 hours of field sampling and laboratory analysis while undergoing research training.

ELIZABETH M. HERNDON

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PROFESSIONAL PREPARATION

Washington University in Saint Louis	B.A. Earth and Planetary Sciences, 2007
	B.A. Chemistry: Biochemistry concentration, 2007
The Pennsylvania State University	Ph.D. Geosciences (dual-title Biogeochemistry), 2012
Oak Ridge National Laboratory	Postdoctoral, Environmental Sciences Division, 2012-2014

APPOINTMENTS

Assistant Professor of Geology	Kent State University, 2014 – present
Postdoctoral Researcher	Oak Ridge National Laboratory, 2012 – 2014
Instructor in Geosciences	The Pennsylvania State University, 2012
Research Assistant	The Pennsylvania State University, 2007 – 2012

PRODUCTS

Herndon EM, Martínez CE, and Brantley SL (2014, *in review*) Spectroscopic (XANES/XRF) characterization of contaminant manganese cycling in a temperate watershed. *Biogeochemistry*.

Herndon EM, Jin L, Andrews DM, Eissenstat DM, and Brantley SL (2014, *in review*) Vegetation acts as a capacitor for manganese contamination at the Susquehanna/Shale Hills Critical Zone Observatory. *Global Biogeochemical Cycles.*

Herndon EM (2012) Biogeochemistry of manganese contamination in a temperate forested watershed. The Pennsylvania State University, PhD Dissertation.

Herndon, EM, Jin, L, and Brantley SL (2011) Soils reveal widespread manganese enrichment from industrial inputs. *Environ. Sci. Technol.* 45(1), 241-247.

SYNERGISTIC ACTIVITIES

Session Chair, AGU Fall Meeting; 2013
Chair, Professional Development Committee, Oak Ridge Postdoctoral Association; 2013
Session Chair, 22nd V.M. Goldschmidt Conference; 2012
Elementary educational outreach, Shake Rattle and Rocks; 2010-11
Steering committee, Environmental Chemistry Student Symposium; 2010-11

COLLABORATORS AND OTHER AFFILITATIONS

Collaborators (last 48 months):

Oak Ridge National Laboratory: Taniya Roy Chowdhury, David Graham, Baohua Gu, Liyuan Liang, Benjamin Mann, Stan Wullschleger,
Penn State: Danielle Andrews, Susan Brantley, Ashlee Dere, David Eissenstat, Pamela Sullivan
University of Texas – El Paso: Lixin Jin, Lin Ma
Stanford Synchrotron Light Source: John Bargar
Cornell University: Carmen Enid Martínez

Graduate Advisors and Postdoctoral Sponsors

Susan Brantley, Penn State; Baohua Gu, ORNL; Liyuan Liang, ORNL

CURRENT AND PENDING SUPPORT

Investigator: Elizabeth M. Herndon

CURRENT

None

PENDING

Title: (This Proposal) Investigating inorganic and organic-mediated cation transport from soils to streams
Source of Support: Susquehanna Shale Hills Critical Zone Observatory (SSHO)
Total Requested Amount: $9,902
Award Period Covered: 08/15/2014 – 08/15/2015
Location of the Project: Kent State University
Person-months/year committed to the project: 0 months