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AGU-FM13

December 07 - 13, 2013

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Saturday, December 07, 2013

You have nothing scheduled for this day

Sunday, December 08, 2013

You have nothing scheduled for this day

Monday, December 09, 2013

Time	Session Info
8:00 AM-10:00 AM, 2003 (Moscone West), **Thresholds in Soil Response to Global Change I**	
8:45-9:00 AM	**EP11A-04. Developing approaches to hindcast and earthcast climate controls on solute fluxes during shale weathering in the Critical Zone** P.L. Sullivan; Y. Godderis; Y. Shi; J. Schott; C. Duffy; S.L. Brantley
1:40 PM-6:00 PM, Hall A-C (Moscone South), **Thresholds in Soil Response to Global Change II Posters**	
1:40-1:40 PM	**EP13C-0876. Depth and Topographic Controls on Soil Gas Concentrations and Fluxes in a Small Temperate Watershed** E.A. Hasenmueller; L. Jin; L.A. Smith; M.W. Kaye; H. Lin; S.L. Brantley; J.P. Kaye
4:00 PM-6:00 PM, 3009 (Moscone West), **Measurement and Modeling of Root-Zone Processes Influencing Water, Carbon and Nitrogen Cycles at Various Scales II [SWIRL_GS]**	
4:00-4:15 PM	**H14D-01. Scaling root processes based on plant functional traits** ***(Invited)*** D.M. Eissenstat; M.L. McCormack; K. Gaines; T. Adams
4:00 PM-6:00 PM, 3002 (Moscone West), **Hydraulic Fracturing: Knowns, Unknowns, and Communication to the Public I [SWIRL_CU] (Virtual Option)**	
4:15-4:25 PM	**PA14A-02. Water Resource Impacts During Unconventional Shale Gas Development: The Pennsylvania Experience** S.L. Brantley; D. Yoxtheimer; S. Arjmand; P. Grieve; R. Vidic; J.D. Abad; C.A. Simon; J. Pollak
6:15 PM-7:15 PM, 304 (Moscone South), **Critical Zone Science and Observatories**	
6:15-6:15 PM	**TH15D-01. Critical Zone Science and Observatories** S.L. Brantley; T.S. White; S.P. Anderson; R.C. Bales; J. Chorover; W.H. McDowell

Tuesday, December 10, 2013

Time	Session Info

1:40 PM-6:00 PM, Hall A-C (Moscone South), **Hydropedology: Synergistic Integration of Soil Science and Hydrology in the Critical Zone I Posters [SWIRL_GS]**	
1:40-1:40 PM	**H23F-1330. Temporal and Spatial Patterns of Preferential Flow Occurrence in the Shale Hills Catchment: From the Hillslope to the Catchment Scales** H. Liu; H. Lin
1:40-1:40 PM	**H23F-1331. Temporal stability of soil matric potential in the Shale Hills Critical Zone Observatory** H. Yu; H. Lin; W. Berger; P. Yang
1:40-1:40 PM	**H23F-1332. Resolving the High Resolution Soil Moisture Pattern at the Shale Hills Watershed Using a Land Surface Hydrologic Model** Y. Shi; D.C. Baldwin; K.J. Davis; X. Yu; C. Duffy; H. Lin

Wednesday, December 11, 2013

Time	Session Info
1:40 PM-6:00 PM, Hall A-C (Moscone South), **Connecting Natural Landscapes to Experimental and Numerical Models of Earth and Planetary Surface Evolution III Posters**	
1:40-1:40 PM	**EP33A-0858. A New Hydrologic-Morphodynamic Model for Regolith Formation and Landscape Evolution** Y. Zhang; R.L. Slingerland; C. Duffy
1:40 PM-3:40 PM, 3011 (Moscone West), **Pore Structure, Fluid Flow, and Mass Transport in Porous Media II [SWIRL_CM]**	
1:40-1:55 PM	**H33L-01. Water-Organic-Rock Reactions Recorded in Pores in Shales from the Marcellus and Rose Hill Formations *(Invited)*** S.L. Brantley; L. Jin; G. Rother; D.R. Cole; x. gu; V.N. Balashov

Thursday, December 12, 2013

Time	Session Info
8:00 AM-10:00 AM, 3022 (Moscone West), **Biophysical Functions and Process Dynamics in Soil I**	
9:00-9:15 AM	**H41L-05. The Catchment Isoscape: Theory and Experimental Evidence for the Isotopic Age of Water in a Critical Zone Observatory *(Invited)*** C. Duffy; E. Thomas; P.L. Sullivan; G. Bhatt; X. Yu
10:20 AM-12:20 PM, 102 (Moscone South), **Hydrometeorological Research at the Computational Frontier: Data-Intensive Prediction and Social Impact Assessment of Natural Disasters (Virtual Option)**	

11:20-11:50 AM	**U42A-03. A call for a community strategy to the "Essential Terrestrial Variables" necessary for catchment modeling anywhere in the US** ***(Invited)*** C. Duffy; L.N. Leonard
1:40 PM-3:40 PM, 3014 (Moscone West), **Hydrogeophysical Characterization of the Critical Zone I [SWIRL_GS]**	
3:10-3:25 PM	**H43L-07. Cross-CZO Contrasts: Aspect Controls and Critical Zone Architecture** B.A. Clarke; E. Kirby; D.W. Burbank; N. West
3:25-3:40 PM	**H43L-08. Geologic controls on fracture distributions within the Shale Hills Critical Zone Observatory** K. Singha; B.A. Clarke; P.L. Sullivan; P.B. Chattopadhyay; S.L. Brantley

Friday, December 13, 2013

Time	Session Info
8:00 AM-12:20 PM, Hall A-C (Moscone South), **Biophysical Functions and Process Dynamics in Soil II Posters**	
8:00-8:00 AM	**H51A-1174. Understanding the Hydrological Controls on the Water Chemistry at the Watershed Scale Using an Integrated Hydro-Thermo -Geochemical Model PIHM-RT** C. Bao; L. Li; Y. Shi; C. Qiao; P.L. Sullivan; S.L. Brantley; C. Duffy
8:00 AM-12:20 PM, Hall A-C (Moscone South), **CZ-tope: Using Multiple Isotopes to Understand Watersheds I Posters**	
8:00-8:00 AM	**H51B-1186. Quantifying the signature of the industrial revolution from Pb and Cd isotopes in the Susquehanna Shale Hills Critical Zone Observatory** L. Ma; E. Herndon; L. Jin; D. Sanchez; S.L. Brantley
8:00-8:00 AM	**H51B-1190. Boron isotopes at the Shale Hills critical zone observatory** j. noireaux; P.L. Sullivan; P. Louvat; J. Gaillardet; S.L. Brantley
8:00-8:00 AM	**H51B-1194. Weathering and solute transport to the Salar de Atacama, northern Chile** S.A. Hynek; L.A. Munk; D.F. Boutt
4:00 PM-6:00 PM, 3018 (Moscone West), **CZ-tope: Using Multiple Isotopes to Understand Watersheds II**	
4:30-4:45 PM	**H54A-03. Going Steady: Using multiple isotopes to test the steady-state assumption at the Susquehanna Shale Hills Critical Zone Observatory** ***(Invited)*** N. West; E. Kirby; L. Ma; P.R. Bierman
5:00-5:15 PM	**H54A-05. Using C and S isotopes to elucidate carbonic versus sulfuric acid reaction pathways during shale weathering in the Susquehanna Shale Hills Critical Zone Observatory** L. Jin; N. Ogrinc; T. Yesavage; E.A. Hasenmueller; L. Ma; J.P. Kaye; S.L. Brantley

Final ID: EP11A-04

Developing approaches to hindcast and earthcast climate controls on solute fluxes during shale weathering in the Critical Zone

P. L. Sullivan;[1, 2]; *Y. Godderis;*[3]; *Y. Shi;*[1]; *J. Schott;*[3]; *C. Duffy;*[2]; *S. L. Brantley;*[1];
1. Earth and Environmental Systems Institute, Pennsylvania State University, State College, PA, United States.
2. Department of Civil Engineering, Pennsylvania State University, State College, PA, United States.
3. Géosciences Environnement Toulouse, CNRS-Observatoire Midi-Pyrénées, Toulouse, France.

Body: To quantify the anthropogenic and climatic controls on regolith formation and global weathering fluxes, it is critical to understand the evolution of weathering profiles and the consumption of CO2 associated with weathering. Using a cascade of global circulation, biota, and weathering models, Goddéris et al. (2010) hindcasted the evolution of weathering profiles over the last 10k years along a loess transect in the Mississippi Valley. After using the weathering code, WITCH, in this way to investigate the dissolution and precipitation of silicate and carbonate minerals in loess along the climosequence, Godderis et al. (2013) then used a similar cascade of models to project the response of weathering of the transect through 2100 – we call this forward projection an “earthcast”. The effect of projected climate change on the weathering profile was largely dictated by increasing temperature (which slows the rate of advance of the dolomite reaction front but increases silicate weathering) and changes in drainage (variable along the transect). To a lesser extent, changes in soil CO2 affected weathering. The response of the dolomite reaction front acts like a terrestrial lysocline as it responds to changing CO2 and climate.

Here, we embark on a similar study of shale weathering. Like the loess formations, shale has high surface area of silicates per unit volume, and can contain carbonate minerals. Shale also comprises 25% of the continental landmass. Specifically, to explore how climate evolution controls shale weathering we are beginning to compare soils along a shale climosequence transect that spans from Wales to Puerto Rico (Dere et al. in press)—i.e., like the loess north-south transect, a climosequence of pedons. For the shales, we will also explore the effects of climate variables by comparing soils on the north- and south-facing hillslopes of the Susquehanna Shale Hills Critical Zone Observatory (SSHCZO).

The eventual goal is to utilize our understanding of the climatic controls on shale weathering profiles and solute chemistry from these explorations to “earthcast” the next hundred years. We report our initial efforts to link the meteorological forcing from the North American Land Data Assimilation System (NLDAS-2), the fully-coupled land-surface Penn State Integrated Hydrologic Model (Flux-PIHM), and the geochemical box model WITCH. Our preliminary efforts show that WITCH can elucidate the controls on water and Mg weathering fluxes derived from clay weathering.

Final ID: EP13C-0876

Depth and Topographic Controls on Soil Gas Concentrations and Fluxes in a Small Temperate Watershed

E. A. Hasenmueller;[1, 2]; *L. Jin;*[3]; *L. A. Smith;*[1]; *M. W. Kaye;*[1]; *H. Lin;*[1]; *S. L. Brantley;*[2, 4]; *J. P. Kaye;*[1];
1. Department of Ecosystem Science and Management, Penn State University, University Park, PA, United States.
2. Earth and Environmental Systems Institute, Penn State University, University Park, PA, United States.
3. Department of Geological Sciences, University of Texas at El Paso, El Paso, TX, United States.
4. Department of Geosciences, Penn State University, University Park, PA, United States.

Body: Accurate predictions of soil respiration dynamics are necessary for constructing models of the global carbon (C) cycle and projecting feedbacks between climate change and terrestrial ecosystem C balance. Moreover, quantifying soil CO2 concentrations (pCO2) is important for our understanding of bedrock weathering because it provides an active source of acidity through CO2 dissolution into soil pore water. We seek to determine whether there are predictable patterns in soil pCO2 and CO2 fluxes across landscape positions within a first-order catchment that can lead to better models of soil respiration by using remotely mappable topographic information. Our experimental design captures the spatial variability of soil CO2 by explicitly monitoring both pCO2 and CO2 flux at hillslope transects for a planar slope and swale depression (sampling sites include discrete depths for ridge tops, mid-slopes, and valley floors) over two years in the Susquehanna/Shale Hills Critical Zone Observatory (SSHCZO) catchment. The sampling sites have the same bedrock composition, but different soil series, soil moisture conditions, and vegetation depending on hillslope position.

Our results show that soil pCO2 is controlled by topographic position. The highest pCO2 values for all sites were measured during the growing season, and the average soil pCO2 was highest in the landscape positions with the deepest soils (i.e., swale depression mid-slope: 1.6 m thick soil, pCO2 = 8940 ± 5720 ppmv; planar slope valley floor: 0.7 m thick soil, pCO2 = 5450 ± 4910 ppmv; swale depression valley floor: 0.9 m thick soil, pCO2 = 4850 ± 3130 ppmv). The lowest pCO2 values were found at the ridge tops and the planar slope mid-slope, which had soil depths of < 0.4 m and average pCO2 values of < 1800 ppmv. The pCO2 increased with depth for all sites throughout the year, with the exception of three sites that had high pCO2 anomalies at shallower depths in the profile that only occurred during the growing season and were associated with preferential water flowpaths. Soil pCO2 increased with both soil temperature and moisture, the latter largely being a function of soil depth and landscape position. The observed pattern in soil pCO2 suggests that topographic positions with deeper soils have higher weathering potential.

Like soil pCO2, surface CO2 flux positively correlates with soil temperature and moisture, and on average, is higher for sites in the wetter swale depression (CO2 flux = 4.67 ± 2.96 μmol m-2s-1) than those in the drier planar slope (CO2 flux = 3.67 ± 2.48 μmol m-2s-1). However, flux becomes negatively correlated with soil moisture above 0.25 m3 m-3. Further, there is high spatial variability along the individual transects that does not correlate with hillslope position or soil depth. Rather, the surface CO2 flux pattern along each transect is the result of heterogeneous leaf litter distribution. This relationship is most pronounced during the growing season but persists into the winter. Our results suggest that while topography controls pCO2, the surface CO2 flux is instead influenced by the variability of leaf litter distribution, which is challenging to quantify.

Final ID: H14D-01

Scaling root processes based on plant functional traits *(Invited)*

D. M. Eissenstat; [1]; *M. L. McCormack;* [1]; *K. Gaines;* [1]; *T. Adams;* [1];

1. Pennsylvania State University Main Campus, University Park, PA, United States.

Body: There are great challenges to scaling root processes as variation across species and variation of a particular species over different spatial and temporal scales is poorly understood. We have examined tree species variation using multispecies plantings, often referred to by ecologists as “common gardens”. Choosing species with wide variation in growth rate, root morphology (diameter, branching intensity) and root chemistry (root N and Ca concentration), we found that variation in root lifespan was well correlated with plant functional traits across 12 species. There was also evidence that localized liquid N addition could increase root lifespan and localized water addition diminished root lifespan over untreated controls, with effects strongest in the species of finest root diameter. In an adjacent forest, we have also seen tree species variation in apparent depth of rooting using water isotopes. In particular species of wood anatomy that was ring porous (e.g. oaks) typically had the deepest rooting depth, whereas those that had either diffuse-porous sapwood (maples) or tracheid sapwood (pines) were shallower rooted. These differences in rooting depth were related to sap flux of trees during and immediately after periods of drought. The extent that the patterns observed in central Pennsylvania are modulated by environment or indicative of other plant species will be discussed.

URL : http://ecosystems.psu.edu/research/labs/root-ecology

Final ID: PA14A-02

Water Resource Impacts During Unconventional Shale Gas Development: The Pennsylvania Experience

S. L. Brantley; [1]; *D. Yoxtheimer;* [1]; *S. Arjmand;* [2]; *P. Grieve;* [1]; *R. Vidic;* [2]; *J. D. Abad;* [2]; *C. A. Simon;* [2]; *J. Pollak;* [3];

1. Penn State Univ, University Park, PA, United States.
2. University of Pittsburgh, Pittsburgh, PA, United States.
3. CUAHSI, Medford, MA, United States.

Body: The number of unconventional Marcellus shale wells in PA has increased from 8 in 2005 to more than 6000 today. This rapid development has been accompanied by environmental issues. We analyze publicly available data describing this Pennsylvania experience (data from www.shalenetwork.org and PA Department of Environmental Protection, i.e., PA DEP). After removing permitting and reporting violations, the average percent of wells/year with at least one notice of violation (NOV) from PA DEP is 35 %. Most violations are minor. An analysis of NOVs reported for wells drilled before 2013 revealed a rate of casing, cement, or well construction issues of 3.4%. Sixteen wells were given notices specifically related to migration of methane. A similarly low percent of wells were contaminated by brine components. Such contamination could derive from spills, subsurface migration of flowback water or shallow natural brines, or contamination by drill cuttings. Most cases of contamination of drinking water supplies with methane or brine components were reported in the previously glaciated part of the state. Before 2011, flowback and production water was often discharged legally into streams after minimal treatment, possibly increasing dissolved Br concentrations in some rivers. The rate of large spills or releases of gas-related industrial wastes in the state peaked in 2009 but little evidence of spills has been found in publicly available surface water chemistry data. The most likely indicators of spillage or subsurface release of flowback or production waters are the dissolved ions Na, Ca, and Cl. However, the data coverage for any given analyte is generally spatially and temporally sparse. Publicly available water quality data for before and after spills into Larrys Creek and Bobs Creek document the difficulties of detecting such events. An observation from the Pennsylvania experience is that the large number of people who have complained about their water supply (~1000 letters investigated by state regulators) and the media attention during the fast start in PA may have led to better management practices. Maintaining online databases of observations could similarly drive shale-gas practice to become even more environmentally protective.

Final ID: TH15D-01

Critical Zone Science and Observatories

S. L. Brantley; [1]; *T. S. White;* [1]; *S. P. Anderson;* [2]; *R. C. Bales;* [3]; *J. Chorover;* [4]; *W. H. McDowell;* [5];
1. Earth & Environmental Systems Institute, Penn State University, University Park, PA, United States.
2. Geography, University of Colorado-Boulder, Boulder, CO, United States.
3. School of Engineering, University of California-Merced, Merced, CA, United States.
4. Institute of the Environment, University of Arizona, Tucson, AZ, United States.
5. Natural Resources and the Environment, University of New Hampshire, Durham, NH, United States.

Description: Critical Zone Observatories (CZOs) are natural laboratories for investigating Earth surface processes by monitoring streams, climate and groundwater. CZOs are instrumented for hydrogeochemical measurements of soil, canopy and bedrock. The US CZO network grew to 9 observatories in 2013. The cross-disciplinary teams use field and theoretical approaches, and include education and outreach such as the townhall.

Final ID: H23F-1330

Temporal and Spatial Patterns of Preferential Flow Occurrence in the Shale Hills Catchment: From the Hillslope to the Catchment Scales

H. Liu;[1, 2]; *H. Lin;*[1];
1. Deptment of Ecosystem Science and Management, The Pennsylvania State University, University Park, PA, United States.
2. Cold and Arid Regions Environmental & Engineering Research Institute, Chinese Academy of Sciences, Lanzhou, Gansu, China.

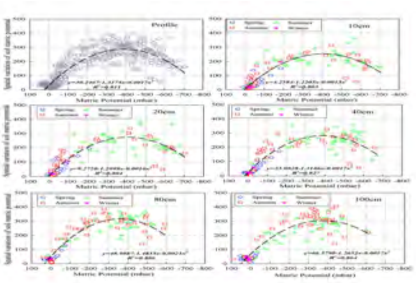
Body: Understanding temporal and spatial patterns of preferential flow (PF) occurrence is important in revealing hillslope and catchment hydrologic and biogeochemical processes. Quantitative assessment of the frequency and control of PF occurrence in the field, however, has been limited, especially at the landscape scale of hillslope and catchment. By using 5.5-years' (2007-2012) real-time soil moisture at 10 sites response to 323 precipitation events, we tested the temporal consistency of PF occurrence at the hillslope scale in the forested Shale Hills Catchment; and by using 25 additional sites with at least 1-year data (2011-2012), we evaluated the spatial patterns of PF occurrence across the catchment. To explore the potential effects of PF occurrence on catchment hydrology, wavelet analysis was performed on the recorded time series of hydrological signals (i.e., precipitation, soil moisture, catchment discharge). Considerable temporal consistence was observed in both the frequency and the main controls of PF occurrence at the hillslope scale, which was attributed largely to the statistical stability of precipitation pattern over the monitoring period and the relatively stable subsurface preferential pathways. Preferential flow tended to occur more often in response to intense rainfall events, and favored the conditions at dry hilltop or wet valley floor sites. When upscaling to the entire catchment, topographic control on the PF occurrence was amplified remarkably, leading to the identification of a subsurface PF network in the catchment. Higher frequency of PF occurrence was observed at the valley floor (average 48%), hilltop (average 46%), and swales/hillslopes near the stream (average 40%), while the hillslopes in the eastern part of the catchment were least likely to experience PF (0-20%). No clear relationship, however, was observed between terrain attributes and PF occurrence, because the initiation and persistency of PF in this catchment was controlled jointly by complex interactions among landform units, soil types, initial soil moisture, precipitation features, and season. Through the wavelet method (coherence spectrum and phase differences), dual-pore filtering effects of soil system were proven, rendering it possible to further infer characteristic properties of the underlying hydrological processes in the subsurface. We found that preferential flow dominates the catchment discharge response at short-time periods (< 3 days), while the matrix flow may dominate the discharge response at the time scales of around 10-12 days. The temporal and spatial patterns of PF occurrence revealed in this study can help advance the modeling and prediction of complex PF dynamics in this and other similar landscapes.

Final ID: H23F-1331

Temporal stability of soil matric potential in the Shale Hills Critical Zone Observatory

H. Yu; [1, 2]; *H. Lin;* [2]; *W. Berger;* [2]; *P. Yang;* [1];
1. College of Water Resources & Civil Engineering, China Agricultural University, Beijing, China.
2. Pennsylvania State University Main Campus, STATE COLLEGE, PA, United States.

Body: This study utilized a 6-yr database consisting of catchment-wide soil matric potential (MP) measurements at 62 locations from the surface down to 1.0 m depth within the 7.9-ha Shale Hills Critical Zone Observatory in Pennsylvania. The objectives were to: (1) assess the temporal stability of soil MP spatial distribution pattern; and (2) examine the temporal variability of soil MP across the catchment. Our results showed that spatial variability of soil MP increased parabolically with decreasing catchment-wide average MP across all measurement depths and different seasons. This relationship is different from the exponential relationship between soil moisture content spatial variability and catchment-averaged volumetric soil moisture, which could be attributed to the nonlinearity of the soil water retention curve. Moreover, the spatial variability of soil MP was also found to be related to topographical characteristics as higher variation of MP was observed in the valley sites. Based on the analysis of Mean Relative Difference, the spatial pattern of soil MP varied among different depths and no one single location had the same ranking more than two layers, indicating the lack of soil moisture correspondence between layers. The spatial pattern of soil MP was more stable over time under wet conditions, but less stable during the drying periods. The results of this study can help optimal design and plan for monitoring and sampling, and provide insights regarding hydropedological processes at the pedon, hillslope, and catchment scales.



Spatial variability of soil matric potential in relation to catchment-wide mean matric potential at each of the five depths and the profile.

Final ID: H23F-1332

Resolving the High Resolution Soil Moisture Pattern at the Shale Hills Watershed Using a Land Surface Hydrologic Model

Y. Shi; [1, 2]; *D. C. Baldwin;* [3]; *K. J. Davis;* [2]; *X. Yu;* [4]; *C. Duffy;* [4]; *H. Lin;* [5];

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2. Meteorology, The Pennsylvania State University, University Park, PA, United States.
3. Geography, The Pennsylvania State University, University Park, PA, United States.
4. Civil Engineering, The Pennsylvania State University, University Park, PA, United States.
5. Ecosystem Science & Management, The Pennsylvania State University, University Park, PA, United States.

Body: Soil moisture is a critical variable for water and energy cycle. It determines the partitioning of available energy into sensible, latent and ground heat fluxes, as well as the partitioning of incoming precipitation into surface runoff and infiltration. The prediction of soil moisture pattern at high spatial resolution, however, is challenging. This project aims to answer the following questions: (1) Can we predict the observed high resolution soil moisture pattern (10^0-10^1 m) using numerical models? (2) What data and modeling techniques are needed to resolve fine scale land surface heterogeneities using numerical models? and (3) Is national soil database sufficient for high resolution modeling?

The model used in this project is a coupled land surface hydrologic model, Flux-PIHM, which adds a land surface balance scheme to the Penn State Integrated Hydrologic Model (PIHM). Flux-PIHM has been implemented at the Shale Hills watershed (0.08 km^2) in central Pennsylvania with an average grid size of 150 m^2. The locally measured soil maps, soil parameters, and tree map, as well as LiDAR topographic data have been synthesized into the Flux-PIHM model to provide soil, land cover, and topography inputs.

Calibrated only using watershed-scale data (i.e., discharge and surface heat fluxes) and point measurements (i.e., soil moisture and water table depth at one location), and driven by spatially uniform forcing data, Flux-PIHM is able to resolve the observed hill-slope scale (10^1 m) soil moisture pattern at the watershed owing to the spatially-distributed physically-based hydrologic component, especially the simulation of horizontal groundwater flow. The model successfully reproduces the seasonal change of soil moisture, and resolves the observed soil moisture pattern. This ability of Flux-PIHM to resolve hill-slope patterns is unique relative to current land surface models, and is especially significant for high-resolution simulations at small watersheds, which represent a large areal fraction of many landscapes.

To test the important factors that drive the fine-scale soil moisture pattern, different Flux-PIHM runs using different combinations of soil maps, soil parameters, and bedrock depths are performed. While different test cases are all able to provide good agreement with catchment-scale observations and point observations, the predicted soil moisture patterns are considerably different among different test cases. Model results show that the prediction of soil moisture distribution is strongly driven by the input soil maps and soil parameters, as well as topography (surface elevation and bedrock depth); water table position is determined by surface topography and bedrock depth. Results suggest that using the filed measured soil maps and parameters significantly improves the predicted soil moisture pattern, compared with using the national database (SSURGO) 30-m resolution product.

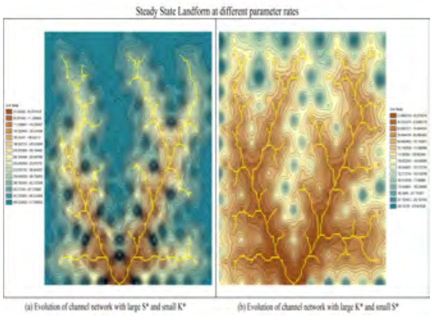
Final ID: EP33A-0858

A New Hydrologic-Morphodynamic Model for Regolith Formation and Landscape Evolution

Y. Zhang; [1, 2]; *R. L. Slingerland;* [2]; *C. Duffy;* [1];
1. Department of Civil and Environmental Engineering, The Pennsylvania State University, STATE COLLEGE, PA, United States.
2. Department of Geoscience, The Pennsylvania State University, STATE COLLEGE, PA, United States.

Body: Abstract

Feedbacks between regolith formation and removal and accompanying hydrological processes require a landscape evolution model coupling vertical uplift, soil production by bedrock weathering, and regolith transport with a hydrologic model. Here we present a new version of the Penn State Integrated Hydrologic Model (PIHM) that computes the feedbacks among infiltration, recharge, groundwater and surface water runoff, creation of regolith and its erosion by streams, and downslope movement by tree-throw. The equation set is solved using the semi-discrete finite volume method. The groundwater table evolves during deposition and erosion of regolith and tree-throw. Three non-dimensional parameters govern the behavior of the system: 1) W*=Po/U, the ratio of the weathering rate of bare bedrock to the rock uplift rate; 2) K*=K/UL, the ratio of hillslope diffusivity to rock uplift rate times a system lengthscale; and 3) S*=D/UL, the ratio of overland sediment transport diffusivity to uplift rate times a system lengthscale. Steady-state landforms of an artificial watershed possess convex and smooth channel profiles if K* relative large and S* is small, whereas S* dominant landscapes possess concave and sharp channel and mountain profiles. The set of analysis also reveal that even though the ratios are the same, higher uplift rate accelerates the time to steady state.



Steady State Landforms at Different Parameter Rates

Final ID: H33L-01

Water-Organic-Rock Reactions Recorded in Pores in Shales from the Marcellus and Rose Hill Formations *(Invited)*

S. L. Brantley; [1]; *L. Jin;* [2]; *G. Rother;* [3]; *D. R. Cole;* [4]; *x. gu;* [1]; *V. N. Balashov;* [1];

1. Geosciences/EESI, Penn State University, University Park, PA, United States.
2. Geological Sciences, University of El Paso, TX, El Paso, TX, United States.
3. Oak Ridge National Laboratory, Oak Ridge, TN, United States.
4. School of Earth Sciences, Ohio State University, Columbus, OH, United States.

Body: The porosity of shales varies depending upon such attributes as the mineralogy, grain size, organic content, depth and duration of burial, and extent of water-rock reaction. Today, shales are being exploited when they contain significant natural gas, and the connectivity of pores are important toward controlling both recovery of gas after hydrofracking. In fact, the fine-scale nature of the pores controls aspects of release of natural gas and brines during hydrofracturing and gas exploitation.

Despite the importance of shale as a source rock for natural gas and petroleum, it remains difficult to quantify and image porosity in shales because of their fine-scale nature. We are using neutron scattering, FIB SEM, CT microtomography, and other techniques to understand pores in a black (Marcellus) and a grey shale (Rose Hill formation) sampled in Pennsylvania. Samples were recovered both from outcrop and from depth in wellbores. We also report a new approach for investigating pores in shales by using neutron scattering before and after removal of organic matter.

Pores in the two shales are observed to be isotropic (i.e. in the plane of bedding) or anisotropic (i.e. perpendicular to bedding), as expected for sediments that have been compacted after burial. Some nanometer-sized pores are observed in the organic matter of the Marcellus to be spherical; other pores are observed to be present in pyrite framboids and among silicate grains in that rock. We have no evidence that significant porosity is present in the organic matter in the Rose Hill formation, a relatively organic-poor shale, but pores are observed between and in clay particles.

We also investigate how progressive water-rock reaction changes the primary porosity in the shales by investigating weathering samples. FIB SEM images document that organic matter is oxidized and removed significantly from the weathering Marcellus before the rock turns to soil, leaving behind porosity. Pyrite oxidation and dissolution also creates pores in the Marcellus bedrock before it turns to soil. Only the latter process is significant in the Rose Hill shale. Unlike other weathering rocks (granites, diabase, basalt), the pores in the shales comprise surface fractals both before and after weathering. Understanding how water enters and transforms pores in shales at depth and near surface will increase our ability to protect our water and soil resources, as well as inform our methods of gas recovery.

Final ID: H41L-05

The Catchment Isoscape: Theory and Experimental Evidence for the Isotopic Age of Water in a Critical Zone Observatory *(Invited)*

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Body: This paper deals with the theoretical controls for the “Age” of water in upland watershed flow systems and present comprehensive experimental evidence to support the theory using stable isotopes of and at the Susquehanna/Shale Hills Critical Zone Observatory (SSH_CZO). In this context “age” is defined as the time since water entered the watershed as precipitation. The paper first examines the theoretical basis for direct simulation of “age” for environmental tracers in the unsaturated zone subject to dynamic flow and transport processes with mobile and immobile flow considered. The theory demonstrates that the residence time and age of an environmental tracer can be directly modeled without knowledge of the form of the underlying residence time distribution function and without adding any new parameters. On the physical side, the theory is applied to the apparent rapid attenuation of event and seasonal isotopic ratios with depth in the soil at the SSH_CZO. Comparison of the age model to experimental data provides evidence for the role of macropore-matrix flow partitioning during the non-growing cold season and root uptake from the immobile store during the growing season via transpiration and evaporation. Flow path changes during storm events are also inferred by comparing the distribution of groundwater and streamflow isotope histories.

Final ID: U42A-03

A call for a community strategy to the “Essential Terrestrial Variables” necessary for catchment modeling anywhere in the US *(Invited)*

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Body: Water is an essential human resource and an agent of earth system processes that is playing an increasing role in global environmental and political issues (NRC 2004). As such there is a national need to provide seamless and fast access to essential geo-spatial/geo-temporal data to support the physics-based numerical models necessary to understand, predict and manage the nations surface and groundwater resources. The heterogeneity of data sources and access methods for data sources across multiple agencies has resulted in a lack of interoperability between data repositories required to support integrative data-intensive computation that addresses national and continental scale water problems.
In this paper we review the existing national data sets necessary to support catchment models that resolve upland stream features (hillslopes, 1st, 2nd and 3rd order streams), and make the case for a community adoption of the “Essential Terrestrial Variables” (ETV) necessary to support hydrologic modeling supported by national data anywhere in the US. The concept of ETV’s evolves from the WMO’s adoption of Essential Climate Variables.
We argue for a community approach for an integrated system of data sources that provides seamless access to the ETV data required to support water models at multiple scales across the continent (WMO, 2011). We envisage collaborative data access arrangements with Federal and other data providers coupled to workflows to parse and repackage data into a form ready for use by models in near real time for retrospective investigation and for scenario development of climate and landuse change impacts.

Final ID: H43L-07

Cross-CZO Contrasts: Aspect Controls and Critical Zone Architecture

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Body: We investigate aspect controls on Critical Zone (CZ) architecture, mobile regolith transport, and landscape morphology, based on a cross-CZO comparison of 1) Niwot Ridge, Boulder Creek CZO (BcCZO), a high alpine site with minimal soil/veg cover, characterized by steep S-facing and shallow N-facing hillslopes and 2) Shale Hills CZO (SSHCZO), a temperate, densely-forested, soil-mantled site with steep N-facing slopes and shallow S-facing slopes. We use high-resolution 2D seismic tomography of P- and S-wave velocities (Vp, Vs) to characterize CZ architecture and constrain depths of weathering fronts, as well as the thickness, character, and transport efficiency of mobile regolith layers. The 2D imagery allows assessment of changes in material properties both lateral and vertical (depth), thus mapping variability in CZ structures along the survey profile. The combination of Vp and Vs are used to better quantify material properties, (i.e., elastics moduli, density, fractures porosity), rock-mass strength, and weathering intensity – and when applied to the very shallow subsurface can help constrain the transport efficiency (strength or erodibility) of mobile regolith layers

On Niwot Ridge, the depth of the weathering front and thickness of mobile regolith are substantially greater on shallower N-facing slopes, consistent with frost/freeze driven processes. However, the depth of the weathering front far exceeds modeled extents of frost-cracking depth (for past or present climates), suggesting additional processes also influence deep weathering. Mobile regolith is considerably thicker on shallow N-facing aspects and composed of large, disintegrated cobbles, however, velocity-based estimates of transport efficiency are higher on S-facing slopes composed of small talus blocks and thin soil/veg cover. Although, thin mobile regolith on S-facing slopes may be weak (slow V), the lower gradient of N-facing slopes and southward asymmetry of the ridge divide, suggests that transport efficiency is greatest on N-facing slopes. This may be explained by the dominance of frost/freeze process, which can readily lift or break, and provide a remarkably efficient process to transport the thick mobile regolith layer of large cobbles.

At SSHCZO, depths of weathering fronts are invariant with slope aspect, suggesting that aspect control is not a predominant mechanism driving regolith production. Mobile regolith thickness, however, is more than 2-fold greater on N-facing slopes. Additionally, the mobile regolith on both slope aspects is primarily composed of well-developed soils. N-facing soils are thicker with greater cohesion, moisture, and inclusion of rock fragments. This is consistent with velocity-based estimates of lower transport efficiency on N-facing slopes relative to the thin, dry, fine grained soils on S-facing slopes.

These results suggest fundamental differences in CZ architecture, weathering processes, and the influence of slope aspect between BcCZO and SSHCZO

Final ID: H43L-08

Geologic controls on fracture distributions within the Shale Hills Critical Zone Observatory

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Body: We investigate the roles of lithologic heterogeneity and spatial patterns of bedrock fracturing within the Susquehanna-Shale Hills Critical Zone Observatory and their feedbacks to groundwater flow and weathering processes. Based on detailed field observations and a series of down-hole geophysical logs from 8 boreholes, we characterize the local structure and geology within the catchment and explore variations in fracture density and orientation across the catchment and with depth, allowing us to look at relationships between geology and fracture distribution. While the geologic template of a catchment system often creates fractures, fractures in turn affect that template by influencing rates of erosion and weathering. The most prevalent fracturing occurs along bedding planes, setting the dominant fracture orientation in the catchment. Variation in rock type and strength control fracture distribution and ultimately groundwater flow and weathering front locations. The prevalence of fracturing within the bedrock likely serves as an important control on the “active depth of flow,” the subsurface zone that responds to annual recharge and climatic variability and has groundwater residence times that become older as a particle moves from recharge to discharge areas.

We find systematic differences in hydraulic conductivity beneath ridgelines and valleys that map fracture density; both were higher beneath the valley floor when compared to the ridgetop. While we see higher fracturing near the surface and in the valley, the orientation of fracturing is not significantly different in terms of location within the watershed. Borehole gamma-ray emission measurements, XRD, and major element analysis suggest a loss of clay minerals near the surface, with slightly greater weathering within the valley when compared to the ridge top. These data demonstrate a potential weathering-fluid flow feedback driven by fracture abundance: valleys may act as “drains” for shallow groundwater flow through watersheds, potentially driving a positive feedback in which water penetrates deeper and faster into deeper valleys, accelerating the weathering that breakdown the bedrock, and enhancing the growth of valley relief. Our results suggest that fractures likely control groundwater flow within the deeper watershed, but patterns in the observational data provide evidence of fairly consistent fracture orientation and rock structure throughout the watershed.

Final ID: H51A-1174

Understanding the Hydrological Controls on the Water Chemistry at the Watershed Scale Using an Integrated Hydro-Thermo-Geochemical Model PIHM-RT

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Body: Hydrological and geochemical processes are intricately coupled at the watershed scale. Despite recent advances, modeling the complex hydro-thermo-geochemical interactions at the watershed scale has been challenging. Many efforts have been put forward to solve the well-known puzzles such as the “double paradox ” raised by Kirchner either mechanistically or through simplified numerical modeling. However, a major gap remains in explicitly modeling and integrating these processes at the watershed scale.

This work presents an integrated approach to understanding and quantifying the hydrologic controls on water chemistry at the watershed scale. A fully coupled finite volume hydro -thermo-geochemical model, PIHM-RT (Penn State Integrated Hydrologic Model --Reactive Transport) has been developed based on the land surface hydrologic model, Flux-PIHM. Flux-PIHM is capable of simulating the terrestrial water cycle and the surface energy balance (SEB) to reproduce the spatially distributed observations of water, temperature, and saturation . Adding the reactive transport module enables explicit modeling of the evolving water chemistry, which is controlled by hydrologic processes and geochemical reactions. The reactions include mineral dissolution, precipitation and ion exchange. PIHM-RT utilizes an a priori database EQ3\EQ6 that is widely used for geochemical thermodynamics and kinetics. The RT module utilizes an operator splitting scheme described in Zysset et al. (1994), to solve for the advection-dispersion-reaction equation (ADR). The advection dispersion equation was solved using the Euler forward method and the reaction process was solved implicitly. In addition, because the reaction and transport processes differ significantly between the unsaturated and saturated zones, we implemented a volume explicit mass conservation law to account for the variable depth of groundwater and the mixing process involved at the boundary between the saturated and unsaturated zone. The use of an unstructured mesh in PIHM-RT provides an optimal representation of heterogeneity in both hydrological and geochemical parameters. In sum, PIHM-RT presents a powerful tool to test hypotheses against key hydrologic and geochemical observations at the watershed scale (HUC-12 sized or less). We will demonstrate the use of PIHM-RT with constraints from field data collected at the Shale Hills watershed (0.08 km2). PIHM-RT is expected to be a general tool for understanding coupled hydro-geochemical processes in the Critical Zone.

Final ID: H51B-1186

Quantifying the signature of the industrial revolution from Pb and Cd isotopes in the Susquehanna Shale Hills Critical Zone Observatory

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Body: Anthropogenic forcings have dominated metal cycling in many environments. During the period of the industrial revolution, mining and smelting of ores and combustion of fossil fuels released non-negligible amounts of potentially toxic metals such as Pb, Cd, Mn, and Zn into the environment. The extent and fate of these metal depositions in soils during that period however, have not been adequately evaluated.
Here, we combine Pb isotopes with Cd isotopes to trace the sources of metal pollutants in a small temperate watershed (Shale Hills) in Pennsylvania. Previous work has shown that Mn additions to soils in central PA was caused by early iron production, as well as coal burning and steel making upwind. Comparison of the Pb and Cd concentrations in the bedrock and soils from this watershed show that Pb and Cd in soils at Shale Hills are best characterized by addition profiles, consistent with atmospheric additions. Three soil profiles at Shale Hills on the same hillslope have very similar anthropogenic Pb inventories. Pb isotope results further reveal that the extensive use of local coals during iron production in early 19th century in Pennsylvania is most likely the anthropogenic Pb source for the surface soils at Shale Hills. Pb concentrations and isotope ratios were used to calculate mass balance and diffusive transport models in soil profiles. The model results further reveal that during the 1850s to 1920s, coal burning in local iron blasting furnaces significantly increased the Pb deposition rates to 8-14 μg cm-2 yr-1, even more than modern Pb deposition rates derived from the use of leaded gasoline in the 1940s to 1980s.
Furthermore, Cd has a low boiling point (~760 °C) and easily evaporates and condenses. The evaporation and condensation processes could generate systematic mass-dependent isotope fractionation between Cd in coal burning products and the naturally occurring Cd in the sulfide minerals of coals. This fractionation indicates that Cd isotopes can be used as a novel tracer of materials that have been affected by industrial high temperature processes, distinguishing them from natural Cd sources. Our ongoing Cd isotope measurements in the same soil profiles thus hold significant promise for tracing anthropogenic sources of this highly toxic metal in the environment. This will be the first time that Cd isotopes are characterized for polluted soils related to coal-burning activities. Such information will provide the first Cd isotope dataset to assess the environmental impacts due to the use of coals on a global scale. These new Pb and Cd isotope results, along with previous observations of Mn enrichment at Shale Hills, suggest that historical point sources from the industrial revolution could contribute significant amounts of metal contamination to top-soils. Our study highlights the importance of using multiple isotope systems to investigate Critical Zone processes in identical lithology and environmental settings.

Final ID: H51B-1190

Boron isotopes at the Shale Hills critical zone observatory

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Body: Small catchments are an ideal tool for deciphering the geochemical signature of continental rock chemical weathering processes. Distinguishing between the effect of biological mineralogical and hydrological processes is still a challenge but recent advancements in non-traditional isotopes have proven useful in this endeavor. Among the different isotopic systems of the weathering toolbox, boron isotopic ratios provide an interesting perspective since boron isotopes in the Critical Zone are fractionated both by biological processes (boron is an essential nutrient to the vegetation) and by re-incorporation in secondary minerals.

We analyzed boron isotopes (δ11B) on a variety of hydrologic, biologic, and geologic materials across the Susquehanna Shale Hills Critical Zone Observatory. Boron isotopic ratios were obtained by MC-ICP-MS Neptune following the Louvat et al. (2010) procedure.

Preliminary results indicate that δ11B of the stream water at Shale Hills is slightly lighter at the outlet of the basin (15.28‰ compared to the upper stream values of 16.43‰ and 17.35‰) and is enriched by as much as 20 ‰ when compared to the stream sediments. The groundwater display a contrasting behavior between the upper (15.62‰) and the lower part (5.67‰) of the catchment. Assuming that boron isotopes are not affected by silicate rocks dissolution, the 11B stream water enrichment can be attributed either to water/rock interaction (with the input of isotopically lighter groundwater); 10B being preferentially incorporated into secondary phases, or to the contribution of the vegetation, whose isotopic composition is highly enriched in 11B (values as high as 43‰ have been reported in throughfalls by Cividini et al. (2010) in a granitic critical observatory of the Strengbach basin, France).

These clearly distinct isotopic compositions allow us to constrain the processes that control the stream water composition.

Louvat et al. (2010) Geostand and Geoanal Res 35, 75-88

Cividini et al. (2010) Geochim et Cosmochim Acta 74, 3143-3163

Final ID: H51B-1194

Weathering and solute transport to the Salar de Atacama, northern Chile

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Body: The Salar de Atacama is situated in a tectonic basin on the Tropic of Capricorn, adjacent to the Central Andean Volcanic Zone in hyper-arid northern Chile. This basin has been hydrographically closed for most, if not all, of the Cenozoic. Since the late Miocene, chemical sediment (primarily halite, but also sulphate) and Na-Cl brines have accumulated. The volume of these deposits provides a constraint on long term average solute fluxes. We have undertaken an extensive multiple isotope study of surface and shallow groundwater in the basin to constrain processes and pathways affecting solute fluxes to the basin. By comparing these inflow waters to brackish waters and brines, we are able to place constraints on modern weathering with the ultimate goal of comparing it to longer term fluxes estimated from the geologic record. The volcanic arc and extensive large volume silicic magma chambers provide potential sources of solutes to the basin which are not a direct result of surficial weathering (hydrothermal waters/magmatic brines). For most freshwater, this possibility is ruled out. Oxygen and hydrogen isotopes in water provide no strong evidence for high temperature water-rock interaction. Further, the isotopic composition of helium dissolved in groundwater demonstrates that most groundwater carries an atmospheric signal (air saturated water), though some evidence for the influence of magmatic brines is found in shallow groundwater with high concentrations of helium-3, methane, and carbon dioxide. The strontium isotopic composition of waters and brines exhibits geographic variation that is related to at least four sources; 1) weathering of Andean volcanic arc along the eastern margin of the basin (87/86 ratios ~0.708), 2) thermal waters sourced in the northern headwaters of the Río San Pedro and 3) high calcium weathering fluxes from the Cordón de Lila on the southern margin of the basin, both of which have more radiogenic 87/86 ratios than the Andean volcanic arc, and 4) the least radiogenic 87/86 ratios which are found along the western margin of the basin and may have their source in the Cordillera Domeyko. The Sr isotope composition of brine in Salar de Atacama is dominated by sources from the Neogene to modern volcanic arc along its eastern margin. Lithium isotope ratios of freshwater influx are depleted in lithium-7 compared to the brines, and brackish waters are transitional between the two. These data implicate precipitation and/or dissolution of secondary minerals, as the majority of these processes take place where freshwater interacts with evaporite minerals, brackish water, and brines. The lithium isotopic composition of water draining the volcanic arc suggest a limited role for precipitation of Li-bearing secondary minerals associated with freshwater solute fluxes in surface and shallow groundwater. Near surface solute fluxes are constrained by concentrations of tritium, an anthropogenic radioisotope of hydrogen indicative of groundwater recharge (and residence times) within the last 60 years. This multi-isotope approach demonstrates how isotope geochemistry can identify and constrain important processes, pathways and timescales in the Critical Zone.

Final ID: H54A-03

Going Steady: Using multiple isotopes to test the steady-state assumption at the Susquehanna Shale Hills Critical Zone Observatory *(Invited)*

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Body: Regolith-mantled hillslopes are ubiquitous features of most temperate landscapes, and their morphology reflects the climatically, biologically, and tectonically mediated interplay between regolith production and downslope transport. Despite intensive research, few studies have quantified both of these mass fluxes in the same field site. Here, we exploit two isotopic systems to quantify regolith production and transport within the Susquehanna Shale Hills Critical Zone Observatory (SSHO), in central Pennsylvania. We present an analysis of 131 meteoric ^{10}Be measurements from regolith and bedrock to quantify rates of regolith transport, and compare these data with previously determined regolith production rates, measured using uranium-series isotopes. Regolith flux inferred from meteoric ^{10}Be varies linearly with topographic gradient (determined from high-resolution LiDAR-based topography) along the upper portions of hillslopes in and adjacent to SSHO. However, regolith flux appears to depend on the product of gradient and regolith depth where regolith is thick, near the base of hillslopes. Meteoric ^{10}Be inventories along 4 ridgetops within and adjacent to the SSHO indicate regolith residence times ranging from ~ 9 – 15 ky, similar to residence times inferred from U-series isotopes (6.7 ± 3 ky – 15 ± 8 ky). Similarly, the downslope flux of regolith (~ 500 – 1,000 m^2/My) nearly balances production (850 ± 22 m^2/My – 960 ± 530 m^2/My). The combination of our results with U-series derived regolith production rates implies that regolith production and erosion rates along ridgecrests in the SSHO may be approaching steady state conditions over the Holocene.

Final ID: H54A-05

Using C and S isotopes to elucidate carbonic versus sulfuric acid reaction pathways during shale weathering in the Susquehanna Shale Hills Critical Zone Observatory

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Body: Chemical weathering of silicate minerals via the carbonic acid reaction pathway regulates global climate on geological timescales. However, strong acids are also key dissolution agents that drive silicate and carbonate weathering. In order to assess the potentials of silicate weathering on CO_2 consumption, it is crucial to separate carbonic acid versus sulfuric acid reaction pathways, and also to separate the contribution of stream-dissolved inorganic carbon (DIC) from silicate versus carbonate dissoution. Here we address these two questions using C and S isotopes at the well-studied Susquehanna Shale Hills Critical Zone Observatory (SSHO).

In shallow soils of SSHO, clay dissolution dominates. Here soil waters are charaterized by low [DIC], which is controlled by equilibrium with soil pCO_2. Carbonate minerals, in this Rose Hill Shale formation, are depleted in soils and have only been observed in few bedrock boreholes, i.e. at > 23m depth at ridges and > 2m depth under the valley. Indeed, some groundwaters have much higher [DIC], [Mg] and [Ca], presumably due to ankerite dissolution. Accompanied by the transition from silicate weathering in shallow soils to carbonate weathering below the water table, the source of sulfate shifts with depth from atmospheric deposition to pyrite dissolution. Apparently, the weathering fronts of ankerite and pyrite are at almost the same depth. The $\delta^{13}C_{DIC}$ values of these groundwaters indicate C mixing equally from ankerite and soil CO_2, with only slight modification by the sulfuric acid pathway.

Groundwater chemistry evolves to different extents with respect to ankerite saturation because the depths to ankerite weathering fronts vary due to heterogeneity of the Rose Hill shales and landscape position. Interestingly, groundwaters along the valley floor at the outlet of the first-order catchment are influenced by carbonate dissolution but also show S isotope signatures indicative of anthropogenic sulfate in wet precipitation. This provides another line of evidence that at least some of the carbonate we observe at shallow depths in the valley floor may be secondary. Indeed, C isotopes of some of the shallow carbonates differ from those in Rose Hill bedrock.

Comparison between groundwater and soil water chemistry shows that at SSHO most DIC derives from the dissolution of carbonate minerals, i.e., primary ankerite or secondary carbonate. Sulfate derives almost entirely from atmospheric deposition in soil waters and some groundwater near the outlet; however, its source shifts to pyrite dissolution in groundwaters from ridges and headwater areas. Overall, in this catchment underlain by grey shale, the sulfuric acid pathway is insignicant due to the low pyrite content in comparison to ankerite or secondary carbonate.