Annual Report for Period:10/2011 - 09/2012 **Submitted on:** 09/13/2012

Principal Investigator: Sparks, Donald L. **Award ID:** 0724971

Organization: University of Delaware

Submitted By:

Aufdenkampe, Anthony - Co-Principal Investigator

Title:

CZO: Spatial and temporal integration of carbon and mineral fluxes: a whole watershed approach to quantifying anthropogenic modification of critical zone carbon sequestration.

Project Participants

Senior Personnel

Name: Sparks, Donald

Worked for more than 160 Hours: Yes

Contribution to Project:

Pi - managing overall project with emphasis on ensuring science is being conducted and objectives are being met in each of the hypotheses presented in project. He is one of the leaders of objective 1, investigating Fe speciation and mineralogy and C-mineral complexation mechanisms in the soils using macroscopic and small scale synchrotron based techniques.

Name: Pizzuto, James

Worked for more than 160 Hours: Yes

Contribution to Project:

Pizzuto has participated in overall project coordination and planning, including the hiring of research technicians and post doctoral scientists. His major areas of involvement have been in managing research under Objective 3 - Fluvial Network Controls on Complex Formation & Preservation. He has also been our CZO's primary contact with NCALM regarding LIDAR data collection and analyses.

Name: Kaplan, Louis

Worked for more than 160 Hours: Yes

Contribution to Project:

Kaplan has participated in overall project coordination and planning, including the hiring of research technicians and post doctoral scientists. His major areas of involvement have been on the development of continuous of organic carbon sensors, site selection, and development of work plans for research questions concerning the stability of organo-mineral complexes and organic carbon bioavailability.

Name: Aufdenkampe, Anthony

Worked for more than 160 Hours: Yes

Contribution to Project:

Aufdenkampe has helped lead overall project coordination and planning, including the hiring of research technicians and post doctoral scientists. His major areas of involvement have been on overall project design and integration of all research activities and objectives, data management at both local and national levels, sensor network development, site selection, and development of work plans for research questions concerning all components of the research tasks. Aufdenkampe also manages research under Objective 1 - Properties of Carbon-Mineral Complexes. Additionally, Aufdenkampe participates in the montly
teleconferences for all PIs and has been involved in the data management group for the CZOs.

Name: Yoo, Kyungsoo

Worked for more than 160 Hours: Yes

Contribution to Project:

Co-Pi managing research under Objective 2 - Weathering and Erosion Controls on Carbon-Mineral Complex Formation by exploring the mechanisms by which weathering and erosion determine spatial distributions and fluxes of complexation potential, with the goal of providing a means to extrapolate these processes over a landscape of differing topography and land use.

Name: Newbold, J. Denis

Worked for more than 160 Hours: Yes

Contribution to Project:

Newbold manages, along with Aufdenkampe and Hornberger, research and modeling efforts under Objective 4 - Watershed Integration of Erosion-Driven Carbon Sequestration.

Name: Gill, Susan

Worked for more than 160 Hours: Yes

Contribution to Project:

Gill is the Director of Education at the Stroud Water Research Center. She was the lead PI on a proposal for a 'distributed' REU-RET program to integrate all CZO sites that will be resubmitted in autumn 2010 and was instrumental in the submission of a NSF STEP proposal dealing with transformation of geoscience education.

Name: Dow, Charles

Worked for more than 160 Hours: Yes

Contribution to Project:

Charles Dow will provide support for all data management activities related to the Christina River Basin CZO (CRB/CZO). He has participated in the CZO data management workshop and will be responsible for implementing the data management procedures within the CRB/CZO.

Dow also participated in a national CZO data management meeting in Boulder Co, May 19-20, 2010. The meeting, attended by principle investigators and data managers from most of the CZOs, was a continuation of the effort towards an integrated data management system across all CZOs. This effort builds upon the creation and implementation of the Consortium of Universities for Advancement of Hyrdologic Science (CUASHI) Hydrologic Information System (HIS).

Name: Hornberger, George

Worked for more than 160 Hours: Yes

Contribution to Project:

Hornberger is advising Ph.D. student Mei as they develop several approaches for modeling the flux of Dissolved Organic Matter from hillslopes to streams and testing them against measurements made at the CRB/CZO. Work for the past six months has included development of a two-dimensional hillslope model and associated data collection on a hillslope at White Clay Creek. Hornberger willcontinue to focus on testing models of DOM fate and transport and on extending the PIHM framework to include carbon transport modeling at the whole-catchment scale.

Name: Michael, Holly

Worked for more than 160 Hours: Yes

Contribution to Project:

Working on Objective 2 - Weathering and Erosion Controls on Carbon-Mineral Complex Formation and advising post-doc and coastal zone aspects of the CZO project.

Name: Levia, Delphis

Worked for more than 160 Hours: Yes

Contribution to Project:

Working on objective 2, managing graduate students during summer 2010 on LIDAR vegetation survey, and advising undergraduate students.

Name: Inamdar, Shreeram

Worked for more than 160 Hours: Yes

Contribution to Project:

Advising graduate students and working on objective 2 - Weathering and Erosion Controls on Carbon-Mineral Complex Formation

Name: Jin, Yan

Worked for more than 160 Hours: Yes

Contribution to Project:

Yan Jin participates in Objective 1: Formation and Stabilization of Organo-Mineral Complexes, by bringing perspectives on inorganic colloids and their transport. She is the primary supervisor for Graduate Student Jing Yan.

Name: Imhoff, Paul

Worked for more than 160 Hours: No

Contribution to Project:

Paul Imhoff participates in Objective 2, and is focused on the exchange of gases CO2 and O2 through soils and modeling our data to better explain temporal and spatial variability in soil pH and soil and shallow groundwater redox.

Name: Aalto, Rolf

Worked for more than 160 Hours: Yes

Contribution to Project:

Rolf Aalto is one of the primary contributors to the hypotheses being tested by our CZO. He is one of the leads for Objective 3. As a faculty at a foreign University (Exeter, UK), Rolf does not receive salary funds from our CZO. He receives analytical funds for some speciality analyses, but primarily leverages other UK funds.

Name: Claessens, Luc

Worked for more than 160 Hours: No

Contribution to Project:

Luc Claessens is a new faculty member at UD (starting Sept. 2010), but has begun actively participating with our CZO. He is teaching watershed science field course in Spring 2011 that is centered around GIS and biogeochemical study of White Clay Creek, one of the focal watersheds within our CZO. In addition, Luc is beginning to efforts (and looking for supplemental funding) to implement the RHESSys ecohydrology model for our CZO.

Name: Arscott, David

Worked for more than 160 Hours: No

Contribution to Project:

David Arscott is the Assistant Director at the Stroud Water Research Center, and actively participates in helping implement watershed research infrastructure efforts.

Name: Zaslavsky, Ilya

Worked for more than 160 Hours: Yes

Contribution to Project:

Ilya Zaslavsky and his staff assist with our data management system and integration with CUAHSI's data holdings, in addition to providing guidance and training for local data management team.

Name: Mayorga, Emilio

Worked for more than 160 Hours: No

Contribution to Project:

Emilio Mayorga, from the University of Washington?s Applied Physics Laboratory, is helping to implement a map-based data browser, similar to one that Emilio and collegues have developed for the Northwest (http://www.nanoos.org/nvs/nvs.php?section=NVS-Assets).

Name: Kan, Jinjun

Worked for more than 160 Hours: Yes

Contribution to Project:

Dr. Kan is a microbial ecologist and his research on the CRB/CZO project involves identifying the role of microorganisms in biogeochemical and erosional processes.

Post-doc

Name: Rosier, Carl

Worked for more than 160 Hours: Yes

Contribution to Project:

Carl Rosier received his PhD from the University of Montana in soil microbiology. He began his Post-Doc in Aug. 2010 to carry out research under Objectives 1 and 3, and will study organo-mineral aggregates within both erosional 'source' locations and depositional locations in floodplains and wetlands and microbial impacts on C cycling in the soils.

Name: Lazareva, Olesya

Worked for more than 160 Hours: Yes

Contribution to Project:

Hired in Aug. 2010 to carry out research under Objectives 1 and 2 - Weathering and Erosion Controls on Carbon-Mineral Complex Formation.

Name: Tsang, Yinphan

Worked for more than 160 Hours: Yes

Contribution to Project:

Tsang worked on extending and incorporating previous watershed hydrological modeling research (funded by NSF award EAR-0450331) within our CZO watersheds to new efforts to use the Penn State Integrated Hydrological Model (PIHM) within these same watersheds. She helped mentor graduate student Yi Mei in his early modeling efforts for several months, before accepting another job elsewhere

Name: Karwan, Diana

Worked for more than 160 Hours: Yes

Contribution to Project:

Dr. Karwan received her degree from Yale University in forest hydrology and sediment transport. She started her Post-Doc on Sept. 9, 2010 to carry out research on Objective 3 - Fluvial Network Controls on Complex Formation & Preservation.

Name: Sawyer, Audrey

Worked for more than 160 Hours: Yes

Contribution to Project:

Audrey is quantifying surface water-groundwater exchange in a stream and estuary as part of a broader effort to understand carbon budgets in a watershed subject to land use change.

Graduate Student

Name: McLaughlin, Christine

Worked for more than 160 Hours: Yes

Contribution to Project:

Christine McLaughlin, a PhD. Candidate at the University Pennsylvania, is investigating water flow paths that deliver carbon to stream ecosystems. The goal of her research is to understand the controls on material export from the landscape by explicitly considering how streams connect with the rest of the land-based environment.

Name: Mei, Yi

Worked for more than 160 Hours: Yes

Contribution to Project:

Mei is a Ph.D. candidate at Vanderbilt University and is developing several approaches for modeling the flux of DOM from hillslopes to streams and testing them against measurements made at the CZO. Work for the past six months has included development of a two-dimensional hillslope model and associated data collection on a hillslope at White Clay Creek. Yi Mei participated in a PIHM Workshop sponsored by the Penn State CZO and, along with other investigators on the Christina CZO, did a preliminary calibration of the hydrological model to White Clay Creek. His work, with mentoring from George Hornberger, will continue to focus on testing models of DOM fate and transport and on extending the PIHM framework to include carbon transport modeling at the whole-catchment scale.

Name: Chen, Chunmei

Worked for more than 160 Hours: Yes

Contribution to Project:

Conducting research under objectives 1 and 2 - Weathering and Erosion Controls on Carbon-Mineral Complex Formation. She is advised by D.L. Sparks.

Name: Pearson, Adam

Worked for more than 160 Hours: Yes

Contribution to Project:

Graduate student working on objective three - Fluvial Network Controls on Complex Formation & Preservation. He is dealing with DOM cycling and is advised by J. Pizzuto.

Name: Pan, Weinan

Worked for more than 160 Hours: Yes

Contribution to Project:

Weinan Pan is a graduate student working on objective 2. She is advised by S. Inamdar and D.L. Sparks.

Name: Yan, Jing

Worked for more than 160 Hours: Yes

Contribution to Project:

Jing Yan is supported full time by CZO funds, and is focusing his research on the formation and transport of colloids under conditions of varying redox. He is advised by Y. Jin.

Name: Van Stan, John

Worked for more than 160 Hours: Yes

Contribution to Project:

John is working with Drs. Rosier and Levia to study the effects of tree species, stemflow, and the spatial heterogeneity of microbial communities on soil carbon stocks. John is also working on compression sensors to measure whole-tree interception of precipitation.

Name: Wenell, Beth

Worked for more than 160 Hours: Yes

Contribution to Project:

Graduate student with Kyungsoo Yoo at the Univ. of Minnesota, starting in Sep. 2011 and supported full time by the CRB-CZO grant.

Undergraduate Student

Name: Iuliano, Kayla

Worked for more than 160 Hours: Yes

Contribution to Project:

Part-time undergraduate intern from the Univ. of Delaware, assisting Post-Doc Audrey Sawyer, from Sept. 2011 to May 2012. Kayla continued with the CZO as a time undergraduate intern working in Shree Inamdar's lab for Summer 2012.

Name: Shaw, Alfred

Worked for more than 160 Hours: Yes

Contribution to Project:

Full time undergraduate intern, assisting with all aspects of CZO fieldwork and with labwork within the Aufdenkampe lab. Started Winter 2011 as capstone project with West Chester University then continued full time to April 2012. Graduated in May 2011.

Name: Vazquez, Erika

Worked for more than 160 Hours: Yes

Contribution to Project:

Part-time undergraduate intern from the Neumann University, assisting Post-Doc Diana Karwan, from May 2011 to Aug. 2012. Graduated in Dec. 2011.

Technician, Programmer

Name: Montgomery, David

Worked for more than 160 Hours: Yes

Contribution to Project:

David Montgomery is the watershed manager for the Stroud Water Research Center experimental watershed. He will provide logistical support and coordination for monitoring installations and research use within the watershed.

Name: Hicks, Steven

Worked for more than 160 Hours: Yes

Contribution to Project:

The main responsibilities for Steven Hicks on the CZO are to design and implement a network of environmental sensors throughout the study watersheds. He will use existing sensor and wireless technologies as well as develop custom sensor devices to record a variety of environmental measurements and then aggregate all of the data for processing by the data management group.

Name: Hicks, Naomi

Worked for more than 160 Hours: Yes

Contribution to Project:

Naomi Hicks received her PhD in Forest Hydrology from Princeton University. Since May 2010, she has worked 20-30 hours per week on our CZO project, helping in the design and placement of stream flumes for discharge measurements and the processing LIDAR and other data.

Name: Arnold, Melanie

Worked for more than 160 Hours: Yes

Contribution to Project:

Melanie is a staff member at the Stroud Water Research Center who actively works on our data management tasks, in collaboration with CUAHSI and the San Diego Supercomputer Center.

Name: Hendricks, Gerald

Worked for more than 160 Hours: No

Contribution to Project:

Jerry is lab manager for Don Sparks and also has been maintaining our current, temporary website (http://www.udel.edu/czo) that we use as we wait for the national web system to be developed by David Lubinski at Boulder.

Name: Whitenack, Thomas

Worked for more than 160 Hours: Yes

Contribution to Project:

Tom, who works for Ilya Zaslavsky at the San Diego Supercomputer Center (SCSC), has been assisting with setting our data systems to interface with CUAHSI-HIS and CZO-central. His time is funded through the CRB-CZO subcontract to SDSC.

Other Participant

Name: Doremus, Kelly

Worked for more than 160 Hours: Yes

Contribution to Project:

Administering and monitoring financial accounts for CZO, scheduling conferences, meetings and calls.

Research Experience for Undergraduates

Organizational Partners

USGS-Pennsylvania Water Science Center

CRB-CZO has collaborated with Kirk White to process all historical continuous water quality data since 1986 in order to provide unit value (i.e. 15 minute) time series datasets for the Christina River Basin. Currently those datasets are only provided as daily values. Funding is partially provided by a supplemental grant from NSF (to our LTREB project) but nearly have is provided by USGS as in-kind support.

Other Collaborators or Contacts

The University of Delaware and the Stroud Water Research Center co-lead this project as equal partners. In addition, several senior staff are funded at other institutions via subcontracts:

George Hornberger at Vanderbilt University. See description under senior personel.

Ilya Zaslavsky at San Diego Super Computing Center. See description under senior personnel.

Rolf Aalto, Associate Professor at the Univ. of Exeter in the United Kingdom and Adjunct Associate Professor at the University of Washington, has been an important collaborator on this project. He will oversee the preparation of samples for cosmogenic radio isotopes at the Univ. of Washington, and is actively participating in Objective 3 - Fluvial Network Controls on Complex Formation & Preservation. A subcontract to Univ. of Washington covers laboratory supplies and materials. Aalto's salary, and that of his student, are covered by UK funds.

Julia Marquard, graduate student with Rolf Aalto at the University of Exeter, and funded with UK funds.

In addition, we are actively collaborating with a number of other CZO researchers funded by one of the other CZO projects. These include:

Alain Plante, at the University of Pennsylvania, and his graduate student, Wenting Feng, on organo-mineral complexation.

Beth Boyer, at Penn State University, and Diane McKnight at Univ. of Boulder, on Dissolved Organic Matter characterization.

Chris Duffy and his students Gopal Bhatt and Lorne Leonard, at Penn State Univ., on modeling with the Penn State Integrated Hydrological Model (PIHM).

Henry Lin and his graduate student Danielle Andrews, on improving the design and construction of low-cost, in-situ redox sensors (platinum electrodes). Also, Del Levia from our CZO recently co-wrote a proposal with Henry Lin to look at the effects of different tree species on soil moisture.

Mark Williams, from Univ. of Boulder, David Tarboton and Jeff Horsburgh from Utah State Univ., Kerstin Lehnert from Columbia, and a long list of other colloaborators from various institutions, on the national CZO data management system.

We are collaborating with Kirk White of the USGS Pennsylvania Water Science Center, to process 15 min (or unit value) historical water quality data. This work is partially funded by an NSF Rapid Award but also by USGS funds.

We are actively developing collaborations with a wide range of local partners who either produce or need/use data on the Christina River Basin (CRB). These include: federal (EPA, USGS), interstate (CRB Watershed Management Committee, Delaware River Basin Commission), state (DE Dept. of Natural Resources, DE Geological Survey, DE Water Resources Agency), and local (Chester County Water Resources Agency, Chester County Conservation District, White Clay Creek Watershed Management Committee (CCWRA), Red Clay Valley Association) agencies in addition to several non-profit non-governmental organizations (Brandywine Conservancy, Natural Lands Trust). Representatives from most of these groups have been meeting quarterly for several years under the name 'Christina River Basin Task Force'. We have attended many of these meetings and are beginning discussions for data sharing efforts.

Collaborators outside the CZO network or not funded by the CZO program:

Joshua LeMonte, Ph.D. student with Don Sparks and working within the CRB-CZO for his dissertation, is funded by a US DOE Science, Mathematics And Research for Transformation (SMART) Scholarship.

Dan Leathers, lead PI for the Delaware Environmental Observing System (DEOS, http://www.deos.udel.edu/). We have initiated substantial data sharing efforts which will continue in coming years, in addition to collaborating on sensor design ideas.

Chris Sommerfield, a coastal geomorphologist at UD, is collaborating with us (co-PI on pending proposal) to better expand our CZO toward the coastal zone.

Anne Kraepiel and Francois Morrel at Princeton Univ. have been funded (NSF EAR 1024545) to work as collaborators within the CRB-CZO to study trace metal limitation of nitrogen fixation.

Lee Slater and Dimitrios Ntarlagiannis (Rutgers University at Newark) and Jonathan Nyquist (Temple University) led a 2-day geophysical field trip within CRB-CZO in April 2012 with ~20 students including members of the Rutgers Newark Geophysical Society (RN-GS), a very active student chapter of the Society of Exploration Geophysicists (SEG) and students from Temple University. In collaboration with CRB-CZO researchers, they collected a very interesting preliminary dataset at our 100% forest Spring Brook research catchment, which we hope to continue annually and use as a preliminary dataset for a proposal to NSF.

Activities and Findings

Research and Education Activities: (See PDF version submitted by PI at the end of the report)
See attached Activities File.

Findings: (See PDF version submitted by PI at the end of the report)
See attached Findings file.

Training and Development:
The major training and development for this project has focused on the 9 Ph.D. students and
5 post-doctoral scientists working directly on this project (2 of the students receive money from non-NSF sources, 1 of the post-docs found a job after 6 months).

For the Ph.D. students this takes to form of advising on course selection, research topics, research planning, technical aspects of sample collection, processing, and analyses, data analysis, oral presentation, and writing. Given the collaborative and interdisciplinary nature of

our investigations it is not unusual for a Ph.D. student to receive input from multiple investigators, but one CRB/CZO scientist has the primary responsibilities of a mentor. Graduate students have been encouraged to participate in national and international meetings
and have numerous opportunities to share their research efforts during either all scientists meetings or the individual objective meetings.

For the post-doctoral scientists weekly meetings attended by all of the post-doctoral scientists and several of the CRB/CZO investigators have been the primary mechanism for planning and an exchange of ideas. Initially these meetings were scheduled and run by the investigators, but now that the post-doctoral scientists have had a chance to develop their research programs, it is they who take turns scheduling the meetings, preparing the agendas,
and running the meetings. Other one-on-one meetings between post-doctoral scientists andCRB/CZO investigators occur frequently and individual investigators have provided feedback to post-doctoral scientists preparing research proposals.

One of the major coordinated training activities in year 2 has focused on developing a shared
set field skills within our team. In Nov. 2010, Aufdenkampe, Aalto and Yoo conducted a series of workshops during a 2-week intensive field campaign in the CRB. We continued that
training with repeated gatherings throughout the spring and early summer of 2011. The result is that graduate students, post-docs and faculty are all now using similar field sampling techniques.

Outreach Activities:

Susan Gill, Director of Outreach and Education at the Stroud Water Research Center, is the lead on CRB-CZO Outreach and Education activities. She is the lead PI on a number of NSF projects that directly interface with the CRB-CZO project. These include:

EAR-1034961 'Introducing the Principles and Processes of Earth?s Critical Zone to Teachers,
Informal Educators and Academically At-Risk Youth.' The project includes a 1 week summer
workshop and graduate courses for teachers and informal educators and an after-school and
summer activities for children of local migrant agricultural workers. The after school programs were provided in the spring of 2011, and focused on teaching students how to build basic environmental sensors, using the same open-source technologies that we are using to build our wireless sensor network.

DRL-0929763 'Collaborative Research - Model My Watershed: Developing a Cyberlearning Application and Curricula to Enhance Interest in STEM Careers'. This project provides students and teachers with online tools to visual and model the hydrology of their backyard
watershed. This project is a component of a larger envisioned project called WikiWatershed
(http://wikiwatershed.org/), which will put 'research-grade' data and modeling tools in the hands of the public in visually appealing and self-explaining forms. The first phase of the WikiWatershed visualization system (beta version at
http://www.nanoos.org/nvs_crb/nvs.php)
was co-funded by the CRB-CZO project and the Cabot Foundation.

A large multidisciplinary Critical Zone STEP Center proposal was submitted in early 2011. Although the CZ STEP Center at UD was not funded, the process of bringing together this

regional team is likely to have a lasting effect. This project was a collaboration among nine institutions of higher education, research, and outreach. The objective of the Center was to increase the geoscience literacy of a diverse suite of undergraduate cohorts within the context
of a data rich world. The Center would seek to not only guide undergraduates to ?take the pulse of the planet? by collecting environmental data in the field and on the Internet but also
to help them interpret that information within a larger sociopolitical or economic context.

Last, Sparks and Aufdenkampe have presented the CRB-CZO to numerous groups of policymakers and laypersons, including: the environmental section of the Delaware Bar Association, the Brandywine and Christina Conservancies, the Christina River Basin Task Force, the PA State Water Symposium, the UD Academy of Lifelong Learning, retired UD faculty, and the Delaware Department of Natural Resource Conservation (DNRC).

PI Sparks presented a paper on historical aspects of Critical Zone Science at the Soil Science Society of America.

Journal Publications

Levia, DF; Van Stan, JT; Mage, SM; Kelley-Hauske, PW, "Temporal variability of stemflow volume in a beech-yellow poplar forest in relation to tree species and size", JOURNAL OF HYDROLOGY, p. 112, vol. 380, (2010). Published, 10.1016/j.jhydrol.2009.10.02

Melack, JM; Finzi, AC; Siegel, D; MacIntyre, S; Nelson, CE; Aufdenkampe, AK; Pace, ML, "Improving biogeochemical knowledge through technological innovation", FRONTIERS IN ECOLOGY AND THE ENVIRONMENT, p. 37, vol. 9, (2011). Published, 10.1890/10000

Aufdenkampe, AK; Mayorga, E; Raymond, PA; Melack, JM; Doney, SC; Alin, SR; Aalto, RE; Yoo, K, "Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere", FRONTIERS IN ECOLOGY AND THE ENVIRONMENT, p. 53, vol. 9, (2011). Published, 10.1890/10001

Yoo, K., J. Ji, A. Aufdenkampe, and J. Klaminder, "Rates of soil mixing and associated carbon fluxes in a forest vs. tilled agricultural field: implications for modelling the soil carbon cycle", Journal of Geophysical Research - Biogeosciences, p. G01014, vol. 116, (2011). Published, doi: 10.1029/2010JG001304

Inamdar, S., N. Finger, S. Singh, M. Mitchell, D. Levia, H. Bais, D. Scott and P. McHale, "Dissolved organic matter (DOM) concentration and quality in a forested mid-Atlantic watershed, USA", Biogeochemistry, p. 55, vol. 108, (2012). Published, DOI: 10.1007/s10533-011-9572-4

Tsang, Y-P., L. A. Kaplan, J. D. Newbold, A. K. Aufdenkampe, and G. M. Hornberger, "A variable source area for groundwater evapotranspiration: impacts on modeling stream flow", Water Resources Research, p. , vol. submitt, (2011). Submitted,

Mei, Y., G. M. Hornberger, L. A. Kaplan, J. D. Newbold, and A. K. Aufdenkampe, "Estimation of Dissolved Organic Carbon Contribution from Hillslope Soils to a Headwater Stream", Water Resources Research, p. W09514, vol. 48, (2012). Published, 10.1029/2011WR010815

Karwan DL; Aalto R; Aufdenkampe AK; Newbold JD, Pizzuto JE, "Characterization and Source Determination of Stream Suspended Particulate Material in White Clay Creek, USA", Applied Geochemistry, p. 5356, vol. 26, (2011). Published, 10.1016/j.apgeochem.2011.03.058

Chen C; Yoo K; Aufdenkampe AK, "An Exploratory Study of Carbon Mineral Complexation and Their Responses to Soil Erosion, Deposition, and Mixing within a Mixed Land Use Watershed", Journal of Geophysical Research - Biogeosciences, p. , vol. , (2012). Submitted,

Books or Other One-time Publications

Inamdar, S. P, "The use of geochemical mixing models to derive runoff sources and hydrologic

flow paths in watershed studies", (2011). Book, Published
Editor(s): D. Levia, D. Carlyle-Moses, and T. Tanaka
Collection: Forest Hydrology and Biogeochemistry: Synthesis of Research and Future Directions
Bibliography: Springer; 1st Edition. 762 pages
ISBN-10: 9400713622; ISBN-13: 978-9400713628

Zaslavsky, Ilya; Whitenack, Thomas;
Williams, Mark; Tarboton, David;
Schreuders, Kim; Aufdenkampe, Anthony, "The Initial Design of Data Sharing Infrastructure for the Critical Zone
Observatory", (2011). Peer reviewed Conference Proceedings, Accepted
Collection: Proceedings of the Environmental
Information Management Conference
2011
Bibliography: doi:10.5060/D2NC5Z4X

Web/Internet Site

URL(s):

http://www.udel.edu/czo/

Description:

This is a temporary website that provides basic information on our activities. Active development of this web site has been limited in anticipation of of a complete redesign of an integrated national CZO website built upon a modern content management system (CMS) framework. This national website is currently under development and should be unveiled by the end of 2010.

Other Specific Products

Contributions

Contributions within Discipline:

Although our project was only initiated in Oct. 2009, our stated hypotheses have already begun to contribute to critical zone research. Our hypotheses, if shown to be correct, have the potential to substantially transform perceptions on landscape scale controls on carbon sequestration. Aufdenkampe, Yoo, and Aalto have each given many invited presentations describing our core CZO hypotheses, which have been well received. Some of these hypotheses have been published (Aufdenkampe et al. 2011). Preliminary data, collected for this and previous projects are already supporting our hypotheses.

Contributions to Other Disciplines:

The science we have conducted so far will contribute to a number of disciplines including geochemistry, soil science, and environmental chemistry.

We believe that our early achievements at harnessing open source electronics hardware for very low-cost yet robust wireless sensor networks has the potential to radically transform critical zone science. For example, Campbell Scientific, the long-time leader in environmental data logging, sells 16-channel data loggers with wireless radio communication for $2000 to $3000. We can snap together open source parts to achieve the same or better capabilities for $60 to $150.

Contributions to Human Resource Development:

We have been successful in recruiting some highly talented postdoctoral researchers to conduct research on the CZO project including Olesya Lazavera, Carl Rosier, Diana Karwan and Audrey Sawyer; excellent graduate students Adam Pearson, Beth Wenell, Chunmei Chen, Christine McLaughlin, Yi Mei, Jing Yan and Weinan Pan; Kelly Doremus as Financial Manager; Steve Hicks to develop and manage sensor technology; and David Montgomery as watershed manager.

The students and postdoctoral researchers are obtaining excellent training with new instrumentation and be involved in research that serves to link spatial and temporal scales that address C cycling and impacts on climate change. They will also benefit by having opportunities to communicate their research to scientists and the public, enhancing their verbal and written communication skills. These training activities are described in more detail in the Training and Development section above.

Contributions to Resources for Research and Education:

CRB-CZO supported activities have contributed substantially to resources for research and education in three specific areas.

Hicks and Aufdenkampe are developing a wireless environmental sensor system that is based on low cost open-source electronics. The design of this system and its components will be freely available online and thus has transformative potential. Details are described in the Activities section, above.

CRB-CZO data managers -- Aufdenkampe, Dow and Arnold -- have actively participated in the development of the national CZO data system. Details are described in the Activities section, above.

Gill and Aufdenkampe have been developing the WikiWatershed and Model My Watershed (http://wikiwatershed.org/) web applications for formal and informal science education. These applications are built upon cyberinfrastructure that was developed for and by the CZO, including the CRB-CZO data visualization system that was funded by this project (beta version available at http://www.nanoos.org/nvs_crb/nvs.php). These intent is that these systems will be a resource to many other research and education efforts.

Contributions Beyond Science and Engineering:

Sparks and Aufdenkampe have given a number of public talks to educate the public about the importance of understanding the interplay between land use, carbon cycling and climate change.

Conference Proceedings

Special Requirements

Special reporting requirements: None

Change in Objectives or Scope: None

Animal, Human Subjects, Biohazards: None

Categories for which nothing is reported:

Any Product

Any Conference

Year 3 (Oct. 2011 to Sep. 2012)

2. Research Findings

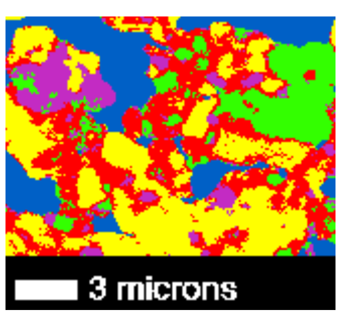
As we approach the 3-year mark on this project many of our research findings are beginning to mature into publications in preparation and in press. In the last year we have also presented a large number of posters and oral presentations from national and international scientific meetings. Here we provide highlights, organized by CRB-CZO objectives.

Objective 1 – Properties of Carbon-Mineral Complexes

Soft X-ray Spectromicroscopy Study of Mineral-Organic Matter Associations in Pasture Soil Clay Fractions

Chunmei. Chen, Yan Jin, Olesya Lazareva and Don Sparks

There is a growing acceptance that associations with soil minerals may be the most important overarching stabilization mechanism for soil organic matter. However, direct investigation of organo-mineral associations has been hampered by a lack of methods that can simultaneously characterize soil organic matter and soil minerals. In this study, Scanning transmission X-ray microscopy (STXM) combined with near edge X-ray absorption fine structure (NEXAFS) spectroscopy at the C1s, Ca 2p, Fe 2p, Al 1s and Si 1s edges were used to investigate C distribution and speciation and its associations with Ca, Fe, Al and Si species in pasture soil clay fractions. Results demonstrated that carbon was intimately associated with soil minerals and was heterogeneously distributed on mineral surfaces. Good C-Ca spatial correlations were found for the soil clays. Calcium carbonate was not present, suggesting a strong role of Ca in C-mineral association. The Fe in the soil clays, investigated by Mossbauer and X-ray absorption spectroscopies, was mainly in the Fe(III) oxidation state. Al and Si were strongly correlated, due to predominance of aluminosilicates minerals in soils, which were predominately hydroxy-interlayered vermiculite, illite and kaolinite. There were also discrete SiO_2 particles. Carbon was associated with both aluminosilicate clay minerals and Fe oxides, with the latter being more highly correlated with C. Little C was found associated with SiO_2 particles. The major C forms associated with soil clays were aromatic C, carboxylic-C and polysaccharides. Polysaccharides appeared to be preferentially associated with the thinner regions of clay particles (Fig. 1). These direct microscopic determinations can help to improve our understanding of C-mineral interactions in soils and to identify C stabilization processes and responses to a changing environment.



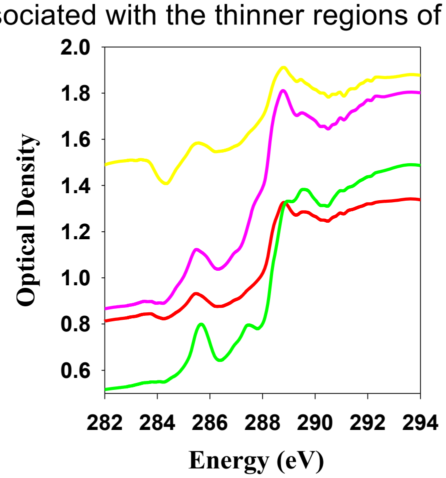


Fig.1 Principal component and cluster analysis (PCA-CA) showing heterogeneous distribution of C functional groups with four distinct regions (green, purple, red, and yellow) in soil clay fractions and C 1s NEXAFS spectra of the regions shown in the right figure.

2. Characterization of soil solid-phase iron speciation from floodplain soils along a redox gradient using X-ray absorption spectroscopy and Mössbauer spectroscopy. Iron (Fe) oxides are of particular importance for C-mineral complexation because of their abundance in soils and their high reactive surface area. Iron is susceptible to redox variability along landscape gradients. Fe (III) minerals predominate in well-drained upland soils, while under poorly - drained conditions at lowland locations, such as floodplains and streams, reductive dissolution of Fe (III) oxides occurs. These redox fluctuations drive local mobilization of Fe^{2+}(aq), which can be either removed from soil by leaching, re-oxidized and precipitated as Fe(III)-oxide and –hydroxide coatings on soil mineral surfaces, or incorporated into ferrous-bearing minerals. Additionally, reductive dissolution and transformation of Fe minerals governs the amount, form and transport of sequestered C. Using Mössbauer spectroscopy at the Environmental Molecular Science Laboratory at Pacific Northwest National Laboratory, we have investigated changes in soil Fe solid-phase speciation from a floodplain soil profile, which demonstrates a significant redox gradient. Based on continuous in-situ redox sensor monitoring, post-colonial (legacy) sediments and gravel are under oxic conditions (Eh = 480-730 mV) while buried wetland sediments are under an anoxic environment with an Eh ranging from -200 mV to -50 mV. The detailed Mössbauer study has indicated that Fe(III) in clays is significantly reduced in the buried wetland compared to legacy sediments and gravel (Fig.2).

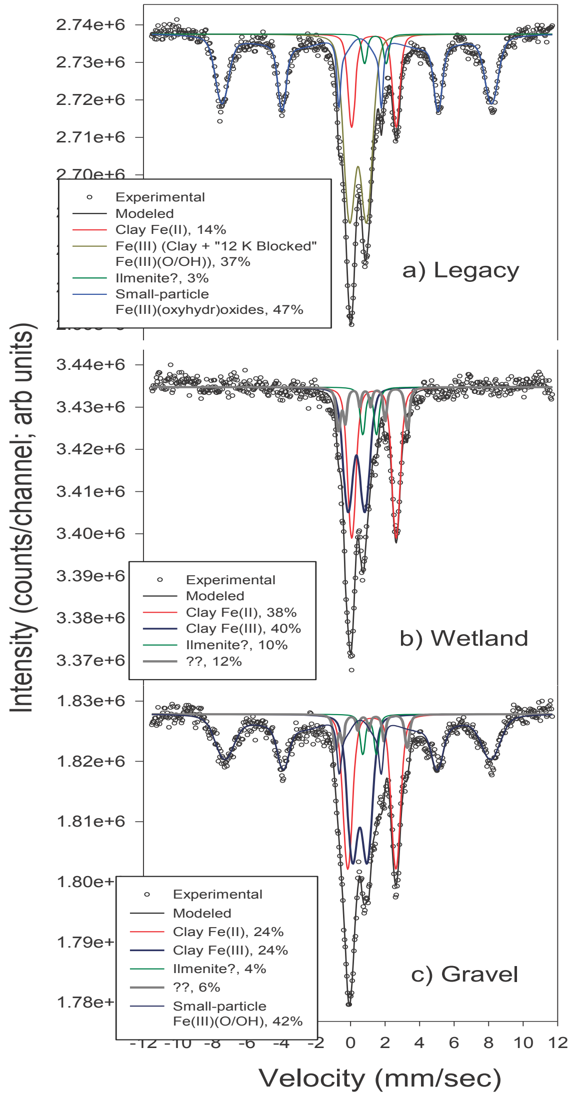


Fig.2 Fe Mossbauer spectra of floodplain soils.

Also, this study demonstrated that Fe(III) (oxyhydr)oxides were absent in the wetland (Fig.2). The linear combination fitting (LCF) results of Fe EXAFS spectra are consistent with the Mössbauer study. In the anoxic buried wetland, the Fe(II) bearing clay minerals are biotite and chlorite. Fe(III) clay minerals throughout the floodplain profile are vermiculite with trace amounts of mica, while the majority of Fe(III) (oxyhydr)oxides are goethite with minor amount of ferrihydrite in the oxic legacy sediments and gravel layer. LCF results also show that there are no Fe(III) (oxyhydr)oxides present in the anoxic buried wetland. These findings highlight that in addition to reductive dissolution of Fe(III)-(oxyhydr)oxides, the anoxic redox conditions of the floodplain soils lead to clay structural Fe reductive cycling in the natural field. Detailed spectra fitting are being conducted.

3. Stabilization of Organic Matter by Adsorption to and Coprecipitation with Ferrihydrite

Ferrihydrite, because of its ubiquitous occurrence in the environment and its high surface area, contributes significantly to the sorption of organic matter and protects it against microbial degradation in soils and sediments. In addition, ferrihydrite often forms in the presence of dissolved organic matter in the natural environment, which leads to coprecipitation of organic matter with ferrihydrite. However, the extent and mechanisms of organic matter adsorption to or coprecipitation with ferrihydrite, and the consequences of such reactions for the properties of sorbed versus coprecipitated organic matter remain largely unknown. In this study, we compared adsorption and coprecipitation with dissolved organic matter from a forest litter layer. Results have shown that: (1) coprecipitation leads to greater maximum OC loadings on ferrihydrite than adsorption (Fig.3); (2) the mineral surface achieves full C coverage at a normalized OC to mineral surface area ratio (OC loadings) of 1 mg C m^{-2} SA and multilayers of C on ferrihydrite are likely formed by hydrophobic interactions, when OC loadings are greater than 1 mg C m^{-2} SA; (3) micropores and mesopores are important in C-ferrihydrite interactions by adsorption and coprecipitation; (4) ligand exchange between carboxylic C and Fe in ferrihydrite is likely the major mechanism for adsorption and coprecipitation; (5) Coprecipitated C is much more stable than the adsorbed C, based on a desorption study (Fig.4).

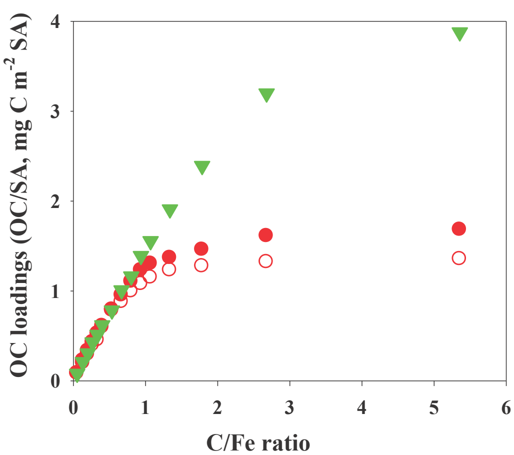


Fig.3 Adsorption and coprecipitation of DOM as a function of the initial C/Fe ratios

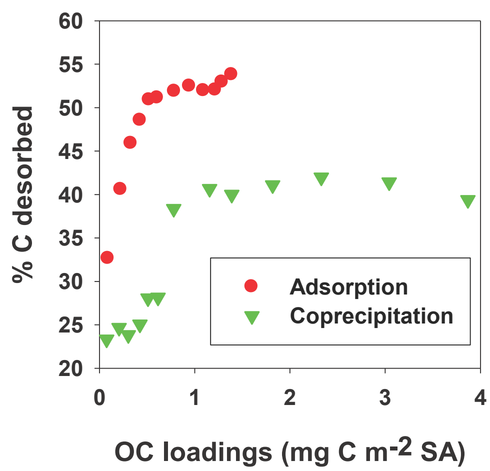


Fig.4 Desorption of the adsorbed C and coprecipitated C by 0.1M NaOH

In-situ sensitivity of the mineral surface area of soils to changes in redox conditions
Olesya Lazareva, Steve Hicks, Anthony Aufdenkampe, Jinjun Kang, and Donald Sparks

The major objective of this part of the study is to evaluate the in-situ sensitivity of the mineral surface area of soils to changes in redox conditions (reducing versus oxidizing) across a wide range of landscape positions and uses, within transect A of the White Clay Creek Watershed (WCC). Specifically, we want to understand the role of Fe- and Mn- redox transformations on carbon cycling and sequestration in a mixed land use watershed, including floodplain forest, upland forest and agriculture sites.

The proposed research questions include the following: (1) How do redox conditions in soils affect mineral surface area via the dissolved phase? (2) How deep and fast does O_2 penetrate through soils under different land use types and landscape positions? (3) Does O_2 diffusion back into riparian soil/sediments facilitate complexation between C and newlyprecipitated Fe- and Mn-oxides in the pore water? (4) How do soil properties, such as composition, mineralogy, mineral surface area, as well as redox state, vary depending on different types of land use and topographic position? (5) How do microbial communities within soils and pore and stream water respond to redox gradients and seasons, and what groups of bacteria interact extensively with C cycling under redox fluctuations?

Starting in the Spring of 2011, we have been constructing and installing field instrumentation, conducting field sampling and analyzing a combination of soil, soil pore-waters, and stream water within the floodplain of transect A in the White Clay Creek Watershed (Figure 5). The instrumentation included multiple redox sensors, soil moisture/temperature probes, in-situ soil pore-water samplers (borosilicate glass), and pressure transducers. The sensors and probes were placed on the eastern and western sides of the stream bank at different depths including in post-colonial deposits, and pre-colonial buried wetland and gravel layers (Figure 1). The sensor data have been collected continuously since April 2011 using Campbell and homemade low cost high efficiency data loggers manufactured by Steve Hicks. The soil pore-water samplers were installed from the stream bank as well to understand the composition of soil pore-water and microbial communities at different depths. Water samples from soils and stream have been collected bi-weekly and analyzed for pH, temperature, alkalinity, Fe^{2+}, conductivity, major anions (F, Br, Cl, SO_4, NO_3, NO_2, PO_4), major cations/metals (Ca, Mg, Na, K, Al, Si, Sr, Fe, Mn, As), stable isotopes of water ($\delta^{18}O$, δD), dissolved organic carbon (DOC), dissolved organic matter (DOM) quality using UV–visible absorbance and fluorescence excitation emission matrices (EEMs), and microbial communities. Soil samples were analyzed for total chemistry, surface area, Fe speciation (Mössbauer spectroscopy), microbial communities, using microscopy (SEM, confocal). The analyses were performed at the Stroud Water Research Center, University of Delaware (Soil Testing Laboratory, Watershed Hydrochemistry Group), Delaware Biotechnology Institute (Bioimaging Center), and Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National

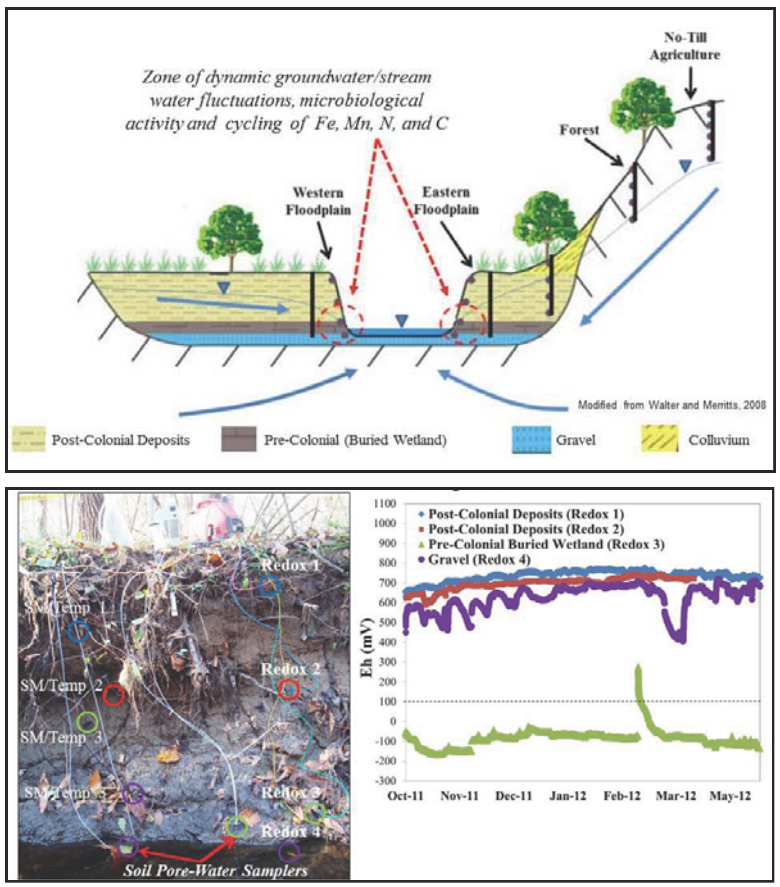


Figure 5. Top: Transect A floodplain, White Clay Creek Watershed (WCC). Current research is focused on the floodplain forest it will be applied to other land uses such as upland forest, and no-till agriculture. Note: black lines = soil cores; red circles = in-situ sensors; **Bottom:** Continuous in-situ monitoring of redox environment within the western floodplain. Note: dynamic fluctuations in gravel deposits are crucial for biogeochemical cycling of Fe, Mn, and C.

Laboratory (PNNL) collaborating with Drs. R. Drs. R. Kukkadapu, E. Walter, H. Michael, A. Sawyer, D. Karwan, J. Kan, S. Inamdar, K. Czymmek and graduate students C. Chen and W. Pan.

In addition, redox sensors, soil moisture/temperature probes, soil pore-water and gas samplers were installed at the agricultural site of transect A and currently are being developed at the upland forest site.

Our preliminary results demonstrated that DOC, Fe, and Mn concentrations vary in time and space within the floodplain forest and stream. The highest Fe and Mn were observed in the eastern wetland layer while the western wetland had 5-7 times lower concentrations. The distributions of DOC versus Fe and Mn were not linearly correlated. DOC, Fe, and Mn concentrations were substantially lower within gravel deposits due to formation of Fe and Mn oxides/hydroxides facilitating the sorption of C along a redox gradient. Redox conditions across the western side of the floodplain ranged quite substantially from very reducing within the wetland soil (Eh ≈ -300 mV) to oxidizing within the post-colonial deposits (Eh ≈ +700 mV). There is a significant redox gradient across the interface between anoxic wetland and valley-bottom gravel layers. The redox potential fluctuated with storms, especially in the gravel layer, where advective transport was greatest (Sawyer et al., unpublished data). Variations in redox gradients near the streambed may drive changes in Fe- and Mn-oxide precipitation or dissolution affecting OC complexation or destabilization (Lazareva and Sawyer unpublished data). Therefore, this zone could be very dynamic in terms of groundwater/stream water fluctuations (Maurice and Leff, 2002; Gilbert et al., 1994) and biogeochemical redox cycling of Fe, Mn and C (Emerson et al., 2010; Lovely, 2006; Lovely, 1993). Sawyer et al. (unpublished data) showed that during storms, the water table in the banks rose almost as fast as the stream. Groundwater flow reversals into the banks (negative q) were common but short-lived. Reversals carried oxygenated surface water into the banks and could disturb redox gradients in the riparian aquifer. Groundwater discharged to the stream along the east and west banks, but the steeper hill slope and potentially stronger groundwater discharge on the eastern side may contribute to a sharper redox gradient which could be crucial for the cycling of Fe, Mn and C (Lazareva et al., 2011; Sawyer et al., 2011).

Solid-phase Fe speciation in floodplain soils using Mössbauer spectroscopy showed that Fe(III) in clays was significantly reduced within the wetland soils compared to the post- colonial deposits and gravel. Additionally, Fe(III) (oxyhydr)oxides were absent in the wetland soils. These results highlight that in addition to reductive dissolution of Fe(III)-(oxyhydr)oxides, the anoxic redox conditions of the floodplain soils lead to clay structural Fe reductive cycling in the natural field.

Preliminary analyses of DOM quality in the selected samples indicated the existence of humic regions for all samples. At the same time, the microbial regions (bioavailable DOM) had distinctive peaks only in the eastern and western wetland, and eastern gravel samples. These results clearly demonstrate the importance of defining the quality of DOM especially with seasonal variations.

Microbiology data from our recent studies include microscopic observation and microbial community characterizations by molecular approaches. Abundant and diverse prokaryotic cells were detected in pore waters from the east and west wetlands. Additionally, close interactions of microbes and minerals were observed by 3D confocal microcopy using Multiphoton Microscope Zeiss 510 NLO at the DBI Bioimaging Center, which is a very powerful tool for 3D depth imaging of the localization of cells within matrices. This confirmed the ubiquitous distribution of bacterial cells within the mineral matrix (Fe- or Mn oxides) in soil and pore-water samples. For a more comprehensive understanding of this system, other microscopy techniques (SEM, TEM), as well as molecular analysis of microbial communities are required. Finally, microbial DNA extracted from the pore water was amplified and analyzed with PCR-DGGE. Different band patterns occurred in the pore-water samples, which showed distinct spatial (across the transect from wetland, gravel to stream water) and temporal variations.

Colloidal-scale transport and carbon-mineral complexation
Yan Jin and Jing Yan

Soil colloids, often defined as entities with sizes < 1.0 mm, have attracted much attention because they have small size and large surface area, leading to their high reactivity with and ability to facilitate the transport of contaminants in the subsurface environment. However, the role of colloids in carbon complexation and transport and effects of natural organic matter on colloids stability and mobilization is largely unknown. Our goal for the study is to investigate the complex dynamic interactions of colloids, DOM, and Fe oxides, and their implications in colloid mobilization and carbon cycling.

Dr. Jin and Jing Yan efforts in the last year have included 1) conducting batch experiments to quantify colloid release and stability under aerobic and anaerobic conditions in the presence of DOM at different concentrations and 2) field sampling and analysis for colloidal fractions of < 0.45 mm.

We collected high iron content soils from agricultural sites near Stroud's Water Research Center, PA. Soils were air-dried, sieved through 2-mm screen. We conducted the first set of batch experiments having four treatments: (1) soil slurry in DI water under reduced and oxidized condition, (2) same soil slurry in DI water with DOM concentration of 19.35 mg/L TOC. Soil suspension was made at solid and solution mass ratio of 1:10 in 160-ml amber serum bottles, which are kept under aerobic (ambient) and anaerobic (in glove box) conditions. Samples were taken periodically for 3 weeks and analyzed for pH, conductivity, colloid concentration. Our main findings are the following:

1) More colloids were released under anaerobic conditions;
2) Colloids were more stable under aerobic conditions over time;
3) Colloids settled out under anaerobic conditions;
4) DOM facilitated colloid aggregation under anaerobic conditions but not under aerobic conditions.

Conductivity increased after DOM addition in both aerobic and anaerobic samples, and further increased at later time for anaerobic samples, which we speculate to be due to iron reduction. We also suspect that the aggregation behavior may depend on DOM concentration. To gain a more complete understanding of how DOM concentration affect colloids' release and stability, a new set of experiments with additional treatments at different DOM concentrations has been conducted. The results are largely similar and more quantitative analysis including Fe^{2+} concentration and colloid characterization (SEM-EDX and XRD) are being completed.

In addition, we sampled stream water during a storm event at White Clay Creek, PA. We fractionated samples by filtering them with 1.2 µm glass fiber filter, 0.45 µm and 0.22 µm mixed cellulose ester filters successively. The concentration of colloids was calculated by their dry mass on the filters. We found the concentration of colloids at 0.45-1.2 µm is 1.4 ppm, while 0.22-0.45 µm is 0.95 ppm. It indicated that the small colloids may play a very important role during storm events. We will collect more samples and relate finding to environmental and land use variables.

Objective 2 - Weathering and Erosion Controls on Carbon-Mineral Complex Formation
Paul Imhoff, Shree Inamdar, Del Levia, Holly Michael, Fang Tan, Beth Wenell and Kyungsoo Yoo

The primary focus of the Christina River Basin Critical Zone Observatory (CRB-CZO) is to quantify human impact on Critical Zone carbon sequestration. A key hypothesis is that human-induced changes to the land surface alter mineral weathering and mineral supply to the watershed, which may change the rate of carbon sequestration. In this project we focus on the impact of land use on mineral weathering. We hypothesize that the conversion of forests to crop or livestock farming alters the fluxes of water, solutes, and gases to mineral weathering zones. Further, we postulate that these changes will result in greater weathering rates and subsequently larger mineral supply to near-surface groundwater and subsequently streams. Agricultural land use may alter mineral weathering through 1) chemical inputs associated with liming and fertilization; 2) increases in water flux, due to irrigation and a reduction in evapotranspiration because of the removal of forest land cover; and 3) increases in gas flux, because of shorter distances between land surface and weathering zones and the lower moisture content of agricultural soils, which promotes increased gas diffusion.

Fang Tan, a new PhD student in fall 2011, began working on this project in 2011/2012. Her first task was to test this hypothesis outlined above using data gleaned from the literature in watersheds with similar climate and bedrock but different land use: either agriculture or forest. Using data obtained from the United States Geological Survey, the quality of near-surface groundwater in the Connecticut Housatonic and Thames River Basins was examined for differences that might be associated with land use and changes in mineral weathering. We use T-test to determine whether water chemistry is affected by land use at level of significance $\alpha=0.05$. The results showed that concentrations of base cations (Ca^{2+}, K^+, Na^+, Mg^{2+}), dissolved inorganic matter, and nutrients (P, Cl^-, SO_4^{2-}, NO_3^-, NH_4^+,) all differed significantly among groundwater associated with different land use. While we are still piecing together the mechanisms causing these differences, the data support the hypothesis that land use affects chemical inputs to the mineral weathering zone.

In addition to the analysis of existing datasets, we are in the process of collecting cores from land with the same bedrock and landform, but different land use. We have selected a ridge along Transect A in the CRB-CZO where a forest (> ~100 years old) is adjacent to land that has been extensively farmed for approximately 80 years. Soil pits have been installed in both regions and instrumented with water samplers, redox sensors, and devices for measuring moisture content and water pressure. We have designed and tested probes for collecting gas samples with depth to assess gas fluxes, which will be installed this summer. The most important field data will likely be obtained from borings at these locations, where intact core will be removed and the mineralogy quantified. Drilling at these locations is scheduled for July 2012. Once the cores are removed, samplers will be installed in the holes to remove gas and water samples. To assist in the interpretation of data from these sites, reactive transport modeling will be employed.

One paper by Chen et al was submitted to Journal of Geophysical Research. Two major field trips were undertaken in Nov.2011 and Mar.2012, which resulted in collecting ~100 soil and saprolite samples from a hillslope transect at the Laurel Preserve (forest end member of CRB-CZO) and forest-agricultural transect within the Stroud watershed. These samples are being analyzed for elemental chemistry (ICP), mineralogy (XRD), particle size distribution (hydrometer), specific surface area (BET), and in-situ 10Be analysis (in collaboration with

Aalto). Yoo has also actively participated in (1) deciding locations for geophysical ground survey (completed in April 2012) and (2) deciding locations and techniques for drilling and well installation (scheduled for July-August 2012).

Beth Wenell was recruited for this project in the fall 2011. She is currently enrolled in MS. program at the UMN and will switch to Ph.D. program starting this fall. Wenell attended CZO meeting at the Biosphere II in May 2011 and completed two major field trips in Nov. 2011 and Mar. 2012 respectively. Her field trips have been guided by Yoo and Aufdenkampe. TheNov. 2011 field trip was further coordinated with Aalto who was sampling collaboratively with us for meteoric 10Be analysis. In the spring 2012, Wenell was trained by and worked with Ed Nater (UMN) on clay mineralogy of the samples from the CZO with XRD technique. Wenell is currently characterizing grain size distribution of soil samples from the CZO site. This laboratory works also involve undergraduate students.

(1) Yoo presented to 6th grade science class at Mary Open school in Minneapolis school district. The presentation includes introduction of carbon cycle and hand on experience with soil sampling tools. (2) Yoo gave a 1 hour 15 min lecture on introducing the concept of critical zone and CRB-CZO's goals and activities to new graduate students entering Land and Atmospheric Science graduate program at UMN. (3) Yoo participated in the NSF-sponsored workshop, "Critical Zone Observatories International Meeting", Newark, Delaware, Nov. 7- 10.

Canopy and stem water and solute fluxes
Del Levia, Courtney Siegert, and Diana Karwan

Dr. Levia activities in conjunction with the CRB-CZO are centered in three areas: (1) ^{7}Be radioisotopes work to formulate a ^{7}Be budget of the forest and to dovetail these measurements with sediment and C transport within our experimental watersheds; (2) stemflow-microbe-fungi soil C cycling to gain insights on the heterogeneity of C cycling in forests in relation to hydrological and biological parameters; and (3) whole-tree canopy interception measurements using compression sensors. Updates on each of these three are provided below.

^{7}Be radioisotopes: forest budgets and C transport
The project is supporting, overseeing, and working with postdoctoral researcher Dr. Diana Karwan and graduate student Courtney Siegert on the beryllium isotope work. As of the end of July 2012, we will have a full year of sampling completed. The gamma counter measurements and ICP-MS measurements are proceeding well. We have discussed plans to submit a major paper to *Geochimica et Cosmoschimica Acta*. We will begin manuscript preparation later this summer and anticipate the paper will be submitted in winter 2013. This Objective 2 work dovetails nicely with the work of Objective 3.

Stemflow-microbe-fungi- soil C cycling
Del Levia, Carl Rosier and John Van Stan

Dr. Levia is supporting, overseeing, and working with postdoctoral researcher Dr. Carl Rosier and Dr. John Van Stan (recently graduated student) on stemflow-microbe-fungi- soil C cycling. Dr. Jinjun Khan at Stroud Water Research Center also is involved with this work. Carl has collected some very interesting data on soil C flux in relation to stemflow-induced hot zones for biogeochemical reactivity. Data collection continues but some intriguing patterns are emerging. This work is significant for Objective 2 and brings a biological component to our CZO work. We have three or four papers planned from this ork. The first is already being written and we will target *Frontiers in Ecology and Environment*. This paper couples some data collected thus far with theories of biogeochemical reactivity over space and time. We are working on outlines of other papers. The first will be a seasonally based paper examining soil C cycling in relation to stemflow and microbial community development and the second will focus on stemflow influences on soil C storage. Possible target journals are *Plant and Soil* and *Soil Biology and Biochemistry*, respectively.

Whole-tree canopy interception
Dr. John Van Stan, a former graduate student, and I are working with interceptometers at Fair Hill in an effort to better understand the effects of plant canopies on subcanopy water fluxes that affect C cycling. Data have been collected and a paper is in draft form for submission to *Water Resources Research* within the next month or so. This study is in conjunction with an international collaborator and dovetails with Objective 2.

Inamdar: Nothing significant to report at this time (conference presentations provided below)

Geophysical Study of Spring Brook Catchment Hydrogeology
Lee Slater and Dimitrios Ntarlagiannis (Rutgers Univ.), Jonathan Nyquist (Temple Univ.) and their students at the invitation of Holly Michael and Anthony Aufdenkampe

Geophysical measurement techniques such as those used under EAR-1045084 have the potential to provide unique information on subsurface architecture and processes over a broad range of scales from field plots to entire watersheds. In October 2011, Lee Slater (Rutgers University at Newark) visited the Christina River Basin Critical Zone Observatory (CRB-CZO) to discuss opportunities for transferring some of the field techniques being used to investigate carbon cycling in northern peatlands to studies of water, mineral and carbon cycling within the CRB-CZO. During this visit, Slater met with key CRB-CZO scientists (including Anthony Aufdenkampe of Stroud Water Research Center and Holly Michael of University of Delaware) to discuss some of the key scientific questions of the CRB-CZO research effort that could be addressed with geophysical imaging methods.

In April 2012, student members of the Rutgers Newark Geophysical Society (RN-GS), a very active student chapter of the Society of Exploration Geophysicists (SEG), ran a two-day field campaign within a key watershed of the CRB-CZO. This field campaign was student organized and student led, with Slater and CRB-CZO scientists engaging as participants. Jonathan Nyquist and students from the SEG student chapter at Temple University also participated in the field work performed during the first day. Similarly, students and faculty from a recently formed SEG student chapter at Queen’s College (New York City) also participated in the first day of field research. In total, this field campaign was attended by approximately 25 participants, including undergraduate students, graduate students, postdoctoral scholars, early-career faculty and mid-career faculty.

A range of geophysical measurements were performed within the Spring Brook catchment of the Laurel's preserve, being a critical watershed within the CRB-CZO network as it represents a forested watershed that is relatively unaffected by human activities. Furthermore, Spring Brook exhibited a unique hydrological response following the passage of Hurricane Irene on August 28, 2011, suggesting that significant intra-basin transfer of water occurs to limit overland flow. This watershed is also being used to study geomorphological controls on carbon accumulation rates. Students led the acquisition of multiple resistivity/induced polarization and ground penetrating radar (GPR) transects at different elevations with the watershed, as well as electromagnetic and magnetic measurements over the entire watershed (Figure 6).

Figure 6: Selected examples of student-led geophysical measurements performed at the CRB-CZO: (a) surface nuclear magnetic resonance soundings (SNMR); (b) ground penetrating radar (GPR); (c) magnetometry, and (d) electrical resistivity imaging

Preliminary processing of the geophysical datasets suggests that a wealth of information relevant to better understanding water, mineral and carbon cycling within the catchment can be extracted from the geophysical datasets. Figure 7a shows examples of resistivity inversions on transects crossing the site, where spatial variability in the depth to a key lithological contact has been non-invasively mapped. Figure 7b shows GPR (100 MHz) profiles where the stratigraphy of the weathered soil horizon is clearly highlighted as a result of variations in moisture content connected to variations in grain size and weathering. One striking aspect of both these geophysical datasets is that the data quality; such data quality results from the fact that the physical and chemical characteristics of this watershed are very conducive to geophysical investigations.

The team from Temple University also compared GPR transects collected with 250 MHz vs 500 MHz antennae (Fig. 8). The 250MHz antenna offered deeper penetration without sacrificing too much resolution in comparison with 500MHz antenna. Initial findings include:

- The rapid and continuous data collected on site provides insight into sub surface (≈4 m) soils structures which include but are not entirely limited to; depth to saprolite, depth to bedrock, tree root balls, large tree roots, soil creep/slump, and rocks (Figure 9).
- Depth to water table in the channel area was unable to be determined via the 250MHz antenna. No strong reflectors or attenuation boundaries were found in the post-processed radiogram data. Returning to the field with a higher frequency antenna (500-800MHz) could provide this information where the depth to water table is shallow (<2m).
- Soil horizons were gradational at best and are not immediately distinguishable in the GPR data. Jim Doolittle has found at the Shale Hills CZO that recent rainfall can change

layer and bedrock contrast remarkably in GPR data. Another argument for returning to the site.

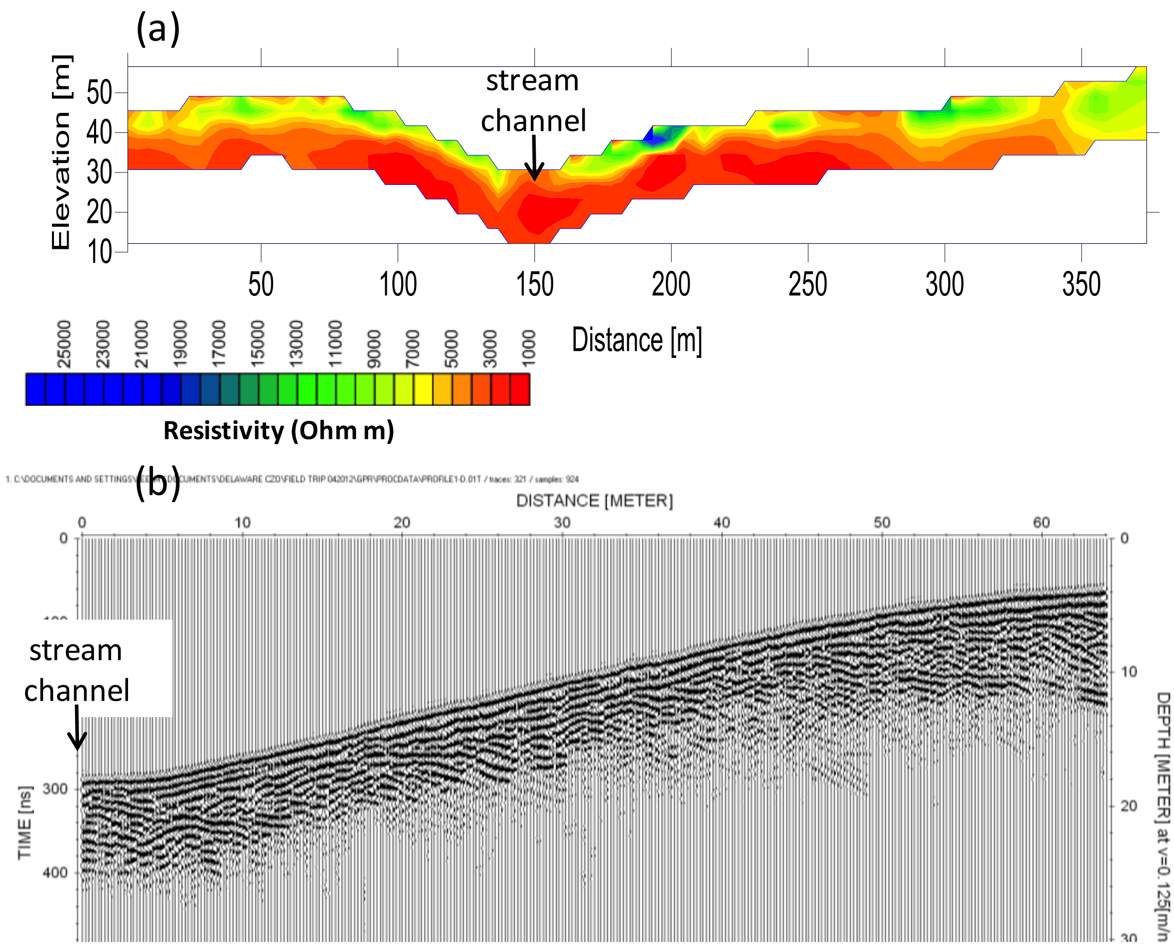


Figure 7: (a) Example 2D resistivity profile across the Spring Brook catchment showing an upper resistive layer with strong spatial variability (b) 2D Ground Penetrating Radar (GPR, 100 MHz) traverse showing excellent resolution of the stratigraphy of the upper resistive sediments imaged with resistivity

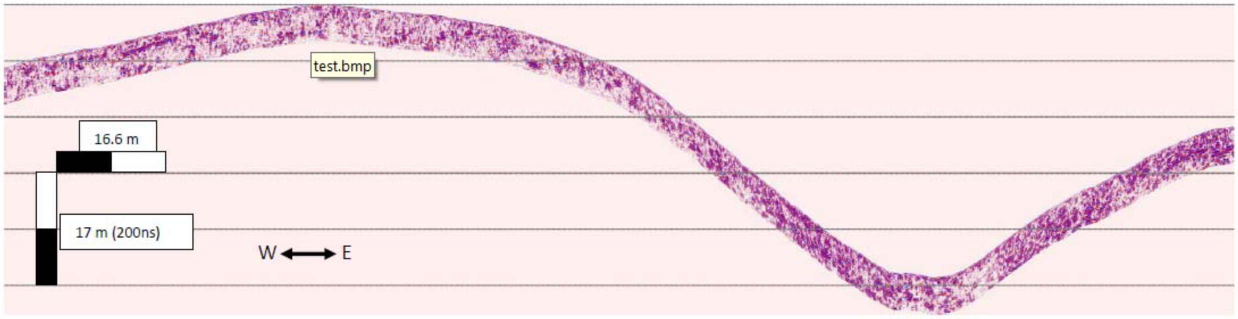


Figure 8. Entire 250 MHz GPR Transect Mirroring Resistivity Transect.

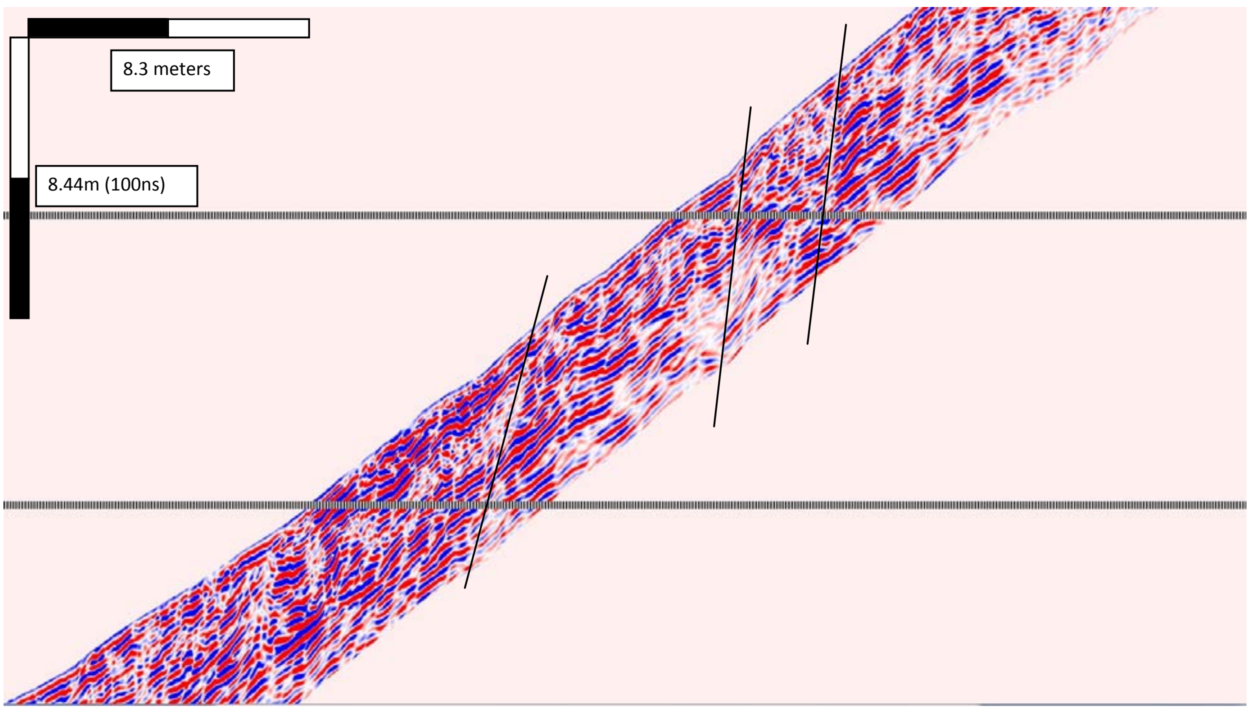


Figure 5- Possible Detachment Surfaces

Figure 9. Possible detachment surfaces visible in 250 MHz GPR data.

Objective 3. Fluvial Network Controls on Carbon-Mineral Complex Formation & Preservation

PI Pizzuto's role in this project is to work with a group of scientists studying how sediment and carbon are received from hillslope sources and transported down the fluvial valley system to estuarine receiving waters. Pizzuto is directing three Ph.D students and one M.S. student. One PhD student started in Sept. 2010, while the other students started in Sept. 2011, so all the work is in its initial stages. The students and their projects are:

Adam J. Pearson (PhD): Fluvial process, morphology, and history of colonial mill dams in the Christina River Basin.

Dale Lambert (PhD): Influence of bedrock on river channel form and process in the Christina River Basin

Margaret Christie (PhD): Anthropogenic and geological influences on sedimentation in the Christina River Estuary.

Elyse Williamson (M.S.): The effect of particle storage on time-averaged suspended sediment transport velocities along the White Clay Creek, Pennsylvania.

Sediment Erosion and Fingerprinting using radio-isotopes and elemental compostion
Diana Karwan, Julia Maquard, Rolf Aalto, Jim Pizzuto, Kyungsoo Yoo and Anthony Aufdenkampe.

In this study we will (1) quantify the composition and sources of suspended particulate material (SPM) to the White Clay Creek Watershed, (2) examine longitudinal trends in SPM composition and source in first to fourth reaches of the White Clay Creek, and (3) quantify the differences in composition and source with hydrologic variations produced by storms and seasonality.

Dr. Diana Karwan has conducted sampling and analysis of stream sediments during storms and their potential watershed sources through the summer of this year. In-stream samples were collected in the Boulton Tributary and White Clay Creek at Spencer Road sites. Watershed sources were collected from agricultural and forested areas on each of the six bedrock types in the 7.2 km^2 watershed (Fig. 10). In addition to surface soils, materials from gullies, road cuts, and road dust were also collected. Many samples for the sediment fingerprinting study continue to undergo geochemical analysis for short-term radioisotopes (Beryllium-7, Cesium-137, Lead-210), elemental composition, carbon and nitrogen content and stable isotopes, mineral surface area, and grain size. Dr. Karwan conducts and oversees the geochemical analysis at the Stroud Water Research Center and University of Delaware. Additional analyses are conducted by Ms. Julia Marquard and Dr. Rolf Aalto at the University of Exeter. While these analyses continue, preliminary results indicate that erosion from the watershed surface does contribute to the suspended solids in the stream during storms.

Longer-term, catchment scale erosion continues to be evaluated using Beryllium-10. Dr. Rolf Aalto and Ms. Julia Marquard have collected sediment samples in the White Clay Creek watershed and Ms. Marquard has prepared these samples, as well as some of the suspended sediment samples collected by Dr. Karwan for Beryllium-10 analysis.

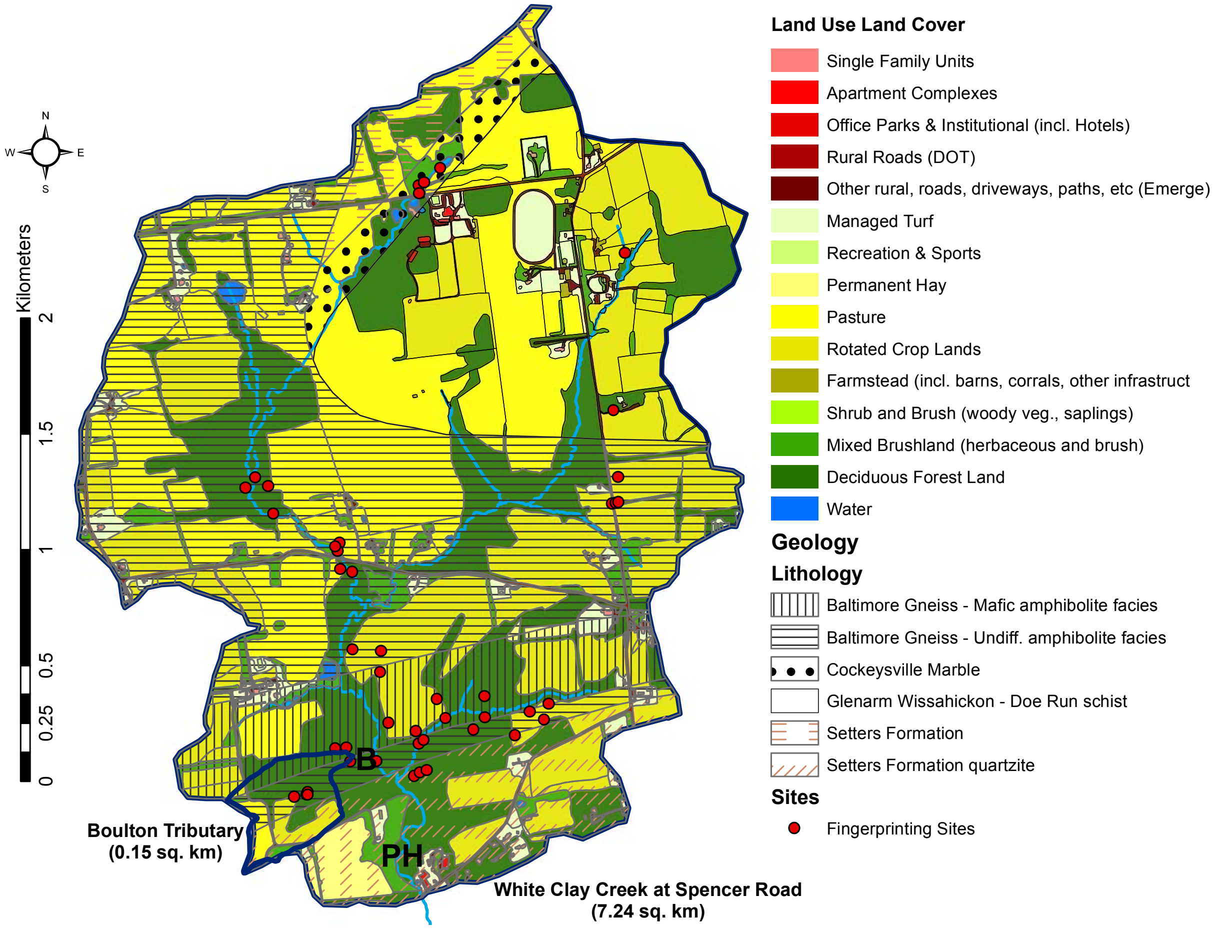


Figure 10. Map of sediment source fingerprinting sampling sites stratified by landuse and lithology.

Dr. Diana Karwan has also been awarded a National Science Foundation, Division of Earth Sciences Postdoctoral fellowship (EAR-1144760) to conduct cross-CZO research in the Susquehanna Shale Hills Critical Zone Observatory.

Objective 4. Watershed Integration of Water, Mineral and Carbon Cycles

PennState Integrated Hydrological Model (PIHM) for Dissolved Organic Carbon

Yi Mei, George M. Hornberger, Louis A. Kaplan, J. Denis Newbold and Anthony K. Aufdenkampe with CRB-CZO

In collaboration with Christopher J. Duffy; Qu, Yizhong, Kumar, Mukesh, Bhatt, Gopal; Xuan Yu from Shale Hills CZO.

We are developing a DOC model coupled with PIHM to explore DOC dynamics at catchment scale. This model is highly related to CZO projects in terms of carbon cycle of watersheds. Vanderbilt University graduate student Yi Mei has spent each of the last two summers working at Stroud Water Research Center and Penn State University to develop a version of PIHM that handles the generation, transport and reaction of DOC in catchments (Fig. 6). Yi also participated as an Teaching Assistant in the international modeling workshop held in Crete in July 2012 and organized by Chris Duffy.

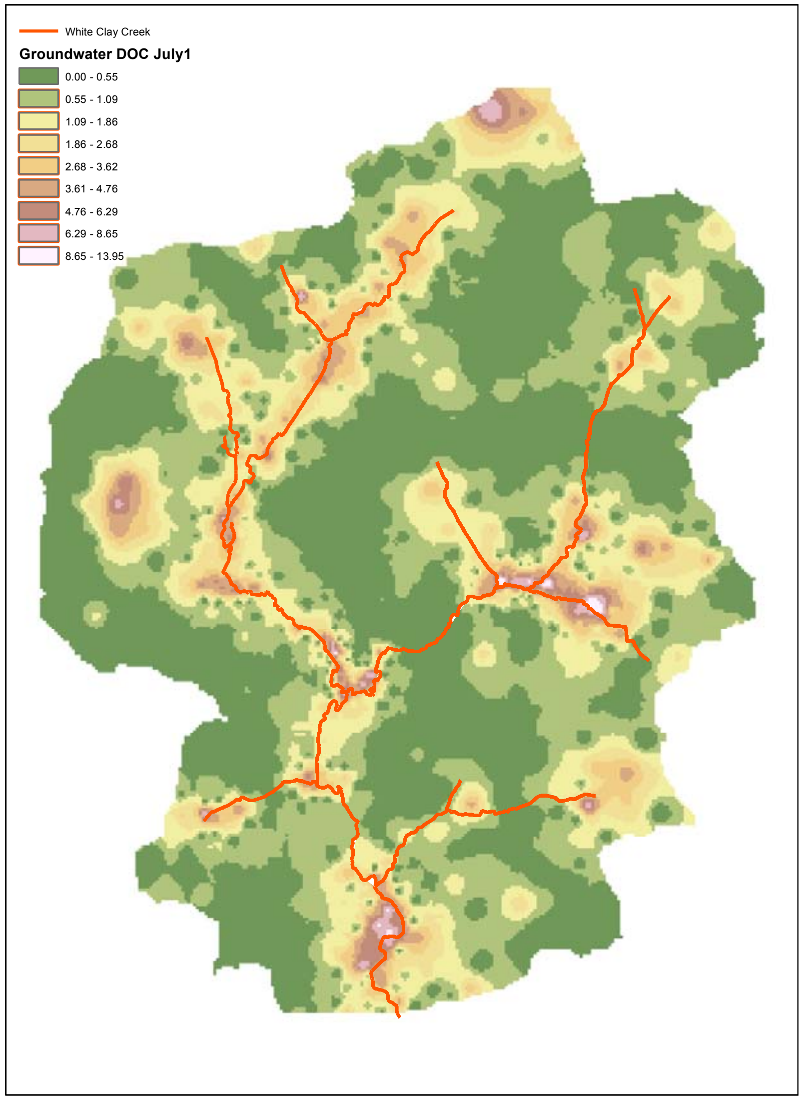


Figure 6. DOC concentration distribution in groundwater for White Clay Creek watershed simulated by PIHMdoc

Surface water-groundwater exchange processes from land to sea
Audrey Sawyer and Holly Michael

The goal of this work is to quantify surface water-groundwater exchange and implications for carbon and mineral fate in three unique watershed settings: stream, tidally influenced river, and estuary. Processes that drive surface water-groundwater interactions are unique in fluvial and coastal settings. Within streams, hydraulic gradients formed by the interaction of currents with channel morphology drive vertical and lateral exchange across the sediment-water interface. In between streams and estuaries, the tidally influenced freshwater zone within rivers is a hydrologically dynamic setting where tidal pumping and reversing currents may enhance exchange. In estuary sediments, vertical exchange can occur due to currents, tides, and waves. Sediment-water interfaces in these settings may be highly active zones for reactive solute transport.

Three field sites have been targeted for comparing surface water-groundwater exchange rates and carbon-mineral reactions. Below is a report of progress at each site.

Stream site (White Clay Creek near Avondale, PA). Three transects of piezometers with pressure transducers have been installed in the floodplain perpendicular to the stream to monitor lateral surface water-groundwater exchange during base flow and storm events. Piezometer transects compliment the existing sensor network, which includes redox potential and soil moisture probes. An additional 11 wells have been installed throughout the floodplain to monitor multidimensional groundwater flow patterns and water table dynamics away from the three transects. Monitoring shows that groundwater discharges to the stream during baseflow, but flow reversals occur from the stream into the floodplain aquifer during storm events due to rising stream stage. Plans are underway to sample DOC and redox-sensitive N, Fe, and Mn species in riparian groundwater and hyporheic water along a transect over a storm event this summer (2012). Storm sampling at high spatial and temporal resolution will indicate how redox-sensitive groundwater chemistry, surface water-groundwater interactions, and chemical fluxes change with storms.

Tidally influenced river site (White Clay Creek near Stanton, DE). A field site has been selected in the tidally-influenced freshwater zone of White Clay Creek just above the confluence with the Christina River. We have received land access permission from DE DOT and United Water, and we have installed a transect of in-stream piezometers and bank piezometers. This summer, we plan to monitor water table fluctuations, vertical head gradients, and hyporheic redox chemistry over several tidal cycles to characterize how tides impact hyporheic exchange and reactive transport of DOC, N, Fe, and Mn.

Estuary site (Holts Landing State Park, DE). Two locations in the subtidal nearshore estuary have been identified with different rates of fresh groundwater discharge: the “Offshore West Site” is at the edge of a buried paleochannel and has moderate fresh groundwater discharge rates, and the “Nearshore East Site” is far from the paleochannel in a zone of rapid fresh groundwater upwelling. Vertical pore water samplers were installed to measure salinity, redox potential, and dissolved oxygen in shallow sediment (Figure 6). Each location has unique pore water chemistry and depths of shallow surface water-groundwater exchange. The Nearshore East Site has a shallow zone of surface water-groundwater mixing (salinity declines rapidly in the upper 25 cm of sediment). The Offshore West Site has a deeper zone of surface water-groundwater mixing (salinity declines more gradually with depth). Dissolved oxygen is greater at the Nearshore East Site, and NO3- concentrations are ~ 200 uM. Redox potential favors Mn reduction at both sites and Fe reduction at the Offshore West location.

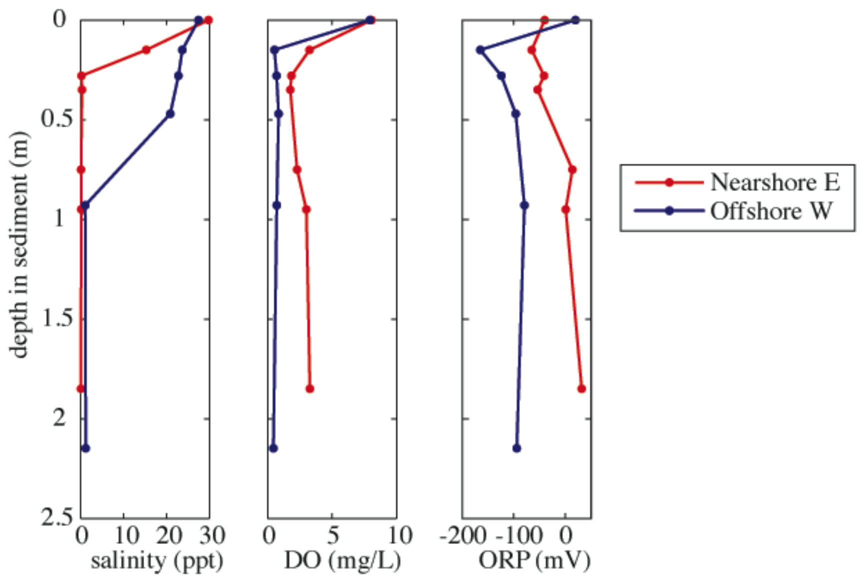
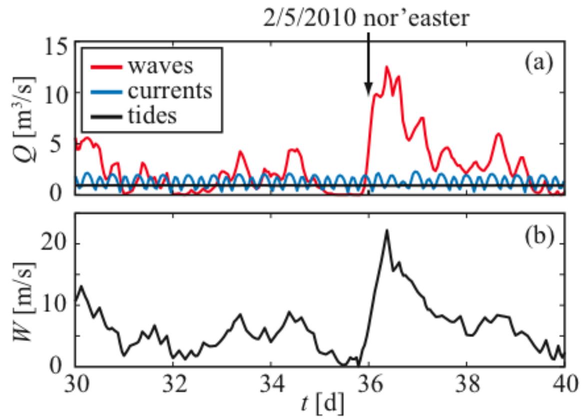


Figure 7: Salinity, dissolved oxygen concentration, and redox potential versus depth for pore water samplers with rapid groundwater upwelling (Nearshore E) and diffuse upwelling (Offshore W).

During the week of June 4, 2012, we deployed vertical arrays of conductivity-temperature sensors at each site to monitor mixing between surface water and groundwater over storm and tidal timescales. At the end of June 2012, redox probes will be installed to monitor changes in redox chemistry. To link hydrochemical dynamics in the sediment with surface water dynamics, we will also deploy an acoustic Doppler velocimeter and rotary sonar to measure currents and sediment mobilization. Pore water sampling before and after storms and over tidal cycles will constrain potential fluxes of dissolved oxygen, Fe, Mn, and C between groundwater and the bay.

Our two subtidal monitoring stations will provide insights into local surface water-groundwater exchange dynamics and reactive transport, but we seek to scale-up these processes across the entire estuary. Toward that end, we have conducted numerical experiments to constrain surface water-groundwater exchange rates due to tidal pumping, wave pumping, and current-bedform interactions. Simulations show that shallow surface water-groundwater exchange rates are highly heterogeneous in both space and time (Figure 8). Storms can increase wave pumping by an order of magnitude in downwind regions of the estuary. Exchange rates also vary over tidal timescales due to oscillating currents and water depths. Saline recirculation is a significant portion of the estuary fluid budget, approaching rates of runoff and fresh groundwater discharge. Saline recirculation may also contribute substantially to geochemical budgets for the estuary, depending on chemical reaction rates in shallow subtidal sediment. These findings are in revision for publication.

Figure 8: (a) Simulated volumetric benthic flux, *Q*, integrated across the Delaware Inland Bays and (b) measured wind speed, *W*, during a nor'easter storm.



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- Aufdenkampe, A.K., E. Mayorga, P.A. Raymond, J.M. Melack, S.C. Doney, S.R. Alin, R.E. Aalto, and K. Yoo, (2011), Riverine coupling of biogeochemical cycles between land, oceans and atmosphere, Frontiers Ecology Environ., 9(1), 53-60, doi:10.1890/100014.
- Chen, C., J. Dynes, J. Wang, T. Regier, and D.L. Sparks. 2012. Soft X-ray Spectromicroscopy Study of Mineral-Organic Matter Associations in Pasture Soil Clay Fractions. *Environmental Science and Technology*, in preparation.
- Chen, C., J. Dynes, J. Wang, T. Regier, and D.L. Sparks. 2012. Soft X-ray Spectromicroscopy Study of Mineral-Organic Matter Associations in Soil Clay Fractions along a Redox Gradient. *Environmental Science and Technology*, in preparation.
- Chen, C., J. Dynes, J. Wang, T. Regier, and D.L. Sparks. 2012. Stabilization of Organic Matter by Adsorption to and Coprecipitation with Ferrihydrite. *Geochimica et Cosmochimica Acta, in preparation.*
- Pearson, A.J., and Pizzuto, J.E., in preparation, Morphology and sediment transport processes of run-of-the-river colonial mill dams, White Clay Creek, Delaware and Pennsylvania, U.S.A.
- Karwan, D.L., R. Aalto, A.K. Aufdenkampe, J.D. Newbold, J.E. Pizzuto. 2011. Characterization and Source Determination of Stream Suspended Particulate Material in White Clay Creek, USA. *Applied Geochemistry* 26:5354-5356.
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- Kyungsoo Yoo, Aufdenkampe, A.K., Chen, C., Sparks, D. **(Invited)** Christina River Basin Critical Zone Observatory: Carbon-Mineral Interactions from Molecular to Basin Scales in the Anthropocene, Goldschmidt Conference, Aug. 14-19, 2011, Prague, Czech Republic.
- Aufdenkampe, A., R. Aalto, K. Yoo, E. Mayorga, (2011), **(Invited)** Is mineral erosion the ultimate control on organic matter sequestration in tropical watersheds?. International Symposium on Soil Organic Matter, Leuven, Belgium.
- Rosier C.*, K. Yoo, J. Kan, A. Aufdenkampe. 2011, Soil organic matter dynamics: Assessment of abiotic and biotic factors controlling soil organic matter complexation and stabilization with mineral surface. American Geophysical Union, Dec.5-Dec.9 2011, San Francisco.
- Yoo, Kyungsoo, CHEN, Chunmei*, AUFDENKAMPE, Anthony, and JI, Junling. 2011. IMPACTS OF LAND USE ON MINERALS' INTERACTION WITH ORGANIC CARBON: FROM SOILS TO WATERSHED SCALES. Geological Society of America Annual Meeting, Oct 9th-12th, 2011, Minneapolis.
- Lazareva O., D.L. Sparks, A. Aufdenkampe, K. Yoo, S. Hicks, J. Kan. 2011. Role of Fe- and Mn- redox coupling on the carbon cycle in a mixed land use watershed: Christina River Basin Critical Zone Observatory. Goldschmidt Conference, Prague, Czech Republic
- Chen, C. and D.L. Sparks. 2011. Soil Organic Matter-Mineral Interactions Along Hillslope Transects: Importance of Iron-Redox Coupling Processes. ASA-CSSA-SSSA International Annual Meetings, San Antonio, TX.
- Chen, C. and D.L. Sparks. 2012. Stabilization of Organic Matter by Adsorption to and Coprecipitation with Ferrihydrite. The 4th International Congress of ECSSS, Bari, Italy, 2012.

- **Chen, C., and D.L. Sparks. 2012.** Biogeochemical Transformations of Iron-bearing Soil Minerals along a Redox Gradient: Implication for C Cycling. The 97th Ecological Society of America International Annual Meeting, Portland, Oregon. (Invited).
- **Lazareva, O.**, Sparks, D.L., Pan, W., Kan, J., and Aufdenkampe, June 2012. A. Biogeochemical dynamics of aqueous Fe and Mn in soil pore-waters and stream with respect to dissolved organic matter (DOM) quantity and quality. Goldschmidt Conference on Geochemistry, Montreal, Canada; Poster Presentation
- Sparks, D.L., Chen, C., **Lazareva, O.**, LeMonte, J., Wang, J., Regier, T., and Dynes, J.J. June 2012. The role of metal redox coupling processes in carbon cycling and stabilization. Goldschmidt Conf. on Geochemistry, Montreal, Canada; Keynote Presentation.
- **Lazareva, O.**, Sparks, D.L., Aufdenkampe, A., Kan, J., Hicks, S., LeMonte, J., Pan, W., and Chen, C. March 2012. Biogeochemical transformation of Fe- and Mn- along a redox gradient: Implications for carbon sequestration within the Christina River Basin Critical Zone Observatory. ACS National Meeting, San Diego, CA, USA; Oral Presentation.
- **Lazareva, O.** March 2012. Biogeochemical Transformation of Fe- and Mn- Along a Redox Gradient: Implications for Carbon Sequestration within the Christina River Basin Critical Zone Observatory. Department of Plant and Soil Sciences Seminar, University of Delaware.
- **Lazareva, O.**, Sparks, D.L., Aufdenkampe, A., Yoo, K., Hicks, S., Kan, J. January 2012. Biogeochemical Transformation of Fe- and Mn- Along a Redox Gradient: Implications for Carbon Sequestration. DENIN Research Symposium, University of Delaware, Newark, DE. Poster Presentation.
- Sawyer A.H., Karwan, D.L and **Lazareva, O.** December 2011. An integrated monitoring network for hydrologic, geochemical, and sediment fluxes to characterize carbon-mineral fate in the Christina River Basin Critical Zone Observatory. AGU Fall Meeting, San Francisco, CA; Poster Presentation.
- Pearson, A.J., Walker, J., Teoli, K., Hubacz,D., Kauffman, G.J., Pizzuto, J.E., and O'Neal, M.A., 2011, Conceptual model of fluvial landforms and bed material transport in 200 year-old run-of-the-river impoundments on gravel-bed streams of the Christiana River Basin, Delaware. EP23B-0735 presented at 2011 Fall Meeting, AGU, San Francisco, Calif., 5-9 Dec.
- Participated in the International Workshop on Design of Global Environmental Gradient Experiments Using International CZO Networks, University of Delaware, Newark, DE. November 2011.
- **Lazareva, O.**, Sparks, D.L., Aufdenkampe, A., Yoo, K., Hicks, S., Kan, J. August 2011. Role of Fe- and Mn- redox coupling on the carbon cycle in a mixed land use watershed: Christina River Basin Critical Zone Observatory. 21th Annual Goldschmidt Conference on Geochemistry, Prague, Czech Republic; Poster Presentation.
- Hicks, S., Anthony, A., **Lazareva, O.**, Karwan, D. Montgomery, D. June 2011. A wireless environmental sensor network using open-source electronics for the Christina River Basin CZO. Joint USGS- CUAHSI Workshop on Optical Water Quality Sensor Networks, Shepherdstown, W
- W. Pan, S. Inamdar, D. Sparks, A. Aufdenkampe, and K. Yoo. 2011. Controls of landuse and landscape position on dissolved organic carbon and mineral complexation: A watershed approach. International Workshop on Design of Global Environmental Gradient Experiments using International CZO Networks, Newark, Delaware, November 8-9 .
- O. Lazareva, A. Sawyer, D. Sparks, A. Aufdenkampe, S. Hicks, K. Yoo, J. Kan, C. Chen, J. LeMonte, S. Inamdar, and W. Pan. 2011. An integrated monitoring network for geochemical and hydrologic fluxes to characterize carbon-mineral fate in the Christina River Basin Critical Zone Observatory: White Clay Creek Watershed, Transect A, International Workshop on Design of Global Environmental Gradient Experiments using International CZO Networks, Newark, Delaware, November 8-9

Year 3 (Oct. 2011 to Sep. 2012)

1. Research and Education Activities

1.1 Project Management and Coordination

The integration of research and education activities across our 37-member team continues to be a priority for the PIs of the CRB/CZO. During the past year we have had periodic conference calls involving the 5 co-PIs, 2 all-scientists meetings for the entire research and education team, and continuous informal post-doctoral scientists discussions. Given the multi-disciplinary nature of our investigations into the dynamics of water, carbon, and minerals within the critical zone, samples are generally split among several scientists, placing a premium on coordinated field sampling campaigns, group decisions concerning sensor installation placement, and data management.

1.2 New Hires

In project year 3 we have continued to bring on new graduate students and interns. Beth Wenell officially began her PhD graduate studies in September 2011 with Yoo in the Land and Atmospheric Science Graduate program at the University of Minnesota and already dedicated nearly 30 days of fieldwork on three separate trips to the CRB-CZO to to characterizing the soil profiles in order to study landscape evolution. Julia Marquard has began work in Sept. 2011 toward her Ph.D. with Aalto at the University of Exeter, kicking off her work with meteoric 10-Be with a 3-week field champagne in Nov. 2011. Fang Tan began her PhD studies in fall 2011 with Paul Imhoff and Holly Michael, with an interest in modeling weathering and solute transport in groundwaters.

In project year 3, we employed 4 undergraduate interns and one high school volunteer to assist post-docs in their last year of field and laboratory work.

1.3 Site Development

We have continued to develop infrastructure at a number of intensive research sites within the CRB. In the aftermath of Hurricane Irene, two small first order catchments were elevated to highest priority due to the observed contrasting storm runoff. Our 100% forested 8.5 ha Spring Brook catchment, in the Brandywine Conservancy's Laurels Preserve, only discharged ~0.1 cm of the 15 cm of precipitation received during Hurricane Irene. In contrast, our 70% forested 15 ha Bolton Run catchment within SWRC's 750 ha research watershed had more than 10 times the runoff. In addition, our towed Acoustic Doppler Current Profiler (ADCP, RDI StreamPro) measurements at other CZO stream study sites during these channel-altering storms showed a need to develop sensitive but exceptionally stable control structures or cross-sections for our discharge gauging.

Stream gauging infrastructure. In project year 3 we significantly upgraded stream gauging infrastructure at 5 stream sites – in two smaller streams by installing trapezoidal flumes and in three larger streams by constructing rock-lined control structures.

In the July of 2012 we installed a 13-foot-long trapezoidal flume to precisely and continuously measure stream discharge in our flashy first order Boulton Run (Fig. 1). Not only is this stream of interest for our studies of hydrology in catchments of different land use, but it is also an intensive sediment fingerprint site for Post-Doc Diana Karwan. Fiberglass trapezoidal flumes have a number of advantages over alternative approaches:

- Pre-engineered, accurate depth-to-discharge rating curves for an exceptionally large dynamic range (i.e. 2 to 6200 gallons per minute for our selected design).
- No upstream pool for trapping and storage of sediment
- Do not require free-fall discharge as for V-notch weirs

We mounted our flume on a level plastic lumber deck set in concrete footings and with plastic lumber wing-walls backed and underlain with rubber pond liner. The installation took three handymen 2.5 days to complete. All materials and labor were directly funded with CZO funds.

Figure 1. A trapezoidal flume (60° V, 3.0 ft high and 13 ft long) installed at Boulton Run in White Clay Creek and designed to precisely measure flashy flows from 2-6200 gallons per minute.

In Oct. 2012 we will install another, smaller trapezoidal flume at the 100% forested Spring Brook in the Brandywine Conservancy's Laurels Preserve.

In early 2012 we selected straight, narrow, stable, tall-banked pool-riffle locations near three stream gauging stations and lined channel cross sections in the riffles with 100-150 lb step stones to create very stable flow control structures (Fig. 2). We placed high precision Solinst LevelLogger Edge pressure transducers in the pools upstream of each of these structures and have begun the process of developing new stage vs. discharge rating curves, which already show the high sensitivity and stability of our new gauges. We decided on this approach after thorough evaluation of all alternatives because:

- These streams are too large for traditional Parshall, trapezoidal and H-flumes

- V-notch weirs back up water, catch sediment and constrain fish movement
- Long-throated flumes and other concrete control structures (http://www.usbr.gov/pmts/hydraulics_lab/pubs/wmm/chap08_08.html) are too expensive to construct and permit for widespread deployment

Fig. 2. Stream discharge gaging control structure at White Clay Creek near Spencer Rd Bridge, economically constructed for long-term stability and sensitivity from locally quarried 100-150 lb step stones. We have installed such structures at 3 similarly sized stream gaging stations and will construct 2 more in late 2012.

The drawback to our less engineered and less expensive stone approach is that we need to develop the full rating curve between water depth/stage and discharge by measure discharge at a variety of stage heights. Measuring low flow discharges in our streams is relatively straightforward using traditional wading rod approaches to measuring velocity profiles, and in early 2012 we upgraded our precision making these measurements by purchasing a Sontek FlowTracker Accoustic Doppler Velocity Profiler (ACVP) wading rod system which we purchased by leveraging SWRC institutional instrument endowment funds. However, measure high, storm flows in many of our streams is much more difficult because of the logistical challenges of making these measurements during the 1-2 hour storm peaks that often occur at night. For that purpose, we also purchased a stationary, upward-looking Sontek IQ+ ACDP, also by leveraging SWRC institutional instrument endowment funds. With the Sontek IQ+, we can thus estimate discharge every 5 minutes over the full hydrograph of many storms at each site, which we can combine with our low-flow wading rod measurements to create full hydrograph rating curves in months rather than years. Our plan is to move the Sontek IQ+ from one site to the next to develop rating curves for all of our stream gaging stations over the next year or two.

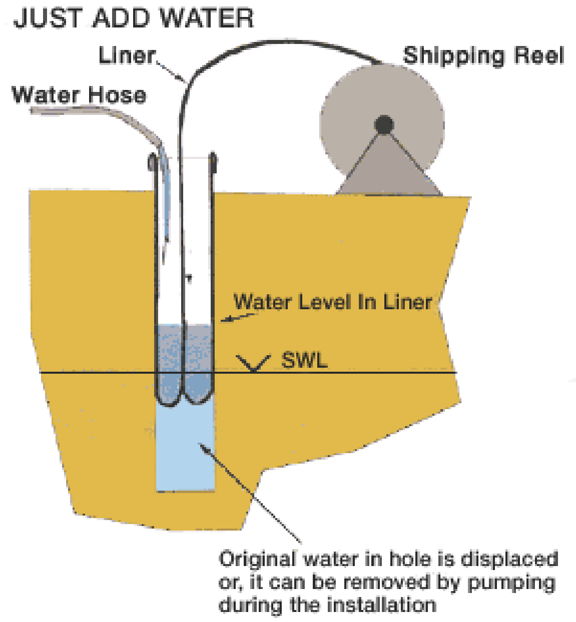
Drilling for Geochemistry and Hydrogeology.

Our original CRB-CZO proposal budgeted for drilling – to collect a continuous profile of materials to assess bedrock weathering and soil formation processes in an unglaciated meta-sediment landscape, and to install multi-depth sensing and sampling wells into the groundwater. This effort was also energized by a call for all CZOs to “drill the ridge”, which was a concept developed at the 2011 International CZO meeting in Delaware. The idea behind “drill the ridge” is that ridgelines provide the simplest weathering profiles because the do not receive any uphill contributions of sediment, colluvium or solutes. In addition, the ground water depth at the ridgeline provides the ultimate control on groundwater gradients in a catchment.

We selected the 100% forest Spring Brook catchment in the Laurels preserve for our first drilling effort because of its uniform landuse, uniform lithology and uniform geomorphology (i.e. planar hillslopes). The provocative results from Hurricane Irene (i.e. ~0.1 cm of runoff during a 15 cm rainfall event) further motivated the choice, by raising the question of whether mature forest on uncompacted soil can really make such a difference, or whether there may be a geologically driven subsurface inter-basin transfer of water to the adjacent catchment. In the full spirit of CZO science, we decided to approach that and other scientific questions with a multi-pronged approach including modeling, geophysical surveys of the subsurface and drilling cores and monitoring wells along the ridgelines.

Figure 3. Roto-sonic coring and drilling activities within a mature forest ridge top in the Spring Brook catchment.

Drilling on the top of a forested ridge in ecological preserve presents both logistical and conservation issues. Not only did we need to be able to bring a drilling rig to the desired location, but we also wanted to ensure that it did minimal damage to the forest and in particular did not cover the forest soil with drilling mud. The later requirement is a scientific one as well, given our interest in studying the geochemistry of soil, rock core and well water, we do not want contamination on the surface by drilling mud. After considerable investigation of different drilling approaches, including field visits by two different drillers, we settled on what we believe is the perfect solution -- roto-sonic drilling with a has a small 6ft x 14 ft rig that still has the capability to extract continuous sample cores through solid bedrock only using small amounts of water for lubrication. We contracted with Aquifer Drilling & Testing, Inc. (ADT, http://www.aquiferdrilling.com/) for the work, which occurred July 30 to Aug. 3, 2012. We succeeded in coring two 70-ft deep bore holes – one on a ridgeline above a planar slope on which we have a soil pit transect, and the other in the valley near the bottom of the soil pit transect. Water table depths in each of the holes were approximately 65 and 25 feet respectively, and bedrock depths were 55 and 30 feet respectively.



We completed the boreholes by casing the top 10 ft with PVC pipe, but then lining the remaining hole with removable flexible liners from Flexible Liner Underground Technoloigies (FLUTe, http://flut.com/).

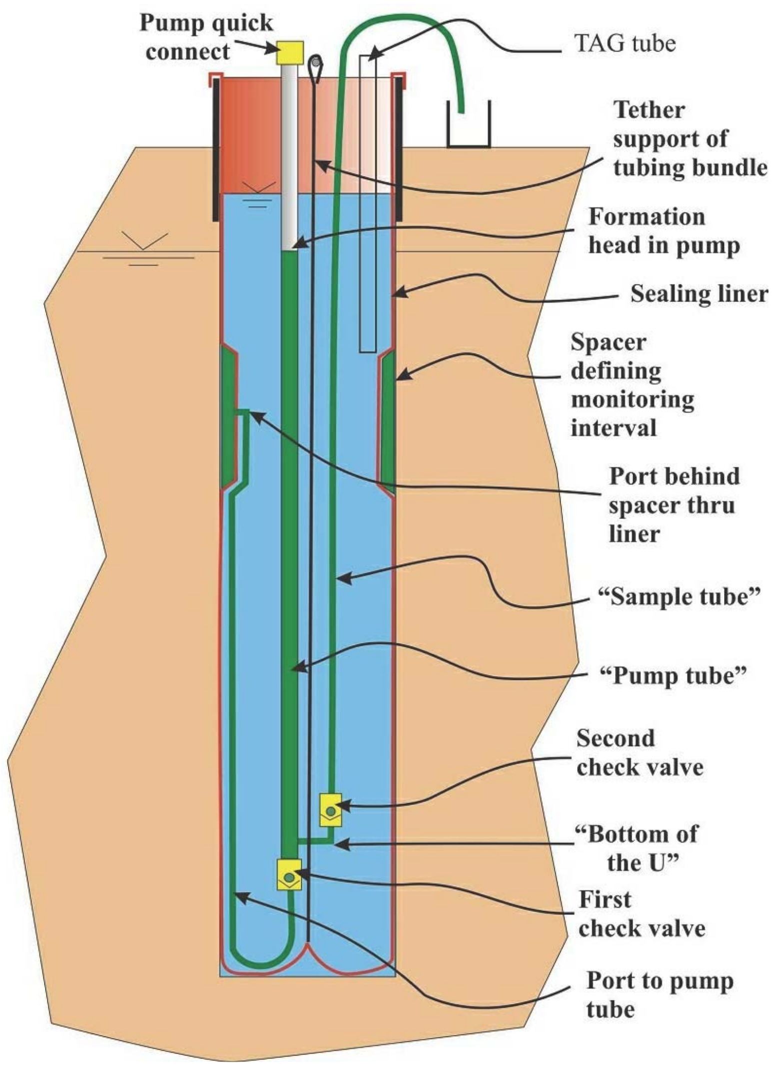


Figure 4. Flexible Liner Underground Technoloigies (FLUTe) multiport sampling.

Immediately after drilling we installed a “blank” liner with no sampling ports to seal and stabilize our borehole. Once the data come back from the cores, we will order custom liners with multiple sampling ports at specified depths.

Coastal Sites. As part of the hydrogeology studies, we have established one study site on the tidally influenced stretch of White Clay Creek just above the confluence with the Christina River near Stanton, DE and two estuarine sites in the subtidal nearshore estuary at Holts Landing State Park, DE. The estuarine sites were chosen, in part, because they have different rates of groundwater upwelling. The Nearshore East site has focused fresh groundwater discharge and a shallow zone of surface water-groundwater mixing, while the Offshore West site has more diffuse fresh groundwater discharge and a deeper zone of surface water-groundwater mixing. More details are described in Section 2, Findings.

1.4 Development of an Advanced Sensor Network

We have continued to develop our wireless environmental sensor networks using open-source electronics. Specfically, we now have deployed throughout our CZO study sites:

- Loggers:
    - 15 Stroud loggers with ArduinoPro/AdafruitLoggerShield
    - 3 Stroud loggers with SeeeduinoStalker/StroudAnalogInterfaceShield & solar panels
    - 8 Campbell Scientific loggers for redox
    - 2 Decagon Em50 loggers at Audrey's bay site.
    - 2 Hypnos redox loggers next month (48 sensor channels on each)
- Sensors:
    - 24 pressure transducers
    - 26 Decagon 5TM soil moisture probes deployed, 16 more in the lab for later
    - 12 Decagon MPS-2 water potential sensors in the lab for later
    - 26 single-element redox probes installed; others in the lab to be deployed soon: 22 single-element platinum probes, 9 nine-element probes, and 5 four-element probes
    - 3 Arduino Dial-a-pumps
    - 10 Decagon CTD sensors for Audrey's bay site
    - 20 Sensorex conductivity sensors to be deployed whenever we build the circuit based on Carnegie-Mellon's design, of which we have 5 of their loggers deployed
    - 2 Licor LI-840 gas analyzers for respirometers (1 lab, 1 portable)
    - Sontek IQ-Plus uplooking acoustic doppler
    - S::can spectrolyser

1.5 Cyber-infrastructure for Data Management

Our major data management effort for project year 3 has been the development of a data system to efficiently parse out streaming, real-time data from our wireless sensor network, automatically tag it with the full set of metadata required to comply with CUAHSI's Hydrological Information System, and feed it into our Aquarius hydroserver (http://aquaticinformatics.com/) for easy quality control and data manipulation. These efforts are nearing completion and we hope to have a very high quality streaming data system posting live data to web services, including a web client that has been customized for our CZO by Emilio Mayorga at the Unversity of Washington's Applied Physics Laboratory (http://www.nanoos.org/nvs_crb/nvs.php),

1.6 Sample Collection, Sample Processing, and Laboratory Experiments

The majority of sample collection, processing and analysis activities are described in section 2, findings.