COVER SHEET FOR PROPOSAL TO THE NATIONAL SCIENCE FOUNDATION

PROGRAM ANNOUNCEMENT/SOLICITATION NO./CLOSING DATE/if not in response to a program announcement/solicitation enter NSF 13-1 **NSF 12-575** **02/05/13**	FOR NSF USE ONLY NSF PROPOSAL NUMBER
FOR CONSIDERATION BY NSF ORGANIZATION UNIT(S) (Indicate the most specific unit known, i.e. program, division, etc.) **EAR - CZO: CRITICAL ZONE OBSER SOLIC**	

DATE RECEIVED	NUMBER OF COPIES	DIVISION ASSIGNED	FUND CODE	DUNS# (Data Universal Numbering System)	FILE LOCATION
				003403953	

EMPLOYER IDENTIFICATION NUMBER (EIN) OR TAXPAYER IDENTIFICATION NUMBER (TIN)	SHOW PREVIOUS AWARD NO. IF THIS IS ☒ A RENEWAL ☐ AN ACCOMPLISHMENT-BASED RENEWAL	IS THIS PROPOSAL BEING SUBMITTED TO ANOTHER FEDERAL AGENCY? YES ☐ NO ☒ IF YES, LIST ACRONYM(S)
246000376	**1239285**	

NAME OF ORGANIZATION TO WHICH AWARD SHOULD BE MADE **Pennsylvania State Univ University Park**	ADDRESS OF AWARDEE ORGANIZATION, INCLUDING 9 DIGIT ZIP CODE **Pennsylvania State Univ University Park** **110 Technology Center Building** **UNIVERSITY PARK, PA. 168027000**
AWARDEE ORGANIZATION CODE (IF KNOWN) **0033290000**	
NAME OF PRIMARY PLACE OF PERF **Pennsylvania State Univ University Park**	ADDRESS OF PRIMARY PLACE OF PERF, INCLUDING 9 DIGIT ZIP CODE **Pennsylvania State Univ University Park** **225B Earth-Engineering Sci Bldg** **University Park ,PA ,168025000 ,US.**

IS AWARDEE ORGANIZATION (Check All That Apply) (See GPG II.C For Definitions) ☐ SMALL BUSINESS ☐ FOR-PROFIT ORGANIZATION ☐ MINORITY BUSINESS ☐ WOMAN-OWNED BUSINESS ☐ IF THIS IS A PRELIMINARY PROPOSAL THEN CHECK HERE

TITLE OF PROPOSED PROJECT **Using the Susquehanna - Shale Hills CZO to Project from the Geological Past to the Anthropocene Future**

REQUESTED AMOUNT	PROPOSED DURATION (1-60 MONTHS)	REQUESTED STARTING DATE	SHOW RELATED PRELIMINARY PROPOSAL NO. IF APPLICABLE
$ **5,000,000**	**60** months	**11/01/13**	

CHECK APPROPRIATE BOX(ES) IF THIS PROPOSAL INCLUDES ANY OF THE ITEMS LISTED BELOW

☐ BEGINNING INVESTIGATOR (GPG I.G.2)
☐ DISCLOSURE OF LOBBYING ACTIVITIES (GPG II.C.1.e)
☐ PROPRIETARY & PRIVILEGED INFORMATION (GPG I.D, II.C.1.d)
☐ HISTORIC PLACES (GPG II.C.2.j)
☐ EAGER* (GPG II.D.2) ☐ RAPID** (GPG II.D.1)
☐ VERTEBRATE ANIMALS (GPG II.D.6) IACUC App. Date ________
PHS Animal Welfare Assurance Number ________
☐ HUMAN SUBJECTS (GPG II.D.7) Human Subjects Assurance Number ________
Exemption Subsection ________ or IRB App. Date ________
☐ INTERNATIONAL COOPERATIVE ACTIVITIES: COUNTRY/COUNTRIES INVOLVED (GPG II.C.2.j)
____

PI/PD DEPARTMENT **Earth & Environmental Systems Institute**	PI/PD POSTAL ADDRESS **2217 Earth & Engineering Sciences Bldg.** **University Park, PA 16802** **United States**
PI/PD FAX NUMBER **814-865-3191**	

NAMES (TYPED)	High Degree	Yr of Degree	Telephone Number	Email Address
PI/PD NAME **Susan L Brantley**	**PhD**	**1987**	**814-865-1619**	**brantley@essc.psu.edu**
CO-PI/PD **Kenneth J Davis**	**PhD**	**1992**	**814-863-8601**	**kjd10@psu.edu**
CO-PI/PD **Christopher J Duffy**	**Ph.D.**	**1982**	**814-863-4384**	**cxd11@psu.edu**
CO-PI/PD **David M Eissenstat**	**PhD**	**1986**	**814-863-3371**	**dme9@psu.edu**
CO-PI/PD **Li Li**	**PhD**	**2005**	**814-867-3547**	**lili@eme.psu.edu**

CERTIFICATION PAGE

Certification for Authorized Organizational Representative (or Equivalent) or Individual Applicant

By electronically signing and submitting this proposal, the Authorized Organizational Representative (AOR) or Individual Applicant is: (1) certifying that statements made herein are true and complete to the best of his/her knowledge; and (2) agreeing to accept the obligation to comply with NSF award terms and conditions if an award is made as a result of this application. Further, the applicant is hereby providing certifications regarding conflict of interest (when applicable), drug-free workplace, debarment and suspension, lobbying activities (see below), nondiscrimination, flood hazard insurance (when applicable), responsible conduct of research, organizational support, Federal tax obligations, unpaid Federal tax liability, and criminal convictions as set forth in the NSF Proposal & Award Policies & Procedures Guide,Part I: the Grant Proposal Guide (GPG). Willful provision of false information in this application and its supporting documents or in reports required under an ensuing award is a criminal offense (U.S. Code, Title 18, Section 1001).

Conflict of Interest Certification

When the proposing organization employs more than fifty persons, the Authorized Organizational Representative (or equivalent) is required to complete the following certification regarding Conflict of Interest:
By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is certifying that the organization has implemented a written and enforced conflict of interest policy that is consistent with the provisions of the NSF Proposal & Award Policies & Procedures Guide, Part II, Award & Administration Guide (AAG) Section IV.A;
that to the best of his/her knowledge, all financial disclosures required by that conflict of interest policy have been made; and that all identified conflicts of interest will have been satisfactorily managed, reduced or eliminated prior to the organization's expenditure of any funds under the award, in accordance with the organization's conflict of interest policy. Conflicts which cannot be satisfactorily managed, reduced or eliminated must be disclosed to NSF.

Drug Free Work Place Certification

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent), is providing the Drug Free Work Place Certification contained in Exhibit II-3 of the Grant Proposal Guide.

Debarment and Suspension Certification

(If answer "yes", please provide explanation.)

Is the organization or its principals presently debarred, suspended, proposed for debarment, declared ineligible, or voluntarily excluded from covered transactions by any Federal department or agency? Yes ☐ No ☒

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) or Individual Applicant is providing the Debarment and Suspension Certification contained in Exhibit II-4 of the Grant Proposal Guide.

Certification Regarding Lobbying

This certification is required for an award of a Federal contract, grant, or cooperative agreement exceeding $100,000 and for an award of a Federal loan or a commitment providing for the United States to insure or guarantee a loan exceeding $150,000.

Certification for Contracts, Grants, Loans and Cooperative Agreements

The undersigned certifies, to the best of his or her knowledge and belief, that:
(1) No Federal appropriated funds have been paid or will be paid, by or on behalf of the undersigned, to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with the awarding of any Federal contract, the making of any Federal grant, the making of any Federal loan, the entering into of any cooperative agreement, and the extension, continuation, renewal, amendment, or modification of any Federal contract, grant, loan, or cooperative agreement.
(2) If any funds other than Federal appropriated funds have been paid or will be paid to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with this Federal contract, grant, loan, or cooperative agreement, the undersigned shall complete and submit Standard Form-LLL, ''Disclosure of Lobbying Activities,'' in accordance with its instructions.
(3) The undersigned shall require that the language of this certification be included in the award documents for all subawards at all tiers including subcontracts, subgrants, and contracts under grants, loans, and cooperative agreements and that all subrecipients shall certify and disclose accordingly.

This certification is a material representation of fact upon which reliance was placed when this transaction was made or entered into. Submission of this certification is a prerequisite for making or entering into this transaction imposed by section 1352, Title 31, U.S. Code. Any person who fails to file the required certification shall be subject to a civil penalty of not less than $10,000 and not more than $100,000 for each such failure.

Certification Regarding Nondiscrimination

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is providing the Certification Regarding Nondiscrimination contained in Exhibit II-6 of the Grant Proposal Guide.

Certification Regarding Flood Hazard Insurance

Two sections of the National Flood Insurance Act of 1968 (42 USC §4012a and §4106) bar Federal agencies from giving financial assistance for acquisition or construction purposes in any area identified by the Federal Emergency Management Agency (FEMA) as having special flood hazards unless the:
(1) community in which that area is located participates in the national flood insurance program; and
(2) building (and any related equipment) is covered by adequate flood insurance.

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) or Individual Applicant located in FEMA-designated special flood hazard areas is certifying that adequate flood insurance has been or will be obtained in the following situations:
(1) for NSF grants for the construction of a building or facility, regardless of the dollar amount of the grant; and
(2) for other NSF grants when more than $25,000 has been budgeted in the proposal for repair, alteration or improvement (construction) of a building or facility.

Certification Regarding Responsible Conduct of Research (RCR)
(This certification is not applicable to proposals for conferences, symposia, and workshops.)

By electronically signing the Certification Pages, the Authorized Organizational Representative is certifying that, in accordance with the NSF Proposal & Award Policies & Procedures Guide, Part II, Award & Administration Guide (AAG) Chapter IV.B., the institution has a plan in place to provide appropriate training and oversight in the responsible and ethical conduct of research to undergraduates, graduate students and postdoctoral researchers who will be supported by NSF to conduct research.
The AOR shall require that the language of this certification be included in any award documents for all subawards at all tiers.

CERTIFICATION PAGE - CONTINUED

Certification Regarding Organizational Support

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is certifying that there is organizational support for the proposal as required by Section 526 of the America COMPETES Reauthorization Act of 2010. This support extends to the portion of the proposal developed to satisfy the Broader Impacts Review Criterion as well as the Intellectual Merit Review Criterion, and any additional review criteria specified in the solicitation. Organizational support will be made available, as described in the proposal, in order to address the broader impacts and intellectual merit activities to be undertaken.

Certification Regarding Federal Tax Obligations

When the proposal exceeds $5,000,000, the Authorized Organizational Representative (or equivalent) is required to complete the following certification regarding Federal tax obligations.
By electronically signing the Certification pages, the Authorized Organizational Representative is certifying that, to the best of their knowledge and belief, the proposing organization:
(1) has filed all Federal tax returns required during the three years preceding this certification;
(2) has not been convicted of a criminal offense under the Internal Revenue Code of 1986; and
(3) has not, more than 90 days prior to this certification, been notified of any unpaid Federal tax assessment for which the liability remains unsatisfied, unless the assessment is the subject of an installment agreement or offer in compromise that has been approved by the Internal Revenue Service and is not in default, or the assessment is the subject of a non-frivolous administrative or judicial proceeding.

Certification Regarding Unpaid Federal Tax Liability

When the proposing organization is a corporation, the Authorized Organizational Representative (or equivalent) is required to complete the following certification regarding Federal Tax Liability:

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is certifying that the corporation has no unpaid Federal tax liability that has been assessed, for which all judicial and administrative remedies have been exhausted or lapsed, and that is not being paid in a timely manner pursuant to an agreement with the authority responsible for collecting the tax liability.

Certification Regarding Criminal Convictions

When the proposing organization is a corporation, the Authorized Organizational Representative (or equivalent) is required to complete the following certification regarding Criminal Convictions:

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is certifying that the corporation has not been convicted of a felony criminal violation under any Federal law within the 24 months preceding the date on which the certification is signed.

AUTHORIZED ORGANIZATIONAL REPRESENTATIVE	SIGNATURE	DATE
NAME		

TELEPHONE NUMBER	EMAIL ADDRESS	FAX NUMBER

* EAGER - EArly-concept Grants for Exploratory Research
** RAPID - Grants for Rapid Response Research

PROJECT SUMMARY

Overview. Humans are changing the Critical Zone (CZ) over large spatial scales at geologically unprecedented rates. Maintaining ecosystem services requires that we project the future of the CZ across space and time. Only with concerted efforts to measure and model the landscape will we learn to make forward projections or "*earthcasts*" of both the fast and slow changes occurring in the CZ.

Intellectual Merit. We are working to develop models to use in earthcasting the CZ. Over short timescales and large spatial extents, we are using an atmosphere-land surface model that couples meteorological and ecological processes with hydrological and biogeochemical processes in regolith (Fig. 1) by parameterizing i) depth to bedrock; ii) permeability; iii) water uptake by roots; iv) distribution of fractures and macropores. Over long timescales and smaller spatial extents, we are developing models that predict these regolith characteristics as a function of geological and climatological history. Both the land-atmosphere and the regolith models describe changes in water, energy, sediment, and solute (WESS) fluxes, but over vastly different timescales from 10^{-3} y (water) to 10^{6} y (regolith). For the sedimentary rocks underlying our CZO, we use these models to explore how the geological past has impacted the structure of regolith, and, in turn, how this structure contributes toward controlling today's hydrobiogeochemical fluxes.

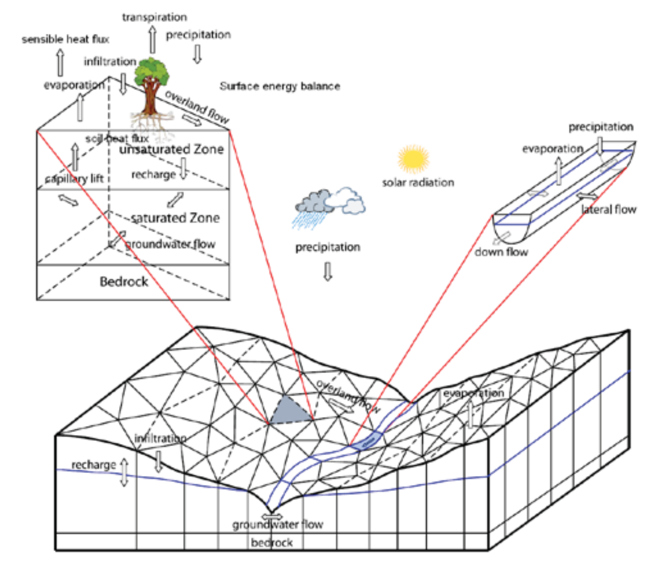

Figure 1. SSHO seeks to understand the Critical Zone (CZ) from canopy to fractured bedrock. We measure and model the system across timescales from those of the meteorologist to the geologist. We will use our knowledge to project, or "*earthcast*," into the future. Our models rely on characterization of water, gases, biota, and regolith (altered material at earth's surface that overlies pristine bedrock). The PIHM model framework is shown here.

The focus of our current work is the monolithologic, forested Shale Hills watershed (~0.1 km^2). In the next 5 years, we will upscale to the multilithologic, multiple-landuse Shavers Creek watershed (165 km^2). These nested watersheds will comprise the expanded Susquehanna Shale Hills Observatory (SSHO). This upscaling will force us to learn to transition from measuring "*everything everywhere*" to measuring "*only what is needed*" and to grapple with the effects of multiple lithologies and land use characteristics. We will use our regolith models as well as publicly available satellite and map data (e.g., soils, land use) to extrapolate from spot measurements of soils and fluxes to the broader watershed. We will test the over-arching hypothesis: *To project CZ evolution into the future requires knowledge of geological history, observations of CZ processes today, and scenarios of human activities tomorrow.*

Broader impacts. Our biggest impact will be to educate 8 grad students, 1 postdoc, and 8 undergrads in state-of-the-art interdisciplinary research focused on 9 sub-hypotheses facilitated by 11 faculty. At the same time, we will engage scientists from within and outside the CZO community using multiple approaches, including provision of seed grants. An important new focus of *Broader Impacts* will be to transfer our knowledge from SSHO into the development of hydrological models for two PA watersheds in the region of drilling and hydrofracking for shale gas. For those catchments, we will work with multiple entities to develop models to understand environmental impacts. We will also engage the public by generating the first "*CZO Four Seasons*" music concert, where Penn State musicians will create a music score from many years of WESS-flux time series data at the CZO. This public concert will be presented at the Penn State Shavers Creek Environmental Center and online.

TABLE OF CONTENTS

For font size and page formatting specifications, see GPG section II.B.2.

Appendix Items:

*Proposers may select any numbering mechanism for the proposal. The entire proposal however, must be paginated. Complete both columns only if the proposal is numbered consecutively.

PROJECT DESCRIPTION

Scientific Justification

Vision. The Critical Zone (CZ) is the Earth surface system that most directly supports humanity. Humans are changing the CZ over large spatial scales at rates that are geologically unprecedented [1-4]. To maintain healthy ecosystems requires that we learn to project the future of the CZ with models that can describe and quantify CZ processes accurately. At present we cannot “earthcast” the evolution of the CZ and its response to environmental perturbations. For example, we cannot *a priori* predict the streamflow in a catchment even if we know the average climate conditions and current vegetation because we are uncertain how much water is lost to evapotranspiration and to groundwater. Likewise, we cannot *a priori* predict the depth or chemistry of regolith on a ridgetop even if we know its lithology and exposure age because we do not know how to project rates of regolith formation. Perhaps even more unsettling, *we do not even agree upon which minimum measurements are needed to answer these questions at any location*.

Such difficulties are largely due to two factors: i) we cannot adequately quantify spatial and temporal variations in the reservoirs and fluxes of mass and energy; and ii) we do not adequately understand the interactions and feedbacks among chemical, physical, and biological processes. These problems are the target of the six Critical Zone Observatories (CZOs), built upon the premise that to project what will happen *tomorrow* we must measure what is happening *today* and read the geological record of what happened *yesterday*. The CZO network represents a “*time-telescope*” that allows us to understand the changing Earth surface from time scales of seconds (atmospheric fluxes) to millions of years (landscape change). As a result of this effort, our measurements and models will decipher the water, energy, solute, and sediment (WESS) fluxes that are encoded in and modulated by the regolith.

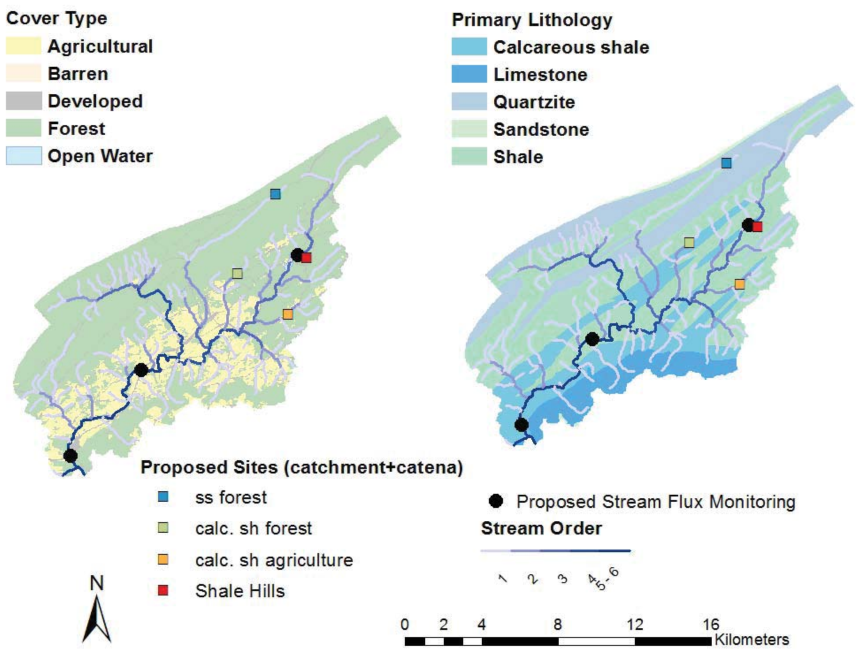

Figure 2. Map of Shavers Creek watershed identifying land cover (left) and primary lithology (right). In the next 5 years we will scale up from the forested, shale-underlain Shale Hills catchment (red square) to the larger Shavers Creek watershed by measuring and modelling three new first-order sub-catchments: forested sandstone (blue square), forested calcareous shale (lime green), and agricultural calcareous shale (orange). Three stations on Shavers creek will be established for monitoring (black circles).

At the Susquehanna Shale Hills observatory (SSHO), we have tackled this challenge by studying the CZ in an 8-hectare watershed -- Shale Hills -- located on Rose Hill shale in Pennsylvania, as well as a climosequence of ridgetop satellite sites on shale from Wales to Puerto Rico (see *Facilities*). Established for research in the 1970s [5] but expanded as a CZO in 2007, Shale Hills now provides a huge dataset to understand the CZ. Using these data, we are implementing predictive models to understand today’s WESS fluxes as well as the geologic record of those fluxes written in regolith. For the next 5 years, we will enlarge the spatial focus of the *time telescope* at Shale Hills by upscaling to the Shavers Creek watershed (Fig. 2).

Goals. The expansion from 8 hectares in Shale Hills to 163 km^2 in the Shavers Creek watershed is an expansion from a zeroth-order catchment to a watershed with 3 HUC-12 watersheds. While the expansion allows us to remain in the Valley and Ridge physiographic province, the expansion will compel us to understand new lithologies (sandstone, calcareous shale, minor limestone), and the impact of multiple land uses including farming and small towns. *Our goal is to understand the interaction of WESS fluxes in a multilithologic and mixed landuse catchment by moving from our Shale Hills paradigm of "measure everything everywhere" to a new approach of "measure only what is needed*". Underlying our proposal is the approach we have pioneered to upscale data collection and modeling from 1D (boreholes, ridgetops) to 2D (hillslope transects, i.e. catenas) to 3D systems (catchments). In this regard, upscaling to Shavers Creek represents a moderately small but important step towards developing CZ expertise for the entire Susquehanna River Basin (SRB), the largest river basin in the Chesapeake Bay watershed in the mid-Atlantic region, U.S.A.

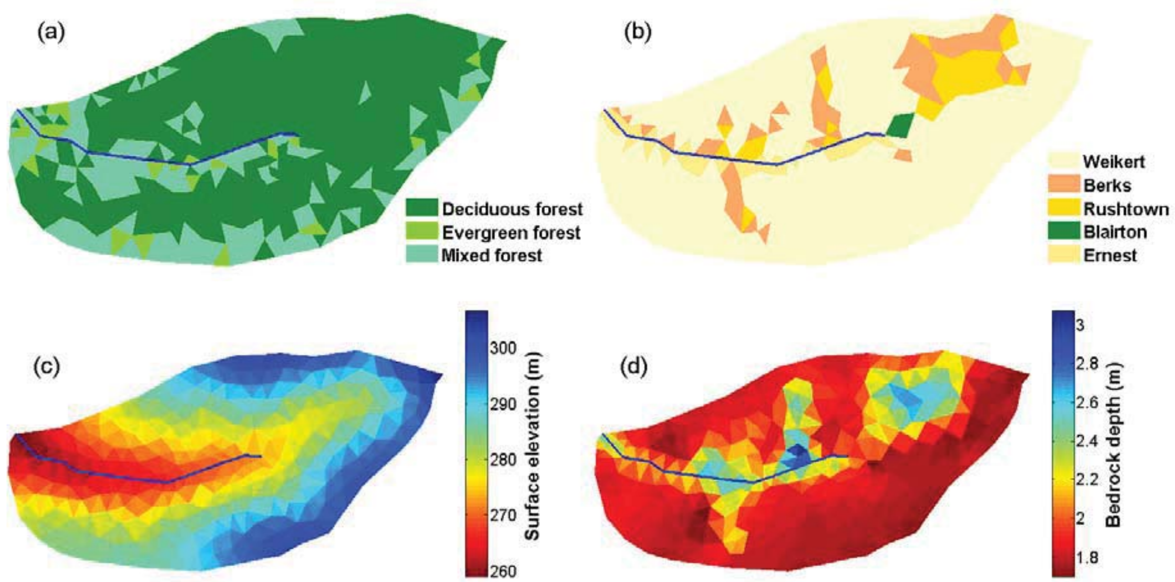

Figure 3. Maps of the Shale hills catchment summarizing extensive surveys which provide input for Flux-PIHM (Penn State Integrated Hydrologic Model, Fig. 1). The model simulates discharge, ground water transport, surface energy balance and soil moisture. Input data include leaf area index (LAI) and plant functional type (a), hydraulic properties for soil series (b), digital elevation from LiDAR (c), and bedrock depth (d). To model discharge we had to add 1 m to all bedrock depths. In the renewal, we explore how this "extra" 1 m is related to fractures, how we can use fracture data to predict stream discharge, and how spatial variations in soil moisture are related to variations in soil and macropore properties. These figures derive from PhD of Y. Shi (2012) in Meteorology.

It is important to note that approximately 85% of the western SRB is underlain by shale and that much of the shale region in the Appalachian plateau is now being drilled for natural gas. Recognizing this significant anthropogenic impact, our *Broader Impacts* will build upon our expertise in understanding the CZ on sedimentary rocks to study 2 satellite watersheds in northern PA, *Young Woman's Creek* and *Snake Creek* (see *Facilities*). Like Shavers Creek, these watersheds overlie mostly shale and sandstone. But unlike Shavers Creek, they are targets for shale-gas drilling. The development of the Marcellus shale for gas is occurring at an extraordinarily rapid pace: in PA alone, >3,000 wells have been drilled and >6,000 wells permitted over the last 7 years. We thus have an opportunity to offer our data, models, experience and knowledge (Fig. 3) to resource managers who are making decisions about shale gas development with limited knowledge of environmental impacts. Of our two satellite watersheds, one has not yet been drilled (YWC) and one contains 13 well pads (Snake Creek). Penn State's Marcellus Center for Outreach and Research anticipates that drilling will begin in YWC during the next 5 yrs; thus, we will work on a watershed both before and after development. Large datasets are available for YWC from the U.S. Geol. Survey and for Snake Creek from collaborators (see *Broader Impacts* section). Using existing non-CZO data, we will create regolith and watershed models that will help communities in those areas and provide a test of the assertion that intensive research at Shale Hills and Shavers Creek can help earthcast in other similar watersheds.

Focus Questions and Anticipated Outcomes. We will focus on four broad questions: *i) What is the best strategy to scale-up from "measuring everything everywhere" to "measuring only what we need" in larger watersheds? ii) What aspects of the geological legacy of a landscape must be incorporated into models of CZ form and function? iii) What are the important imprints of trees on WESS fluxes and the landscape? iv) What approaches can we use to understand how anthropogenic impacts are propagating through the CZ from bedrock to canopy and ridgetop to base level?* As will be documented in the hypotheses section, in answering these questions we plan to i) measure and model ecosystem-atmosphere-subsurface exchanges of water, energy and carbon across the watershed; ii) understand the distribution of fractures in bedrock to reveal how the last glacial maximum affects subsurface flow; iii) learn how trees interact with regolith and how bio-modulated distributions of O_2 and CO_2 control weathering, and iv) assess solute and discharge throughout a mix-landuse catchment that incorporates human disturbance.

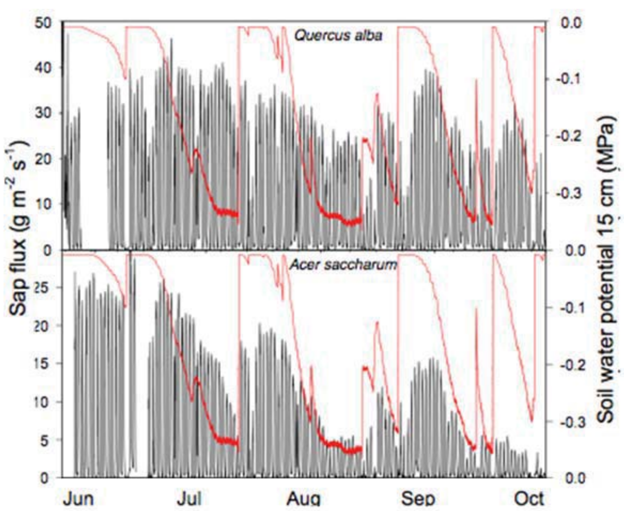

Figure 4. Sap flux (black bars) of white oak (*Quercus alba*) and sugar maple (*Acer saccharum*) at Shale Hills in 2010 with associated soil water potential (red lines). During that growing season, strong periods of low soil moisture were observed in late July, late August and late Sept. Even during the later season drought, the oaks maintained substantial sap flux whereas sugar maples showed minimum sap flux. This may be at least partly because, as shown by natural abundance of oxygen isotopes ($\delta^{18}O$; data not shown), the isotopic signature of sap water in oaks (*Q. prinus*) looks like the ground water, consistent with the deeper rooting depths of the oaks.

We anticipate these outcomes: i) measurement of variables needed to project CZ evolution in the Shavers Creek Watershed; ii) development of several coupled models to project CZ evolution in the watershed over either decadal or millennial timescales; iii) testing of these models using spatially and temporally intense observations from Shale Hills and less intensive measurements in Shavers Creek; iv) development of data assimilation systems that can be applied across CZ disciplines; v) development of hydrological models for two other watersheds relying only upon public data and data from collaborators; vi) interdisciplinary training of 8 grad students, 8 undergrads, and 1 postdoc; vii) maintenance of an instrumented facility, sample archive, and database that welcome outside researchers; viii) exchange of all of our research with other CZOs; ix) dissemination of our science to students, scientists and the public both as a single CZO and as a national CZO network.

Current Knowledge: CZO Research to Date

SSHO operates as both an observatory that provides instrumentation, data and samples for the community (see *Facilities*), and as a site of intensive research. In this section, research accomplishments of the funded CZO since 2007 are summarized and linked with new hypotheses. The discussion is organized to reflect the theme of projecting from the geological past to the Anthropocene future.

Research progress to date: Landform geometry and regolith chemistry and structure. We completed a comprehensive study of chemistry of regolith, bedrock, waters, and vegetation at SSHO and samples and data have been archived [6-13] (see *Data Management*). The primary goals of this work were to 1) map landform geometry / regolith chemistry, and 2) determine rates of weathering, regolith production, and downslope transport, and 3) develop numerical models of hillslope evolution.

Observations of landform geometry and regolith chemistry: We have discovered that the upper 5-7 m of shale underlying the catchment is fractured, perhaps due to ice-related phenomena during the last glacial maximum (Fig. 5) [6-8; 10; 14; 15]. Above the fractured layer lies hand-augerable regolith which varies in depth from 20-50 cm on convex ridgecrests to > 1 m in concave swales and the valley floor. Depth of regolith on hillslopes also shows pronounced north vs. south asymmetry and the southern hillslope retains a mantle of colluvial material (attributed to frost shattering in periglacial climates) that is not present under soil on the north side. In hypothesis H1, we propose to expand these observations to other lithologies to further develop aspect-fracturing-regolith development linkages.

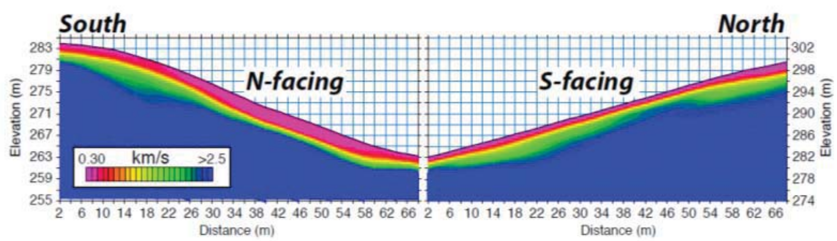

Figure 5. Two tomographic images of the subsurface velocity structure beneath the north and south hillslopes within Shale Hills. The low-velocity zones reveal the depth of soils (pink colors) and highly weathered/fractured rock (red to green) in the shallow subsurface (<6 m). Less-fractured bedrock is shown in blue. Seismic data collected by postdoc B. Clarke.

We recently integrated measurements of regolith chemistry into a conceptual model of nested reaction fronts detailed in Fig. 6 [8]. This model will be further tested in H2. Within the clay reaction front, the degree of weathering is asymmetric (Fig. 7) [6; 11]. Specifically, soils become progressively more depleted in elements such as Mg upward in regolith and downslope, but soils are more depleted on the south than the north hillslopes. Porewater chemistry also shows more variations with depth on the south than the north side [13; 16]. We have attributed this to preferential flow pathways along soil horizon interfaces that have developed more fully on the south side. However, if water chemistry is averaged, the mean chemistry is roughly the same on the two sides. Given that ET is higher on the sun-facing (north) side, less water flows through regolith on that side and more water flow is captured by swales [9; 17]. A synthesis of these observations and a hypothetical explanation are addressed in H3-H5.

Stream water chemistry reveals 3 solute types in SSHO: i) so-called "chemostatic solutes" that show little change with discharge (Na, Mg, K), ii) "organomarker elements" that decrease in concentration due to dilution during increasing discharge (Fe, Mn), and iii) solutes whose concentrations increase with discharge (sulfate) (Fig. 8). Chemostatic behavior is attributed here to release of cations during weathering of clays in the low-flow matrix. These ions sorb to the cation exchange capacity (CEC) of the matrix. This CEC releases solute to porewaters quickly, buffering changes in concentration during storms. Changes in concentrations of organomarker elements, in contrast, vary with dissolved organic carbon (DOC) and are spatially related to soil organic carbon (SOC). Swales, hot spots of SOC and DOC [18; 19], may be sources of Fe and Mn releases to the stream [13]. We test these links in H6.

Rates of regolith production and transport: To quantify the regolith timescales, we conducted the first-ever measurement of both U-series and ^{10}Be *on identical samples from a single catchment* [20-22]. The measured rates of ridgetop regolith production based on U series are equal within error (but slightly higher than) the measured rates of erosion based on ^{10}Be. Given that the catchment was perturbed by the last glacial maximum when SSHO was periglacial, we infer that ridgetop soils could still be thickening with time. Data are consistent with sediment in the valley floor derived from stripping of hillslopes during the periglacial. We expand this work to other lithologies with H1 and we expand the approach of measuring multiple isotopes on the same samples to an international outreach effort, *CZ-Tope*.

In addition to measuring rates, we also seek to understand mechanisms of downslope soil transport (see H3). We are parameterizing a tree throw-driven erosion model by characterizing pit-mound microtopography using terrestrial laser scanning (TLS). One interesting discovery has occurred during these investigations: the concentration of manganese in the soils is greater than expected from the underlying shale [23; 24]. Everywhere in the catchment -- and throughout PA, WV, and OH -- Mn is enriched in upper soil due to atmospheric deposition during the industrial age. We are using Mn enrichment to date pit-mounds for the tree-throw erosion model.

The tree-throw model and a model for freeze-thaw creep are being incorporated into numerical models of coupled regolith erosion and transport along planar hillslopes, including explicit treatment of cosmogenic isotopes. A 3D landscape evolution module is also being built to include sediment flux into the Penn State Integrated Hydrologic Model (PIHM, Fig. 1). This new version is now the basic computing engine for PIHM-Sed and will be tested during May 2013 and applied to hypotheses H7 and H8.

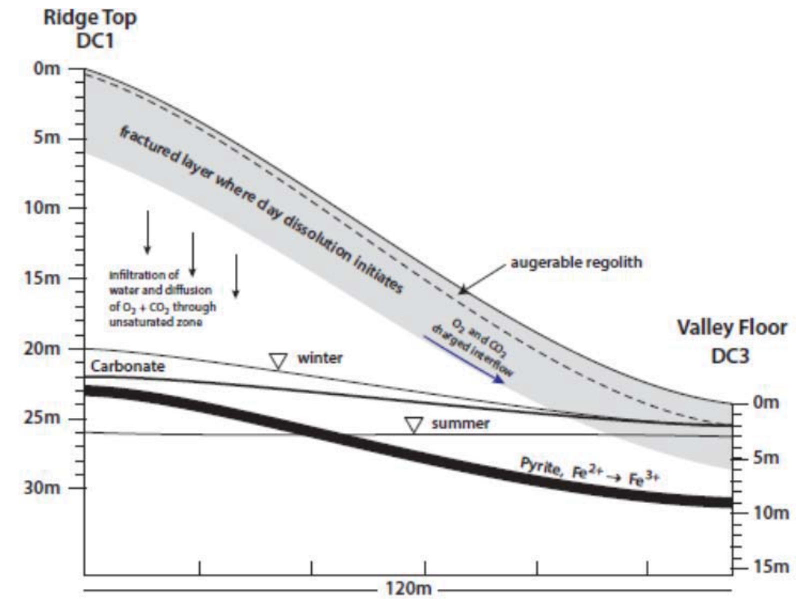

Figure 6. Nested chemical reaction fronts are hypothesized to lie subparallel to the surface under Shale Hills. In this schematic, fronts are plotted at the ridgetop and the valley floor (based on a few boreholes) and projected to one cross-catchment section. Inverted triangles indicate water table. Pyrite appears to be depleted down to the bold dark line and carbonate is depleted down to the labeled carbonate line. We infer that carbonate and pyrite are both dissolved above these fronts. K and Mg are observed in variable concentrations in the upper 6-7 m at ridge and valley, perhaps documenting loss of clay minerals. This upper ~7 meter-thick layer underlying the land surface is highly fractured under both ridge and valley. The layer is thought to host significant interflow downslope (blue arrows). Under the ridge, diffusion of O_2 to the pyrite oxidation front (vertical black arrows) is fast because it is through the unsaturated zone. Pyrite oxidation beneath the water table at the valley is attributed to transport of O_2 in interflow. Degassing of CO_2 from interflow at the valley floor may cause precipitation of carbonate at ~7 m depth.

Research progress to date: Water, energy, and solute fluxes . SSHO hydrometeorology research has focused on the interplay between state-of-the-art modeling tools (Fig. 1) and spatially and temporally intensive hydrometeorological data (e.g. Figs. 3, 4). Observations available for Shale Hills over a 40+ year span have been supplemented by intensive measurements over the last 5 yrs [5; 16; 25-29], including whole-watershed land-atmosphere energy fluxes using eddy covariance, and continuous monitoring of stream discharge, soil moisture and water table depth. These observations have informed the development of a catchment scale model (Fig. 1) that includes explicit coupling among the subsurface, vegetation and atmosphere. The model is referred to as Flux-PIHM [25; 30-36]. Key parameters such as macropore conductivity and leaf stomatal resistance are optimized by fitting model output to catchment-scale measurements using an ensemble Kalman filter [37; 38]. The importance of parameters such as stomatal resistance and macropore conductivity illustrates coupling between groundwater hydrology and ecosystem processes that are not captured in most land-air-ecosystem modeling systems. These model-data syntheses will be enhanced by new processes (H3 – H7), and extended across space (H8) and time (H9) (Fig. 9).

Research on dual-domain water flow. The SSHO hydrology group have coupled observations of soil moisture (Fig. 10), pore water chemistry [16], hydrogeophysical properties (Fig. 5), and water isotopes [29] for all hydrologic components by using new models to provide one of the most comprehensive characterizations of fast and slow water fluxes ever developed for a watershed. The Lin hydropedology group has collected multiple years of soil moisture data in 116 sites from the surface down to 1.1 m [9; 39-41]. We mapped preferential flow paths by coupling soil moisture observations with ground-penetrating radar (GPR), x-ray tomography, *in situ* observations, and modeling (Fig. 10 and H4). To promote others to do similar work, Lin's group has also developed a *Hydropedograph Toolbox* [40] that provides soil and hydrologic information in an efficient way that will streamline work for hypothesis H4.

In addition, hydrogeophysical measurements (Fig. 5) have highlighted the presence of a fractured layer beneath the watershed (Fig. 6). When bromide tracers are injected into the subsurface, the concentration-time curves that result show long tails that that cannot be fit by classical advection-dispersion equations [10]. Rather, the data are best fit by a model that incorporates "immobile domains" where solutes remain for long residence times. Long-residence time water was also invoked to explain the chemistry of SSHO soil porewaters [16]. "Immobile domain porosity" (or "matrix porosity") likely results from low-flow soil layers or porosity inside shale fragments. Immobile water contains concentrated Mg and other elements which are released during clay weathering and retained on matrix exchange sites [16]. Hypotheses H1-H6 will advance understanding of links between dual-domain flow and chemistry.

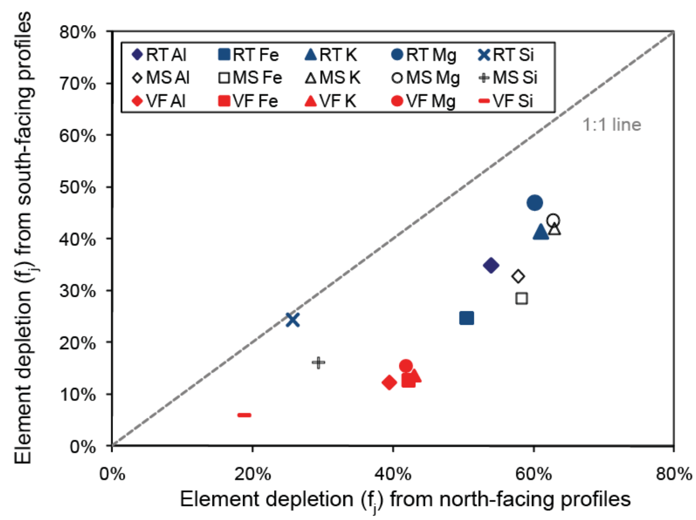

Figure 7. Fractional extent of depletion of Al, Fe, K, Mg, Si in regolith on the two sides of SSHO. Symbol types refer to different elements and hillslope positions as noted: RT = ridgetop, MS = midslope, VF = valley floor. Depletion is more significant at almost all sites for most elements on the north-facing side (south side). Data collected by Lin Ma.

Sorting out the pathways of water and the resultant solute chemistries is enabled by our dataset of >6000 isotopic and geochemical sample measurements for SSHO. We are using ^{18}O, D/H, and solute data to address the "old water-new water" paradox [16; 28; 42]. C. Duffy, CZO postdoc P. Sullivan and H. Lin are working to develop a quantitative analysis of seasonal water isotope dynamics and Duffy has developed a general theory for the isotopic age of waters at SSHO [28-30]. This effort will be developed further in H8.

Research progress to date: Ecohydrology. SSHO vegetation has been characterized by mapping every canopy tree (see Fig. F2, *Facilities*). We observe that patterns of tree water use are influenced at the physiological, community and evolutionary time scales. These temporal measurements are elucidating how a temperate forest affects water, energy and weathering fluxes [43; 44]. Our campaigns to measure up-looking LAI (Leaf Area Index) at ~40 locations across Shale Hills, in parallel with 2 summers of sapflow measurements, demonstrate that the effect of summer drought on tree canopy growth varies with species [45; 46] (Fig. 4). Specifically, oak i) maintains sap flux and leaf area better than maple during droughts, and ii) recovers leaf area and sap flux better after drought. Oaks accomplish this by accessing deeper sources of water, as shown in oxygen isotope data. Weekly LAI data were used in Flux-PIHM to constrain transpiration [25; 47] and future modeling will incorporate tree species effects on water use, especially during droughts (H7, H8). New field work will link tree species and weathering in H2-H5.

Ecology-water synthesis. Based on our observations and their integration with PIHM, the following conceptual model is emerging. The isotopic/chemical signature of snowmelt and winter precipitation is unique compared to summer precipitation which is almost completely utilized by vegetation (Fig. 3,4). Understanding the thresholds between matrix- and macropore-flow is key to simulating subsurface recharge. Summer soil moisture is limited and generally remains below the macropore-flow threshold. Recharge takes place in the cold season when plants are inactive and soil moisture accumulates, eventually crossing the matrix-macropore threshold and infiltrating below the root zone into intermittently-saturated high-flow zones above permeability barriers (e.g. horizon interfaces). We continue to test the essential elements of this conceptual model in H4-H9.

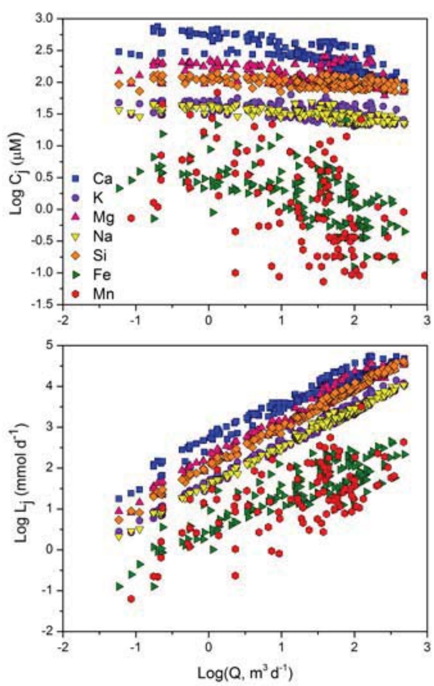

Figure 8. Plots of concentration (C) or load (L) versus discharge (Q) for SSHO streamwaters. Ca, Mg, K, Na and Si concentrations (C) show relatively little variation with stream discharge (Q) and are thus termed "chemostatic". In contrast, "organomarker elements" like Fe and Mn behave like DOC (not shown), becoming diluted at higher discharge. Release of Fe and Mn may be dominated by swales.

Research progress to date: SSHO shale transect. In the first 5 years we designed a "shale transect" of ridgetop sites on the Rose Hill formation (or stratigraphic / compositional equivalent) to investigate rates of regolith formation as a function of climate (see Fig. F3, *Facilities*). In addition, we established one site on black shale of the Marcellus formation within 30 miles of SSHO to investigate composition [48; 49]. The climosequence of satellite sites span 43º of latitude from Wales and New York (NY) to Puerto Rico (PR).

From high to low latitude, the depth and extent of weathering increases on the shale transect ridgetops. Models developed by team members (Fig. 11) predict this along the climosequence, as long as erosion rates are relatively constant. Using approaches developed by Brantley [50; 51] and collaborations with the Arizona CZO [52], we used an activation energy approach [53] to model feldspar weathering along the transect [113]. The constancy of regolith thickness on hillslopes along the transect may be explained by our observation that the density of pits and mounds decreases but the total volume per tree throw increases from high to low latitudes. Thus, compensation between density and volume of tree throw may result in constant erosion rates [54]. We will advance our understanding of tree throw with H3 and improve the model for climate effects with H7 and H9.

Implementation Plan: Hypotheses and Timelines

Our 11 faculty-member team spans a broad range of disciplines and timescales of inference. Each faculty will co-advise 1 or more grad students and each grad student will have two co-advisors. We request funds from NSF for 20 grad-years and 2 postdoc years at Penn State as well as support for one Masters student at Univ of Vermont (UVM) with P. Bierman. Given PSU and UVM teaching requirements, we can thus support 8 grad students to Ph.D. (7) or M.S. (1). The 8 grads and 1 postdoc will focus on 9 hypotheses outlined below. We ordered the hypotheses along the lines of projecting from the geological past to the Anthropocene future and from model conceptualizations that span from 1D (boreholes) to 2D (hillslope catenas) to 3D (catchments). We have argued based upon our first 5 years of research that this upscaling from 1D to 2D to 3D is a convenient strategy toward understanding the fully coupled biogeochemical regolith system [6][16].

Specifically, in hypothesis H1 we focus on the imprint of the recent geological past (fractures in the upper 5 – 7 m layer below the soil) that we believe control WESS fluxes today. H1 focuses on drilled boreholes and sets the stage for hypotheses H2-H4 that similarly focus on regolith production. These hypotheses culminate in creation of 1D and 2D models of regolith formation (H5). While fracture hypothesis H1 focuses on a few boreholes, each of the other regolith hypotheses (H2-H5) focus on observations collected along hillslope transects (i.e., catenas). Each of the catenas will be contained within a sub-catchment of Shavers Creek watershed that will in turn be used for the final 4 hypotheses (H6 - H9) wherein air-land-ecosystem coupling will be measured and modeled, informed by the understanding gained at the borehole and catena scales. Our hypotheses motivate the development of a range of models that are sometimes merged (e.g., 1D processes incorporated into a 3D model) and other times compared as a test of required model complexity, in support of our evaluation of essential measurements. This overall approach is based on our belief that we need multiple model approaches at various scales to unravel the complexity of the CZ.

Working across point (borehole), catena, and sub-catchment scales will be the key to the upscaling strategy (Fig. 2). The 3 new sub-catchments which we target within Shavers creek are first-order catchments like Shale Hills that are situated in one of the three main physiographic regions in Shavers Creek: i) forested and sandstone-underlain; ii) forested and calcareous shale-underlain; iii) agricultural and calcareous shale underlain. These sites will thus complement our work in Shale Hills (forested, shale). Our observations and models will target these sub-catchments, spanning climate, water, soil, chemistry, geology, and biota. The data will constrain and inform the development of models, which will then be used to upscale to the entire Shavers Creek. In this approach, we will begin to understand the coupled physical, chemical and biological processes that formed the CZ. Our coupled modeling systems will be exchanged with and evaluated across the national CZO network. Each hypothesis is delineated below and team members are delineated in *Management Plans*.

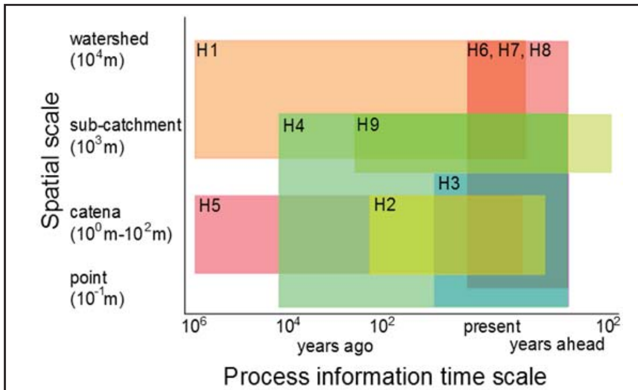

Figure 9. Schematic showing how the processes targeted by hypotheses and models interlink across time and space. The highly coupled nature of chemical, physical, and biological processes in the CZ demand an integrated effort such as shown here. Note that another scale of observation and collaboration – across the CZO network – is also important to SSHO. Personnel and site locations are also summarized for each hypothesis in the *Management Plan*.

H1. The fracture hypothesis: ***Feedbacks among frost shattering, weathering reactions, and the evolution of topography have resulted in an asymmetric distribution of fractures that in turn controls the observed differences in fluid flow in the subsurface between the sun-facing and shaded sides of catchments within Shale Hills and much of the Susquehanna River Basin.***

In the last year, we began a campaign to characterize subsurface heterogeneity in the SSHO. We are currently i) measuring fracture distribution and weathering extent in a deep (25 m) ridgetop and several shallow (5-8 m) boreholes, ii) characterizing seismic velocity of regolith and shallow bedrock and calibrating rock properties to relate velocity to fracture density [e.g., 55], iii) measuring ^{10}Be inventories on hillslopes of varying gradient (~10° to 25°) in parallel watersheds to the north and south of the SSHO. We are integrating data with models of fracture generation that incorporate thermal forcing (i.e., the model proposed by the Boulder CZO [56]), weathering reactions [57], and topography [14].

Results from these studies will yield a predictive understanding of fracture distribution across lithologies throughout Shavers Creek. In the next 5 years, we will conduct seismic investigations of fracture distribution and regolith thickness in both sandstone and shale catenas within the target sub-catchments. These will be compared to several ridgetop boreholes that we are drilling as part of the cross-CZO "Drill the Ridge" campaign (see description below). This drilling will allow quantification of fracture distribution, rates of groundwater movement and recharge. Calibration of seismic velocities will allow estimation of these properties across broader regions. We will continue to coordinate our efforts with ongoing efforts in the Boulder Creek CZO where similar seismic measurements and drilling are ongoing. This cross-CZO collaboration will be facilitated by K. Singha, an original member of the SSHO CZO, who has now moved to Colorado School of Mines and is working with the Boulder CZO, and by Penn State postdoc B. Clarke who has received NSF funding to promote cross-CZO measurements.

One of our goals is to predict regolith distribution on landscapes within Shavers creek. To do this, we need to understand the dependence of fracture distribution, regolith thickness, and weathering extents on variations in erosion rate. Erosion influences weathering through feedbacks between regolith thickness, residence times of water, and supply of weatherable material [58-61]. As part of *Broader Impacts*, we will be developing a hydrologic model for Young Woman's Creek (see *Facilities*). This watershed, similar to Shavers creek in that it lies on clastic lithologies, was chosen because it will soon be drilled for Marcellus shale gas. However, it also provides an opportunity because ^{10}Be measurements in stream sediments [54] suggest that erosion rates in YWC may be 2-3 times greater than those in Shaver's Creek. This has been attributed to transient incision along trunk rivers [62]. By selecting hillslopes in both Shavers Creek and YWC we will test whether erosion and removal of regolith leads to predictable differences in the extent and intensity of fracturing and regolith development.

Timeline and team personnel (Kirby, Bierman, Singha, Brantley, Lin): In year 1 we will complete the "*Drill the Ridge*" campaign started in 2012 at Shale Hills by drilling at least 2 ridges in Shavers Creek (sandstone, calcareous shale) and one sandstone ridge in YWC. We will also complete seismic surveys for each borehole and along the targeted catenas for H2-H5. In year 2, televiewer images from year 1 will be analyzed for fractures, and samples chemically analyzed. In year 3, samples for cosmogenic isotopes will be collected for the catenas within Shavers Creek on sandstone and calcareous shale. In year 4 these samples will be analyzed for ^{10}Be and samples collected in YWC. In year 5, rates of erosion will be calculated and models published.

H2. Imprint of biota on acid- and redox-weathering hypothesis: ***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, DOC) and O_2.***

We have advanced the hypothesis that deep weathering at Shale Hills can be described as nested reaction fronts (Fig. 6). Pyrite is completely weathered to the water table under the ridge but even deeper in the valley [8]. Carbonates are completely weathered by CO_2 or pyrite-produced H_2SO_4 to a depth near the pyrite front under the ridge but meters above the pyrite front under the valley where carbonate precipitation also occurs. Under the ridge, these patterns can be understood in terms of mass balance calculations showing that O_2 and CO_2 should be consumed by ~ 20 m based on the Fe(II) and base metal cation oxides in the shale [63]. In contrast to these deep reactions, clay weathering is ongoing in the shallow regolith and is related to variations in soil CO_2 and DOC [16; 18; 19].

In the next 5 yrs, we will instrument the three new catenas within the target sub-catchments (forested sandstone, forested calcareous shale, agricultural calc. shale, Fig. 2) with co-located lysimeters for pore water chemistry (ions, DOC) and gas-sampling tubes and sensors (CO_2 and O_2). We have published limited soil pO_2 data from Shale Hills [64], and in the next 5 years we will assess pO_2 more broadly and deeply, working closely with W. Silver of the Luquillo CZO who introduced us to the use of Apogee oxygen sensors. Our work at Shale Hills taught us that analysis of weathering processes is best accomplished using carefully located catena transects of ridgetop, midslope and valley floor locations along planar slopes and swales. Therefore, we will place lysimeters (coordinating with H2-H5), soil gas sampling tubes (point measurements), buried soil CO_2 continuous sensors, and Apogee soil O_2 sensors at depths in the B horizon (matrix flow) and at the high-flow AB and BC horizon interfaces. These measurements will be made within the context of measurements of soil moisture and hydrometeorological data using the portable array (H7-H8). In addition, we will explore the use of O_2 and CO_2 sensors in boreholes (H1) to compare gas chemistry to chemical and mineralogical variations with depth.

We will compare CO_2 and O_2 depth profiles to mineralogy and pore water chemistry to link production and consumption of acids and O_2 with weathering reactions. Soil organic matter and CO_2

produced from microbial respiration is typically enriched in ^{13}C relative to root respiration [65]. Using ^{13}C natural abundance, we will investigate the role of deep roots and microorganisms in generating weathering acids. As part of this effort, we will test the Effective Energy and Mass Transfer (EEMT) model developed by the Arizona CZO for their semi-arid climate regime [66]. EEMT is the sum of net primary production (NPP) and precipitation energy available to do work (e.g., weathering). We are measuring all the parameters required to test EEMT in Shale Hills, the shale transect (see *Facilities*), and the new catenas within Shavers Creek. As time allows, this work will be amplified by measurements of soil N_2O. Production of N_2O in soil is mainly controlled by microbial activity and O_2 and NO_3 concentrations. It is difficult to predict N_2O emissions at the ecosystem scale [67]. Our measurements may allow modeling of N_2O if we can map DOC, CO_2, O_2 and NO_3 from digital elevation (swales vs planar slopes) and preferential flow paths. Measurements will be analyzed to assess effects of lithology (sandstone, shale, calcareous shale) and land use (forested versus agricultural).

Timeline and team personnel (Kaye, Brantley, Eissenstat, Li): Sensors will be installed in year 1; monitoring will continue in years 3-4. Frequency for monitoring of soil pore fluids (lysimeters, soil gas tubes) will be roughly 2X per month in the growing season as possible. We will collect pilot C isotope and N_2O data in year 1, and then add targeted isotope measurements in year 3, and N_2O measurements in year 4. Analysis and publications will be fostered in years 4-5.

<u>H3. The tree-root hypothesis</u>*: Trees with deeper roots (oaks) are associated with less frequent tree throw, slower hillslope erosion rates, fewer vertical macropores, faster weathering at depth, and deeper regolith than trees with shallower roots (maples).*

Not only do plants affect land-air water and carbon fluxes (Fig. 4, H7, H8), but different plants also affect regolith weathering differently due to variations in depths of rooting, mycorrhizal fungi, and rates of water use. As climate changes, the effect of vegetation will change. In PA climate change may transform much of the beech/sugar maple forest towards oak/hickory [68; 69]. This change could have important ecosystem consequences, as we have observed that oaks access deeper water and sustain transpiration much more during summer droughts than maples (Fig. 4).

For H3, a grad student will contrast mechanisms of regolith deepening by oaks versus maples on three catenas (forested shale (Shale Hills); forested calcareous shale; forested sandstone) and between forests and pasture (calc shale: agric vs. forest). We will also analyze root traits above and below the regolith and will correlate measurements with pit and mound distributions. In addition to their deeper roots and lower sensitivity to vapor pressure deficits, oaks are colonized by ectomycorrhizal (EM) fungi whereas maples are arbuscular mycorrhizal (AM). Compared to AM, EM produce more extramatrical hyphae and exude much more extracellular enzymes, causing more decomposition and weathering [70].

We expect that the greatest differences in rooting depth will be observed at midslope. At the ridgetop where soils are thinnest and weathering is fastest [20], the density of roots for both species should be high in the fractured bedrock just below the augerable regolith. Conversely, in the deeper soils of the toe slope, root density in the fractured bedrock will be lower (or roots may not access bedrock). At midslope, we expect large differences in species' impact because the oaks' deeper rooting will interact with bedrock, whereas such deep interactions will be unlikely for maples.

To test H3 regarding mechanisms of regolith thickening, we will coordinate with H2 and H5 to measure water chemistry, regolith chemistry, soil gas chemistry, root density, root hydraulic conductivity and mycorrhizal colonization both above and below augerable regolith. In addition, we will continue to measure water isotopes that are indicators of rooting depth. Measurements of plant litterfall, trunk growth (for forested sites) and leaf chemistry along the 3 new catenas as well as in Shale Hills will aid in estimating plant nutrient uptake and overall proton and mass balance of vegetation. The catena measurements will be used to extrapolate for the broader Shavers Creek watershed. Root length distribution will be examined by profile wall mapping [71]. Distribution of mycorrhiza [72] and root hydraulic conductivity [73] will be measured as a function of depth in pit walls and related to observed patterns of pore water and soil gas chemistry as measured by researchers involved in H4 and H2.

Timeline and team personnel (Eissenstat, Davis, Kaye, Brantley): Pits will be dug with a back hoe and jack hammers along the catena in the forested shale site (Shale Hills) in yr 1, in the calcareous shale in yr. 2, in the sandstone site in yr 3, and in the agricultural calc. shale site in yr 4. After pits are dug, pit faces will be smoothed and root distribution mapped. Immediately after root mapping, root and soil parameters will be collected and analyzed. Team will participate in all tree measurements years 1-5.

H4. <u>The soil macropore hypothesis</u>*: Macropores are important in controlling fluid flow and chemistry in soils derived from various lithologies, but the nature and effects of these macropores differ significantly among shale, calcareous shale, and sandstone.*

Water flow and chemical transport in macropores is a frontier in vadose zone hydrology. Macropores are zones of faster flow (cracks or fissures, pore space among aggregates or soil matrix and rock fragments, animal burrows, channels formed by roots). Macropores often lead to spatial distributions of water and solutes that are poorly described by classical models. For instance, macropores often trigger "hot spots" and "hot moments" of biogeochemical reactions and ecological functions [(e.g.74; 75)]. Interpretations of point measurements require an understanding of macropores and their distribution [(e.g. 76; 77)], because stagnant or high velocity flowpaths such as macropores result in highly variable mass flux rates. We have found that much of the heterogeneity in solute concentration with depth in Shale Hills soils is due to high-flow lateral macropores that subtend low-flow matrix zones [(6)]. Likewise, the chemostasis that is observed for Na, K, and Mg in concentration-discharge curves (Fig. 8) is probably due to cation-exchange sites within the low-flow matrix that quickly release solutes to the lateral macropores.

Building on the knowledge gained at Shale Hills [(41; 78)], we will investigate macropore characteristics, distributions, and impacts along the three target catenas (forested sandstone, forested calcareous shale, agricultural calcareous shale, Fig. 2). Two complementary approaches will be used: 1) noninvasive geophysical surveys (including ground penetrating radar or GPR), and 2) a real-time soil moisture sensor network. We will use high-density, time-lapsed GPR survey grids (Fig. 10) and high-frequency soil moisture sensor networks to detect and quantify macropores and related preferential flow features and flow dynamics. We will also use and expand *The Hydropedograph Toolbox* [(79)] for analysis of time series soil moisture profiles to reveal macropore flow. This work will be linked to the investigations of fractures (H1), weathering (H2), and tree roots (H3). The generalized understanding of macropore properties gained here will also support upscaling (H6, H7, H8).

Timeline and team personnel (Lin, Duffy, Eissenstat, Davis): In the 1^{st} yr, we will conduct general EM soil mapping and GPR surveys in the Shavers Creek watershed to select the three target catenas for H2-H5. We will also install the soil moisture sensor network in the 3 catenas. In the 2^{nd} and 3^{rd} yrs we will complete high-density, time-lapsed GPR surveys in both sandstone and calcareous shale areas. In the 4^{th} yr we will analyze all time-series data of soil moisture profiles using the enhanced *Hydropedograph Toolbox*. In the final year we will synthesize all the data collected and link to other hypotheses investigated in this project and publish manuscripts.

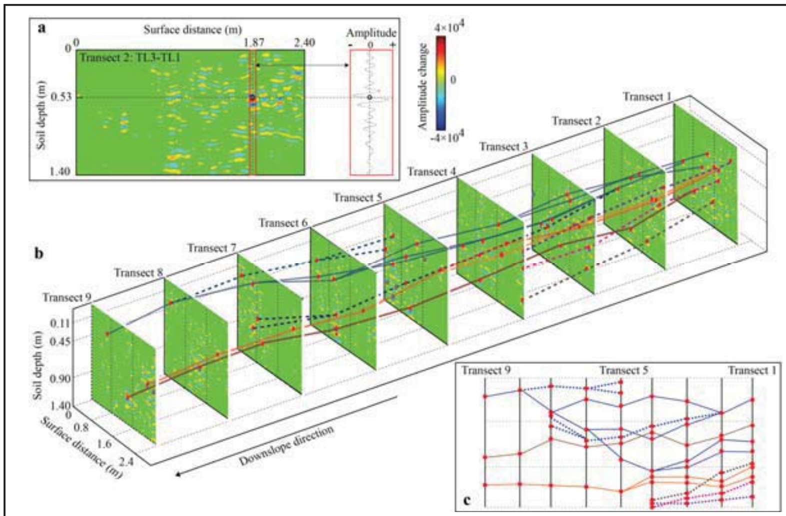

Figure 10. (a) Identification of subsurface lateral flow (SLF) radar signatures based on reflection differences between time-lapsed radargrams over the same transect. (b) Connection of macropores and SLF reflections on neighboring transects into a 3D SLF network. Red dots indicate nodes of the SLF network on each radargram, while gray dots indicate the SLF reflections that could not be connected between transects. (c) 2D projection of the 3D SLF network developed in (b) from upslope transect 1 to down-slope transect 9. Dashed lines represent the SLF pathways that did not cross over the entire surveyed soil, while solid lines represent SLF pathways that extend across all survey transects. Different colors indicate different SLF pathways.

<u>H5. The regolith-modeling hypothesis</u>*: Greater evapotranspiration on the sunny, north side of Shale Hills means that less water recharges to the stream, explaining why Mg and other cations are less depleted in the regolith on the north compared to the south hillslopes.*

We will use Shale Hills as a natural laboratory to develop regolith formation models. Specifically, Fig. 7 shows that elements are less depleted in regolith on the north compared to the south side [11; 21]. Various properties are similar on both sides, including erosion rate [22], regolith depth [9], and tree species (see Fig. F2, *Facilities*), while some properties are different, including underlying stratigraphy and fracturing (Fig. 5), evapotranspiration, slope, extent of preferential flow, and water recharge. We hypothesize that water throughflux exerts the strongest control on elemental depletion and regolith formation [80-82]. The north-side versus south-side observations at Shale Hills will be used as a natural experiment to parameterize models of regolith formation (10^3 -10^6 y) to test H5.

We are currently developing weathering models for ridgetops (1D) and hillslope catenas (2D) with data from Shale Hills. We are exploring existing reactive transport codes that represent different levels of complexity (CrunchFlow, MK76 (Fig. 11), and WITCH (see H9)). The models will be constrained with measurements of water and soil chemistry, regolith formation rate, erosion rate, soil moisture, and weathering duration – all of which have been measured at Shale Hills [9; 21; 22]. The 2D models will also be informed by observations of distributions of fractures (H1) or macropores (H4). Starting from the bedrock, the models will reproduce the spatial and temporal evolution of major elements, water chemistry, porosity, hydraulic conductivity, surface area, and regolith thickness. These models will yield an integrated understanding of the controls on regolith depth throughout the catchment and will inform our ability to parameterize the hydrologic models with respect to depth to bedrock.

Our overall intent is to develop models of regolith formation for the well-characterized Shale Hills that can then be used for the catenas studied in Shavers Creek watershed. With process-based regolith formation models, we will develop more accurate maps of soil properties across the entire Shavers Creek watershed, supporting H7 and H8.

A student of Li is already developing a 1D model for the Marcellus Shale to simulate data from our shale transect site [48; 49] using CrunchFlow. That code has been used for weathering systems and biogeochemical simulations[83; 84]. In addition, CZO postdoc P. Sullivan is already collaborating with Y. Godderis using the code WITCH [103] to generate 1D models. Weathering models in 2D will require incorporation of weathering and erosion, as Brantley and Penn State colleague M. Lebedeva have already done using MK76 (Fig. 11).

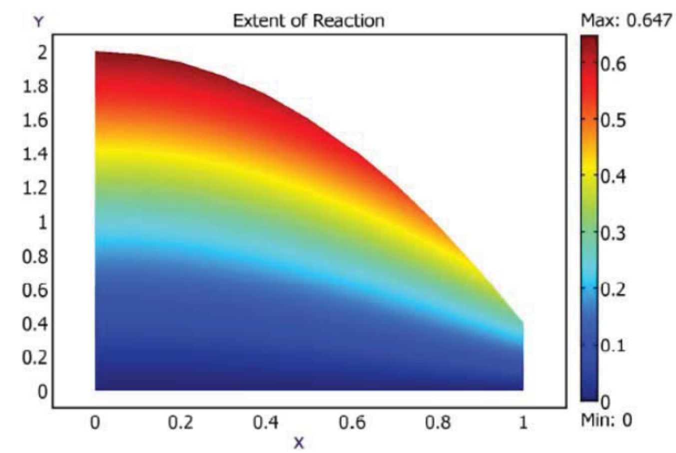

Figure 11. Contours of the extent of depletion of a dissolving element in regolith as a function of depth and position along a hillslope as calculated by Lebedeva and Brantley (2013, subm.). The simulation was run for a system with a slow chemical weathering rate but fast erosion rate, as expected for Shale Hills. For the convex hillslope, y is elevation and x is distance from ridgetop. Simulations are based on the assumption that regolith formation is due to chemical weathering and that all regolith moves downslope. The simulation shows that extent of depletion of an element only reaches 60% at ridgetop, consistent with observations at Shale Hills.

Timeline and team personnel (Li, Brantley, Kaye, Gooseff): Using existing data, 1D ridgetop simulations will be run in the first 3 years to model regolith formation at Shale Hills. Hillslope catena models (2D) will be developed in yrs 2-4 with more realistic chemistry and hydrology, also for Shale Hills. In years 3-5 we will further develop and publish the models. In years 1-4, this team will also analyze soil chemistry and mineralogy for the new catenas in Shavers creek. If time permits, the 1D and 2D models developed for Shale Hills will be used for these new catenas.

<u>H6. Stream solute flux hypothesis</u>*: 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.*

Stream solute fluxes integrate the biotic, geologic, and anthropogenic processes occurring in watersheds making it difficult to predict streamwater chemistry as a function of discharge [42; 81; 85]. For example, several major ions have been found to be chemostatic (concentrations change little with discharge variation) in watersheds across the U.S.A. [85]. In contrast, other chemical species such as dissolved organic carbon (DOC) show increasing concentrations with increasing discharge (i.e., flushing behavior [86]). Other solutes such as nitrate appear related to anthropogenic impact [87].

One reason for complexity is that the spatial distribution of hydrologic connectivity between hillslopes, swales, valley streams, and groundwater varies over time. At Shale Hills we propose that Mg, Na, and K are chemostatic (Fig. 8) because these ions are released rapidly from ion exchange sites located throughout the catchment in the shale matrix: these ions are therefore not sensitive to changes in the parts of the watershed that are connected to the stream. In contrast, Fe and Mn are largely released in pulses of DOC out of swales, somewhat similar to observations in other streams [88]. We hypothesize that the convergent-flow swales and the nonconvergent-flow planar hillslopes largely control the behavior of release of water and solutes in Shale Hills, in concert with ground water inputs.

Our investigation for H6 will emphasize the locations shown in Fig. 2: we will compare our "natural laboratory experiment" of forested shale vs. forested sandstone and agricultural shale vs. forested shale subcatchments. In addition, we are working closely with the *s::can* instrumentation company (letter attached, J. Irving) and the Christina River CZO, to understand and use *s::can* sensors to measure stream chemistry. As a culmination of H6 work, we will couple a reactive transport model to PIHM to simulate water chemistry throughout the sub-catchments (and, time-permitting, Shavers Creek). This effort will be led by Gooseff and Li and will be related to work on H5; however, the H5 regolith formation models will simulate millennial timeframes whereas the H6 stream models will simulate decadal timeframes.

Timeline and team personnel (Gooseff, Brantley, Li, Kaye, Duffy): We will start in Year 1 to measure discharge, temperature, and electrical conductivity at 3 locations on the main stem of Shavers Cr. (Fig. 2). At the watershed outlet, discharge will be measured using an ADCP (acoustic doppler current profiler, to be purchased with funds already in hand). At the 3 main-stem sites, we will also use ISCOs already owned by the PSU group to collect samples for analysis of solutes and stable isotopes (D/H, $^{18}O/^{16}O$). In years 2-3, we will deploy 2 mobile *s::can* monitoring units (one *s::can* already at PSU and one to be purchased) March to November to measure dissolved organics, NO_3, NH_4, K, F, Cl, pH, electrical conductivity, oxidation reduction potential, and dissolved oxygen in the paired sub-catchment experiments. In years 3-5, we will conduct synoptic flow-measurement and chemistry sampling field campaigns (including dissolved inorganic carbon, DIC)[89; 90]. In years 3-5, we will implement a watershed-wide chemistry model using PIHM plus a reactive transport model.

<u>H7</u>. <u>The land – air – ecosystem coupling hypothesis</u> . *Land-atmosphere fluxes of carbon (C) and water, ground-water hydrology, and ecosystem change are coupled processes at time scales of months to decades. This coupling varies with the lithology and land use and position on the hillslope*.

This hypothesis targets the synthesis of the spatially intensive measurements of water, energy and carbon (H2, H3, H4, H6) at the catchment scale using the Penn State Integrated Hydrologic Model (PIHM) [25; 30; 34; 35; 91; 92]. We have shown that fully 3D, high temporal resolution land-atmosphere fluxes of energy and water can be simulated accurately with Flux-PIHM[25; 47]. For H7, we will 1) explore the impact of rooting depth and tree species (H3) on watershed hydrology, 2) add C cycle biogeochemistry and, if possible, vegetation dynamics to our measurement and modeling system, and 3) evaluate the degree to which variability in the key parameters of this modeling system can be explained by lithology and land use (H1, H6). We will also explore the utility of this modeling system for "earthcasting" (H9) and compare Flux-PIHM to lower dimensional models (H5). This effort builds upon the C cycle measurements at Shale Hills including eddy covariance measurements of net ecosystem-atmosphere exchange (NEE) of CO_2, soil and leaf chemistry, litter fall and tree diameter increments.

In the next 5 years, the ongoing Shale Hills measurements will be complemented with a relocatable array that will be deployed to the three new sub-catchments (forested sandstone, forested calcareous shale, agricultural calc. shale). The array will measure an essential subset of the C and water cycle parameters measured at Shale Hills by testing innovative measurement technology (see H8 and *Management Plan*). To complete the work for H7, we will utilize the plant distribution / rooting depth (H3) and macropore/soil mapping data sets (H4) for the target catenas. Flux-PIHM will be modified to include rooting depth as a function of plant species and location on the catena (ridge, midslope and valley), macropore properties that vary with lithology, C cycle biogeochemistry and, if possible, plant demography. The C cycle/ ecosystem modules will be adapted from either the Community Land Model (CLM) or the Ecosystem Demography model (ED2). Model-data synthesis methods [25; 47] will be applied at each catchment to optimize the model with respect to catchment data. As a result we will 1) test the impact of spatially variable tree species, rooting depth, and macropore properties on C and water cycles, 2) elucidate the parameters and processes that couple groundwater hydrology, rooting depth and C fluxes, and 3) evaluate the degree to which key model parameters (e.g., macropore properties) are a function of lithology and position on the catena. We will also integrate C, DOC, and DIC data (H6) to assemble 3D-C-cycle reanalyses of our catchments. We thus use results from catena studies (H2, H3, H4) to inform Flux-PIHM in concert with integrative catchment-scale C and water data to provide a watersehed model.

Timeline and team personnel (Davis, Eissenstat, Duffy, Lin, Kaye): Year 1: We will deploy the relocatable array (described in H8) in Shale Hills and begin measurements while integrating data for advanced rooting depth, macropore and carbon cycle biogeochemistry into Flux-PIHM. In year 2 we will complete the model-data synthesis studies at Shale Hills. In years 2-5, we will deploy the relocatable array in the 3 new sub-catchments and begin model-data synthesis. In year 4 we will begin implementing ED2/CLM into the modeling system. In year 5 we will evaluate the relationship between lithology, land use, and key model parameters.

<u>H8. Water-data integration hypothesis</u>: *Co-located, intensive, relocatable measurements of soil moisture, tree sap flux, sapwood area, LAI, ground water depth, temperature, ^{18}O and D/H along with a 4-component radiometer, laser precipitation monitor and landscape-level soil moisture (COSMOS) can be assimilated within a multi-scale distributed modeling framework to project physical processes from Shale Hills to Shavers Creek to YWC and Snake Creek watersheds.*

This team proposes i) to design and use a relocatable, real-time, multi-sensor array (as noted in H7) to test the fidelity of scaling up predictions from the catchment scale (intensive observations over 600 m to 1 km domains) to that of Shavers Creek (163 km^2); ii) to apply the modeling with existing data at Young Womans Creek and Snake Creek.

This hypothesis builds upon H7's continued development of Flux-PIHM for WESS fluxes into an integrated model and the degree to which integrated and co-located measurements of physical variables for soil water, groundwater, stream water and vegetation can be used for scaling up observatory measurements to scales that allow a new set of relevant science questions. We will focus on the following questions: 1) Do seasonal changes in the depths of water uptake by different tree species (Fig. 4) in different lithologies affect transpiration locally and across watersheds? 2) How can we best assimilate soil type, landform characteristics, and land use to project spatial and temporal patterns of surface and subsurface soil moisture storage, the distribution of macropore development, and the relationship of vegetation state to groundwater recharge and stream flow? 3) Can an intelligent deployment of a relocatable array with intensive multi-sensor measurements on dominant lithologies and landuse serve as a "minimum" observing system while still allowing adequate prediction of water and energy fluxes and pathways? In other words, can we learn from intensive observatory measurements and models developed at Shale Hills to model and estimate uncertainty in other watersheds with less intensive monitoring?

To answer these questions, we will pursue an extensive modeling effort to evaluate model performance as a function of the addition or removal of data across scales, including catchment scales using the existing high density Shale Hills array and the entire Shavers Creek using the relocatable array deployments. We will thus use the data assimilation methods (H7) to test the robustness of modeling. With this effort, we will utilize the upscaled modeling-data synthesis system to assess how tree species influence watershed estimates of transpiration and spatial and temporal patterns of soil moisture under different climate scenarios and land use distributions over the Shaver Creek domain including the interpretation and assimilation of ^{18}O and D/H data.

Timeline and team personnel (Duffy, Davis, Eissenstat, Lin): Year 1-2: Data measurement continues in Shale Hills; design and initial deployment of the relocatable array in Shale Hills (shared effort with team for H7). Years 2-4: Deployment of the relocatable array in each of the 3 sub-catchments (forested sandstone, forested calc. shale, agricultural calc. shale); upscaling of the PIHM modeling effort from Shale Hills to Shavers creek. Years 4-5: Extension of upscaled models to YWC, Snake Creek.

H9. <u>Earthcasting hypothesis</u>*: Increasing atmospheric CO_2 in the future will cause higher temperatures and faster weathering of clays in the catchment, increasing streamwater solute loads.*

A first effort at earthcasting soil weathering was pioneered by Y. Godderis and Brantley for soils developed on Peoria loess along the Mississippi valley climosequence [93]. We will apply this technique to project weathering in the SSHO and the shale transect under future climate conditions. The approach demonstrated by Godderis et al. (2013) uses global scale climate/vegetation models because we were unable to develop models capable of projecting decades into the future with the full resolution of our CZ data. Here, we will explore how CZ data and models can be used to enhance and evaluate this projection using competing modeling systems and CZ data for multiple systems.

We will follow Godderis et al. (2013) and run an atmospheric global circulation model (ARPEGE [94; 95]) under the A1B IPCC carbon emission scenario [96]. The output will yield values for mean air temperature and diurnal temperature range, rainfall, relative air humidity, cloud cover and surface horizontal wind speed. The climate model ARPEGE, part of the international stretched-grid model inter-comparison project (SGMIP), is capable of reproducing the North American climate evolution over 12 years (1987-1998 period) [97]. We will also examine higher resolution climate downscaling if possible.

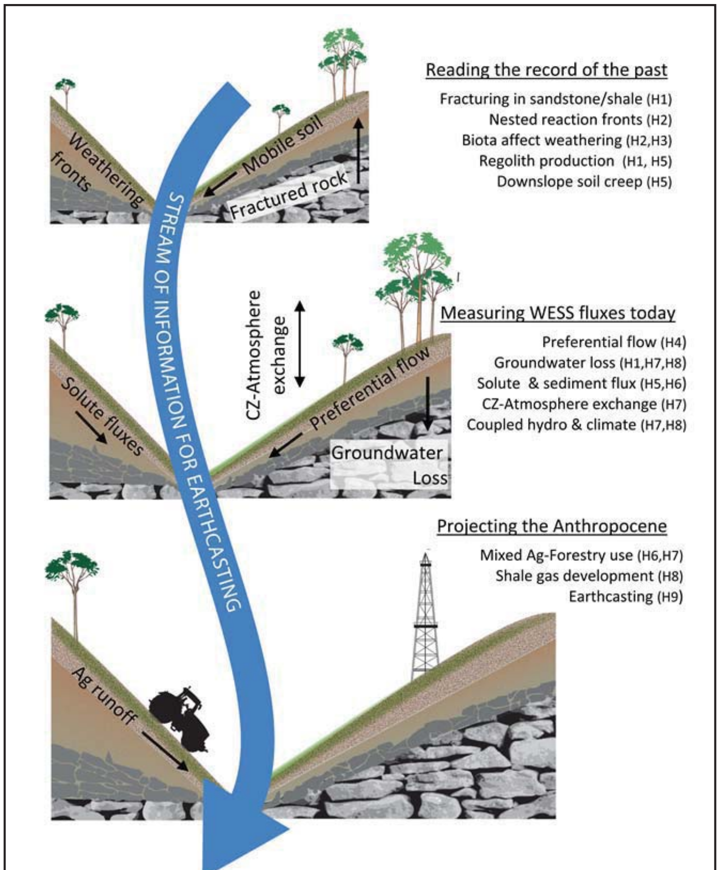

Fig. 12. A schematic showing how we will use geological observations of the past, measurements of fluxes today, and models to earthcast the future of target watersheds.

The climate data will be used to force a global dynamic vegetation model (CARAIB [98]). CARAIB is a dynamic vegetation model initially developed for the global scale [99] which has been evaluated over all continents [100] and shown to produce plausible global vegetation distribution maps [101]. Here, a globally tested classification of plant functional types (PFT) will be updated [102]. CARAIB will then be used to predict vegetation cover, biospheric productivity, below-ground hydrology and CO_2 production for Shale Hills and for the N-S climosequence along the shale transect (Fig. F3, *Facilities*). The carbon cycle functionality of CARAIB will be compared to CZO data and high-resolution models to evaluate its suitability for the CZO scale. If possible, CZ models will be used in a parallel projection. These subsurface carbon and water projections will be used to force WITCH, a process-based model of weathering [103; 104] which has been used to simulate water-mineral interactions from the arctic to tropics [103; 105-107]. We will run the model cascade to simulate 1950-2100.

Timeline and team personnel (Brantley, Godderis, Li, Duffy, Davis): Year 1: Model development and testing of the climate simulations along with the higher resolution climate downscaling. Year 2-3: Analysis of WITCH output and interpretations and comparison of model output to CZO measurements. Years 4-5: Re-running and analyzing the modeling systems for preparation of final publications.

Summary: Hypothesis-Driven Science in the New SSHO

As described in the last section, we propose to foster 9 teams of researchers to measure and model the CZ in the SSHO. The hypotheses target 1D (boreholes) and 2D (catena) systems within 4 sub-catchments of Shavers creek watershed (Shale Hills, forested sandstone, agricultural calcareous shale, forested calcareous shale) as shown in Fig. 2. The hypotheses cross scales of space and time as shown schematically in Fig. 9. The hypotheses also provide the essential framework to enable our goal of learning how to earthcast the Anthropocene future as shown in Fig. 12.

Implementation Plan: CZO National Cross-Network activities

The 6 original CZOs together have proposed the following 5 activities to facilitate and promote cross-site science among the CZOs. This text was placed on the national CZO website to enable other CZO proposers to include in their proposals.

CZ Network Cyberseminar Series. The CZOs will work with R. Hooper, Director of CUAHSI, to run six cyberseminars/yr. Seminars will follow frameworks established for CUAHSI cyberseminars; all viewers can see the slides; the speaker can point and annotate, and participants can comment and question by voice or text. This cyberseries will build upon the series of 6 talks run for CZO by CUAHSI in 2011-2012. In the next 5 years, we will highlight scientists and students working on CZ questions, regardless of whether they are a member of a CZO team. In some cases, a cyberseminar may be scheduled as follow-up after one of the cross-network activities outlined below. All CZ topics will be included.

CZ Network Research (CZNR) Workshop ($15k/CZO). Shale Hills will run one ~2.5-day CZNR Workshop on a cross disciplinary topic. SSHO will run, "*Trees in the CZ*", to be led by tree physiologist and ecologist D. Eissenstat. Workshop will include ~12 scientists/students from in/outside the CZO network. We will provide travel allowances, housing, and meals. The intent is to stimulate researchers to work together and across disciplines. The broadly advertised workshop will result in a proposal, synthesis paper, or integrative model. SSHO data will be highlighted appropriately with data from other sites. The workshop will focus on tree interactions including sap flux, LAI, rooting depth, and tree impacts on weathering/ erosion. The workshop will improve understanding of trees, water, and landscape evolution.

Drill-the-Ridge ($5k). Access to the bottom of the weathered rock zone is difficult to gain but is widely recognized as the CZ region we understand the least. In recognition of this, the CZO network is producing a special issue in Earth Surface Processes and Landforms [108], and ran a special session at AGU. Pilot coring projects have been run at all six original CZOs, and will be extended. The idea, called "Drill the Ridge" was proposed at the International Workshop on Design of Global Environmental Gradient Experiments using International CZO Networks (8-9 Nov 2011, Univ. of Delaware). The goal at each site will be to reach the water table and fresh rock, typically by wireline drilling, extracting core and overburden. Downhole logging will also be pursued, i.e., electrical logging, calipers, acoustic televiewer, optical televiewer, compensated density caliper, thermal neutral (relative porosity), heat pulse flowmeter, and hydrophysical logging. If possible, the borehole will be completed as a well, and instrumented with water level and temperature sensors, and will be used to collect water samples monthly using the method of choice (bailing or pump) at each site. These pilot coring projects will provide training for students in drilling technologies. Data from this initial Drill-the-Ridge campaign will be used to inform future proposals to core in more locations, with accompanying geophysical surveys, pump testing, and microbiological sampling. The depth of these initial pilot holes will vary from site to site. Holes will vary from 10 to 300 m in depth across all CZOs. At SSHO, boreholes will be drilled to approximately 20 m by professional drillers or with a PSU drill rig maintained by Duffy. Funding for SSHO "Drill the Ridge" derives from our recent renewal funds plus a new request here for $5k.

Joint Research Field Campaigns ($15k/CZO). All observatories will run three 5-day CZ Joint Research Field Campaigns spread over the next five years. Each site will host one field campaign, similar in format but with different foci. The host will support travel and accommodation for a total of 12 students, postdocs or scientists from other CZOs in each campaign. The intent is to stimulate researchers to develop shared data, to work together across disciplines, and to introduce students to new sites and techniques. It is expected that results from each Campaign will become part of the CZO community data resources. If appropriate, the CZOs may use the CZ Network Research Workshops to develop focused questions for the field campaigns, or for the CZ Network Research Workshops. For the SSHO campaign, For SSHO, Gooseff will lead a campaign to conduct a spatially intensive synoptic sampling of stream solute and heat fluxes (measuring stream chemistry, temperature, and discharge) in the larger Shavers Creek watershed. The goal of this work will be to enhance the spatial collection of observatory data and to discuss the approach being used, benefits/limitations, and study design for interested students.

Cross-CZO modeling ($10k/CZO). Ongoing modeling activities at each of the CZOs will be communicated and integrated across the network through a series of cross site visits to other CZOs. During those visits, modelers will be cross-fertilized in terms of conceptualizations and codes and will learn how to make best use of available data. To facilitate this, each CZO is pledging $10k for travel to enable modelers to visit or travel to other CZOs. CoIs Li and Duffy among others will participate.

Other SSHO-specific Cross-CZO efforts. Several one-by-one CZO cross-site efforts are also furthered by PSU: 1) SSHO is installing a *s::can* sensor similar to the sensors used by Christina River CZO to measure solutes. The Christina River CZO already has several *s::cans* installed and have tested global calibration algorithms for DOC. The two CZOs are collaborating on testing calibrations. D. Karwan (Univ. Minn.) is working with both CZOs to measure and understand total suspended sediment fluxes. Several cross-CZO modeling initiatives are also underway as described in the Hypotheses.

Broader Impacts: SSHO Engagement Plan

SSHO Will Attract Other Scientists by Cyberseminars and Scientific Special Sessions. One of our biggest goals, to stimulate science and education for those outside CZO, will be promoted by our participation in the CUAHSI cyberseminar series described above. In addition, SSHO investigators have many contacts across all relevant disciplines. We will use these contacts to engage nonCZO scientists in SSHO. In addition, the CZO will work with other CZOs to promote sessions at scientific meetings to highlight findings (see *Management Plan*) and we will also post info on our website that will facilitate visitors using our CZO. We also will annually invite one nonCZO visitor to give a talk at Penn State about CZ science. This visitor will be introduced to SSHO, inviting collaboration. A special thrust of SSHO will be to collaborate with CZO and nonCZO scientists to advance community approaches to design and operation of relocatable observing systems and modeling approaches based on a minimal set of essential measurements to enable scaling up from plot to hillslope to catchment. SSHO will foster web-based sharing of data and open-source access to models, tutorials and test cases (www.pihm.psu.edu).

SSHO will Engage Other Scientists through External Seed Grants. We will provide $10k in seed grants for two non-PSU researchers per year to work at SSHO. (A few will also be given to PSU researchers not currently on the budget.) These seeds will be awarded competitively and targeted to both new and returning researchers (see Table 4 in *Facilities* for summary of collaborators not explicitly included in this proposal – but we will also seek researchers not in Table 4). We will particularly encourage seed grant proposals from undergraduate-only or minority-serving institutions by using our shale transect contacts. The seed grant program is described more fully in the *Management Plan*. A CZO-China Visiting Scholar program will also be facilitated by H. Lin, who has many contacts in China in the CZ community. Currently, many CZ scholars in China have their own funding to work abroad, and Lin will connect Chinese scholars with CZOs in the U.S. to promote interactions.

SSHO Will Be a Community Resource. To enable the CZO as a community resource, the next 5 yrs of funding will provide 1.5 mos/y for Brantley and fulltime support each for the Watershed Specialist, the Program Coordinator, and the Cyberspecialist. One of the big jobs of these four CZO participants will be to enable outsiders to use our CZO (see *Management Plan*). We maintain and share our models, data, outreach, and samples and our site is open to all. We will work with nonSSHO researchers to i) make sure their work does not interfere with or duplicate ongoing work (Program Coordinator/Sample-based Data Specialist), ii) facilitate use of our sensors and power network (Watershed Specialist) and our data and samples (Program Coordinator/Sample-based Data Specialist and the Cyberspecialist).

Broader Impacts: SSHO Dissemination Plan for Sharing Models, Data, Outreach, Samples

Of course, the biggest push within our *Dissemination Plan* is to publish our work in peer-reviewed journals and to educate students in cross-disciplinary science. In the first 6 y of CZO, we have produced a cohort of students (see *Results of Prior NSF Support*) who worked across disciplines. We have found that a new paradigm for education and research has grown at PSU and that the students feel free to cross disciplinary boundaries. Many aspects of our *Management Plan* are aimed to facilitate this.

Sharing Models with Scientists and the Public: Sharing PIHM Modelling Tools and Models at Young Woman's Creek and Snake Creek. Throughout this proposal, we have emphasized Duffy's development of the Penn State Integrated Hydrologic Model, PIHM, and how it is being shared. Duffy will continue to run workshops to guide grad and postdoctoral students on the implementation of PIHM. In addition, he will continue to facilitate members of the European CZOs (*SoilTrec*) with whom we are collaborating to build catchment models (Czech Republic, Crete, Plynlimon, Damma Glacier). PIHM modeling is presently being carried out at the Christina R. CZO and other CZO sites are under discussion.

In addition, the CZO team argues that the biggest contribution we can make with respect to dissemination of our work is *to promote the notion that scientists have much to contribute in helping local communities deal with environmental problems*. The most controversial environmental problem in the PA region today is shale-gas development, including hydrofracking. As discussed earlier, the number of hydrofracked wells in PA has increased dramatically since 2006. So has public pushback. As a test of the implicit, underlying CZO hypothesis that "*intensive efforts at one watershed will inform our understanding of other watersheds*", we will build hydrologic models for two nonCZO watersheds, i.e. Young Woman's Creek (YWC) and Snake Creek (Snake) (Facilities, Fig. F4). These watersheds are roughly the same size as Shavers Creek and are underlain by similar sedimentary rocks. Snake creek watershed hosts 13 well pads for unconventional shale gas. YWC also lies in the area of shale gas drilling and we anticipate it will be drilled during our 5-yr grant timeframe.

To inform these models, we will utilize the HydroTerre geospatial data web services which have harmonized and automated access to data for geospatial soils (USDA, SSURGO), climate reanalysis (NOAA, LDAS-2), terrain (USGS, NED), land cover (USGS, NLCD-2) and the national hydrographic network (USGS, NHD). In addition, we work with G. Llewellyn (Appalachian Hydrogeologic Consulting), a hydrogeologist working in the Snake Creek watershed on shale gas issues who provides us data and logistical support (see letter). Furthermore, we are initiating a collaboration with V. Heilweil, a geologist at the U.S.G.S., who is investigating how to measure gas fluxes in stream networks and who seeks to start a project with us to monitor methane in Snake creek (see letter). Finally, we also collaborate with Prof J. Graney of SUNY Binghamton who is monitoring Snake Creek with the Susquehanna River Basin Commission (SRBC), Wilkes University, and the E.L. Rose Conservancy (NPO). The SRBC operates a multiparameter sonde on Snake Creek (SC) that transmits stage, conductivity, dissolved oxygen, pH, and temperature in real time to the web (srbc.net). Upstream from the SRBC sonde, Wilkes operates a multi-parameter sonde at the confluence on Silver Creek and Fall Brook (FB). The Binghamton team also has deployed stage/conductivity/temperature sondes in SC and FB in Salt Springs State Park. The Salt Springs brines are a natural laboratory in that the chemistry of the seeps mimics flowback water chemistry from gas wells that potentially could leak into streams in the region. The information from the sondes, surface and groundwater sampling will inform our watershed modeling. Graney has provided a letter of collaboration to assist in data sharing. As described in the next paragraph, these partners will be attending the Penn State-hosted Shale Network annual workshop.

Sharing Data through Data Management and the Shale Network. SSHO manages its data in concert with the other CZOs (see *Data Management Plan*). SSHO has also taken the lead with K. Lehnert (Columbia Univ., EarthChem) in organizing geochemical data for regolith [109-111]. In the next five years, this effort will continue along with a new push to upload water quality data into the CUAHSI (Consortium of Universities for the Advancement of Hydrologic Sciences, Inc.) Hydrologic Information System (HIS). In the past, the CZOs agreed to only post this water chemistry data as flat files on CZO websites; SSHO will now upload this data to HIS and teach the other CZOs how to do this as needed.

This latter effort has been accelerated because PI Brantley has been funded by NSF to work with CUAHSI to provide a water quality database accessible for the shale-gas region of the northeast. This effort, called *ShaleNetwork*, is uploading water chemistry datasets to the HIS that were collected by industry, government, universities, and citizen scientists. The Shale Network has uploaded 607,577 data entries for 1244 localities from 18 organizations including153 analytes to the HIS from 7 different sample media, including stream, ground, and flowback water. Brantley's leadership of Shale Network will now extend so that CZO students can participate in outreach concerning Marcellus gas development. Shale Network will host workshops in 2013 and 2014 for people interested in water quality in areas of shale gas, and CZO faculty and students will be invited to participate. The Shale Network also has started TeenShaleNetwork to teach 9-12th graders about shale gas and water quality, and CZO personnel will be invited to participate. Duffy similarly works with the State College Area High School to teach about wireless environmental sensors and this effort will be tied to TeenShaleNetwork.

Sharing Outreach with Environmental Music Concerts. The Watershed specialist and Cyberspecialist will collaborate with one Masters of Fine Arts (MFA) student working with Penn State Prof. B. Orland in the Dept of Landscape Architecture and Prof. Mark Ballora in the School of Music to explore sonification of CZO stream discharge and solute concentration time series data. Both Orland and Ballora work with StudioLab, an initiative that promotes artist-scientist collaborations. Orland and Ballora will mentor the MFA student who will also gather pilot data on the utility of sonification as a discovery mechanism for the CZO. This effort will culminate in an environmental data concert and outreach display at the Penn State Shavers Creek Environmental Center (>10,000 visitors/yr) and will also be posted online: *CZO Four Seasons* (apologies to Vivaldi; see collaboration letters from Wentzel, Orland). No NSF money is requested for Orland/Ballora. If this first concert is a success, we will pursue research on sonification as a new avenue of data analysis and public understanding. For example, this effort could eventually be promoted at the U.S. and European CZOs with a long-term goal of presenting a *CZO Four Seasons* concert of environmental data for different CZOs. Different types of time series data (e.g. precipitation, stream discharge, CO_2 flux, DOC and Mg concentrations in stream water) will have different characteristics that in some cases will produce cacophony and other times melodiousness.

Sharing Samples through CZ-Tope. SSHO is initiating an international effort, *CZ-Tope*, to promote isotopic measurements on identical CZ samples. This is highly useful right now because many "nontraditional" isotopic systems are being newly developed and have not yet been tested thoroughly in the field. For CZ-Tope so far, these isotopes have been measured or proposed for Shale Hills on identical samples: Fe [64], ^{10}Be [6; 22], U series [20; 21], Mg (L. Ma, Univ TX El Paso; F. Zhen [112]), S and C (L. Jin, Univ TX El Paso), Si (F. von Blanckenburg, see letter), B (J. Gaillardet, see letter), Li (M. Feinemann, PSU), and Ca (M. Fantle, PSU).

Results from Prior NSF Support

Brantley, Duffy, Lin, Eissenstat, Kirby, and Singha were all part of the initial 5-year CZO project NSF EAR-0725019 (Duffy, PI, Regolith and Critical Zone in the Susquehanna River Basin: The Shale Experiment, 11/1/07-10/31/13, $5,004,688), and Davis and Kaye joined the group for the 1-year renewal, NSF EAR- 1239285 (Brantley, PI, An Accomplishment-based Request for Renewal of the Susquehanna Shale Hills Critical Zone Observatory, $1,000,000, 9/1/12-8/31/13). Prior NSF Results from the CZO are summarized for these researchers. Results for researchers not salaried through CZO (Bierman, Gooseff and Li) are summarized at the end of this section.

Broader Impacts for CZO

CZO Education: Graduate students and postdoctoral fellows. 11 postdoctoral fellows and 20 grad students were partially supported with CZO funds to date (Soil Science, Meteorology, Ecology, Geosciences, Civil & Environmental Engineering). Of these, 50% were female.

Education: Undergraduate students, REUs, international CZO Field School, and satellite sites. Our original grant provided funding for REU students -- especially from the institutions associated with our shale transect sites (see Fig. F3 in *Facilities*) -- to work on shale. From 2008-2011, we funded 26 undergrads from PSU or the shale transect institutions (Univ. Puerto Rico, Alabama A&M, Univ. of Tenn., Washington & Lee, Juniata, and Colgate). Of the undergrads, 14/26 were female, 4/26 self-reported as African-American, and 6/26 self-reported as Hispanic-American. 15 undergrads have completed senior theses or given presentations at national meetings (6/15 from outside PSU). Three papers include student±faculty authors from the satellite sites [48; 49; 113].

REU field work organized by PSU targeted our Appalachian transect sites (see Fig. F3 in *Facilities*). The work was combined in 2010 with a field school organized in coordination with European *SoilTrec*. In this international CZO Field School fostered by PSU, we taught 10 students from 8 countries. Several international collaborative research projects were initiated. In addition, PSU students A. Dere and N. West are working on satellite site data with our satellite-site colleagues.

Education: K-12 students. PSU students participate in outreach. Students and the CZO watershed specialist helped the local State College Area High School run a Summer Science, Technology, Engineering and Math (STEM) Academy to deploy environmental sensors.

Education: Beyond CZO. One of the SSHO coIs, K. Singha, conducted three 3-week hydrogeophysics field camps from 2008-2010 focusing on Shale Hills. Funding derived from Singha's CAREER grant: ~10 undergrads / year; half from PSU and half from minority-serving institutions. SSHO also works closely with *SoilTrec*, a funded program of European CZ scientists. For example, Duffy is funded to build watershed models at 4 *SoilTrec* sites with US CZO-*SoilTrec* grad student collaboration. Two modeling workshops were held (2009, 2011) with US and international participation. This hydrologic research is fundamental to management of land and water within the Chesapeake Bay watershed. A workshop was held by Duffy for instruction on PIHM in Aug 2010: 27 participants (17/27 grad students) were taught to use PIHM for terrestrial hydrologic simulation.

Intellectual Merit for CZO

Results from Prior NSF Support for Scientists in the CZO. SSHO researchers have published 45 papers [6-8; 10-12; 14; 16; 17; 19-24; 26; 29; 30; 36-38; 40; 43; 45; 46; 48; 49; 62; 64; 79; 110; 111; 113-125]; students have completed 11 theses [13; 15; 18; 27; 28; 31; 32; 47; 126-128]; and SSHO has fostered two special issues [108; 129]. Successes and lessons learned have been described throughout this proposal. We have also collected extraordinary datasets as part of our CZO effort (see *Facilities, Data Management*) and used these to test and advance predictive modeling schemes for the CZ. We are providing the CZ community with the opportunity to tackle many long-standing problems in hydrogeology [16; 42] , geomorphology [21; 130] soil science and ecology [43; 131]. In addition, the CZO led us to discover a previously unreported phenomenon -- widespread but patchy manganese addition to soils in industrialized areas in the U.S. and Europe [23; 24].

Results from Prior NSF Support for Scientists New to the CZO*: 1) Gooseff*. NSF OPP-0327440 (PIs: Bowden, Gooseff (1 mo/y), w/ McNamara, Bradford), "Will climate change affect hyporheic processes in arctic streams? An assessment of interactions among geomorphology, hydrology, and biogeochemistry in Arctic stream networks", $608,709, 08/03 – 07/06. 11 peer-reviewed publications, 1Ph.D. dissertation, 2 M.S. theses. Two undergraduates involved. Professional presentations: 21. Data: http://water.engr.psu.edu/gooseff/arctic_proj.html. 2) *Li*. Assistant Prof. Li has been funded by DOE but not NSF. 3) *Bierman*. NSF ARC-0713956, "Detrital cosmochronology of Greenland Ice Sheet", $273,052, 9/15/07-10/30/11; 3 MS theses, 5 publications, 14 abstracts. Bierman, funded 29 times by NSF since 1993, has used that support to publish ~50 papers, including several in last 3 years [54; 132-139].

References

(1) Vitousek, P. M., Aber, J. D., Horwath, R. W., Likens, G. E., Matson, P. A., Schindler, D. W., Schlesinger, W. H., and Tilman, D. G., 1997. Human alteration of the global nitrogen cycle: sources and consequences. *Ecological Applications* **7**, 737-750.

(2) Vitousek, P. M., Mooney, H. A., Lubchenco, J., and Melillo, J. M., 1997. Human domination of Earth's ecosystems. *Science* **277**, 494-499.

(3) Crutzen, P. J., 2002. Geology of mankind. *Nature* **415**, 23-23.

(4) Wilkinson, B. H. and McElroy, B. J., 2007. The impact of humans on continental erosion and sedimentation. *Geological Society of American Bulletin* **119**, 140-156.

(5) Lynch, J. A., 1976. Effects of antecedent soil moisture on storm hydrographs, Penn State University, PhD.

(6) Jin, L., Ravella, R., Ketchum, B., Bierman, P. R., Heaney, P., White, T., and Brantley, S. L., 2010. Mineral weathering and elemental transport during hillslope evolution at the Susquehanna/Shale Hills Critical Zone Observatory. *Geochimica et Cosmochimica Acta* **74**, 3669-3691.

(7) Jin, L., Rother, G., Cole, D. R., Mildner, D. F. R., Duffy, C. J., and Brantley, S. L., 2011. Characterization of deep weathering and nanoporosity development in shale – a neutron study. *American Mineralogist* **96**, 498-512, DOI:10.2138/am.2011.3598.

(8) Brantley, S. L., Holleran, M., Jin, L., and Bazilevskaya, E., 2013, in press. Probing deep weathering in the Shale Hills Critical Zone Observatory, Pennsylvania (U.S.A.): The hypothesis of nested chemical reaction fronts in the subsurface. *Earth Surface Processes and Landforms*.

(9) Lin, H. S., 2006. Temporal stability of soil moisture spatial pattern and subsurface preferential flow pathways in the Shale Hills Catchment. *Vadose Zone Journal* **5**, 317-340.

(10) Kuntz, B., Rubin, S., Berkowitz, B., and Singha, K., 2011. Quantifying solute transport behavior at the Shale Hills Critical Zone Observatory. *Vadose Zone Journal* **10**, 1-15, doi:10.2136/vzj2010.0130.

(11) Ma, L., Jin, L., and Brantley, S. L., 2011. How mineralogy and slope aspect affect REE release and fractionation during shale weathering in the Susquehanna/Shale Hills Critical Zone Observatory. *Chemical Geology* **290**, 31-49.

(12) Ma, L., Jin, L., and Brantley, S. L., 2011. Geochemical behaviors of different element groups during shale weathering at the Susquehanna/Shale Hills Critical Zone Observatory. *Applied Geochemistry* **26**, S89-S93.

(13) Herndon, E., 2012. Biogeochemistry of manganese contamination in a temperate forested watershed, Pennsylvania State University, Department of Geosciences, Ph.D.

(14) Slim, M., Perron, J. T., Martel, S., and Singha, K., 2013, subm. Influence of topographic stress on rock fracture: A numerical model for arbitrary surface topography and comparisons with borehole observations. *Earth Surface Processes and Landforms*.

(15) Kuntz, B., 2010. Laboratory, Field, and Modeling Analysis of Solute Transport Behavior at the Shale Hills Critical Zone Observatory. Masters, Pennsylvania State University, Geosciences, Master of Science Thesis.

(16) Jin, L., Andrews, D. M., Holmes, G. H., Lin, H., and Brantley, S. L., 2011. Opening the "black box": water chemistry reveals hydrological controls on weathering in the Susquehanna Shale Hills Critical Zone Observatory. *Vadose Zone Journal* **10**, 928-942, doi:10.2136/vzj2010.0133.

(17) Takagi, K. and Lin, H. S., 2012. Changing controls of soil moisture spatial organization in the Shale Hills Catchment. *Geoderma*, 289-302.

(18) Andrews, D., 2011. Coupling Dissolved Organic Carbon and Hydropedology in the Shale Hills Critical Zone Observatory. Dissertation, Pennsylvania State University, Doctor of Philosophy.

(19) Andrews, D. M., Lin, H., Zhu, Q., Jin, L., and Brantley, S. L., 2011. Hot spots and hot moments of dissolved organic carbon export and soil organic carbon storage in the Shale Hills catchment. *Vadose Zone Journal* **10**, 943-954, doi: 10.2136/vzj2010.0149.

(20) Ma, L., Chabaux, F., Pelt, E., Blaes, E., Jin, L., and Brantley, S., 2010. Regolith production rates calculated with uranium-series isotopes at the Susquehanna/Shale Hills Critical Zone Observatory. *Earth and Planetary Science Letters* **297**, 211-225.
(21) Ma, L., Chabaux, F., West, N., Kirby, E., Jin, L., and Brantley, S. L., 2013, in press. Regolith production and transport in the Susquehanna Shale Hills Critical Zone Observatory, Part 1: Insights from U-series isotopes. *Journal of Geophysical Research -- Earth Sciences*.
(22) West, N., Kirby, E., Bierman, P., Slingerland, R., Ma, L., Rood, D., and Brantley, S. L., 2013, subm. Regolith production and transport at the Susquehanna Shale Hills Critical Zone Observatory: Part 2 - Insights from meteoric ^{10}Be. *Journal of Geophysical Research - Earth Surface*.
(23) Herndon, E. M. and Brantley, S. L., 2011. Movement of manganese contamination through the Critical Zone. *Applied Geochemistry* **26**, S40–S43.
(24) Herndon, E. M., Jin, L., and Brantley, S. L., 2011. Soils reveal widespread manganese enrichment from industrial inputs. *Environmental Science & Technology* **45**, 241-247.
(25) Shi, Y., Davis, K. J., Duffy, C. J., and Yu, X., 2012. A watershed scale groundwater-land-surface model. *Journal of Hydrometeorology* **in preparation**.
(26) Takagi, K. and Lin, H. S., 2011. Temporal dynamics of soil moisture spatial variability in the Shale Hills Critical Zone Observatory. *Vadose Zone Journal* **10**, 832-842.
(27) Takagi, K., 2009. Static and Dynamic Controls of Soil Moisture Variability in the Shale Hills Catchment, Masters Thesis, Pennsylvania State University, Crop and Soil Science, Master of Science Thesis.
(28) Holmes, G. H. I., 2011. Using δ^2H and $\delta^{18}O$ to Determine the Flowpaths and Timescales of Water at the Susquehanna Shale Hills Critical Zone Observatory, Pennsylvania State University, Civil and Environmental Engineering, Masters of Science Thesis.
(29) Thomas, E., Lin, H., Duffy, C., Sullivan, P., Holmes, G. H., Brantley, S. L., and Jin, L., 2013, subm. Spatiotemporal patterns of water stable isotope compositions at the Shale Hills Critical Zone: Linkages to subsurface hydrologic processes. *Vadose Zone Journal*.
(30) Duffy, C. J., 2010. Dynamical modeling of concentration-age-discharge in watersheds. *Hydrological Processes Journal* **24**, 1711-1718.
(31) Li, W., 2010. Implementing the Shale Hills Watershed Model in Application of PIHM, Pennsylvania State University, Civil Engineering, Master of Science Thesis.
(32) Kumar, M., 2009. Toward a Hydrologic Modeling System, Pennsylvania State University, Civil Engineering, Doctor of Philosophy.
(33) Kumar, M., Bhatt, G., and Duffy, C. J., 2009. An efficient domain decomposition framework for accurate representation of geodata in distributed hydrologic models. *International Journal of Geographical Information Science* **23**, 1569-1596.
(34) Kumar, M., Bhatt, G., and Duffy, C. J., 2010. An object-oriented shared data model for GIS and distributed hydrologic models. *International Journal of Geographical Information Science* **24**, 1061-1079.
(35) Kumar, M., Duffy, C. J., and Salvage, K. M., 2009. A second-order accurate, finite volume-based, integrated hydrologic modeling (FIHM) framework for simulation of surface and subsurface flow. *Vadose Zone Journal* **8**, 873-890.
(36) Li, S. and Duffy, C. J., 2011. Fully coupled approach to modeling shallow water flow, sediment transport, and bed evolution in rivers. *Water Resource Research* **47**, 1-20, doi:10.1029/2010WR009751
(37) Shi, Y., Davis, K. J., Duffy, C. J., and Yu, X., 2013, subm. Development of a coupled land surface hydrologic model and evaluation at a critical zone observatory. *Journal of Hydrometeorology*.
(38) Shi, Y., Davis, K. J., Zhang, F., and Duffy, C. J., 2013, subm. Evaluation of the parameter sensitivity of a coupled land surface hydrologic model. *Journal of Hydrometeorology*.
(39) Lin, H., Kogelmann, W. J., Walker, C., and Bruns, M. A., 2005. Soil moisture patterns in a forested catchment: A hydropedological perspective. *Geoderma* **131**, 345-368.

(40) Graham, C. and Lin, H. S., 2011. Controls and frequency of preferential flow occurrence: A 175-event analysis. *Vadose Zone Journal* **10**, 816-831.
(41) Doolittle, J., Zhu, Q., Zhang, J., Guo, L., and Lin, H. S., 2012. Geophysical Investigations of Soil-Landscape Architecture and Its Impacts on Subsurface Flow. In: Lin, H. (Ed.), *Hydropedology: Synergistic Integration of Soil Science and Hydrology*. Academic Press/Elsevier.
(42) Kirchner, J. W., 2003. A double paradox in catchment hydrology and geochemistry. *Hydrological Processes* **17**, 871-874.
(43) Naithani, K. S., Gaines, K. P., Baldwin, D., Lin, H. S., and Eissenstat, D. M., 2013, subm. Spatial distribution of tree species governs the spatio-temporal interaction of leaf area index and soil moisture across a forested landscape. *PLOS ONE*.
(44) Naithani, K. J., Gaines, K., Baldwin, D., Lin, H., and Eissenstat, D. M., 2011. Spatio-temporal dynamics of vegetation structure and hydrology at Shale Hills Critical Zone Observatory in central Pennsylvania*1st Conference on Spatial Statistics*, Enschede, Netherlands.
(45) Johnson, D. M., McCulloh, K. A., Meinzer, F. C., Woodruff, D. R., and Eissenstat, D. M., 2011. Hydraulic patterns and safety margins, from stem to stomata, in three eastern US tree species. *Tree Physiology* **31**, 659-68.
(46) Meinzer, F. C., Woodruff, D. R., Eissenstat, D. M., Lin, H. S., Adams, T. S., and McCulloh, K. A., 2013, in press. Above- and belowground controls on water use by trees of different wood types in an eastern United States deciduous forest. *Tree Physiology*.
(47) Shi, Y., 2012. Development of a land surface hydrologic modeling and data assimilation system for the study of subsurface-land surface interaction, The Pennsylvania State University, Meteorology Ph.D. Thesis.
(48) Mathur, R., Jin, L., Prush, V., Paul, J., Ebersole, C., Fornadel, A., Williams, J. Z., and Brantley, S. L., 2012. Cu isotopes and concentrations during weathering of black shale of the Marcellus Formation, Huntingdon County, Pennsylvania (USA). *Chemical Geology* **304-305**, 175-184, doi:10.1016/j.chemgeo.2012.02.015.
(49) Jin, L., Mathur, R., Rother, G., Cole, D., Bazilevskaya, E., Williams, J., Carone, A., and Brantley, S. L., 2013, subm. Evolution of porosity and geochemistry of Marcellus Formation black shale during weathering. *Chemical Geology*.
(50) Williams, J., Pollard, D., Bandstra, J., and Brantley, S. L., 2010. The temperature dependence of feldspar dissolution determined using a coupled weathering - climate model for Holocene-aged loess soils. *Geoderma* **156**, 11-19.
(51) Lebedeva, M. I., Fletcher, R. C., and Brantley, S. L., 2010. A mathematical model for steady-state regolith production at constant erosion rate. *Earth Surface Processes and Landforms* **35**, 508-524.
(52) Rasmussen, C., Brantley, S. L., de B. Richter, D., Blum, A. E., Dixon, J., and White, A. F., 2011. Strong climate and tectonic control on plagioclase weathering in granitic terrain. *Earth Planetary Science Letters* **301**, 521-530,doi:10.1016/j.epsl.2010.11.037.
(53) Chen, Y. and Brantley, S. L., 1997. Temperature- and pH-dependence of albite dissolution rate at acid pH. *Chemical Geology* **135**, 275-292.
(54) Portenga, E. W. and Bierman, P. R., 2011. Understanding Earth's eroding surface with ^{10}Be. *GSA Today* **21**, 4-10.
(55) Clarke, B. A. and Burbank, D. W., 2011. Quantifying bedrock-fracture patterns within the shallow subsurface: Implications for rock mass strength, bedrock landslides, and erodibility. *Journal of Geophysical Research* **116**, 1-22, doi:10.1029/2011JF001987
(56) Anderson, R. S., Anderson, S. P., and Tucker, G., 2013, in press. Rock damage and regolith transport by frost: An example of climate modulation of critical zone geomorphology. *Earth Surface Processes and Landforms*.
(57) Fletcher, R. C., Buss, H. L., and Brantley, S. L., 2006. A spheroidal weathering model coupling porewater chemistry to soil thicknesses during steady-state denudation. *Earth and Planetary Science Letters* **244**, 444-457.

(58) Riebe, C. S., Kirchner, J. W., Granger, D. E., and Finkel, R. C., 2001. Strong tectonic and weak climatic control of long-term chemical weathering rates. *Geology* **29**, 511-514.
(59) Stallard, R., 1995. Relating Chemical and Physical Erosion. In: White, A. F. and Brantley, S. L. Eds.), *Chemical Weathering Rates of Silicate Minerals*. Mineralogical Society of America, Washington, D.C.
(60) West, A. J., Galy, A., and Bickle, M., 2005. Tectonic and climatic controls on silicate weathering. *Earth and Planetary Science Letters* **235**, 211-228.
(61) Hren, M. T., Hilley, G. E., and Chamberlain, C. P., 2007. The relationship between tectonic uplift and chemical weathering rates in the Washington Cascades: field measurements and model predictions. *Am. J. Sci.* **307**, 1041-1063.
(62) Miller, S. R., Sak, P. B., Kirby, E., and Bierman, P. R., 2013, subm. Cenozoic rejuvenation of central Appalachian topography: Evidence for recent rock uplift from stream profiles and erosion rates. *Earth and Planetary Science Letters*.
(63) Brantley, S. L., Lebedeva, M., and Bazilevskaya, E., 2013. Relating weathering fronts for acid neutralization and oxidation to pCO_2 and pO_2. In: Farquhar, J., Kasting, J., and Canfield, D. Eds.), *The Atmosphere -- History*. Elsevier Amsterdam, The Netherlands.
(64) Yesavage, T. A., Fantle, M. S., Vervoort, J., Mathur, R., Jin, L., Liermann, L. J., and Brantley, S. L., 2012. Fe cycling in the Shale Hills Critical Zone Observatory, Pennsylvania: An analysis of biogeochemical weathering and Fe isotope fractionation. *Geochimica et Cosmochimica Acta* **99**, 18-38, doi.org/10.1016/j.gca.2012.09.029.
(65) Paterson, E., Midwood, A., and Millard, P., 2009. Through the eye of the needle: A review of isotope approaches to quantiy microbial processes mediating soil carbon balance. *New Phytologist* **184**.
(66) Rasmussen, C., Troch, P. A., Chorover, J., Brooks, P., Pelletier, J., and Huxman, T. E., 2011. An open system framework for integrating critical zone structure and function. *Biogeochemistry* **102**, 15-29.
(67) Groffman, P. M., Brumme, R., Butterbach-Bahl, K., Dobbie, K. E., Mosier, A. R., Ojima, D., Piapen, H., Parton, W. J., Smith, K. A., and Wagner-Riddle, C., 2000. Evaluating annual nitrous oxide fluxes at the ecosystem scale. *Global Biogeochemical Cycles* **14**, 1061-1070.
(68) Iverson, L. R., Prasad, A. M., Matthews, S. N., and Peters, M., 2008. Estimating potential habitat for 134 eastern U.S. tree species under six climate scenarios. *Forest Ecology and Management* **254**, 390-406.
(69) McCormack, M. L., Eissenstat, D. M., Prasad, A. M., and Smithwick, E., 2013, in press. Regional scale patterns of fine root lifespan and turnover under current and future climate. *Global Change Biology*.
(70) Smith, S. E. and Read, D. J., 2008. *Mycorrhizal Symbiosis*. Academic Press.
(71) Dauer, J. M., Withington, J. M., Oleksyn, J., Chorover, J., Chadwick, O. A., Reich, P. B., and Eissenstat, D. M., 2009. A scanner-based approach to soil profile-wall mapping of root distribution. *Dendrobiology* **62**, 35-40.
(72) Brundrett, M., Bougher, N., Dell, B., Grove, T., and Maljczuk, N., 1995. *Working with Mycorrhizas in Forestry and Agriculture, ACIAR Monograph 32*. Australian Center for International Agricultural Research, Canberra, Australia.
(73) Gebauer, R. and Voarik, D., 2012. Root hydraulic conductivity and vessel structure modification with increasing soil depth of two oak species: *Quercus pubescens* and *Quercus robur*. *Trees* doi:10.1007/s00468-012-0805-5.
(74) Bundt, M., Widmer, F., Pesaro, M., Zeyer, J., and Blaser, P., 2001. Preferential flow paths: Biological "hot spots" in soils. *Soil Biology & Biochemistry* **33**, 729-738.
(75) McClain, M. E., Boyer, E. W., Dent, C. L., Gergel, S. E., Grimm, N. B., Groffman, P. M., Hart, S. C., Harvey, J. W., Johnston, C. A., Mayorga, E., McDowell, W. H., and Pinay, G., 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. *Ecosystems* **6**, 301-312.

(76) Gottlein, A. and Manderscheid, B., 1998. Spatial heterogeneity and temporal dynamics of soil water tension in a mature Norway spruce stand. *Hydrological Processes* **12**, 417-428.
(77) Netto, A. M., Pieritz, R. A., and Gaudet, J. P., 1999. Field study on the local variability of soil water content and solute concentration. *Journal of Hydrology* **215**, 23-37.
(78) Guo, L., Chen, J., Cui, X., Fan, B., and Lin, H. S., 2013. Application of ground penetrating radar for coarse root detection and quantification: A review. *Plant and Soil* **362**, 1-23.
(79) Graham, C. B. and Lin, H. S., 2012. Hydropedograph toolbox and its applications. *Hydrology Earth System Sciences Discussions* **9**, 14231-14271.
(80) Salehikhoo, F., Li, L., and Brantley, S. L., 2013, in press. Magnesite dissolution rates at different spatial scales: The role of mineral spatial distribution and flow velocity. *Geochimica Cosmochimica Acta*.
(81) Maher, K., 2010. The dependence of chemical weathering rates on fluid residence time. *Earth and Planetary Science Letters* **294**, 101-110.
(82) Maher, K., Steefel, C. I., White, A. F., and Stonestrom, D. A., 2009. The role of reaction affinity and secondary minerals in regulating chemical weathering rates at the Santa Cruz soil chronosequence, California. *Geochimica et Cosmochimica Acta* **73**, 2804-2831.
(83) Maher, K., Steefel, C. I., DePaolo, D. J., and Viani, B. E., 2006. The mineral dissolution rate conundrum: Insights from reactive transport modeling of U isotopes and pore fluid chemistry in marine sediments. *Geochimica Et Cosmochimica Acta* **70**, 337-363.
(84) Navarre-Sitchler, A., Steefel, C., Yang, L., Tomutsa, L., and Brantley, S. L., 2009. Evolution of porosity and diffusivity associated with chemical weathering of a basalt clast. *Journal of Geophysical Research-Earth Science* **114**, 1-14, doi: 10.1029/2008JF001060.
(85) Godsey, S. E., Kirchner, J. W., and Clow, D. W., 2009. Concentration-discharge relationships reflect chemostatic characteristics of US catchments. *Hydrological Processes* **23**, 1844-1864, doi:10.1002/hyp.7315.
(86) Hood, E., Gooseff, M. N., and Johnson, S. L., 2006. Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon. *Journal of Geophysical Research* **111**, DOI:10.1029/2005JG000082.
(87) Alexander, R. G., SMith, R. A., and Schwarz, G. E., 2000. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. *Nature* **403**, 758-761.
(88) McGlynn, B. L. and McDonnell, J. J., 2003. Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics. *Water Resources Research* **39**, doi:10.1029/2002WR001525.
(89) Payn, R. A., Gooseff, M. N., McGlynn, B. L., Bencala, K. E., and Wondzell, S. M., 2012. Exploring changes in the spatial distribution of stream baseflow generation during a seasonal recession. *Water Resources Research* **48**, doi:10.1029/2011/WR011552.
(90) Jensco, K. G., McGlynn, B. L., Gooseff, M. N., Wondzell, S. M., Bencala, K. E., and Marshall, L. A., 2008. Hydrologic connectivity between landscapes and streams: Transferring reach and plot scale understanding to the catchment scale. *Water Resources Research* **W04428**.
(91) Qu, Y. and Duffy, C. J., 2007. A semidiscrete finite volume formulation for multi-process watershed simulation. *Water Resources Research* **43**, doi:10.1029/2006WR005753.
(92) Reed, P. M., Brooks, R. B., Davis, K. J., DeWalle, D. R., Dressler, K. A., Duffy, C. J., Lin, H., Miller, D. A., Najjar, R. G., Salvage, K. M., Wagener, T., and Yarnal, B., 2006. Bridging river basin scales and processes to assess human-climate impacts and the terrestrial hydrologic system. *Water Resource Research* **42**, 11.
(93) Godderis, Y., Brantley, S. L., Francois, L., Schott, J., Pollard, D., Deque, M., and Dury, M., 2013. Rates of consumption of atmospheric CO2 through the weathering of loess during the next 100 yr of climate change. *Biogeosciences* **10**, 135-148.
(94) Salas y Melia, D., Chauvin, F., Deque, M., Douville, H., J.-F., G., Marquet, P., Planton, S., Royer, J.-F., and Tyteca, S., 2005. Description and validation of CNRM-CM3 global coupled climate model. *Note de centre GMCEC, CNRM* **103**.

(95) Gibelin, A. L. and Deque, M., 2003. Anthropogenic climate change over the Mediterranean region simulated by a global variable resolution model. *Climate Dynamics* **20**, 327-339.
(96) Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., 2007. *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, UK and New York, NY, USA.
(97) Fox-Rabinovitz, M., Cote, J., Dugas, B., Deque, M., and McGregor, J. I., 2006. Variable resolution general circulation models: Stretched-grid model intercomparison project (SGMIP). *Journal of Geophysical Research* **111**, D16104.
(98) Dury, M., Hambuckers, A., Warnant, P., Henrot, A., Favre, E., Ouberdous, M., and Francois, L., 2011. Responses of European forest ecosystems to 21st century climate: Assessing changes in interannual variability and fire intensity. *iForest* **4**, 82-99.
(99) Warnant, P., Francois, L., Strivay, D., and Gerard, J.-C., 1994. CARAIB: A global model of terrestrial biological productivity. *Global Biogeochemical Cycles* **8**, 255-270.
(100) Nemry, B., Francois, L., Gerard, J.-C., Bondeau, A., and Heimann, M., 1999. Comparing global models of terrestrial net primary productivity (NPP): analysis of the seasonal atmospheric CO_2 signal. *Global Change Biology* **5**, 65-76.
(101) Otto, D., Rasse, D., Kaplan, J., Warnant, P., and Francois, L., 2002. Biospheric carbon stocks reconstructed at the last glacial maximum: Comparison between general circulation models using prescribed and computed sea surface temperatures. *Global Planet Change* **33**, 117-138.
(102) Francois, L. M., Utescher, T., Favre, E., Henrot, A.-J., Warnant, P., Micheels, A., Erdei, B., Suc, J. P., Cheddadi, R., and Mosbrugger, V., 2011. Modelling late Miocene vegetation in Europe: Results of the CARAIB model and comparison with palaeovegetation data. *Palaeogeography Palaeoclimatology Palaeoecology* **304**, 359-378.
(103) Godderis, Y., Francois, L., Probst, A., Schott, J., Moncoulon, D., Labat, D., and Viville, D., 2006. Modelling weathering processes at the catchment scale: The WITCH numerical model. *Geochimica et Cosmochimica Acta* **70**, 1128-1147.
(104) Godderis, Y., Williams, J. Z., Schott, J., Pollard, D., and Brantley, S. L., 2010. Time evolution of the mineralogical composition of Mississippi Valley loess over the last 10 kyr : Climate and geochemical modelling. *Geochimica et Cosmochimica Acta* **74**, 6357-6374, doi:10.1016/j.gca.2010.08.023.
(105) Roelandt, C., Godderis, Y., Bonnet, M.-P., and Sondag, F., 2010. Coupled modeling of biospheric and chemical weathering processes at the continental scale. *Global Biogeochemical Cycles* **24**, 1-18.
(106) Violette, A., Godderis, Y., Marechal, J.-C., Riotte, J., Oliva, P., Mohan Kumar, M. S., Sekhar, M., and Braun, J.-J., 2010. Modelling the chemical weathering fluxes at the watershed scale in the Tropics (Mule Hole, South India): Relative contribution of the smectite/kaolinite assemblage versus primary minerals. *Chemical Geology* **277**, 42-60.
(107) Beaulieu, E., Godderis, Y., Labat, D., Roelandt, C., Calmels, D., and Gaillardet, J., 2011. Modeling of water-rock interaction in the Mackenzie basin: Competition between sulfuric and carbonic acids. *Chemical Geology* **289**, 114-123.
(108) Riebe, C. and Brantley, S. L., 2013, in prep. A Special Issue: Probing the Deep Critical Zone. *Earth Surface Processes and Landforms*.
(109) Hofmockel, M., Richter, D., Miller, D., and Brantley, S. L., 2007. Building critical zone research cyberinfrastructure. *EOS Transactions*, *American Geophysical Union* **88**, 560.
(110) Niu, X., Lehnert, K. A., Williams, J. Z., and Brantley, S. L., 2011. CZChemDB and EarthChem: Advancing management and access of critical zone geochemical data. *Applied Geochemistry* **26**, S108–S111.
(111) Niu, X., Williams, J., Miller, D., Lehnert, K., Bills, B., and Brantley, S. L., 2013, subm. An ontology driven relational geochemical database for the Earth's Critical Zone: CZchemDB. *Journal of Environmental Informatics*.

(112) Ma, L., Teng, F.-Z., Ke, S., Yang, W., Jin, L., and Brantley, S. L., 2013, in prep. Mg isotope fractionation during shale weathering in the Shale Hills Critical Zone Observatory: Why Mg in soil minerals are isotopically light. *Chemical Geology*.
(113) Dere, A. L., White, T. S., April, R. H., Reynolds, B., Miller, T. E., Knapp, E. P., McKay, L. D., and Brantley, S. L., 2013, subm. Climate dependence of feldspar weathering along a latitudinal gradient. *Geochimica Cosmochimica Acta*.
(114) Yu, X., Bhatt, G., Duffy, C. J., and Shi, Y., 2013, subm. Parameterization for distributed watershed modeling using national data and evolutionary algorithm. *Computers and Geosciences*.
(115) Lin, H. S. and Zhou, X., 2008. Evidence of subsurface preferential flow using soil hydrologic monitoring at the Shale Hills catchment. *European Journal of Soil Science* **59**, 34-49.
(116) Herndon, E. M., Martinez, C. E., and Brantley, S. L., 2013, subm. Spectroscopic (XANES/XRF) characterization of manganese biogeochemistry in a temperature forested watershed. *Geochimica Cosmochimica Acta*.
(117) Brantley, S. L., Buss, H., Lebedeva, M., Fletcher, R. C., and Ma, L., 2011. Investigating the complex interface where bedrock transforms to regolith. *Applied Geochemistry*, S12–S15, DOI:10.1016/j.apgeochem.2011.03.017
(118) Anderson, S. A., Bales, R. C., and Duffy, C. J., 2008. Critical Zone Observatories: Building a network to advance interdisciplinary study of Earth surface processes. *Mineralogical Magazine* **72**, 7-10.
(119) Jin, L. and Brantley, S. L., 2011. Soil chemistry and shale weathering on a hillslope influenced by convergent hydrologic flow regime at the Susquehanna/Shale Hills Critical Zone Observatory. *Applied Geochemistry* **26**, S51–S56.
(120) Liermann, L. J., Mathur, R., Wasylenki, L. E., Nuester, J., Anbar, A. D., and Brantley, S. L., 2011. Extent and isotopic composition of Fe and Mo release from two Pennsylvania shales in the presence of organic ligands and bacteria. *Chemical Geology* **281**, 167-180.
(121) Lin, H. S., 2011. Three principles of soil change and pedogenesis in time and space. *Soil Science Society of America Journal* **75**, 2049-2070.
(122) Lin, H. S., 2010. Earth's Critical Zone and Hydropedology: Concepts, characteristics and advances. *Hydrology and Earth System Science* **14**, 25-45.
(123) Lin, H. S., Hopmans, J. W., and Richter, D. B., 2011. Interdisciplinary sciences in a global network of Critical Zone Observatories. *Vadose Zone Journal* **10**, 5.
(124) West, N., Kirby, E., Bierman, P. R., and Rood, D., 2011. Preliminary estimates of regolith generation and mobility in the Susquehanna Shale Hills Critical Zone Observatory, Pennsylvania, using meteoric 10Be. *Applied Geochemistry* **26**, S146–S148.
(125) Zhang, J., Lin, H. S., and Doolittle, J., 2013, in press. Soil layering and preferential flow impacts on seasonal changes of GPR signals in two contrasting soils. *Geoderma*.
(126) Baldwin, D., 2011. Catchment-scale soil water retention characteristics and delineation of hydropedological functional units in the Shale Hills catchment, The Pennsylvania State University, Crop and Soil Science, Masters of Science Thesis.
(127) Wubbels, J., 2010. Tree species distribution in relation to stem hydraulic traits and soil moisture in a mixed hardwood forest in central Pennsylvania Pennsylvania State University, Horticulture, Master of Science Thesis.
(128) Zhang, J., 2011. Integrated Approach to Identifying Subsurface Flow in a Forest Catchment Dissertation, The Pennsylvania State University, Crop and Soil Science, Ph.D. Thesis.
(129) Lin, H. S., Hopmans, J. W., and Richter, D. B., 2011. Vadose Zone Journal Special Issue: Critical Zone Observatories.
(130) Heimsath, A. M., Dietrich, W. E., Nishiizumi, K., and Finkel, R. C., 1997. The soil production function and landscape equilibrium. *Nature* **388**, 358-361.
(131) Graham, R. C., Rossi, A. M., and Hubbert, K. R., 2010. Rock to regolith conversion: Producing hospitable substrates for terrestrial ecosystems. *GSA Today* **20**, 4-9.

(132) Graly, J., Reusser, L. J., and Bierman, P. R., 2011. Short and long-term delivery rates of meteoric ^{10}Be to terrestrial soils. *Earth and Planetary Science Letters* **302**, 329-336.
(133) Reusser, L. J. and Bierman, P. R., 2010. Tracking fluvial sand through the Waipaoa River Basin, New Zealand, with meteoric ^{10}Be. *Geology* **10**, 47-50.
(134) Reusser, L. J., Corbett, L. B., and Bierman, P. R., 2012. Incorporating concept sketching into teaching undergraduate geomorphology. *Journal of Geoscience Education* **60**, 3-9.
(135) Reusser, L. J., Graly, J., Bierman, P. R., and Rood, D., 2010. Calibrating a long-term meteoric Be-10 accumulation rate in soil. *Geophysical Research Letters* **37**, DOI: 10.1029/2010GL044751.
(136) Pearce, A., Bierman, P. R., Druschel, G. K., Massey, C., Rizzo, D. M., Watzin, M. C., and Wemple, M. C., 2010. Pitfalls and successes of developing an interdisciplinary watershed field camp. *Journal of Geoscience Education* **58**, 213-220.
(137) Jungers, M. C., Bierman, P. R., Matmon, A., Nichols, K., Larsen, J., and Finkel, R., 2009. Tracing hillslope sediment production and transport with in situ and meteoric ^{10}Be. *Journal of Geophysical Research* **-** *Earth Surface* **114**.
(138) Cox, R., Bierman, P. R., Jungers, M. C., and Rakotondrazafy, M., 2009. Erosion rates and sediment sources in Madagascar inferred from ^{10}Be analysis of lavaka, slope, and river sediment. *Journal of Geology* **117**, 363-376.
(139) Parris, A. S., Bierman, P. R., Noren, A. J., Prins, M., and Lini, A., 2010. Holocene paleostorms identified by particle size signatures in lake sediments from the northeastern United States. *Paleolimnology* **43**, 29-49.

Facilities

The Observation Network at Shale Hills. Shale Hills has a comprehensive instrument base for physical, chemical and biological characterization of water, energy, stable isotopes and geochemical conditions (see Fig. F1). This includes a dense network of soil moisture observations at multiple depths (120), a shallow observation well network (25 wells), soil lysimeters at multiple depths (80+), a research weather station including eddy flux measurements for latent and sensible heat flux/CO_2/water vapor, net radiation, barometric pressure, temperature, relative humidity, wind speed/direction, snow depth sensors, leaf wetness sensors, and a load cell precipitation gauge. A laser precipitation monitor (LPM: rain, sleet, hail, snow, etc.) was installed in 2008, as were automated water samplers (daily) for precipitation, groundwater, and stream water for chemistry and stable isotopes. A snow scale was installed and began operation in 2012.

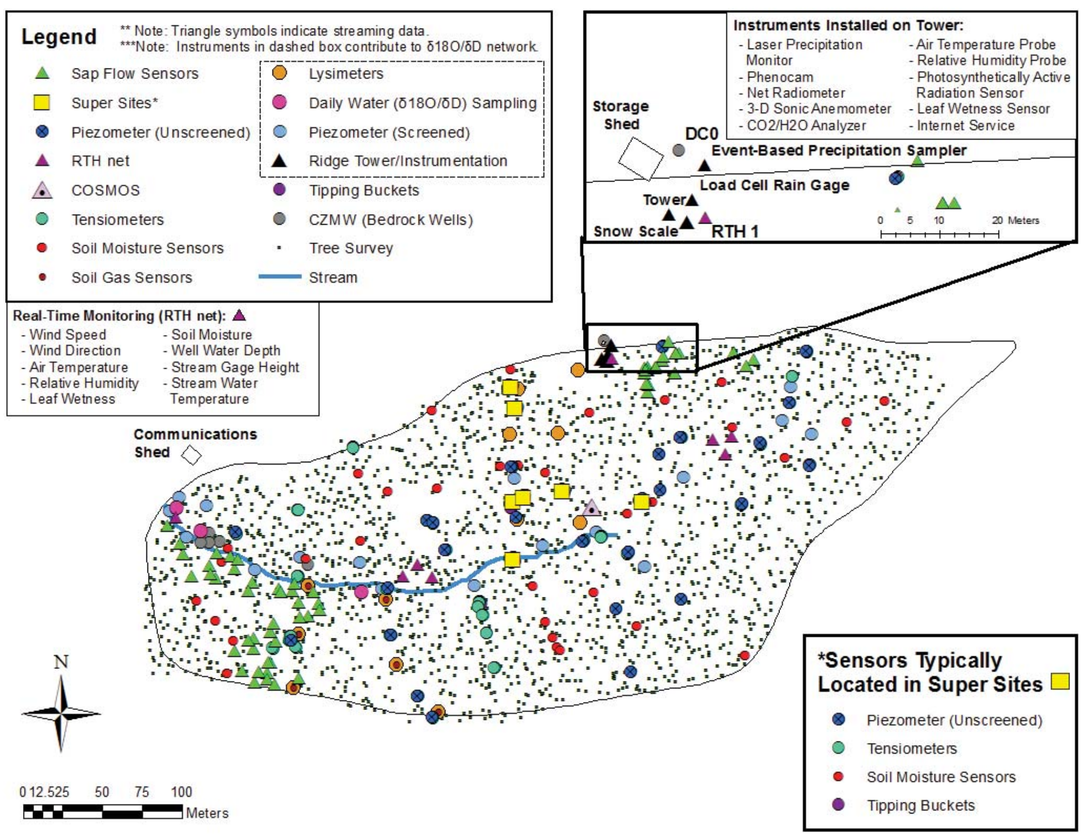

Figure F1. Comprehensive map of instrumentation at Shale Hills, including all trees surveyed. Research infrastructure at Shale Hills will be maintained as part of this proposal.

For approximately 3 years, porous cup tension lysimeters were sampled weekly during the non-winter months and samples are available. Arrays of sapflow measurements have been carried out each year as a function of tree species (25 species in the watershed). Geochemical measurements for solution chemistry, and water isotopes were carried out approximately every other week for more than two years on the soil lysimeter profiles, and continue currently for stream, groundwater and precipitation. Real time observations for soil moisture, groundwater level, streamflow, and weather are collected at 10 minute intervals. Water samples for stable isotopes of precipitation are collected adaptively at 6-hr intervals. Stream samples and groundwater samples (2 sites) are collected and processed daily. Partial pressure of oxygen has been measured *in situ* every ten minutes in the soil atmosphere at several depths at two locations near the valley floor for more than a year. Recently a wireless sensor network has been deployed for groundwater level, ground temperature, and electrical conductance at observation well locations and data from other locations in the watershed will also be transmitted wirelessly for collection.

In addition, A. Richardson (Harvard Univ.) has provided a high resolution video camera (StarDot NetCam SC Megapixel Hybrid IP Camera) that we have mounted at the eddy flux tower at the Shale Hills CZO. This camera monitors phenology (leaf emergence and fall leaf senescence are basic examples) and snow cover with greater temporal resolution than is logistically feasible for individual observers. This camera also helps support a PSU student-initiated project to monitor phenology in central PA (*PennPhen*, www.sites.google.com/site/psuphenology), contributes data to a larger network of phenology observations (http://phenocam.sr.unh.edu/), and provides data that supports ongoing projects at the CZO.

Table 1. Partial list of collaborators working at SSHO who are not listed as co-Investigators but who provide additional data or samples

Name	Institution	Focus of Project	Status of Project
Mezimir Wagaw	Alabama A&M	Soil on shale in AL	Satellite team
Rob Jacob	Bucknell Univ	gravity measurements	Unfunded, ongoing
Brian Reynolds	CEH, Wales	Soil on shale in Wales	Satellite team
Rich April	Colgate Univ	Soil development on shale till	Satellite team
Jed Sparks	Cornell Univ	Sr and Si cycling	NSF prop. Submitted
Lou Derry	Cornell Univ	Sr and Si cycling	NSF prop. Submitted
Andrew Richardson	Harvard Univ	PhenoCam	Unfunded, ongoing
Ryan Mathur	Juniata College	Soil on Marcellus shale	Satellite team
Taylor Perron	MIT	Fractures, fluid flow, topography	Unfunded, ongoing
Anne Krapiel	Princeton Univ	Mo and V cycling	NSF funded, ongoing
Karen Salvage	SUNY Binghamton	Hydrogeological modeling	NSF funded, 1st round
Laura Toran	Temple Univ	Hydrogeophysics	NSF funded, 1st round
Fangzhen Teng	Univ of Arkansas	Mg isotopes at Shale Hills	Unfunded, ongoing
Diana Karwan	Univ of DE	sediment transport, Cs, Pb isotopes	NSF funded, ongoing
Tom Johnson	Univ of Puerto R.	Soil development on shale	Satellite team
Chris Fedo	Univ of Tennessee	Soil on shale in TN	Satellite team
Paul Biermann	Univ of VT	Cosmogenic isotopes	Ongoing
F.-Z. Teng	Univ of Arkansas	Mg isotopes	Ongoing
Lin Ma	Univ TX, El Paso	REE in shale transect sites	USGS funded, ongoing
Lixin Jin	Univ TX, El Paso	C isotopes at Shale Hills	UTEP funded, ongoing
David Woodruff	USDA Forest Service	Sap flux and tree water relations	PSU & Forest Service
Frederick Meinzer	USDA Forest Service	Sap flux and tree water relations	PSU & Forest Service
Elisabeth Knapp	Wash and Lee	Soil on shale in VA	Satellite team
Jonathan Nyquist	Temple Univ	Water at soil-bedrock interface	NSF funded, ongoing
Beth Boyer	Penn State	DOC, precipitation monitoring	Unfunded, ongoing
Mary Ann Bruns	Penn State	Soil microbiology	Unfunded, ongoing
Rudy Slingerland	Penn State	Sediment transport, tree throw	NSF funded, 1st round
Maureen Feinmann	Penn State	Li isotopes at SSHCZO	Unfunded, ongoing
Matt Fantle	Penn State	Ca isotopes at SSHCZO	Unfunded, ongoing
Margot Kaye	Penn State	Assessment of litterfall	PSU funded, ongoing
David Pollard	Penn State	Climate modelling for transect	Unfunded, ongoing
Tim White	Penn State	Transect	NSF funded, 1st round

PSU Geosciences grad students E. Herndon (now a postdoc at Oak Ridge Nat. Lab) and A. Dere worked with Princeton geochemist A. Krapiel (Table 1) to sample and analyze the chemistry of vegetation. Samples are being archived for sharing.

Available datasets from Shale Hills. A large number of datasets have been collected that are either online or will soon be online for the CZO (locations can be found on CZO website). The Shale Hills watershed and the larger Shaver Creek watershed have hosted 3 airborne LIDAR flights with the most recent flights at 0.5 m resolution to evaluate micro-topography and tree species identification. Bedrock elevation surveys have been carried out with ground-penetrating radar and verified at spots with rotary air-drilling and hand augering. Ground-based LiDAR and total station surveys have been carried out for all instrument elevations. A survey of all trees >20cm diameter at breast height (dbh) is available including GIS coordinates, species and crown height. The survey is illustrated in Figure F2. Leaf Area Index (LAI), greenness index, distribution and CO_2 flux are regularly measured. An analysis of microbial cell density, including analysis for Fe-related bacteria, has been completed on a hillslope transect on the south side and a description has been published.

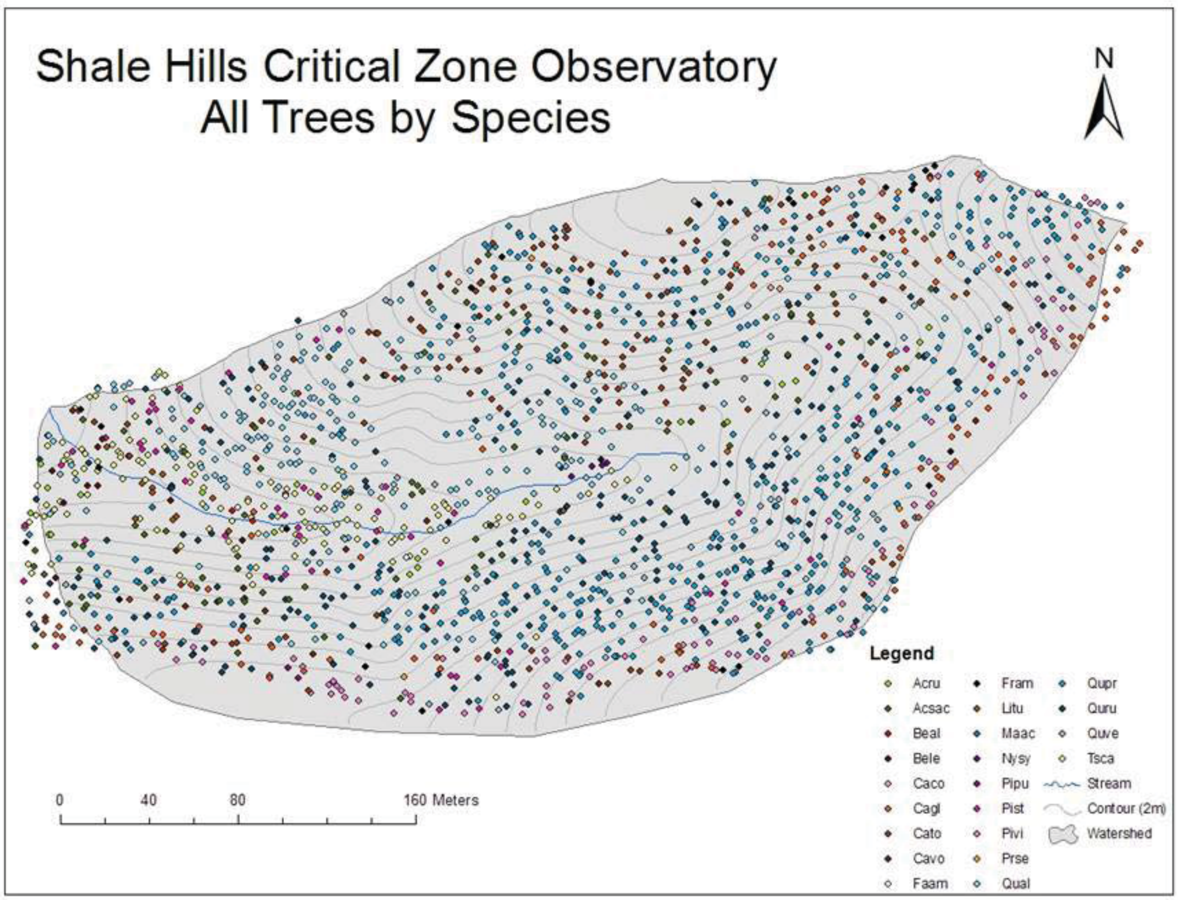

Figure F2. The tree species distribution at Shale Hills Critical Zone Observatory, as surveyed by CZO researchers: legend indicates major tree species. These and the leaf area index (LAI) seasonal data are the most frequently requested data sets from the CZO Ecology group.

A complete suite of borehole logging was done at 4 locations to 17m and complete chemical and mineralogical data is available for the same sites. Logs and geochemical characterization are also available for one deep borehole (25 m) on the north side of the catchment. Some of the boreholes have logs available for (1) spectral gamma – a measure of the U, K, and Th decay within the subsurface materials; (2) caliper -- borehole-diameter log to locate broken and fractured zones; (3) fluid resistivity -- total dissolved solids in the water column; (4) fluid temperature; (5) heat-pulse flowmeter--rate and direction of vertical flow in a borehole; and (6) optical tele-viewer for a continuous, oriented, true-color 360^{o} image of the borehole wall. Additionally hydraulic and tracer tests were done to estimate the effective hydraulic properties in all wells in the field. Other datasets are summarized online or in the *Data Management* section.

Available samples. The following samples from the CZO have also been collected and archived: soils, fractured rock, bedrock, leaf litter, green leaf samples, woody materials, soil porewaters, streamwaters and tree increment cores. These samples are being archived after analysis and labeled using notation developed as part of the geochemical sample data effort described in the *Data Management* section. Samples have already been shared with several researchers outside of PSU (e.g. Ma, L.; Jin, L.; Krapiel, A; Derry, L.; see Table 1).

Regolith samples are also available for the satellite sites, as described in the next section, either through the satellite team institutions (Table 1) or in the PSU archive.

Shale Transect satellite sites. We have established a set of satellite sites on Marcellus shale (PA), Rose Hill shale (in NY, VA, TN, AL), or its compositional or stratigraphic equivalent (Puerto Rico; Plynlimon, Wales; see Figure F3). These sites were monitored using a meteorological station that PSU designed and built for each site. Meteorological stations have not been implemented for the Marcellus because it lies in the same climate zone as SSHO nor for Plynlimon, because it is the site of a very large and well-studied hydrologic investigation by the Center for Ecology and Hydrology, Wales. Colleagues from local institutions (Table 1) operate these sites with Penn State student A.Dere, and the sites comprise part of the foci of the PhD theses of 2 PSU grad students. Samples are available for sites from regolith to bedrock. While the satellite sites are not explicitly part of the current proposal, we will continue relationships with investigators at those sites and maintain the data record and archive from the sites.

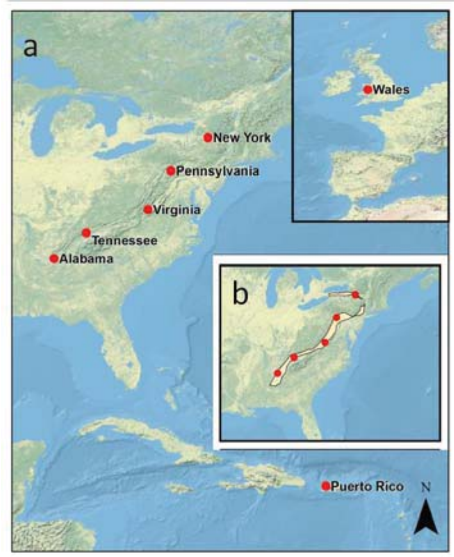

Figure F3. Map documenting the satellite sites. Sites involve collaboration with participants at local institutions as a way of incorporating minority-serving and undergraduate-dominated institutions, as well as one international colleague (see Table 1). Most of the sites lie along a gradient in climate variables that comprise a climosequence developed on identical lithology (Rose Hill Formation or its stratigraphic or compositional equivalent). One additional site plots on the map in the same location as SSHO – this site is managed by our colleague R. Mathur at Juniata College, and overlies organic-rich Marcellus shale.

Planned observation network for Shavers Creek. Testing the hypotheses listed in the *Project Description* and extending the scope of CZ research at SSHO requires expanding the observation network beyond Shale Hills to include other sites that characterize the diversity of CZ environments in the larger Shavers Creek watershed. To accomplish this, we have selected several first-order catchments (Figure 2) that span the lithologic and land use/land cover variation in the watershed. Each catchment will be observed for one year spanning the CZ variables described in the Implementation Plan (see Table in

Management Plan). The studies for each catchment will include deployment of a relocatable array of sensors to measure hydrological and meteorological variables as described in hypotheses H7 and H8. The catchments will be sampled for ecological variables (e.g. leaf area index) and catena transects sampled for soil properties and geochemistry. Deep boreholes in each catchment will characterize the geophysical structure. In addition to the three new catchments, streamflow and hydrochemistry will be monitored at three sites: above and below Lake Perez Dam and at the outlet of Shavers Creek into the Juniata River.

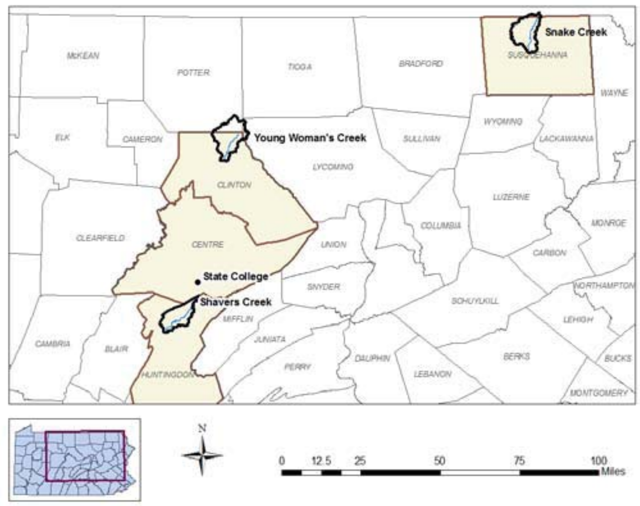

Figure F4. We will use what we learn in the Susquehanna Shale Hills Observatory (labeled Shaver's Creek in Huntingdon county) to develop models for two satellite watersheds, Snake Creek and Young Woman's Creek. Most data collection for the two northern watersheds will be completed by other entities as described in *Project Description.*

Shale Gas Exploration Satellite Sites. Research and data collection currently underway at the two Shale Gas Exploration Satellite sites (Figure F4) will be integrated with conceptual and numerical models from SSHO as described in *Project Description*.

Personnel from Binghamton University (Dr. Joe Graney and students) are actively collaborating with personnel from the Susquehanna River Basin (SRBC), Wilkes University, and the E.L. Rose Conservancy (NPO) in the Snake Creek watershed. As a part of their remote water quality monitoring network, the SRBC operates a multiparameter sonde that transmits stage, conductivity, DO, pH, and temperature in real time to their srbc.net website. Upstream from the SRBC sonde, Wilkes operates a multi-parameter sonde at the confluence on Silver Creek and Fall Brook. Binghamton University (BU) has deployed stage/conductivity/temperature sondes in SC and FB in Salt Springs State Park (SSSP). The springs in SSSP provide a natural laboratory to assess brine seeps that may mimic surficial leakage concerns associated with natural gas extraction in the region. The information from the nested sonde network, as well as ongoing surface and groundwater sampling, will provide information for the watershed modeling in Snake Creek. Graney will act as a collaborator on this project to assist in data acquisition requirements and logistics in the Snake Creek effort. Investigators and students from PSU will collaborate with BU and other partners to apply models adapted from Shale Hills/Shavers Creek at Snake Creek. Also collaborating on Snake Creek are G. Llewellyn (Appalachian Hydrogeologic Consulting) and V. Heilweil (USGS, starting to collaborate with us on techniques of monitoring CH_4 in northern PA watersheds).

Data are collected at the Young Woman's Creek watershed as part of the SRBC's remote water quality network (since August 2012) and a National Atmospheric Deposition Program site has been maintained in the watershed since 1999. The outlet of Young Woman's Creek is gauged by the US Geological Survey and water chemistry is measured and available.

Other Facilities at Penn State. Materials Characterization Laboratory (MCL)/Laboratory for Isotopes and Metals in the Environment (LIME). At Penn State, the MCL and LIME provides analytical services, specialized instruments, personnel and expertise in materials and minerals characterization in support of research and training. Researchers and students can use the facilities to obtain their own data. Other persons may complete work by hiring or collaborating with fulltime MCL personnel.

Equipment available include (underlined equipment will be used for the proposed work while other instrumentation is available): AFM (Digital Instruments Digital Instruments AFM/LFM Scanning Probe Microscope and Digital Instrument Nanoscope IIIa Dimension 3100 microscope); ICP-AES

(Leeman Labs PS3000UV inductively coupled plasma emission spectrophotometer); ICP-MS (Thermo X-Series II quadrupole ICP-MS); EA-IRMS (Coztech elemental analyzer (EA) connected to Thermo Conflo IV device and Combi PAL auto-sampler connected to Thermo Gas Bench); ICP-MS (Thermo-Scientific Neptune Plus multiple collector with UPS); IR (several models of infrared spectrometers are available for both solution and solid state analysis); LECO S analyzer; SEM (ISI SX 40 secondary electron microscope; ISI SX 40A with energy dispersive xray analysis capability; JEOL JSM-6300F with EDS detector and analysis; SIMS (Cameca IMS-3F secondary ion mass spectrometer/ion microscope); DTA and TGA (DuPont 2100 and Netzsch STA 429 thermal analyzers for thermogravimetric analysis and differential thermal analysis); TEM (Hitachi HF 2000 and Philips EM420ST transmission electron microscopes); XPS/AES (Kratos Analytical XSAM800 pci for xray photoelectron spectroscopy and Auger electron spectroscopy); XRD (Rigaku Geigerflex xray diffraction analysis); and BET surface area analyzer (Micromeritics ASAP 2020 using N_2 or Kr gas as adsorbent).

MCL charges user fees to run all instruments according to approved federal guidelines and Penn State's approved federal auditing entities. MCL fees are posted online. Each instrument is maintained by MCL technical staff and supervised by a tenure line faculty. Recently, several of the MCL instruments have become a part of the new Laboratory for Isotope and Metals in the Environment (LIME) which is run identically as a multi-user facility. Shared equipment includes a Dionex ion chromatograph (IC), a coulometer, an inductively coupled plasma mass spectrometer (ICP-MS) and inductively coupled plasma atomic emission spectrometer (ICP-AES). S. Brantley supervises the chemists who run the ICP-AES and ICP–MS, and is also the director of LIME.

Soil Research Cluster Laboratory. The Soil Research Cluster Laboratory (SRCL) in the Department of Ecosystem Science and Management at The Pennsylvania State University is a multi-function, multi-user analytical laboratory that provides common and cutting edge analytical instrumentation in the areas of soil chemistry and biochemistry, soil fertility and nutrient cycling, soil physics, pedology, and hydropedology. The SRCL was established to provide students, faculty and staff access to instrumentation and equipment that may not be available in individual laboratories and that find common use by several research groups. The SRCL analytical instruments and research methods and procedures are not limited to soil; they also have been employed in the analysis of plant and animal extracts and digests; water and waste water; biosolids; and geologic and synthetic materials. Equipment to be used in research outlined in this proposal includes a CE Instruments (Thermo Electron Corp) CHNS-O Elemental Analyzer EA 1110 with a thermal conductivity detector (TCD); a LI-COR CO_2/ H_2O Analyzer (LI- 7000); an INNOVA photoacoustic infrared multi-gas analyzer for analysis of CO_2, N_2O, and NH_3; and a Varian 3800 GC with FID, ECD and TCD detectors for CH_4, N_2O, and CO_2 analyses, respectively.

Computation and Modeling. Institute for CyberScience at Penn State. Senior Personnel Padma Raghavan (Director) directs this Institute to facilitate Penn State research such as the SSHO. Institute includes a peak Terascale networked computing & storage system with high resolution digital display wall for visualization and a high bandwidth parallel storage system. This facility was funded partially through an NSF MRI: Acquisition of a Scalable Instrument for Discovery through Computing (f*or additional information:* http://www.research.psu.edu/ics/index.html*.)* Penn State has computing facilities all over campus available to students, faculty and visitors, including wireless access throughout much of the University. There is wide access to workstations, plotters, printers, digitizing tablets, and other hardware for spatial & temporal data analysis across the campus. The University holds site licenses to major GIS and image processing software such as Arc/Info and ERDAS, and to most major mathematical and statistical software such as MATLAB, S+, and SAS. We have developed the Penn State Integrated Hydrologic Model (http://www.pihm.psu.edu/). The Penn State Integrated Hydrologic Model (PIHM) is a multiprocess, multi-scale hydrologic model where the major hydrological processes are fully coupled using the semi-discrete finite volume method. The model itself is "tightly-coupled" with PIHMgis, an open-source Geographical Information System designed for PIHM. The PIHMgis provides the interface to PIHM, access to the digital data sets (terrain, forcing and parameters) and tools necessary to drive the model, as well as a collection of GIS-based pre- and post-processing tools. Collectively the system is referred to as the Penn State Integrated Hydrologic Modeling System. The modeling system has been written in C/C++, while the GIS interface is supported by Qt. The Penn State Hydrologic Modeling System is open source software, freely available for download along with installation and user guides. In parallel to our model development we will support PIHM with an online geospatial database HydroTerre (www.hydroterre.psu.edu) for soils, geology, climate, land use/land cover, topography and the stream network that automates access to model data for the region.

Shaver's Creek Environmental Center. This center is a Penn State-run facility (http://www.outreach.psu.edu/shaverscreek/) to teach about environmental science. The Center lies within 1 mile of the SSHO and is the host for many camps, scouting projects, summer visitors, and students. Shaver's Creek provides facilities that can facilitate in K-12 education efforts at SSHO. In addition, the SSHO benefits from interactions with the Center for Science and the Schools (CSATS), a unique Penn State facility whose purpose is to develop mutually beneficial and sustainable relationships between P-12 schools, faculty and researchers in Penn State's STEM colleges and College of Education. CSATS conducts external evaluations for projects unrelated to CSATS activities and works closely with Penn State Outreach, Penn State Public Broadcasting and other university entities across the state (http://csats.psu.edu/).

Non-Penn State Laboratory Resources.

University of Vermont Cosmogenic Nuclide Laboratory. The U. of Vermont laboratory has analyzed cosmogenic isotope samples from SSHCZO, specifically ^{10}Be, since 2008. The laboratory provides accurate and precise measurements of ^{10}Be at exceptionally low levels (background process blanks consistently have ^{10}Be/^{9}Be ratios well below 10^{-15}). The lab has separate dedicated space for preparation of quartz mineral separates. With 10 ultrasounds, lab staff can rapidly extract sufficient quantities of pure quartz for analysis (typically 20-40 grams). The lab shares up-to-date rock crushing facilities with the rest of the Geology Department. These facilities include a jaw crusher, plate grinder, sieve shaker, and a high volume, roll-type magnetic separator. Detailed information on the lab's operations, protocols and standards can be found on their website (http://www.uvm.edu/cosmolab).

Colorado School of Mines Hydrology and Geophysics Research Lab. The hydrogeology and geophysics labs possess an array of field equipment, including a portable weather station, pH, redox potential, and fluid conductivity meters, water level tapes, augering and surveying gear, stream velocity meters, and both surface and subsurface pumps. We additionally have Mount Sopris wireline logging equipment, a Pulse EKKO GPR with 50-, 100-, 500- and 1000-MHz antennae, a SuperSting Resistivity Meter, and an IRIS Syscal Pro 10-channel resistivity-induced polarization meter with both surface and borehole cables, and a Radic Instruments Spectral Induced Polarization SIP Lab-II meter. We also own a Sensornet SR fiber optic distributed temperature system, and older seismic, electromagnetic, and gravity equipment. All School of Mines equipment can be shipped as needed for work at SSHO.

Oregon State University. The Active Tectonics group at Oregon State will be fully sufficient for the field aspects of the project, including sample collection, mineral separation, structural and GIS analysis. Because Kirby is moving to OSU in July 2013, these facilities are currently being acquired; we are developing a shared facility with Prof. Andrew Meigs. By Fall 2013, we anticipate that the following will be in place. *Field Equipment*: Kirby's lab facility in tectonic geomorphology will maintain all of the basic field equipment needed for the proposed research, including: optical total station, kinematic differential GPS (Trimble 5800 L1/L2 RTK instrument, Trimble R3 single-frequency post-processed instrument), laser rangefinders, clinometers, hand levels, etc. Kirby has had extensive experience conducting the type of field mapping entailed in the proposed effort. In addition, Kirby is familiar with the regional logistical consideration of managing equipment and power in relatively remote locales. *Computer equipment*: Compilation and analysis of geomorphic surveys, topographic analysis, and modeling will be completed primarily in the active tectonics computer facility. Kirby will acquire a GIS/remote sensing laboratory that includes 4-6 dual Mac/PC workstations and server with RAID storage/backup. The lab has access to all of the necessary GIS software including ESRI products (ArcGIS, Arcpad), remote sensing software (ENVI, IDL, ERDAS Imagine), image processing/DEM generation software (PCI Geomatica), and MATLAB. For direct digital acquisition and compilation of geologic data while in the field, the lab also maintains field-hardened, hand-held (Pocket PC) computers running Arcpad GIS, field-hardened tablet PCs, and iPads. *Sample processing*: The College of Earth, Ocean and Atmospheric Sciences also maintains a full suite of mineral separation facilities.

Data Management Plan

SSHO works closely with the national CZO team to provide data according to all CZO agreements. In addition, team members have been integral parts of the Data Management grants and database developments, including the geochemical data initiative.

The SSHO data management team provides "flat" (text) files of tabular data collected via field campaigns or laboratory projects for discovery on our website (www.czo.psu.edu). We work to do this as soon as available from the investigation team. Files sometimes are password protected; however they are released if they are not within the embargo period (2 years), upon request. All files under embargo are marked as such on the webpage with a request for the user to contact the associated PI for additional information. Password protection allows the investigator who collected the data to work more closely with users as needed, or to embargo the data to protect student research if the data is still within the embargo period. Currently, all data are available under one of three category headings (Time Series, Geospatial, or Geochemical and Geophysical). Each dataset has a corresponding Metadata Worksheet, provided to quickly inform the user of pertinent details regarding dataset. A comprehensive data sharing agreement is in development with National CZO management.

Researchers at Shale Hills have monitored groundwater, streamflow, and soil moisture in 10 minute intervals and hydropedological variables (11 variables at 14 sites) for the catchment. In addition to extensive sensor measurements, the geochemical team and ecological team have collected numerous soil cores, water and biological samples (see *Facilities)*. Water samples derive from the stream, groundwater, soil porewater, and plant sapflux. Physical samples, including soil, rock, water, vegetation, and drilling samples collected from the Shale Hills observatory are routinely registered with SESAR (http://www.geosamples.org), organized and archived (when sample size warrants), and are available upon request for further studies. To date, 1831 terrestrial sections and 60 individual samples have been registered to SESAR on behalf of the CZO. Hydrogeochemical datasets are on the website with password protection and have been registered with EarthChem library and await DOI's.

In coordination with the national CZO network and EarthChem, the SSHO team has been working since 2006 to develop CZchemDB, a relational database for CZO rock and regolith geochemical data, with capability to include the chemistry of other sample media. The database is currently implemented as a MS Access database on SSHO website with no web-based interactions. Data submitted thus far derives from 27 investigators from 11 institutions rendering 44 unique field locations, of which 3 are CZOs (Shale Hills, Luquillo, Jemez River Basin – Santa Catalina Mountains) and one is international (Plynlimon, Wales, UK). Total contributions at present equal 290 cores collected with a total of 34,987analytical values. The SSHO team is working with EarthChem and K. Lehnert (Columbia Univ.) to implement web-based services in EarthChem for the data.

Initial efforts with the National CZO data directives have linked tabular time series data into a relational database with searchable and downloadable files within the CUAHSI HIS system. To date, 4yrs groundwater, 6 yrs stream discharge, 7 yrs precipitation and 2 yrs soil moisture data have been harvested by the San Diego SuperComputing Center, SDSC, and published in the HIS library. These data are accessible through the HydroDesktop application. Although the current search capability for data on the national CZO website page is still under construction, ongoing collaboration between SSHO data management staff (see *Management Plan*) and National CZO data management partners—at other CZOs, SDSC and CUAHSI—is constantly improving data accessibility for all researchers. SSHO personnel also work to fulfill all appropriate requests.

At the national level, the data and website team are formulating a new, concise data use policy to be implemented at all CZOs following collective approval. Members of SSHO data management staff are currently participating in the development of these standards and will continue to contribute to the formulation of data and metadata standards for National CZO management. The new policy will specify the terms and conditions of the data sharing agreement, including intellectual property rights, acknowledgement collaboration with investigators and the production of derivative research, both for published and unpublished datasets. We will adopt a streamlined approach to facilitate data sharing and use and adapt to national formatting and metadata content when applicable. As new data (time series, geospatial, and geochemical/geophysical) are collected at the proposed sites in Shavers Creek, they will be archived according to the existing data management procedure along with ongoing data collection efforts at the Shale Hills site.

We are also working in conjunction with other CZOs to coordinate cross-CZO data collection efforts, *e.g.* the *Drill the Ridge* campaign. Data from drilling at SSHO will be shared prior to full data publication to facilitate the research outcomes specified above. Similarly, collaboration with Christina CZO on water quality data using *s::can* instruments will include direct data sharing for research purposes prior to publication. These data will be linked to similar data at other CZOs via the National CZO database. Models developed via cross-CZO efforts will be retained and hosted by SSHO pursuant to the emerging data use policy.

At SSHO, data management efforts are divided among three staff members (see *Management Plan*). The Sample-based and Sensor-based data specialists are responsible for coordinating among the research groups to collect and format data for ease of use internally among different groups and externally. The Cyberspecialist then coordinates the hosting and accessibility of that data to larger data repositories, including the National CZO database, CUAHSI HIS, SESAR, EarthChem and other relevant databases. In this way, we hope to maximize the value of our data both for SSHCZO investigators and the wider scientific community.

Postdoctoral scholars and post-PhD professional development

Professional development of postdoc: We will provide 2 years of support for 1 postdoctoral researcher who will take a lead role in investigating the fracture hypothesis. The postdoc will be fully integrated into our CZO team and will help identify the links and feedbacks between bedrock fractures and other CZO processes. CZO faculty are committed to providing guidance and professional development activities for the postdoc (as well as grad students). These activities will include campus-specific and cross-CZO programs and opportunities and will follow all recommendations for best practices in research and education. For example, the Penn State Graduate School organizes occasional workshops on preparing grants and research and teaching statements for upper level graduate students or postdoctoral scholars. In addition, the current CZO postdocs have been intensely involved in preparation of this renewal proposal, as part of their training. PSU also hosts the Penn State Postdoctoral Society, which promotes a postdoctoral research exhibition on campus. CZO faculty will encourage the postdoc to take part in these activities. Furthermore, the Earth and Environmental Systems Institute (EESI) at Penn State (of which Brantley is director) provides a video conferencing center that can be used to promote virtual meetings among all the participants of the different CZOs. The postdoc and their supervisor will co-lead a CZO-wide cyberseminar on the impacts of bedrock fractures, which will provide the postdoc with valuable exposure, networking opportunities, and experience leading a multi-institutional workshop. In addition to the CZO-wide cyberseminars, we will use these facilities to promote interactions among all the CZO postdocs at all sites.

The postdoc will be encouraged to enroll in the National Postdoctoral Association, which provides resources for professional development, personal and financial coaching, job and funding announcements. We anticipate that, in collaboration with CZO faculty, the postdoc will co-organize sessions at professional meetings such as the Geological Society of America, American Geophysical Union, the Goldschmidt Conference, or the European Geophysical Union. Postdoc conference participation will be supported from grant travel funds.

Academic career development: CZO faculty members will mentor the postdoc in their quest for an academic career by providing opportunities to interact and/or supervise graduate student research as well as guest lecture in courses, if desired, while receiving constructive feedback. Guidance in the preparation of curriculum materials and in the teaching process itself will be provided. At PSU, a semester-long course is available for PhD students within the Dept of Geosciences on preparing for the academic job market. Materials from this course can be shared with all postdocs and CZO faculty will meet one-on-one with the postdoc to help them define and achieve their career goals. The postdoctoral scholar will be encouraged to learn about alternate career paths by meeting informally with visiting researchers from industry, government labs and stakeholder institutions. Furthermore, the postdoc will be encouraged to engage in outreach activities as appropriate. For example, the postdoc will be encouraged to learn about shale gas in PA where Marcellus shale is under rapid and dense exploitation; this outreach activity is particularly opportunistic because of the strong impact of bedrock fracture on shale exploration (gas, oil, etc) and water quality. As described in the proposal, the postdoc will be able to participate in the TeenShaleNetwork and Shale Network workshops as appropriate.This activity will be mentored by Brantley who is developing an NSF-funded water quality database for the Marcellus development area.

Advising and mentoring: Mentoring will be accomplished by 1) pairing the postdoc with several primary faculty mentors (Kirby, Singha, Brantley, Lin) to focus on the fracture hypothesis and 2) encouraging the postdoc to explore interdisciplinary research/collaborations with other members of the diverse CZO team As PI, Brantley will ultimately be the budgetary supervisor for the postdoc and she will make sure that the scholar's time is not spread too thin and that their work is getting done appropriately. Brantley has significant experience in this type of mentoring because she has previously been PI of an NSF-funded IGERT training grant, and an Environmental Molecular Sciences Institute (CEKA). Postdocs from BRIE and CEKA are now pursuing successful careers as faculty members (e.g., Northwestern Univ., Univ. of FLA, Univ. TX El Paso), workers at government agencies (e.g., Bureau of Land Management, U.S. Geological Survey), or in industry (e.g., 3M).

Timing: We anticipate hiring the postdoc as soon as possible.

Management Plan

Introduction. We have collected extraordinary datasets at Shale Hills and the satellite sites of the CZO (see *Facilities, Data Management*) and we are testing these datasets against predictive modeling schemes. Our experimental and predictive capabilities are now enabling a wide range of Earth Science. We see this 5-year renewal as an exciting opportunity to synthesize and share data and models across disciplines while extending our work to Shavers Creek and, as outreach, to Young Woman's and Snake Creeks. To enable this, we seek funds for 8 graduate students, 1 new postdoc, and 8 undergrads.

Steering committee. SSHO science efforts, including those funded by seed grants described in the *Project Description*, will be managed by a Steering Committee consisting of the PI, Brantley (a geochemist), and 3 members from the PSU team. These members will rotate and be derived from the PSU team: C. Duffy, hydrologist and PI of the original Susquehanna Shale Hills CZO project; D. Eissenstat, tree physiologist and ecologist; K. Davis, meteorologist and specialist in eddy flux measurements; J. Kaye, soil ecologist and specialist in nutrients in soils; H. Lin, soil scientist and specialist in hydropedology; M. Gooseff, hydrogeological engineer (new to CZO project); L. Li, geoenvironmental engineer and specialist in modeling reactive transport (new to CZO project). Funding is requested for higher salaries for the 3 members on the steering committee at any given time and 1.5 months for the Project Director (PI). NonPSU team members include P. Bierman (Univ. Vermont, geomorphologist), K. Singha (Colo. School of Mines, hydrogeologist), and E. Kirby (Oregon State Univ., geomorphologist). Each PSU faculty member + Kirby/Bierman will lead one hypothesis team (see table at end of this section where the first name listed is the team leader). Each team will work with one dedicated student.

One of the main jobs of the Steering Committee will be the equitable distribution of funding among the PIs and students. We have considered the costs of proposed activities and allocated a budget for each project that will be set as cost centers for each PI on a yearly basis. The Steering Committee will ascertain that adequate progress is being made on the part of each student and each team. To evaluate progress, each student will give a talk at the annual All Hands meeting (see below). Lack of progress will be discussed among the Steering Committee, if it occurs, so as to make appropriate decisions about funding. Travel to National CZO meetings will be facilitated for members of the PSU and nonPSU team.

The steering committee will be facilitated by staff of the Earth and Environmental Systems Institute (EESI), a PSU research institute (Brantley is Director). Brantley's job as EESI director is to facilitate cross-disciplinary science such as CZO. EESI funds one yearly CZ Science Seminar to bridge between the Soils and Geosciences programs. Recently, Brantley has been funded by NSF, NASA, and DOE. As PI of the CZO after 2013, she is no longer pursuing funding with the NASA Astrobiology Institute (PSARC). Her NSF funding for Shale Network (see *Project Description*) is synergistic with CZO efforts. Brantley will mentor a junior faculty to take over the CZO directorship as needed after 2018.

Seed grants. The Steering Committee will advertise the Seed Grants. Once Seed proposals are received, the Committee will solicit appropriate internal or external reviews and a funding decision will be made on a competitive basis. We anticipate funding 2 awards/y of $10K each. We expect grants will be used for activities that further Critical Zone science in the observatory. Activities might include: i) funding for researchers to conduct new measurements in the SSHO, ii) funding to deploy novel sensors or instrumentation, or iii) funding for PSU students (i.e students on site) or non-PSU students to work at SSHO. Grants will not be awarded for acquisition of capital equipment. We will particularly encourage seed grant proposals from undergrad or minority-serving institutions: we have strong contacts now based on the shale transect work we completed (Fig. F3, *Facilities*). Criteria for allocation will include diversity of personnel and science, novelty, record of productivity, student participation, complementarity of research to ongoing SSHO and CZO network activities, and significance of proposed research.

SSHO is currently running a very successful seed grant program. So far, we have awarded two external seed grants and one internal grant. For our future program, we will solicit proposals that include the same information we are currently requesting: *Proposed work*, *Proposed SSHO interactions, Results of prior support to work on SSHO* (if applicable), *Brief budget with budget justification*, *CV*, *Summary of proposer's current/pending support* (if proposer has other support), *Letter(s) of support* (no more than 2) showing that the proposer has contacted appropriate researcher(s) at SSHO.

Students. Each hypothesis team will recruit and mentor a student for the project. Each of the 8 students will receive approximately 3 years of funding and will have to teach for one year; one masters student (Univ. Vermont) will finish an M.S. within 2 years (1 year teaching, one year as NSF funded research assistant), and one postdoc will be funded for 2 years on H1. We will annually recruit 2 undergrads from PSU or elsewhere to participate in summer field work.

Fulltime CZO workers. SSHO project coordination will be facilitated by three full-time staff members who will report to the Project Director: i) a Program and Sample Data Manager, ii) a Watershed and Sensor-based Data Specialist, and iii) a Cyberspecialist. Yearly evaluations will be communicated to each person by the Director. In addition, the Director will ensure equitable workloads.

The Program and Sample Data Manager will provide direct administrative support: travel coordination, reporting, field work coordination, meeting management (including the CZ workshop and All Hands), seed grant coordination, and All Hands meeting organization. Internal quarterly reports for field work will be handled by this person. In addition, this person will oversee the compilation and curation of specimens and management of sample-based datasets. The work will include formatting data for uptake to national CZO databases (in conjunction with the Cyberspecialist). J. Williams, a geochemist who holds a Masters degree in Geosciences from Penn State, has held this position since CZO inception.

The Watershed and Sensor-based Data Specialist (currently A. Neal) will be responsible for maintaining infrastructure and equipment related to long-term sensor measurement systems including power supplies, the cross-CZO campaign at SSHO, data loggers and network communications. The Specialist will maintain sensor data and facilitate its integration into the national CZO database (in conjunction with the Cyberspecialist). Along with these duties, the Specialist will be responsible for maintaining and archiving SSHO geospatial data and producing maps. Neal, who holds a Ph.D. in Hydrology, joined the Penn State team from the AZ CZO. Neal will also work closely with at least one undergrad each field season to facilitate and collect tree measurements to support H7 (diameter, height, distribution), LAI every couple of weeks, and litter fall.

The Cyberspecialist (to be determined) will manage the SSHO web content in coordination with the National CZO and other CZO sites as appropriate. The Cyberspecialist will be responsible for data export from SSHO to appropriate online data portals, data visualization and GIS support (in conjunction with the Watershed and Sensor-based Data Specialist). Web activities, including web conferencing and Drupal support will also be in the purview of the Cyberspecialist. To explore the sonification of CZO stream discharge and solute concentration time series data, the Cyberspecialist and Watershed Specialist will work with the CZO team, the MFA student, and Professors Brian Orland in the Dept of Landscape Architecture and Mark Ballora in the School of Music. In this activity, the cyberspecialist will be in charge of facilitating all interactions with the Penn State Shavers Creek Environmental Center. The Cyberspecialist will also work with grad students and the postdoc in terms of data management. This specialist will teach students to use HydroDesktop or CZChemdb, the soil chemical database.

Promoting collaborative CZO science. We will take a multifaceted approach to ensure interdisciplinary collaboration within the SSHO and across the CZO network. At Penn State, each SSHO grad student will be mentored by at least two of CZO faculty. To promote interaction, all teams will participate in SSHO seminars, the CUAHSI-hosted crossCZO seminars, or relevant disciplinary seminars. The Program Coordinator (Williams) will provide a monthly calendar update giving CZO participants information about these seminars of interest. The occasional CZO seminars will be led by CZO faculty, students, and postdocs. In addition, each year the CZO will bring in at least one visiting non-SSHO scientist. The scientist will interact separately and formally with students, postdocs, and faculty and will give feedback to our group about ongoing work. We will thus receive yearly insights about methods, models, and analyses. These visitors may derive from other CZOs or outside of CZO.

All SSHO participants (CZO faculty, postdocs, students) will meet annually for a comprehensive "All Hands" meeting that will include nonPenn State members (Bierman, Kirby, Singha). This meeting will inform the entire SSHO community of the findings, developments and goals of projects and will foster intra-site collaboration. Each research team, organized around the 9 hypotheses, will present their results and future directions. Most of the speakers will be students to evaluate progress. If possible, each year the CZO visitor will attend the All Hands meeting. As part of this meeting, we will also have a set-aside time for investigators to present short proposal presentations (5-10 min) to elicit feedback about potentially new research projects. In general, the All Hands meeting will be held during spring finals week at Penn State and will allow planning for the summer season.

Further, to maintain focus on the cross-cutting questions that motivate our hypotheses, we will host a bi-annual *Big Challenge* meeting that will focus on a specific, complex cross-disciplinary challenge for the PSU personnel. For example, *Big Challenge* could focus on i) differences between north and south sides of the catchments, ii) form and function of macropores; or iii) effects of trees. These meetings will be run as mini-AGU meetings (11 min talks) with ample intervening time to synthesize ideas.

To encourage student and postdoc collaboration, we will provide funds to support an initiative we will call the *Critical Hour*. The purpose of these gatherings will be to share CZ research at all stages—from questions and hypotheses, to model and methods, to results and broader implications. The goal will be to foster a positive but informal setting where students and postdocs can collaborate and seek guidance mostly from peers, but occasionally from faculty. The group will be coordinated by a rotating set of representatives from the postdoc / graduate student populations. Meeting times will be chosen to promote participation. *The Critical Hour* will provide a setting that inspires innovative, critical zone research. Web-conferencing will be explored to engage the nonPSU members.

Team research. As described in *Project Description*, our work is scaling up from 1D (boreholes) to 2D (catenas) to 3D (catchments) as embodied in work so far at Shale Hills (forested shale) and work proposed for Shavers Creek. For example, our proposed effort in Shavers Creek uses boreholes sited within catenas sited within sub-catchments in turn sited within each of 3 physiographic/land use units: forested sandstone, forested calcareous shale, agricultural calcareous shale (Fig. 2). As the teams must interact by sharing locations, samples, data, and models, the work will be coordinated by the 3 fulltime specialists (described above). Not every project will be able to achieve the complete synthesis from Shale Hills to Shavers Creek, as indicated in the table summary below. Nonetheless, our approach is meant as an exploration as well as an exemplar for how such watershed upscaling can occur when informed by geology, hydrology, biogeochemistry, ecology, and soil science.

Implementation Plan Details: SH (Shale Hills), SC (Shavers Creek), YWC (Young Womans creek)

Team	Model	Measurement or data compilation	Spatial area
H1 Kirby		drilling sandstone/shale in SC	boreholes
Bierman		drilling sandstone in YWC	boreholes
Singha		fracture density	boreholes
Brantley		geophysical surveys	8 in SC
Lin		geophysical surveys	8 in YWC
		cosmogenic measurements	40 in SC, 20 in YWC
H2. Kaye		O_2 @ ridge, midslope, valley	3 catenas in SC
Brantley		CO_2 @ ridge, midslope, valley	3 catenas in SC
Eissenstat		soil water @ ridge, midslope, valley	3 catenas in SC
Li		N_2O @ ridge, midslope, valley	3 catenas in SC
H3. Eissenstat		vertical root distribution (oaks, maples)	SH+2 forestd. SC catenas
Davis		root hydraul. conduct. (oaks, maples)	SH
Kaye		mycorrhizal colonization	SH+2 forestd. SC catenas
Brantley		plant water H and O isotopes	SH+2 forestd. SC catenas
H4. Lin	PIHM, others		SH and SC
Duffy		soil maps @ ridge, midslope, valley	3 SC catenas
Eissenstat		macropore maps ridge, midslope, valley	3 SC catenas
Davis		GPR images @ ridge, midslope, valley	3 SC catenas
		soil moisture @ ridge, midslope, valley	3 SC catenas

Table,contd.

H5. Li		soil chemistry (majors, trace, SOM)	3 SC catenas
Brantley		soil mineralogy	3 SC catenas
Kaye		1D ridgetop model	ridgetops SH (maybe SC)
Gooseff		2D hillslope model	catenas SH (maybe SC)
H6. Gooseff		stream campaigns	3 SC subcatchments
Brantley		s::can measurements	3 SC subcatchments
Li			
Duffy	3D PIHM-RT		subcatchments, SC
		stream chem. (majors, DOC, ^{18}O, D, dischg., T, EC)	3 sites on SC stem
H7. Davis	Flux-PIHM w/ tree species+C		SH, SC sub-catchments
Eissenstat			
Kaye	Flux-PIHM parametrztn. + C cycle		SH, SC sub-catchments
Lin			
	Flux-PIHM C and water reanalyses		SH, SC sub-catchments
		turb. fluxes of H_2O, CO_2, T, momentum	SH, SC sub-catchments
		radiation exch.(solar,terrest., up-, downwelling)	SH
		LAI	3 subcatchments, SC
		litter fall, litter chemistry	sub-catchments, SC
		dendrometer bands	sub-catchments, SC
H8. Duffy	PIHM	Climate/watershed reanalysis/data assimilation	SH, SC, YWC, Snake
Davis		Deployment of relocatable real-time array including:	3 subcatchments SC +SH
Eissenstat		COSMOS, laser precip monitor; 4	
Lin		component radiometer, wind, relative humidity, acoustic snow sensors; groundwater levels, temp, EC; soil moisture, temp, and EC deployed annually to new site	
H9.Brantley	PIHM-WITCH		SH and shale transect
Godderis			
Li			
Duffy			
Davis			

GFZ · Postfach 60 07 51 · 14407 Potsdam · Germany

CZO Program

Department 3 "Geodynamics"
Section 3.4 "Earth Surface Geochemistry"
Prof. Dr. Friedhelm von Blanckenburg
Head of Section
Telegrafenberg E220
14473 Potsdam
Telefon: +49 (0)331 288-2850
Telefax: +49 (0)331 288-2852
e-mail: fvb@gfz-potsdam.de

Potsdam, Jan 25, 2013

Using the Susquehanna - Shale Hills CZO to Project from the Geological Past to the Anthropocene Future

By signing below, I acknowledge that I am listed as a collaborator on this CZO renewal proposal, entitled "Using the Susquehanna-Shale Hills CZO to Project from the Geological Past to the Anthropocene Future" with Dr. Susan Brantley as the Principal Investigator. I agree to collaborate on the activities described in the proposal with respect to my involvement.

Sincerely

Friedhelm v. Blanckenburg

Friedhelm von Blanckenburg

GEOSCIENCE ENVIRONNEMENT TOULOUSE
UMR 5563 CNRS / UR 234 IRD / UPS / CNES

To: NSF CZO Program
From: Yves Goddéris
Directeur de recherche CNRS

By signing below, I acknowledge that I am listed as a collaborator on this CZO renewal proposal, entitled "Using the Susquehanna-Shale Hills CZO to Project from the Geological Past to the Anthropocene Future" with Dr. Susan Brantley as the Principal Investigator. I agree to collaborate on the activities described in the proposal with respect to my involvement.

Signed:

Organization: Géosciences-Environnement Toulouse
CNRS-Observatoire Midi-Pyrénées

Date: January 24th 2013

GET - UMR 5563 14 avenue Edouard Belin F-31400 TOULOUSE FRANCE Tél. (33) 5 61 33 25 65 Fax. (33) 5 61 33 25 60

Paris, Jan 24th, 2013

Jérôme Gaillardet

To: NSF CZO Program
From: _____Jérôme GAILLARDET________

By signing below, I acknowledge that I am listed as a collaborator on this CZO renewal proposal, entitled "Using the Susquehanna-Shale Hills CZO to Project from the Geological Past to the Anthropocene Future" with Dr. Susan Brantley as the Principal Investigator. I agree to collaborate on the activities described in the proposal with respect to my involvement.

Signed: _________________
Organization: __INSTITUT DE PHYSIQUE DU GLOBE DE PARIS________________
Date: ____PARIS, JANUARY 24th, 2013._________

PENNSTATE

Department of Landscape Architecture
H. Campbell and Eleanor R. Stuckeman
School of Architecture and Landscape Architecture

College of Arts and Architecture
The Pennsylvania State University
121 Stuckeman Family Building
University Park, PA 16802-1921

T: 814-865-9511
F: 814-863-8137
stuckeman@psu.edu

January 28, 2013

To: NSF CZO Program

From: Brian Orland, Distinguished Professor of Landscape Architecture

By signing below, I acknowledge that I am listed as a collaborator on this CZO renewal proposal, entitled "Using the Susquehanna-Shale Hills CZO to Project from the Geological Past to the Anthropocene Future" with Dr. Susan Brantley as the Principal Investigator. I agree to collaborate on the activities described in the proposal with respect to my involvement.

Signed: Brian Orland

Organization: The Pennsylvania State University

Date: January 28, 2013

Shaver's Creek
Environmental Center

3400 Discovery Road
Petersburg PA 16669-9317

phone: 814-863-2000
fax: 814-865-2706

web: www.ShaversCreek.org
email: ShaversCreek@outreach.psu.edu

PENNSTATE

Great Horned Owl
Bubo virginianus

To: NSF CZO Program

From: Mr. Douglas Wentzel, Program Director

By signing below, I acknowledge that I am listed as a collaborator on this CZO renewal proposal, entitled "Using the Susquehanna-Shale Hills CZO to Project from the Geological Past to the Anthropocene Future" with Dr. Susan Brantley as the Principal Investigator. I agree to collaborate on the activities described in the proposal with respect to my involvement.

Signed: Douglas Wentzel

Organization: Shaver's Creek Environmental Center

Date: January 28, 2013

BINGHAMTON
UNIVERSITY
STATE UNIVERSITY OF NEW YORK

Harpur College of Arts and Sciences
Department of Geological Sciences
and Environmental Studies
PO Box 6000
Binghamton, New York 13902-6000
607-777-2264, Fax: 607-777-2288
geology.binghamton.edu

To: NSF CZO Program

From: Dr. Joseph R. Graney

By signing below, I acknowledge that I am listed as a collaborator on this CZO renewal proposal, entitled "Using the Susquehanna-Shale Hills CZO to Project from the Geological Past to the Anthropocene Future" with Dr. Susan Brantley as the Principal Investigator. I agree to collaborate on the activities described in the proposal with respect to my involvement.

Signed: Joseph R. Graney

Organization: Binghamton University

Date: Jan 28, 2013

s::can
Intelligent. Optical. Online.
s::can Measuring Systems LLC
1035 Cambridge Street, Suite 1
Cambridge, MA 02141

CZO Renewal Proposal

To: NSF CZO Program
From: Justin Irving

By signing below, I acknowledge that I am listed as a collaborator on this CZO renewal proposal, entitled "Using the Susquehanna-Shale Hills CZO to Project from the Geological Past to the Anthropocene Future" with Dr. Susan Brantley as the Principal Investigator. I agree to collaborate on the activities described in the proposal with respect to my involvement.

Signed: ____________

Organization: s::can Measuring Systems LLC

Date 1/29/2013

January 30, 2013

NSF CZO Program
4201 Wilson Blvd.
Arlington, VA 22230

Re: CZO renewal proposal "Using the Susquehanna-Shale Hills CZO to Project from the Geological Past to the Anthropocene Future"

To Whom It May Concern,

By signing below, I acknowledge that I am listed as a collaborator on this CZO renewal proposal, entitled "Using the Susquehanna-Shale Hills CZO to Project from the Geological Past to the Anthropocene Future" with Dr. Susan Brantley as the Principal Investigator. I agree to collaborate on the activities described in the proposal with respect to my involvement.

Sincerely,

Garth T. Llewellyn, MSc, PG
Principal Hydrogeologist
Appalachia Hydrogeologic and Environmental Consulting, Inc.

United States Department of the Interior
U.S. GEOLOGICAL SURVEY
Utah Water Science Center
2329 Orton Circle
Salt Lake City, Utah 84119-2047

TAKE PRIDE IN AMERICA

To: NSF CZO Program
From: Dr. Victor Heilweil

By signing below, I acknowledge that I am listed as a collaborator on this CZO renewal proposal, entitled "Using the Susquehanna-Shale Hills CZO to Project from the Geological Past to the Anthropocene Future" with Dr. Susan Brantley as the Principal Investigator. I agree to collaborate on the activities described in the proposal with respect to my involvement.

Signed: Victor M. Heilweil
Organization: U.S. Geological Survey – Utah Water Science Center
Date: January 30, 2013

University of Minnesota

Twin Cities Campus

Department of Forest Resources
College of Food, Agricultural and Natural Resource Sciences

115 Green Hall
1530 Cleveland Avenue North
St. Paul, MN 55108-6112

612-624-3400
Fax: 612-625-5212
www.forestry.umn.edu

To: NSF CZO Program

From: Diana L. Karwan

By signing below, I acknowledge that I am listed as a collaborator on this CZO renewal proposal, entitled "Using the Susquehanna-Shale Hills CZO to Project from the Geological Past to the Anthropocene Future" with Dr. Susan Brantley as the Principal Investigator. I agree to collaborate on the activities described in the proposal with respect to my involvement.

Signed: Diana Karwan

Organization: University of Minnesota

Date: January 31, 2013

PENNSTATE

Dr. Matthew S. Fantle
Assistant Professor
Department of Geosciences

212 Deike Building
The Pennsylvania State University
University Park, PA 16802

p: 814.863.9968
f: 814.863.7823
mfantle@psu.edu

To: NSF CZO Program

From: Matthew Fantle

By signing below, I acknowledge that I am listed as a collaborator on this CZO renewal proposal, entitled "Using the Susquehanna-Shale Hills CZO to Project from the Geological Past to the Anthropocene Future" with Dr. Susan Brantley as the Principal Investigator. I agree to collaborate on the activities described in the proposal with respect to my involvement.

Signed: ______________________

Organization: Penn State University

Date: 01-31-2013