**Annual Report for Period:** 10/2010 - 09/2011 **Submitted on:** 09/13/2011

**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**

**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

## 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 have submitted an NSF RAPID proposal work with Kirk White, of the USGS Pennsylvania Water Science Center, to process 15 min (or unit value) historical water quality data.

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.

## 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. , vol. in pres, (2011). Accepted, 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 Riparian Zone to a Headwater Stream", Water Resources Research, p. , vol. submitt, (2011). 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. 2011, 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:

Organizational Partners

Any Product

Any Conference

**Year 2 (Oct. 2010 to Sep. 2011)**

## 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, weekly post-doctoral scientists discussions, and monthly discussions for each of the 4 primary research objectives (one per week). 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.

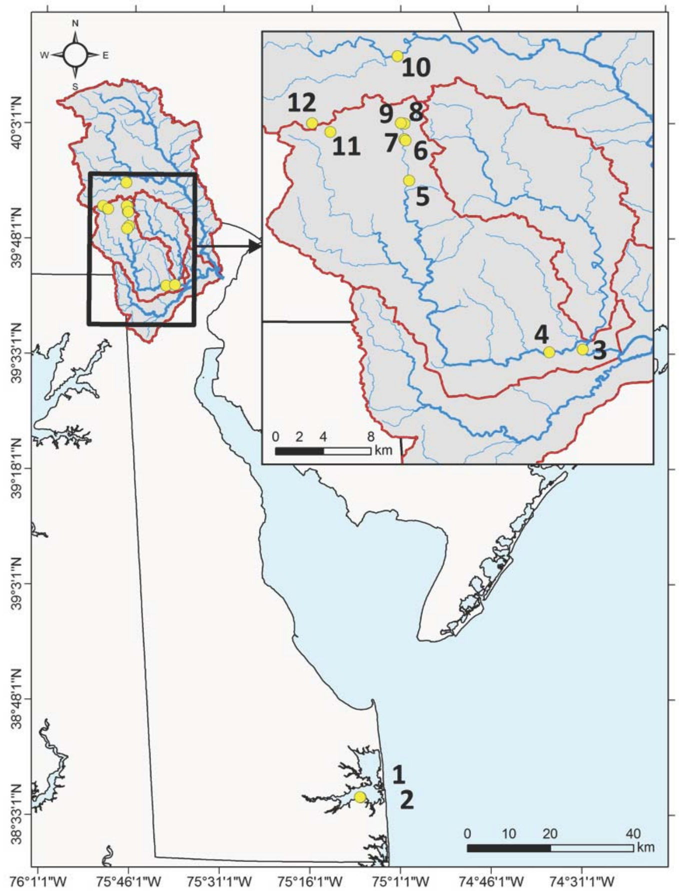



Fig. 1. Map of CRB/CZO study sites: (1,2) estuarine sites at Holts Landing; (3) potential site in tidally influenced White Clay Creek (WCC); (4) USGS 01479000; (5) USGS 01478120; (6) 3rd- order WCC; (7) Boulton's Branch intermittent stream; (8,9) 2nd-order streams WCC; (10) 1st-order Laurels Preserve; (11) 1st-order at SECCRA landfill; (12) 1st-order agricultural site.

The division of research fronts into 4 primary objectives related to our proposal questions and hypotheses has been beneficial. However, to ensure that our CZO provides a robust observatory that constitutes a resource for the larger geosciences community, we are moving to involve CRB/CZO Senior personnel as coordinators for disciplinary efforts including hydrology, soil science, atmospheric fluxes, and GIS.

### 1.2 New Hires

With the addition in May 2011 of Dr. Audrey Sawyer, a hydrogeologist, we now have 4 post-doctoral scientists working in the CRB/CZO (see year 1 report). Audrey is mentored by Dr. Holly Michael and is working on quantifying surface water-groundwater interactions in rivers and coastal settings to understand implications for solute and heat transport. She is particularly interested in dynamic processes such as storms and tides that enhance surface water-groundwater exchanges. Some of Dr. Sawyer's initial research efforts are described below.

Two new students were recruited in the spring of 2011 by CRB/CZO scientists Drs. Rolf Aalto and Kyungsoo Yoo. Julia Marquard has begun work toward her Ph.D. with Aalto at the

University of Exeter and brings extensive experience working with meteoric 10-Be to the project. Beth Wenell has begun her MS graduate studies with Yoo in the Land and Atmospheric Science Graduate program at the University of Minnesota and has an interest in applying geophysical techniques to characterize the regolith within the CRB/CZO.

**1.3 Site Development**

We have continued to develop the infrastructure at a number of intensive research sites within the CRB (Fig. 1).

Three contrasting headwater ($1^{st}$- order) streams identified for the CRB/CZO are: (1) a completely forested watershed that is protected in perpetuity within the Laurels Preserve, managed by the Brandywine Conservancy (Figs. 2, 3); (2) an agricultural watershed that is held under an agricultural conservation easement and dominated by row crops of soybeans and corn (Fig.4); and (3) a watershed impacted by the Southeastern Chester County Refuse Authority (SECCRA) landfill (Fig. 5).

Our 3rd -order White Clay Creek Experimental Watershed at the Stroud Water Research Center (WCC-SWRC) continues to be an important research focus because of our extensive existing infrastructure and 44-year data record. As such, our primary sensor and infrastructure development has occurred in WCC-SWRC and we consider it a test-bed for new infrastructure that we plan to deploy at other CRB-CZO sites.

Two other sites from which we are beginning to collect data are USGS stations at East Branch White Clay Creek at Avondale (USGS 01478120) and at the mouth of White Clay Creek near Newark DE (USGS 01479000).

Fig. 2. Mouth of forested $1^{st}$-order stream in the Laurels Preserve.

Fig. 3. Mid-slope section of forested $1^{st}$-order stream in the Laurels Preserve.


Fig. 4. . Agriculture site with $1^{st}$-order stream.

Fig. 5. Construction site with 1st-order stream at SECCRA.

Fig. 6. Submersible diode-array spectrophotometer (s::can©, spectro::lyser©) installed in 3rd-order White Clay Creek.

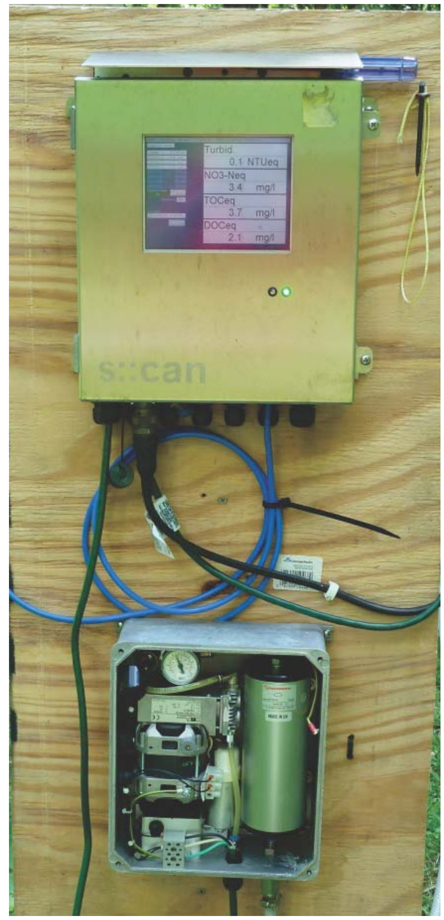



Fig. 7. s::can© showing readout for turbidity, nitrate, and dissolved organic carbon.

During Hurricane Irene we activated automated stream samplers (ISCO samplers) and pressure transducers for stage height measurements at nine locations, eight of which are in the White Clay Creek watershed. These included the six sites described above, an intermittent zero-order forested stream that drains into WCC-SWRC and two 2nd-order streams that are the main tributaries to WCC-SWRC.

As part of the hydrogeology studies, two potential study sites 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 have been identified. Discussions concerning land access permission to the White Clay Creek sites are currently underway with DE Department of Transportation and Artesian Water of Delaware. 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 (Fig. 1).

We continue to have plans to develop infrastructure (samplers and additional sensors) at USGS gauging stations on lower sections of Brandywine Creek in years 3-5, but will first focus on White Clay Creek as described above.

### 1.4 Development of an Advanced Sensor Network

To quantify the flux of minerals and organic carbon from the Christina River Basin we have identified the submersible UV-Vis diode array spectrometer probe, a "spectro::lyser©" manufactured by s::can (http://www.s-can.at/), as the centerpiece of our stream sensor clusters (Figs. 6, 7). Comparison of spectro::lyser values performed using a probe with a sapphire window and a probe with a quartz window and bench-top values for organic carbon, nitrate, and suspended solids were performed and the data presented at the CZO national meeting in Arizona. Following the Arizona meeting, two members of the CRB/CZO team attended a joint USGS-CUAHSI workshop on *In Situ* Optical Water Quality Sensor Networks where our experience with the spectro::lyser was shared. Based on these experiences and other laboratory comparisons we continue to work on improved probe calibration, generation of a remote diagnosis of window fouling, developing ideas for remote cleaning of the probe windows, and reducing the energy consumption of the installations.

Fig. 8. Pressure transducer installation in 3rd-order stream and riparian zone well.

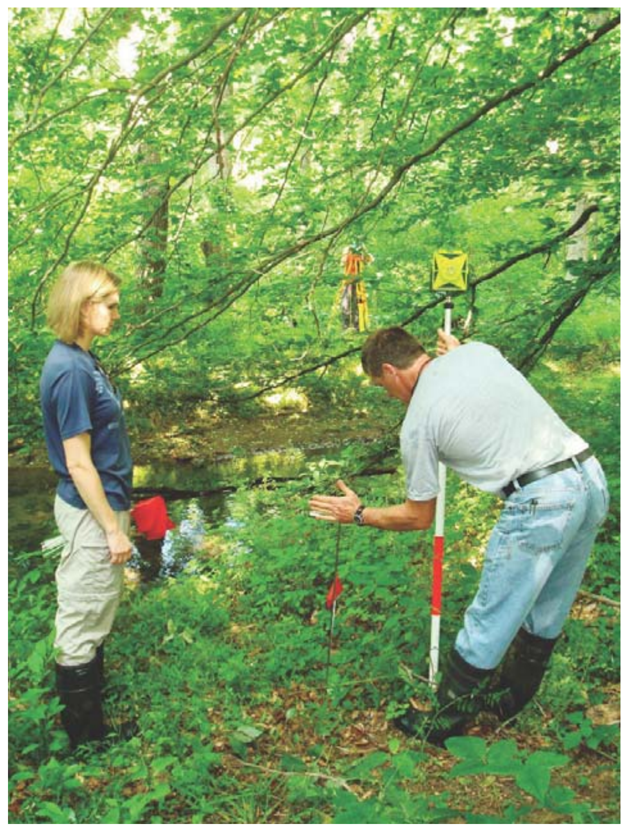


Fig. 9. Mapping a floodplain gravel layer prior to installing piezometer transect.

Our work on wireless environmental sensor networks using open-source electronics has moved from planning into various stages of deployment and development, depending on the specific sensor. Briefly, a variety of sensors have been purchased or constructed, installed, and connected to custom data loggers. The sensors include: (1) pressure transducers placed into streams, riparian zone wells (Fig. 8), and a piezometer transect in a floodplain perpendicular to the stream (Fig. 9); and (2) redox sensors and soil moisture/temperature probes placed within different soil layers exposed at the stream banks on either side of a stream (Fig. 10), and within an upslope soil pit in an agricultural field. Some of these sensors are currently streaming live data into our labs, and we hope to provide public access in the near future. We plan on adding gas sensors for oxygen and carbon dioxide and a conductivity sensor to these arrays in the near future. The advances made in sensor networks with open-source electronics were also presented at the USGS-CUAHSI workshop mentioned above and at an event on Capitol Hill attended by elected officials from Delaware. Some of these efforts are described in more detail below under in the research activities of Dr. Oleysa Lazareva.

Fig. 10. Installation of redox and soil moisture/temperature probes in upland soil pit.

Another development using open-source electronics, while not a sensor per se, has contributed to our ability to target the collection of large volumes of water (200 L) at the peak of material transport during storms. These collections are an integral part of the research led by Dr. Diana Karwan involving cosmogenic radioisotopes, described below. Steve Hicks, an electrical engineer on the CRB/CZO team developed a cell-phone based triggering mechanism for a high volume sample pump used to collect stream water (Fig. 11). By monitoring the storm hydrograph via the internet, Dr. Karwan can pick the appropriate time to start and stop the pump and collect water samples remotely.

Fig. 11. Collection barrel with cell phone trigger attached (upper right) and ISCO sampler prepared for storm sampling.

### 1.5 Cyber-infrastructure for Data Management

We have placed a large amount of data on the CRB/CZO data page (in the 'Data' link from the CRB/CZO home page - http://www.udel.edu/czo/index.html). While not an inclusive list, some highlighted datasets on the site include: (1) 10 yrs of White Clay Creek stream water chemistry data; (2) 5-minute data (beginning in 2006) from the NOAA CRN weather station site located within the White Clay Creek watershed; and (3) 40+ years of 15-minute stream flow data for the White Clay Creek. A majority of the data posted to the CRB/CZO web page has been put in a form that allows for ingestion of our data into CUAHSI's Hydrological Information System (http://his.cuahsi.org/). We continue to work with personnel from the San Diego Supercomputing Center to integrate our data into the larger, cross-CZO effort to compile and make all CZO related data easily accessible.

Emilio Mayorga of the Applied Physics Laboratory, University of Washington, has been working on a map-based data-visualization browser that is scheduled for completion at the end of this year. This web browser will ultimately allow for very easy viewing and downloading of CRB/CZO related data. The initial version uses CUAHSI-HIS web services to pull in USGS data within the

CRB and climate data from NOAA as well as from the Delaware Earth Observing System (DEOS http://www.deos.udel.edu). A prototype of the web-based visualization system is available at: http://www.nanoos.org/nvs_crb/nvs.php.

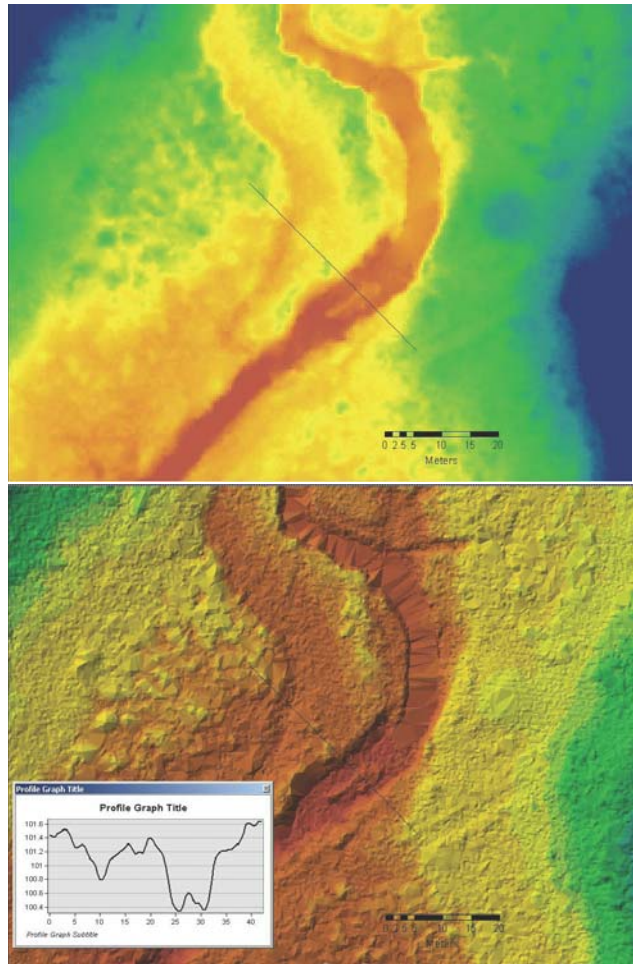



Fig. 12. LiDAR 0.5 m digital elevation model (panel A) and three-dimensional TIN model with channel profile (insert) (panel B) of the same reach of 3rd-order White Clay Creek.

CRB/CZO data managers also continued their active participation in cross-CZO data management efforts. Anthony Aufdenkampe, CRB/CZO co-PI, is an active participant in the national CZO data management committee that is developing the national CZO data system. He has taken a leadership role brining together the hydrological informatics sensor-centric approaches and community (i.e. CUAHSI) and the geochemical informatics sample-centric approaches and community (i.e. EarthChem). Aufdenkampe is co-PI on the recently submitted NSF proposal “Integrated Data Management System for Critical Zone Observatories” (Mark Williams is lead PI), and he is a co-author on a paper describing the CZO data system (Zaslavsky et al. 2011 in press, Environmental Information Management, doi:10.5060/D2NC5Z4X).

CRB/CZO data managers, Charles Dow and Melanie Arnold, participated in near weekly conference calls with the CUAHSI-HIS team to refine data uploading procedures. At the national ‘all-hands’ meeting in May 2011 hosted by the Jemez-Catalina CZO at the Biosphere 2 outside of Tucson AZ, a data management session was held the last day of the meeting and attended not just by CZO data managers, including Melanie Arnold of the CRB/CZO, but also by others working in parallel efforts towards improving environmental data management (e.g. SESAR, Open Topography, CUAHSI-HIS). These cross-project collaborations within the data management arena are a very important aspect of CZO-specific efforts with the potential to radically improve national and international environmental data management efforts.

To further our effort of integrating CRB/CZO data within a larger data compiling/access effort, we have begun working with Chris Crosby of the Open Topography Project (http://www.opentopography.org/) to incorporate all CRB/CZO LiDAR data in this open-source effort that will make LiDAR freely available and easily accessible. We have sent a large amount of LiDAR data including data collected as part of a specific LiDAR effort for the CRB/CZO as well as publicly-available LiDAR data provided through state GIS departments in Pennsylvania, Delaware, and Maryland.

**1.6 Airborne LiDAR Imagery**

Dr. Naomi Hicks of the CRB/CZO is working with LiDAR data for the CRB. These efforts extend beyond our participation in the vegetation survey to ground truth LiDAR imagery under full canopy cover, a project being coordinated by Qinghua Guo at UC Merced and the Open Topography Project mentioned above. Dr. Hicks has created ultra-high resolution surveys of stream geomorphology using high-resolution LiDAR data, which allow for fine scale geomorphic assessment over relatively large spatial extents. Previously available DEMs with a resolution of tens of meters or more do not provide adequate resolution for geomorphic characterization of small streams and watersheds or the identification of changes in stream morphology over time.

High-resolution LiDAR data (9-15 points $m^{-2}$ and 1-2 cm vertical accuracy) for a portion of the CRB/CZO were obtained by the National Center for Aiborne Laser Mapping (NCALM, http://www.ncalm.cive.uh.edu/) during both leaf-off and leaf-on time periods in 2010. Topographic data from these flights were analyzed with the intent of geomorphic applications such as stream morphology, sediment transport studies, and the evaluation of alluvial deposits. These data and resultant products will contribute to hydrologic and biogeochemical modeling and to mechanistic biogeochemical studies of these streams. The LiDAR data also facilitate informed instrument placement and will be used for vegetation studies.

The LiDAR data for the CRB/CZO has been used to create a variety of LiDAR based topographic data products including 10-50 cm Triangular Irregular Networks (TIN) and 0.5-m Digital Elevation Models (DEM) (Fig. 12). LiDAR intensity images have provided additional information, which combined with LiDAR derived slope and elevation products have allowed the identification of stream channel boundaries and stream centerlines for 3$^{rd}$- through1st-order streams. These high precision stream channel and floodplain characterizations would not have been otherwise possible without extensive field surveying. Future LiDAR flights will allow for the identification of changes in channel morphology over time in low order basins and contribute to the long-term data being assembled for the White Clay Creek watershed and larger CRB/CZO. These characterizations are of particular interest in comparisons between forested and meadow reaches, and in studying the effects of changes in land-use on channel morphology. The high-resolution LiDAR data allow for the generation of surface characterizations of importance to a wide range of interdisciplinary researchers.

**1.7 Modeling and Adaption of the Penn State Integrated Hydrologic Model (PIHM)**

Yi Mei, in collaboration with George Hornberger, worked on several modeling approaches to simulate dissolved organic carbon (DOC) dynamics in the White Clay Creek watershed. He calibrated a one-dimensional model using data from soil core experiments and then used these results and a two-dimensional hillslope model to explore the DOC flux along different hydrological flow paths in the watershed. This work was presented at the 2010 Fall AGU meeting. Subsequently a manuscript based on the work was submitted to Water Resources Research. Yi visited Penn State University in July, 2011 to work with Chris Duffy's group on the Penn State Integrated Hydrological model (PIHM), focusing on calibrating PIHM for White Clay Creek watershed and developing new strategies on the simulation of DOC in White Clay Creek using PIHM.

Additional modeling efforts for the White Clay Creek watershed were undertaken by Dr. Yin-Phan Tsang under the direction of Dr. J. Denis Newbold. In that study Topographic Model (TOPMODEL) was calibrated using a 14-yr hydrograph record for White Clay Creek and a groundwater evapo-transpiration (ET) pathway was added to derive a new model, Groundwater Evapotranspiration TOPMODEL (GETTOP). We inspected groundwater elevations and stream flow hydrographs for evidence of groundwater ET, examined the relationship between groundwater ET and topography, and delineated the area where groundwater ET is likely to take place. A manuscript describing this effort has been submitted to Water Resources Research for review.

Fig. 13. Soil core from upslope agricultural field.

Fig. 14. Precipitation samplers for cosmogenic isotope samples.

**1.8 Sample Collection, Sample Processing, and Laboratory Experiments**

Sampling of stream water and its associated suspended load, stream bank sediments, and soils was performed extensively over the past year. Diana Karwan, a post-doctoral researcher, collected suspended sediments during storms as part of her source tracking studies. These samples were analyzed for cosmogenic radioisotopes in Jim Pizzuto's lab at the University of Delaware and Rolf Aalto's lab at the University of Exeter. Additional analyses of the samples included carbon and nitrogen content, stable isotopes of carbon and nitrogen, and mineral surface area. Diana also collected soil core samples from an upslope agricultural site and a floodplain riparian zone site and stream bank sediments from White Clay Creek for geochemical and microbial fingerprint analyses (Fig. 13). Diana set up precipitation collectors (Fig. 14) and stem flow collectors (Fig. 15) to begin her study of cosmogenic isotopes in precipitation and their capture by the tree canopy. As an adjuct to Diana's investigations, soil cores collected within the CRB/CZO have been analyzed for 137-Cs, 210-Pb, and grain size in Rolf Aalto's laboratory. Dr. Karwan presented posters on her research at the

Fig. 15. Construction of stem-flow collection system.

national CZO meeting in Arizona and the Geochemistry of the Earth Surface (GES-9) conference in Boulder, CO. In conjunction with the GES-9 conference, Dr. Karwan gave an oral presentation at a NSF-sponsored young scientists meeting associated with the conference. Additionally, Dr. Karwan wrote a NSF Earth Sciences Post Doctoral fellowship proposal that was submitted for cross-CZO geochemical sediment analysis.

Adam Pearson, a Ph.D. student mentored by Dr. J. Pizzuto in the Geology Department, University of Delaware, has been working with Dr. Pizzuto and others to develop a conceptual model of fluvial landforms and bed material transport in 200 year-old run-of-the -river impoundments on gravel-bed streams within the CRB/CZO. Data have been collected from nine ~200 year-old run-of-the-river impoundments on medium-sized (drainage basin areas of 120-230 $km^2$), gravel-bed ($D_{50}$ ~ 25 mm), pool-riffle channels with an average dam height of 1.5 m (range 1-2 m). The impoundments have an average length of 1400 m (range 1100-1437 m), or about 940 times the average dam height. Accommodation space behind the dams is not completely filled with sediment – maximum water depths of the impoundments range from 1.3-2 m, or 1-1.3 times the average dam height. The upstream extents of impoundments are being defined by the downstream end of pool-riffle bed morphology and by a gradual increase in reach-averaged thickness of stored sandy bed material, which averages about 0.2 m in unimpounded reaches and has been documented by depth of refusal surveys. Upstream reaches of impoundments are also often characterized by a sloping front of gravel-sized bed material that rapidly transitions to the sand-dominated bed ($D_{50}$ < 2-7 mm) that characterizes most of the impoundment. A depth of refusal survey has indicated that the thickness of impounded (mostly sandy) bed material ranges from 0.4 – 1.3 m for one impoundment with a 1-m high dam. On all impoundments, coarser bed material ($D_{50}$ of 3-14 mm) accumulates into a sloping ramp just upstream of the dam that merges smoothly with the dam crest.

Additional studies by Pearson and Pizzuto involve analyses of floodplain cores and monitoring an area upstream of a dam scheduled to be removed on the White Clay Creek. They have obtained 4 cores from the floodplain of the White Clay Creek a few miles upstream of Newark, Delaware. Two of these cores were taken from an area just upstream of an existing mill dam, and the other two are from a section of the stream that is not influenced by an existing mill dam. The cores are being analyzed for the fallout radionuclides Cs137, Pb210, and Be7 to determine if mill dams are currently influencing rates of overbank sedimentation along the White Clay Creek. The monitoring involves an area of the White Clay Creek upstream of a small mill dam near the mouth of the creek at the Delaware Park Golf Course. The mill dam is slated for removal in November, 2011. The monitoring program will continue after the dam is removed to document how the stream changes. These studies will help determine if mill dams construction and removal has had (and continue to have) a significant influence on the movement of sediment and other related constituents in the Christina River Basin.

Studies performed by Drs. Pizzuto and Yoo from the CRB/CZO and others involves the measurements of annual sediment flux, sediment exchange involving the floodplain, deposits formed in the lee of large woody debris, and the hyporheic zone and mean downstream sediment transport distances. These data are being used to estimate the mean transit time for stored sediments and the long-term average downstream velocity of suspended particles.

Christine McLaughlin, a Ph.D. student at the University of Pennsylvania, sampled stream water, spring seeps, and overland flow for an end-member mixing analysis to determine the terrestrial source waters that control stream water chemistry and deliver terrestrial DOC to the stream. She has also measured the quality of DOC in terrestrial source water and has separated stormflow waters into constituent lability classes using plug-flow bioreactors. Christine presented a poster on her CRB/CZO research at the 96th Ecological Society of America annual meeting in Austin, TX in August.

Fig. 16. One of 30 ADCP cross-section measurements of current and discharge measured at WCC-SWRC during Tropical Storm Lee.

During Hurricane Irene and Tropical Storm Lee, which respectively brought approximately 15.5 cm and 18 cm of rain to the CRB/CZO in 8 days, a major effort involving a field and laboratory team of 12 individuals prepared sample labels, sample bottles and secured ISCO samplers at the 9 locations mentioned in Section 1.3 above. Samples were collected over the entire storm and then processed during the following week for organic carbon and nitrogen, major elements of minerals, cosmogenic radioisotopes, major anions and cations, and stable isotopes of carbon and nitrogen. These data will provide our first major integrated assessment of the impact of land use on carbon and mineral fluxes within the CRB/CZO under flood conditions. In addition, our advance preparations enabled us to characterize the entire hydrograph of TS Lee in the 3$^{rd}$ order WCC-SWRC, from 300 L/s to 22,000 L/s and back down, deploying our new RDI Stream Pro Acoustics Doppler Current Profiling for over 30 cross sections over 6 hours (Fig. 18). Comparing these measurements to our four deployed pressure transducers (at three nearby locations) will give a full stage rating curve of exceptional quality, and will allow us to evaluate the best future placement of our stage recorder. Tropical Storm Lee produced our third largest flood to measured since 1968.

Numerous research studies and experiments are being performed on soils and Dr. Carl Rosier, a postdoctoral researcher, led the effort to collect and process reference samples that could be used in his studies and by others. Soil pits were dug in an upland agricultural soil (1.5 m deep, Fig. 17) most recently planted in corn and in a forested floodplain riparian zone soil (1.0 m deep). Initially the soil profiles were described and characterized visually. Extensive soil samples were collected at various depths throughout the soil profiles and will be analyzed for C14, total-C, mineral surface complexed carbon, and bulk density. B-horizon soil was removed

Fig. 17. Detailed pit sampling in 1.5 m agricultural soil pit.

from both soil pits, air-dried and sieved to 2000 µm. Elemental analysis of subsamples are currently being conducted at the Soil Testing Facility at University of Delaware and surface area and total-C analysis are underway at the Stroud Water Research Center. We are currently investigating the potential for STERIS to sterilize a portion of collected soil via gamma-irradiation. These soils will be stored at the Stroud Water Research Center and available for future research requests.

Three experiments are being started by Dr. Rosier that focus on interactions between soil biology, chemistry, and organic matter (OM) dynamics to improve our ability to model and predict numerous soil processes including nutrient cycling, soil water dynamics and OM storage potential. The first experiment is a laboratory incubation study designed to determine the degree to which iron oxide concentrations and biological processing complex and stabilize soil organic matter on mineral surfaces. That experiment will examine macro-scale biological processing (i.e. mixing) in conjunction with increased iron oxide concentrations to see whether they significantly affect the complexation potential of organic matter to mineral surfaces. To date a detailed experimental design, collection/analysis test soil, and construction of incubation chambers have been completed with the anticipation that this experiment will generate a soil carbon budget from measurements of $CO_2$ mineralization, particulate organic matter, carbon complexed to mineral surfaces and the biomass of soil organisms.

A second investigation that has been planned involves assessing whether tree species that conduct greater amounts of stemflow to the soil surface maintain higher soil moisture levels over longer timeframes, leading to increased mineralization of labile organic matters pools and ultimately lower the microbial diversity of wetter soils. This investigation will involve measuring differences in tree species stemflow production, soil organic matter dynamics, and soil microbial community structure. A sampling plan has been developed and sampling sites have been identified.

The third study targets the mountain pine beetle to determine if infestation and the associated disruption of fixed photosynthate translocation to the soil influences soil organic matter dynamics and soil microbial community structure. An anticipated decline in mycorrhizal community followed by reduction in saprophytic fungi coupled with the production of needle fall (low C:N) following several years of infestation could lead to an increase in the bacterial component of the soil community. To date collaboration with Drs. P. Brooks and E. Pendall of the University of Arizona has been established and a sampling plan developed.

Dr. Olesya Lazareva, a post-doctoral scientist in the CRB/CZO, has been conducting research 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. These include a floodplain forest, upland forest, and an upslope agricultural field under row crop cultivation, all within the White Clay Creek watershed. Her proposed research questions include: (1) How do redox conditions in soils affect the transport of 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 newly-precipitated 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 the C cycling under these redox fluctuations?

In year 2 Dr. Lazareva has been working with Steve Hicks to construct and install extensive field instrumentation, conduct field sampling and analyze a combination of soil cores, soil pore waters and gases along the floodplain forest, upland forest, agriculture, as well as stream water, and groundwater. Currently, the floodplain is the most instrumented area including multiple redox sensors, soil moisture/temperature probes, in-situ soil pore-water samplers, and pressure transducers. The sensors and probes were placed on the eastern and western sides of the stream bank at different depths including the post-colonial legacy sediments, pre-colonial buried wetland and gravel layers. The sensor data have been collected continuously since April 2011 using Campbell and data loggers manufactured by 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. The water samples from soils and stream have been collected bi-weekly and analyzed for pH, temperature, alkalinity, $Fe^{2+}$, conductivity, DOC, POC, 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), and stable isotopes of water ($d^{18}O$, dD). The analyses are performed at the Stroud Water Research Center and the University of Delaware. In addition, the installation of redox sensors, soil moisture/temperature probes, soil pore-water and gas samplers are currently in progress within the agricultural site of transect A and expected to be completed this summer.

Dr. Lazavreva presented four different posters on her research at state, national, and international scientific conferences, most recently the Goldschmidt Conference in August, and at an event on Capitol Hill in Washington, D.C. Additionally, she wrote a proposal entitled, "Biogeochemical transformation of soil Fe- and Mn- mineral phases along a redox gradient: Implications for C sequestration" that was submitted to the DOE Wiley Environmental Molecular Science Laboratory to employ high precision Mössbauer and EPR spectroscopies to: (1) investigate soil solid-phase Fe and Mn species along a redox gradient of different landscape positions and uses; (2) assess how Fe and Mn speciation change seasonally; (3) characterize short-range-ordered Fe in the soils; and (4) evaluate the effect of OM association with ferrihydrite on its reduction and transformation. This study will enhance our understanding of the fate and distribution of C in soil/sediment–water systems under various redox conditions.

The research efforts of Dr. Audrey Sawyer are designed to quantify surface water-groundwater exchange and understand their implications for carbon-mineral complexation. Three unique watershed settings are being considered: stream, tidally influenced river, and estuary. Processes that drive surface water-groundwater interaction are unique in fluvial and coastal settings. Within streams, persistent hydraulic gradients formed by the interaction of currents with channel morphology drive vertical and lateral exchange across the sediment-water interface. In estuary sediments, vertical exchange can occur due to currents, tides, and waves. 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. These typically unmonitored settings may be highly active zones for reactive solute transport.

Since her arrival at the CRB/CZO in May, Dr. Sawyer has targeted and made progress at three field sites for comparing surface water-groundwater exchange rates and carbon-mineral reactions. At a 3^rd^-order stream site within the White Clay Creek watershed a single transect of five piezometers and pressure transducers has been installed in the floodplain perpendicular to the stream to monitor lateral surface water-groundwater exchange during base flow and storm events. This piezometer transect complements the existing sensor network developed by Dr. Lazareva and others, which includes redox potential and soil moisture probes. Preliminary data indicate 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. Slug tests have been conducted to characterize aquifer permeability in the five piezometers. Additionally, the top of a gravel layer has been surveyed throughout the floodplain. Plans are to install piezometers in two more stream-perpendicular transects and a distributed grid within the floodplain aquifer over the course of the fall. Downstream of this site where the White Clay Creek is tidally influenced, two potential study sites have been identified just above the confluence with the Christina River.

The estuary site for Dr. Sawyer's research represents the coastal end-member within the CRB/CZO. Two locations in the subtidal nearshore estuary have been identified with different rates of groundwater upwelling based on seepage measurements. Vertical pore water samplers were installed to measure salinity, redox potential, and dissolved oxygen in shallow sediment. The chosen locations have unique pore water chemistry and depths of shallow surface water-groundwater exchange. The Nearshore East site has focused fresh groundwater discharge and a shallow zone of surface water-groundwater mixing (salinity declines rapidly in the upper 25 cm of sediment). The Offshore West site has more diffuse fresh groundwater discharge and a deeper zone of surface water-groundwater mixing (salinity declines more gradually with depth). Dissolved oxygen is greater at the nearshore site, and NO3- concentrations are ~ 200 uM. Redox potential favors Mn reduction at both sites and Fe reduction at the Offshore West location.

Numerical hydrologic models have been created to examine surface water-groundwater exchange due to tidal, wave, and current pumping in estuaries using Comsol, a finite-element solver. Model parameters will later be adjusted to reflect conditions at Holts Landing, and reactive solute transport will be added to the models. Long-term goals are to deploy conductivity-temperature sensors and redox probes in bay sediments at the East and West profile locations to monitor changes in surface water-groundwater exchange and constrain potential fluxes of dissolved oxygen, Fe, Mn, and C between groundwater and the bay. Design construction, and testing of these sensors is underway.

Graduate students at the University of Delaware including Jin Yang, working with Dr. Yan Jin, Weinan Pan, working with Dr. Shreeram Inamdar, and Chunmei Chen, working with Dr. Donald Sparks, all are conducting research projects with CRB/CZO soils. Jin's research, focusing on soil colloids, often defined as entities with sizes < 1.0μm, seeks to understand the dynamic interactions of colloids, carbon, and Fe oxides and their implications in colloid mobilization and carbon cycling. His particular focus is on smaller colloidal fractions (0.01-0.45μm).

Over the past year Jin developed methods for column experiments and colloid characterization and analysis. These activities included collecting soil samples with different iron oxides and soil organic matter contents from various sites in Delaware and Pennsylvania. The collected soils were air-dried, mixed thoroughly, and sieved to pass a 2-mm screen. These soils have been incorporated into column leaching experiments where effluent samples were separated using 0.45μm and 0.22μm size membrane filters successively. Colloid concentrations in effluent samples of various size fractions were quantified by UV-VIS and the colloids were examined with an upright confocal microscope (Zeiss 780, Carl Zeiss USA) and revealed that colloids of different sizes exhibit different fluorescent responses, suggesting that they have different chemical compositions.

Weinan's research addresses how DOC concentration and composition influence carbon-mineral complexation, the role of redox conditions in carbon-mineral complexation, the variability of DOC and redox conditions along hillslope-stream transects in watersheds with varying land use (forested, agricultural, and urban), and how these regulate the potential for carbon-mineral complexation. She has collected leaf litter and humus litter from a forested area within the White Clay Creek watershed, extracted the litter with water, filtered the extracts through 0.7 μm filter and measured their DOC concentrations in the laboratory of Dr. L. Kaplan. DOC quality has been characterized using ultra-violet (UV) absorbance and fluorescence spectroscopy in Dr. Inamdar's laboratory. Leaf and humus litter extractions were used as solutions in the sorption experiments. Two soils with contrasting properties, one from the agricultural site and another from the flood plain site were used as sorbents under 3 solid to solution ratios and 2 DOC concentration levels. The sorbed amount of DOC was measured by the difference in DOC solution concentration before and after sorption. DOC quality change has also been evaluated by comparing ultra-violet (UV) absorbance and fluorescence measurements before versus after conditions. Two posters describing aspects of these studies have been presented at the National CZO meeting in Arizona, one by Weinan and one by Dr. Inamdar.

Chunmei is investigating changes in soil iron concentration and its solid-phase speciation across a pasture and forest hillslope transects as well as a floodplain soil profile subjected to a redox gradient within the CRB/CZO. Quantitative speciation of soil solid-phase iron has been constrained by combining XAS, micro-XAF, micro-XAS, XRD and selective chemical extractions. This approach has allowed her to partition iron into (1) organic bound Fe, (2) crystalline $Fe^{III}$-(oxy)hydroxides, (2) amorphous $Fe^{III}$-oxides, (3) Fe-bearing silicates, and (4) ferrous iron mineral phases. $Fe^{II}$-mineral phases were found only in one sample which is the soil from the buried A horizon at the floodplain soil profile. This soil sample is under the groundwater saturated zone and undergoing the greatest reductive dissolution of minerals, as indicated by the soil color. In order to assess the effect of OM association with ferrihydrite on its transformation, Chunmei synthesized a series of ferrihydrites using solutions with increasing amounts of dissolved organic matter (DOM) extracted from the forest O-horizon and conducted batch experiments with synthesized products at a temperature of 70°C at pH7 as a function of reaction time (0h, 4h, 1d, 2d, 3d, 5d, 7d). The transformed products were characterized by synchrotron-based XAS.

Chunmei has focused on soils from a pasture, forest hillslope, and a floodplain soil profile to investigate the nature of soil mineral-organic associations using synchrotron-based scanning transmission X-ray microscopy-near-edge X-ray absorption fine structure (STXM-NEXAFS) spectroscopy techniques. Additionally, synthesized organic matter-ferrihydrite-kaolinite coprecipitates in the laboratory are being studied as model organo-mineral complexes in the soil to identify distinctive binding mechanisms of OM and specific mineral components, determine the major mineral species for OM-mineral complexation formation, and characterize solid-phase carbon speciation along hillslope transects. The results of Chunmei's research have been presented at the National CZO meeting in Arizona , were included in Dr. Yoo's invited presentation at the Goldschmidt 2011 conference in August, and are the basis of a manuscript that is in preparation.

**Year 1 (Oct. 2009 to Sep. 2010)**

## 1. Research and Education Activities

### 1.1. Project Management and Coordination

In the first seventeen months of the project, our research team thoroughly re-evaluated and reaffirmed project hypotheses, objectives and tasks. Integration of all research activities in this project toward our overall goal – to integrate the net carbon balance (sink or source) due to mineral production, weathering, erosion and deposition over landscapes of contrasting land use – has been a high priority to project PIs. Coordination of the project during the initial period was through monthly PI and all-scientist meetings, and included the selection of team leaders for our 4 primary research objectives.

Our research team grew substantially at the end of our first year, with the arrival of three Post-Docs (all starting in early Fall 2010) and six graduate students (3 continuing from other projects and 3 starting fresh in Fall 2011). This required a continuation and intensification of coordination activities, including a weekly 2-hour meeting primarily focused on developing post-doctoral and graduate student projects and recently culminating in a 1-day project retreat (Feb. 18, 2011).

Scientists from outside of the University of Delaware and the Stroud Water Research Center have joined these discussions via conference calls. Weekly meetings have occurred with PI's and postdoctoral researchers as well as meetings with the entire team. In February, we held a retreat where work plans were discussed and presentations were made by postdoctoral researchers and graduate students. This thoughtful coordination has been required because water, carbon and minerals are transported and transformed across geophysical boundaries that also traditionally separate scientific disciplines. We believe that these coordination efforts are already providing strong intellectual payoffs.

### 1.2. New Hires

In year 1, the Christina River Basin CZO advertised for new positions, interviewed candidates, and hired new personnel for the project, including three post-doctoral scientists, an installations engineer, and a watershed manager. In year 2, we are in the process of hiring a fourth post-doctoral scientist

Our new post-doctoral scientists are Dr. Diana Karwan, Olesya Lazareva, and Carl Rosier. Dr. Karwan received her degree from Yale University in forest hydrology and sediment transport, Dr. Lazareva received her degree from University of South Florida in environmental geochemistry, and Dr. Rosier received his degree from University of Montana in soil microbiology. Our fourth post-doctoral position will be filled by one of the many excellent candidates we are interviewing this month, all with expertise in groundwater-surface water interactions.

In year 1, we also successfully recruited six outstanding graduate students to conduct research on the project. Three – Chunmei Chen, .Chris McLaughlin and Yi Mei – were top students recruited from other projects, and three – Weinan Pan, Adam Pearson and Jing Yan – are new students, all arriving with Master's degrees and strong previous research experience.

Our CZO has placed a strong emphasis on the development and deployment of sensor technology and wireless transmission of data from remote sensor platforms. To assist with this process we have hired Steve Hicks, an electrical engineer with a background in hillslope hydrology. Steve is being joined by David Montgomery, a long-term Stroud Water Research Center employee who has been hired to fill a newly created position of watershed manager. The primary responsibilities for Montgomery are to facilitate watershed access and manage watershed installations. Both Hicks and Montgomery will closely interface with our data management team to assure the continuous flow of data from sensor platforms.

**1.3. Site Selection**

To understand the impact of natural versus human-accelerated mineral cycling on the carbon flux between lands and the atmosphere, we have chosen to instrument three headwater streams that differ in their land uses: forested; agriculture; and construction. We used aerial photographs and ground-truthing to identify the appropriate sites. These include: (1) a completely forested watershed that is protected in perpetuity within the Laurels Preserve, managed by the Brandywine Conservancy; (2) an agricultural watershed that is held under an agricultural conservation easement and dominated by row crops of soybeans and corn; and (3) a watershed impacted by the Southeastern Chester County Refuse Authority landfill. The landfill, which is active and has capacity for at least the next decade, moves soil almost on a continuous basis, so it represents an appropriate surrogate for a major construction site. We have been in active contact with landowners for each of these sites, and all are very open to working with our CZO project into the future. We are currently finalizing our proposed infrastructure plans for each site, which includes a stream discharge flume and a suite of sensors (see 1.4 below).

In addition to these three contrasting headwater streams, we will place sensors hubs and other research infrastructure at three downstream locations in order to integrate the larger watershed-scale and coastal processes within our Objectives 3 and 4. These include: (1) the 3rd -order White Clay Creek Experimental Watershed gauging station at the Stroud Water Research Center; (2) the mouth of the White Clay Creek near Newark DE at USGS gauging station 01479000; and (3) the mouth of Brandywine Creek in Wilminton DE at USGS gauging station 01481500.

**1.4. Development of an Advanced Sensor Network.**

The search for hydrological and geochemical “hot spots” and “hot moments” that control landscape and ecosystem level processes requires a rethinking of how we measure critical zone properties. Despite increasingly automated and rapid laboratory-based analytical methods, these improvements can not hope to meet the increase in frequency of spatial and temporal measurement required to realize the two, three or four dimensional maps necessary to identify important physical locations and the timing of these processes. The Critical Zone Observatory program was in part founded on the need for data with high spatial and temporal frequency, and we envision an advanced, real-time, environmental sensor network as a central component of our CRB-CZO project. To that end, we have hired an electrical engineer with extensive experience designing, deploying and maintaining hydrological sensors and using wireless data communication strategies. We have begun the testing and deployment of several novel technologies that will both meet our immediate needs very well and also serve as a strong foundation for rapid and limitless future expansion. Where possible, we will leverage the revolution in micro-manufacturing and open-source hardware projects to maximize the number and diversity of deployed sensors.

The core of our sensor network will be built around six field computers, which will serve as sensor hubs at each of our six primary stream gauging sites (see 1.3 above). Each field computer will be networked to the internet via continuous bidirectional 3G broadband "mobile" wireless and will control a number of advanced commercial geochemical sensors (below) in addition to a basic suite of hydrological and climate sensors. In addition, each field computer will be able to control any chosen assortment of relay switches that will enable logical triggers for sample collection and nearly limitless possibilities for home-engineered instrumentation. Last, each field computer will serve as a data and web-services hub for a broader ranging wireless sensor network that will extend as much as several kilometers throughout the gauged watershed.

Given the importance of quantifying mineral and carbon mass fluxes to our CZO's objectives, we will invest in a number of advanced hydrological and geochemical sensors at each stream gauging station. The centerpiece of each of our stream sensor clusters is a submersible UV-Vis diode array spectrophotometer (a spectro::lyser by s::can, http://www.s-can.at ). For the last 14 months we have been putting a spectro::lyser to the test at the 3rd order White Clay Creek site adjacent to the Stroud Water Research Center. Every 3 minutes it has been collecting absorbance values at 256 wavelengths at ~2 nm resolution from 220 to 720 nm. This wide range allows for the calculation of turbidity-compensated spectra of dissolved species, and highly accurate multivariate parameterization of dissolved organic carbon, biochemical oxygen demand, nitrate, total suspended solids and other parameters (Langergraber et al. 2003; Aufdenkampe & Kaplan, unpublished data). In addition, the raw and turbidity-compensated full-spectrum data from the Spectrolyzer can be exported for external parameterizations, such as calculation of spectral slopes, which are correlated to molecular weight (Helms et al. 2008). All of these parameters will contribute substantially to our understanding of dynamics of carbon transport and processing in our observatory. Other water chemistry sensors – for temperature, conductivity, dissolved oxygen, dissolved carbon dioxide and pH – have been or will soon be deployed at our test site. We plan to deploy this stream sensor station at our 5 other sites within the next 6 months.

Understanding critical zone processes within the gauged watersheds requires a large array of other sensors on hillslopes, in soils, in the groundwater and in the canopy. We will wirelessly network these sensors for near-real-time data collection using the open source electronics "Arduino" platform that now has over half a million users worldwide (http://www.arduino.cc/) in combination with SNAP wireless modules widely used in industry (http://www.synapse-wireless.com/). The advantages of this combination are numerous. First is cost. For $50-$100, we can replicate and even exceed the capabilities of a $3000-$4000 wireless data-logger from Campbell Scientific. Thus, we can invest our money in sensor hardware, rather than data collection hardware. Second is ease of use. The Arduino electronics prototyping platform was initially designed "for artists, designers, hobbyists, and anyone interested in creating interactive objects or environments." As such, the Arduino family of electronics hardware is exceptionally easy to snap together and program, yet it is also capable of nearly any task we might imagine. Thus, the sensor network system that we are developing on this platform will be easy to disseminate to graduate students and other researchers. We are successfully testing a large system within the 3rd order White Clay Creek research watershed. Using this system, each of the watersheds feeding our three headwater study streams will be instrumented with hillslope sensor nodes that will all include at a minimum: water table elevation, soil moisture, soil temperature, soil matrix potential, soil and groundwater redox potential, soil oxygen and carbon dioxide concentration profiles, soil pH, air temperature, air moisture and precipitation.

**1.5. Cyber-infrastructure for Data Management**

In the last year, we have made large strides migrating our data management approaches toward a modern relational database management system that is a hybrid of those developed by CUAHSI's Hydrological Information System team (http://his.cuahsi.org/) and by the EarthChem project (http://www.earthchem.org/).

The Stroud Water Research Center is an institution with a long history of managing continuous hydrological data and more complex geochemical data based on laboratory analyses of sample fractions and subsamples. Because of this, our group has played an integral role in helping form a national CZO data system that merges the best of both the CUAHSI and EarthChem data models, and we have played a leadership role in all cross-site data management efforts over the last year including a 2-day meeting in Boulder in May 2010, a 2-day meeting in Logan Utah in Feb. 2011 and numerous (at least 2 per month) conference calls since September 2009.

At present, we are actively working with Ilya Zaslavski's team at the San Diego Supercomputing Center to load historical data onto a local CUAHSI "Hydro-Server" and to develop web services to automatically load this data to the central CZO data repository.

We are also collaborating with Emilio Mayorga at the University of Washington's Applied Physics Laboratory 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). A prototype should be available by late March at our website (http://www.udel.edu/czo/data.html).

**1.6. Ground Truthing of Airborne Lidar Imagery**

In conjunction with all sites within the CZO network, we conducted a field campaign last summer to ground truth the airborne LiDAR imagery. We followed the sampling protocol established for all CZO sites for the full-leafed canopy. Prior to the field work, aerial photographs and historic knowledge of landscapes within the Christina River Basin were used to identify potential forested plots for the ground truth work. Two University of Delaware graduate students hired for this project conducted the fieldwork under the supervision of the PIs. The vegetation survey yielded the acquisition of the necessary data, including tree dbh, LAI, and canopy closure. All the field data have been sent to UC, Merced for development of algorithms per the standard protocol. The data collected from our field campaign was presented at the National CZO meeting in Boulder, Colorado in September 2010.

**1.7. Adoption of the Penn State Integrated Hydrologic Model (PIHM) and other models.**

We have been actively collaborating with Chris Duffy and his research group at the Penn State Shale Hills CZO over the past year to learn PIHM and get it to run for our watersheds. This collaboration has included three visits by Chris Duffy and his graduate students between January and July of 2010, and attendance at a PIHM workshop at Penn State by five CRB-CZO project members. We now have PIHM running for our 3rd - order research watershed for which we have extensive data, and with five of us conversant in PIHM, we are now designing our sensor network in such a way as to optimally calibrate and validate 3-D watershed models such as PIHM.

This work with PIHM builds upon efforts by Newbold, Hornberger, Mei and others to calibrate TOPMODEL for White Clay Creek, and also to calibrate a 2-D hillslope model, based on groundwater depth and soil moisture data collected during the summer of 2010.

Luc Claessens joined the faculty at UD in Sept. 2010 and has made concerted efforts to integrate his research with our CZO.  One of these efforts includes implementing the RHESSys eco-hydrology model for our CZO.

### 1.8. Sample Collection

In 2010 we kicked off what will eventually be a substantial soil and sediment sample collection effort.  Graduate students Chunmei Chen and Chris McLaughlin collected a large number of soil and groundwater samples from our “Transect A” hillslope for their respective PhD projects (see findings).  Our biggest sampling efforts, however, will be in sediment source and depositional zones throughout the basin.  To train grad students and post-docs in our sampling approaches, in early Nov. 2011 Rolf Aalto, Kyungsoo Yoo and Anthony Aufdenkampe conducted an intensive “field camp” for nearly 2 weeks, coring floodplains and hillslopes and digging soil pits. In 2011-2012, students and post-docs will use this training to collect a wide variety of samples in erosion and depositional zones throughout the CZO watersheds using similar techniques.  This will eventually allow for integrated “fingerprinting” and determination of sediment sources.

In Fall 2011 we also began the collection of a large volume (>200 L) suspended sediments samples, in order to quantify meteoric radio-isotope signatures for “Fingerprinting”.

### 1.9.  Laboratory Experiments

We have begun a series of organo-mineral complexation and incubation experiments, to provide a “smoking gun” test of whether organic carbon stability is determined by the degree of mineral complexation.

## 2. Planned Activities and Future Vision

In each section above, we have described both completed and planned activities.

Our future vision for our CZO is to create:

- A spatially and temporally rich sensor dataset from which our team and others can calculate water, mineral and carbon fluxes and balances for our research watersheds, and explore processes
- An easy to use data system for exploring, obtaining and integrating our many sensor and sample based datasets into models or other data analyses
- A highly integrated team of researchers, who tackle questions and research problems that none would attempt alone, by maximizing synergisms and group capabilities
- A body of evidence to test each of the hypotheses poised in our proposal
- A watershed, sensor and data infrastructure to support new projects to answer new questions within our CZO watersheds

**Year 2 (Oct. 2010 to Sep. 2011)**

## 2. Research Findings

As we approach the 2-year mark on this project many of our research findings are still preliminary and the research efforts are in a very intensive data gathering phase. The major findings of this project to date are largely contained in the posters and oral presentations from national and international scientific meetings and manuscripts that are either in preparation or in review. These presentations are appended to the report and listed as "files" where appropriate below. A list of CRB-CZO publications and presentations is maintained at http://www.udel.edu/czo/publications.html and http://www.udel.edu/czo/presentations.html.

Numerous overview presentations have been given by A. Aufdenkampe, D. Sparks and K. Yoo that summarize activities and early findings for the CRB-CZO project. Many of the concepts that underlie the hypotheses and objectives of the CRB-CZO were published in project year 2 (Aufdenkampe et al. 2011, FIEE, doi:10.1890/100014).

### 2.1 Development of an Advanced Sensor Network (File 1)

Rapid *in situ* measurements of solutes and particles in stream water hold enormous potential to transform our understanding of biogeochemical dynamics in aquatic systems. The foundation of our wireless sensor network, based on open-source electronics, has been presented at numerous conferences and workshops (File 1, poster presented by Hicks at 2011 National CZO Annual Meeting). Some of the underlying concepts in sensor development were published in a review co-authored by A. Aufdenkampe (Melack et al. 2011, FIEE, doi: 10.1890/100004)

Our flagship sensors are submersible UV-VIS spectrophotometers (s::can spectro::lysers) that collect *in situ* absorbance values every 2 minutes to measure turbidity-compensated spectra for dissolved species and suspended solids (File 2, talk by Kaplan presented at the 2011 National CZO Annual Meeting). We have deployed two different spectro::lyser models in White Clay Creek as a pilot test study for eventual deployment of six units throughout the Christina River Basin. One spectrophotometer is constructed with a quartz optical window and 35 mm pathlength and takes readings at 214 wavelengths with 2.5 nm resolution from 200 to 732.5 nm, and the other is constructed with a sapphire optical window and 5 mm pathlength and takes readings at 218 wavelengths with 2.5 nm resolution between 200 and 742.5 nm. With all *in situ* devices biofouling is a common problem and both instruments are equipped with cleaning valves that provide blasts of compressed air for automated removal of biofouling. The cleaning can be manually augmented with a brush. Fouling by metal oxides is not typically encountered or considered, but in this headwater stream with its proximity to groundwater sources and different redox conditions manganese oxide fouling poses a problem. Over a three-week period that included 4 storms and several non-storm days with diel patterns of fluctuating stream discharge associated with snow-melt, both instruments were able to capture the dynamics of solute and suspended solid transport. However, the quartz window out-performed the sapphire window in resisting metal oxide fouling presumably because of the differences between the affinities of the Al-based sapphire versus the Si-based quartz for manganese. A comparison of the accuracy of the *in situ* measurements against laboratory-based measurements showed reasonable agreement. We are working to improve this agreement and extend the *in situ* detection to other analytes by adjusting the calibration of the spectrophotometers with laboratory-based data.

## 2.2. Hydrologic Modeling

The 2-dimensional hillslope model developed by Yi Mei to explore the DOC flux along different hydrological flow paths estimates that in 1997 (a year with fairly complete storm sampling of DOC), the riparian zone contributes more than 90% of total DOC in groundwater. Further, the model-based estimate indicates that subsurface flow contributes about 75% of the total DOC entering the stream from terrestrial sources in that year.

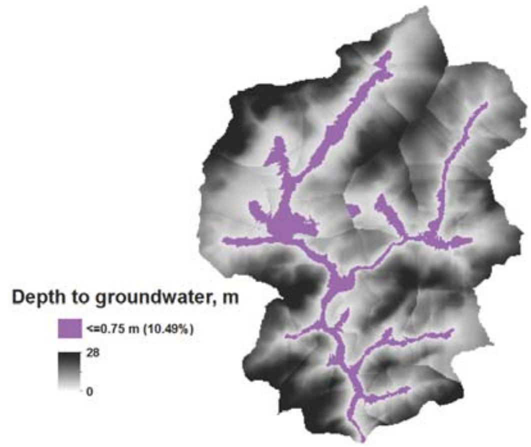


Fig. 1. Area within the White Clay Creek watershed that contributes to ground water evapotranspiration (Tsang et al., submitted).

The Groundwater Evapotranspiration TOPMODEL (GETTOP) developed by Yin-Phan Tsang et al. (manuscript submitted to Water Resources Research) estimated the total groundwater ET flux for the 3rd-order White Clay Creek watershed. Groundwater ET was larger when the topography was flat and the groundwater table was shallow, occurring within about 10% of the area in a headwater catchment and accounting for 6 to 18% of total annual ET (Fig. 1). The addition of groundwater ET to a GETTOP improved the simulation of stream discharge and more closely balanced the watershed water budget.

## 2.3 Sample Collection, Sample Processing, and Laboratory Experiments (Files 2-5)

Extensive sampling and geochemical analyses of soils has been conducted by Chunmei Chen. Many of those results were described in our Year 1 report, and will soon be submitted to JGR Biogeosciences. Our first study of soils within the CRB-CZO was published in early 2011 (Yoo et al. 2011, JGR-B, doi: 10.1029/2010JG001304)

The determination by D. Karwan of chemical and isotopic signatures for suspended sediments over different seasons and storms shows that the geochemical composition of stream sediments changes seasonally and during the course of a single storm (File 3, extended abstract by Karwan for presentation at the 2011 Geochemistry of the Earth Surface meeting).

The data collected by A. Pearson & J. Pizzuto from nine ~200 year-old run-of-the-river impoundments on medium-sized, gravel-bed, pool-riffle channels used to develop a conceptual model of fluvial landforms and bed material transport reveal two landforms that are well-developed below the dams – a plunge pool averaging 16 m long and a mid-channel bar. The mid-channel bar is much larger than the plunge pool (26-51 m long) and contains sediment sizes typical of bed material of unimpounded sections of the river, with surficial deposits of sand and gravel ($D_{50}$ 6-45 mm) overlying a gravel core ($D_{50}$ 28 mm). Large coarse-grained mid-channel bars below impoundments likely store bed material that has been transported through the impoundments during high flows. The speculation is that at least some of the coarsest grains transported by the river are rolled across the sandy bed of the impoundment, up the coarse-grained ramp at the lip of the dam, and through the plunge pool. Initial data suggest that: (1) impoundments reach a quasi-equilibrium morphology soon after dam construction that facilitates continued movement of bed material through the watershed; and (2) these impoundments are never completely filled with sediment.

Measurements by J. Pizzuto of annual sediment flux, sediment exchange involving the floodplain, deposits formed in the lee of large woody debris, and the hyporheic zone and mean downstream sediment transport distances along a 2.43 km long reach of the South River, Virginia, have shown that annual sediment exchanges involving the floodplain, deposits formed in the lee of large woody debris, and the hyporheic zone are 6%, 4%, and 0.02% of the annual suspended sediment flux. This implies that suspended sediment is completely replaced by sediment in storage after a mean downstream transport distance of 28 +/- 13 km. The mean transit time for stored sediment is 4800 +/- 2600 years, and the long-term average downstream velocity of suspended particles is 6 +/- 4 m/yr. These results suggest that most of the sediment currently reaching the terminal Bay is supplied from sources near the estuary and that watershed management plans implemented in upstream reaches may be ineffective for millennia. Although this study was not performed within the Christina River Basin, it has informed our CRB-CZO study design and research efforts.

The EMMA performed by C. McLaughlin for the White Clay Creek watershed indicates that deep ground water contributions are constant throughout the year whereas contributions from spring seeps and overland flow vary significantly. In order to determine how stream water DOC concentrations are affected by hydrologic flow from the terrestrial environment, the ratio of observed to predicted concentration was calculated for each time point in the EMMA model. The average DOC ratio for low flow conditions differed significantly across months and seasons.

DOC quality measured by C. McLaughlin in terrestrial source water decreased with soil depth and was significantly different across source waters. Storm water DOC was separated into labile and semi-labile components and both increased peaking around the time of peak discharge. However, the temporal dynamics of the two lability classes were different indicating important differences in the source pools for the DOC lability classes (File 4, poster by McLaughlin presented at the 2011 ESA annual meeting).

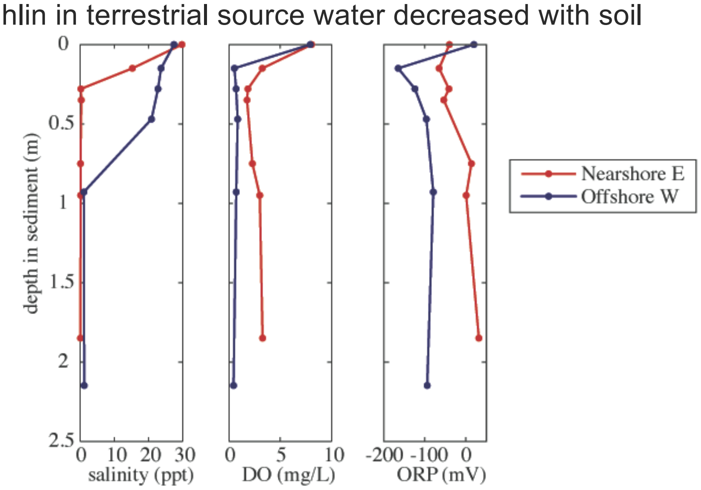



Fig. 2. Salinity, dissolved oxygen concentration, and redox potential versus depth for pore water samplers with rapid groundwater upwelling (Nearshore E) and diffuse upwelling (Offshore W).

Whole stream $^{13}$C-labled DOC tracer experiments conduced by Kaplan, Newbold and Aufdenkampe quantified for the first time the *in situ* mineralization rates of both semi-labile and labile DOC in a stream (File 5, poster by Kaplan presented at the 2011 Goldschmidt conference).

Investigations by O. Lazareva of the roles of Fe- and Mn- redox coupling on the carbon cycle have shown that the section of floodplain affected by high hillslope morphology has an accelerated discharge of groundwater into the stream after heavy rainfall. Furthermore, this creates a substantial redox gradient. This area is characterized by higher DOC and Fe2+ at the buried wetland of the eastern floodplain compared to the western side. Very low DOC and Fe2+ concentrations are found within gravel deposits due to the formation of Fe oxides along a redox gradient (File 6, poster by Lazareva presented at the 2011 Goldschmidt conference).

Preliminary data collected by A. Sawyer from piezometers within a floodplain of WCC show that this is a gaining stream. However, during high flows the water table gradient reverses and forces streamwater into the banks and riparian zone. At Holts Landing the nearshore site has a focused freshwater discharge while off shore there is a more diffuse freshwater discharge and deeper zone of mixing (Fig. 2).

Research by S. Inamdar and D. Levia at the Fairhill Preserve, a CRB-CZO satellite site that was established by NSF EAR-0809205, has resulted in three publications that were partially supported by CZO funding (Levia et al. 2010, JH, doi:10.1016/j.jhydrol.2009.10.028; Inamdar et al. 2011, BGC, doi: 10.1007/s10533-011-9572-4; Inamdar et al. in press, JGRB, doi:10.1029/2011JG001735)

# A Wireless Environmental Sensor Network Using Open-Source Electronics for the Christina River Basin CZO

Steven Hicks[1], Anthony Aufdenkampe[1], Olesya Lazareva[2], Diana Karwan[1], David Montgomery[1]

## Introduction

- The search for biogeochemical "hot spots" and "hot moments" that control ecosystem-level processes requires rethinking how we observe the environment.
- Massive multi-sensor/measurement arrays are required to realize 2D, 3D or 4D maps of environmental properties with sufficient spatial and temporal resolution to find and understand hot spots and hot moments.
- The recent developments in open-source electronics prototyping platforms offer an opportunity for environmental observatories to deploy sensors at massive scales by reducing data logging and communications costs by more than an order of magnitude.
- One particular hardware platform, Arduino, has dozens of low cost boards that allow even novice users to build devices using boards that connect in a modular framework.

## Open-Source Datalogger Hardware

- The Open-Source nature of Arduino means the cost is extremely low compared to similar commercial options. The large user community provides support as well as constant innovation and development of new hardware and applications.
- There are many different types of Arduino-compatible hardware variations, with several designs being very well suited for wireless sensor networks and datalogging.
- Low powered simple nodes collect and transmit basic sensor data short distances to data radio hubs, and the hubs relay the data to a base station.
- High-powered radio units connected to a versatile microprocessor board collect sensor data and transmit long distances via a self-healing mesh network back to base stations.
- In areas with no mesh network, standalone loggers with just a memory card can be deployed.


Standalone logger with memory card: $40


18-bit A/D converter: $12


16 channel multiplexer: $5


Simple node with low power radio: $20

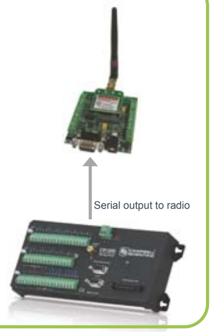

Remote relay control board with prepaid cell phone: $40


High power "smart" radio module: $35


Solar powered node, high power radio: $80

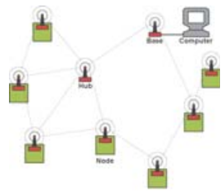
## Compatibility and Integration

- Flexibility and customization of the Arduino platform make the hardware useful for applications other than just sensor interfacing.
- Arduino circuits can control a variety of devices such as relays, motors, and pumps. Interfacing a cell phone to an Arduino node allows users to call the node and trigger remote sampling devices.
- Arduino nodes can also act as "cable replacement" modules by wirelessly transmitting or logging data that would normally be sent on a cable between a sensor and a computer.
- Commercial dataloggers like the Campbell CR1000 can easily join an Arduino mesh network by simply connecting a radio module ($50) and adding a few lines of code to the existing CR1000 program.




## Wireless Datalogging & Mesh Networks

- Self-healing mesh wireless networks are reliable, with nodes spaced hundreds of meters to several kilometers apart.
- Each logging node has a clock that is used to synchronize the sleep and wake cycles of the network.
- The nodes conserve battery power by sleeping most of the time, then waking periodically to take measurements from the sensors, and then transmitting their data through the mesh back to the base before going back to sleep.
- Each node is also equipped with a removable memory card to store all local sensor data in the unlikely case there is a failure in the mesh network.


A Basic Mesh Network


Base Station

- At the base station, the incoming live streaming data can be displayed on a computer, stored in a database, and plotted on a web page for near-real-time viewing and analysis
- Nodes can also be reconfigured or reprogrammed remotely through the mesh network

## Sensor Networks: Cost vs. Coverage

- High-quality commercial sensors are relatively inexpensive and easily available. Most sensors have standard outputs such as analog voltage or digital serial signals that are easily interfaced with the Arduino hardware
- User customization of the Arduino node interface hardware and software means virtually any sensor can be used.
- One Arduino logging node can interface with many different types of sensors at the same time by using multiplexers.
- A 16-channel, solar-powered Arduino datalogger node with self-meshing wireless communications costs approximately $150.


Soil Moisture Sensors


Redox Probes


Water Depth Sensor


Oxygen Sensor


Conductivity Sensor


Carbon Dioxide Sensor

- By significantly decreasing the cost of the datalogging and communication hardware, resources can be focused on installing more sensors for greater spatial coverage.
- Researchers, students, and individuals can easily build and deploy inexpensive dataloggers without the need for electronics experience, complicated software, or specialized tools.
- Implementation of open-source electronics hardware will transform our ability to deploy sensors, field instruments and other electronic "eyes and ears" to unprecedented levels.

The CRB-CZO is a collaborative effort between:
1. Stroud Water Research Center
2. University of Delaware

Funding by NSF's Earth Sciences Division (NSF EAR 0724971 and others)

# In Situ Measurements of Stream Water Organic Carbon, Nitrate, and Suspended Solids with a Submersible UV-VIS Diode Array Spectrometer Probe


Louis A. Kaplan[1,2], Steven Hicks[1], J. Denis Newbold[1,2], Anthony K. Aufdenkampe[1,2]

[1]Stroud Water Research Center
[2]Delaware Environmental Institute


National CZO "All Hands" Meeting
Biosphere II, May 8-12, 2011

## Central Role for Biogeochemistry Studies

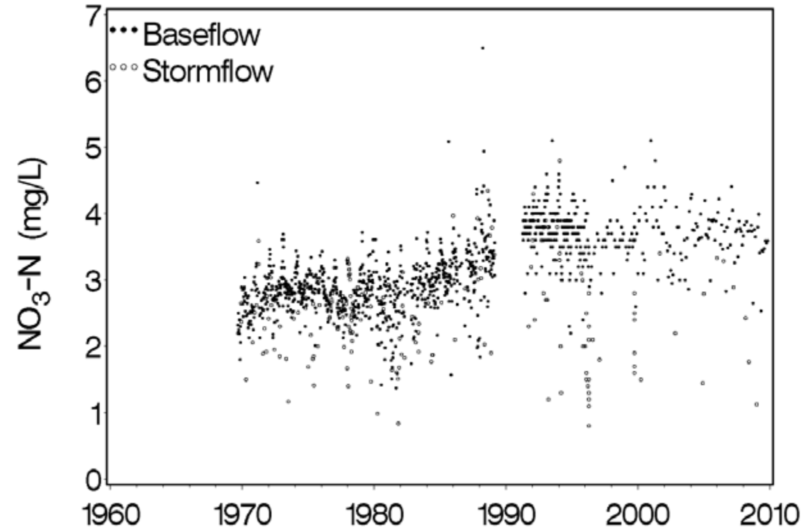
- Insights into chemical dynamics of the critical zone
- Measurements of material fluxes in streams integrate biological processes at the watershed scale
- Highly interdisciplinary and informed by hydrology and geology
- Carbon balance; is the CRB/CZO a C source or sink?

## Outline

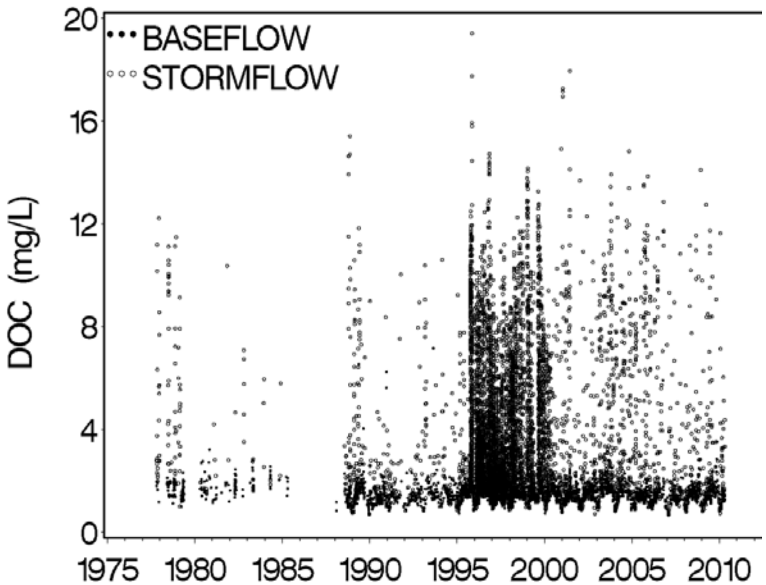
- Biogeochemistry of stream ecosystems as a component of CZO science
- Insights from biogeochemistry studies of White Clay Creek under LTREB program
- The case for biogeochemistry sensors
- Preliminary experiences with a diode array uv-vis spectrometer
- Challenges ahead for "hands-free" sensor deployment

## White Clay Creek, Tributary of the Christina River

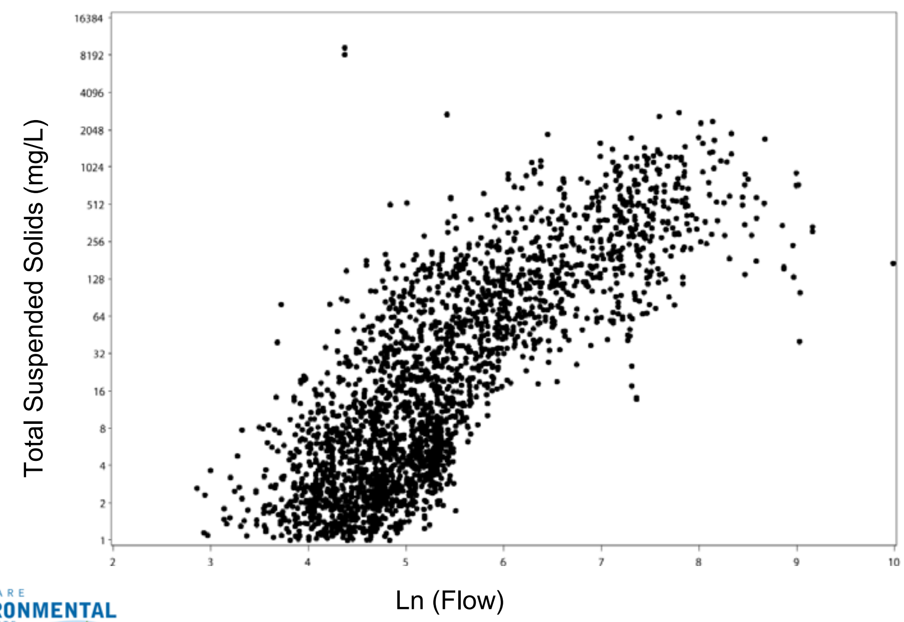
## Nitrate Time Series

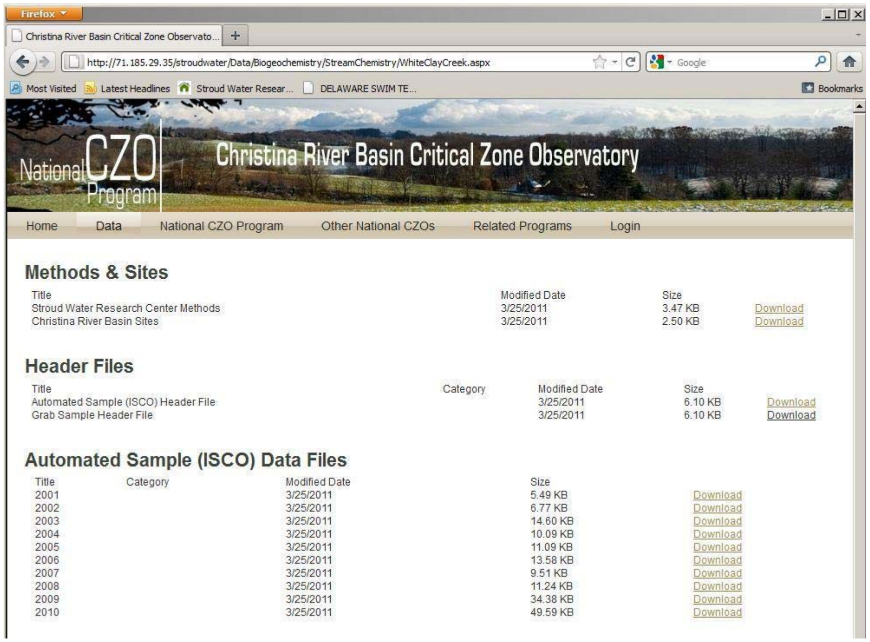



## Dissolved Organic Carbon Time Series




## TSS – Discharge Relationship





Christina River Basin Critical Zone Observatory

National CZO Program

Home | Data | National CZO Program | Other National CZOs | Related Programs | Login

## Methods & Sites

| Title | Modified Date | Size | |
|---|---|---|---|
| Stroud Water Research Center Methods | 3/25/2011 | 3.47 KB | Download |
| Christina River Basin Sites | 3/25/2011 | 2.50 KB | Download |

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| Grab Sample Header File | | 3/25/2011 | 6.10 KB | Download |

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| 2003 | | 3/25/2011 | 14.60 KB | Download |
| 2004 | | 3/25/2011 | 10.09 KB | Download |
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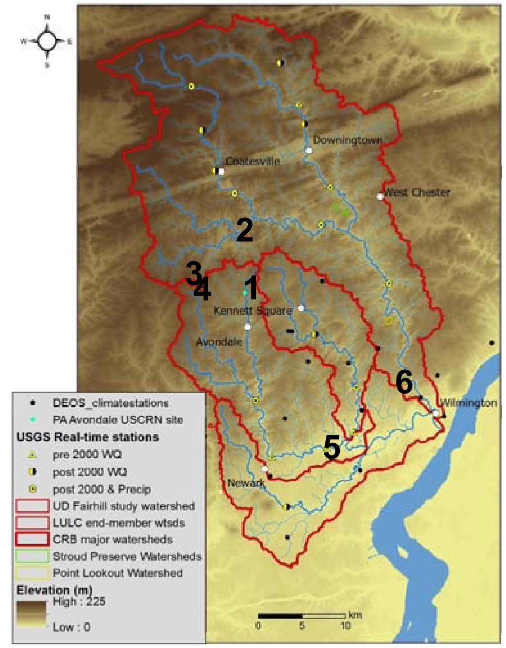
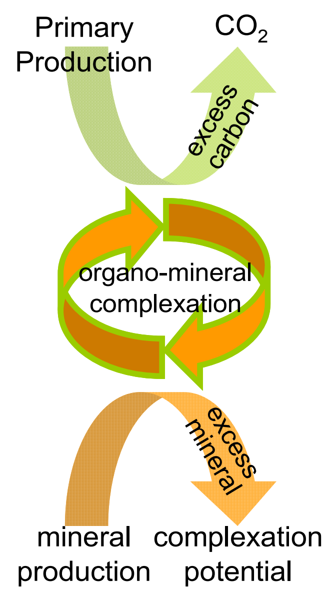
| 2006 | | 3/25/2011 | 13.58 KB | Download |
| 2007 | | 3/25/2011 | 9.51 KB | Download |
| 2008 | | 3/25/2011 | 11.24 KB | Download |
| 2009 | | 3/25/2011 | 34.38 KB | Download |
| 2010 | | 3/25/2011 | 49.59 KB | Download |

- 3rd order White Clay Creek at SWRC, 750 ha
- 1st order forest, 10 ha
- 1st order row crop, ~25 ha
- 1st order construction, ~40 ha
- mouth White Clay Creek, 277 $km^2$
- mouth Brandywine Creek, 842 $km^2$




## White Clay Creek Flood at Stroud Water Research Center

## CRB/CZO Focus on Mineral Surfaces and Organic Carbon



# S::CAN UV-VIS spectrophotometer

(s::can spectro::lysers)


Measurements made at 256 wavelengths over the range of 220 to 720 nm

Dual beam; Xenon lamp

Sapphire window; 5 mm path length

Quartz window; 35 mm path length

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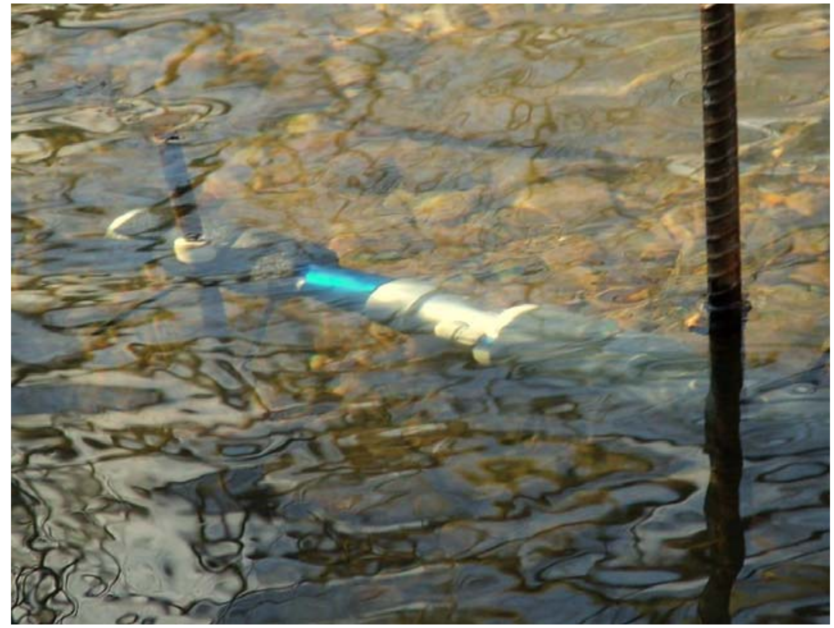

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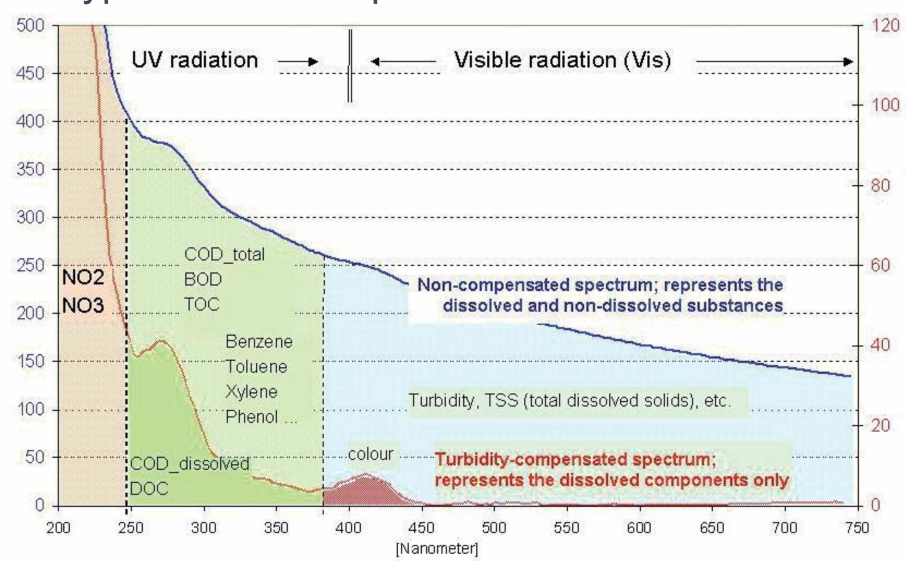
## Typical UV-VIS Spectrum in Natural Waters




## Turbidity Compensated Readings

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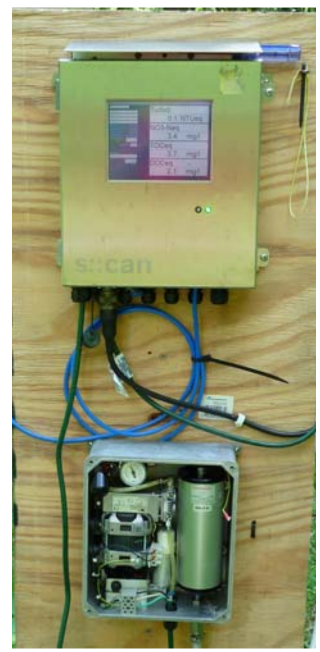


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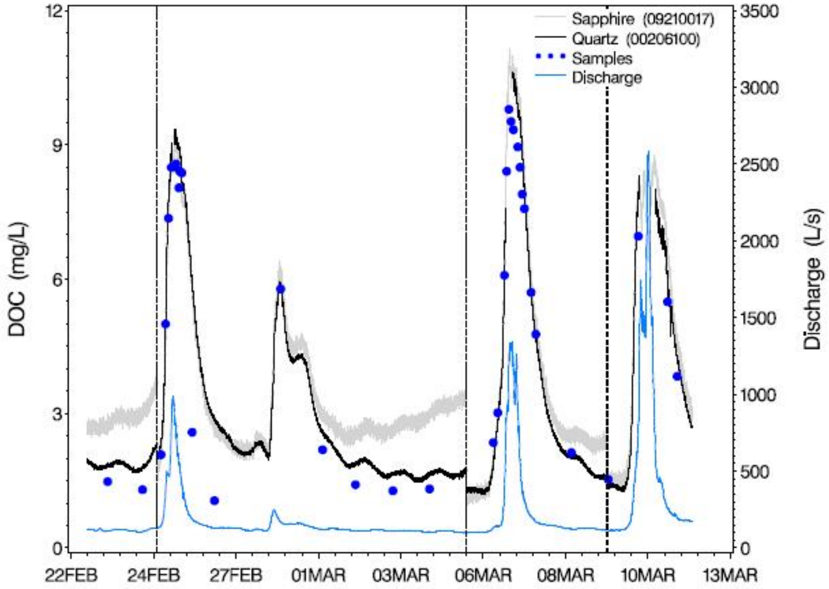
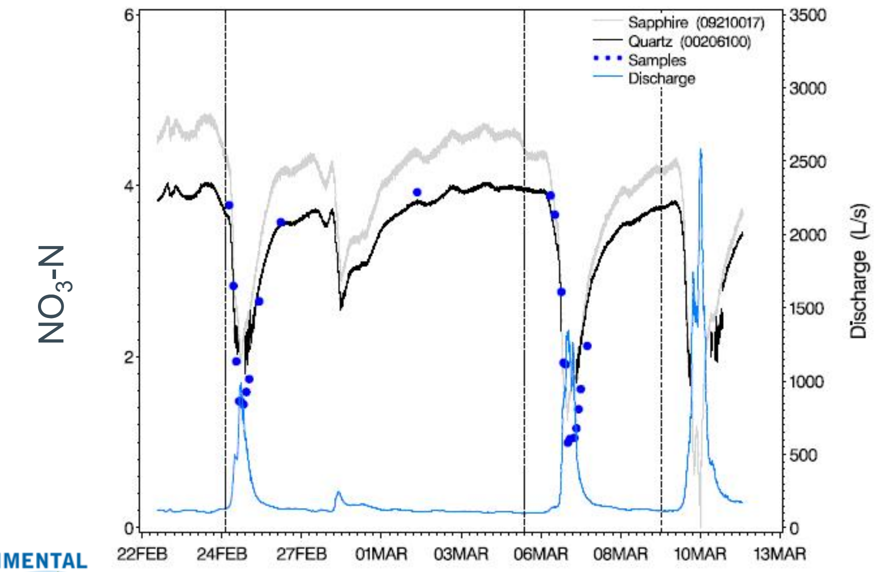
## DOC






## Nitrate

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## Cleaning Sensor Windows

Rinse submerged probe windows 15 ml 10% oxalic acid buffered to pH 2.75

Follow with 1N HCl rinse

Soft brush, soft cloth or cotton swab

Compressed air blast (70 psi)

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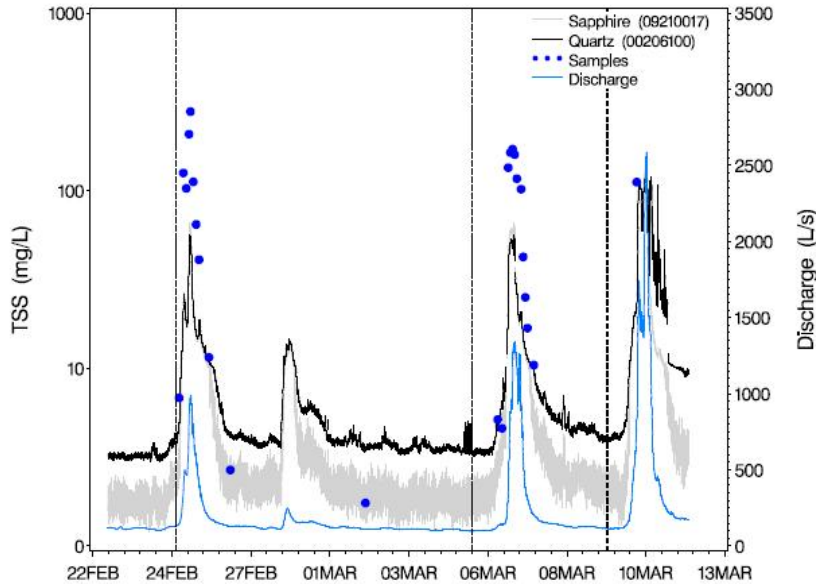
## Total Suspended Solids

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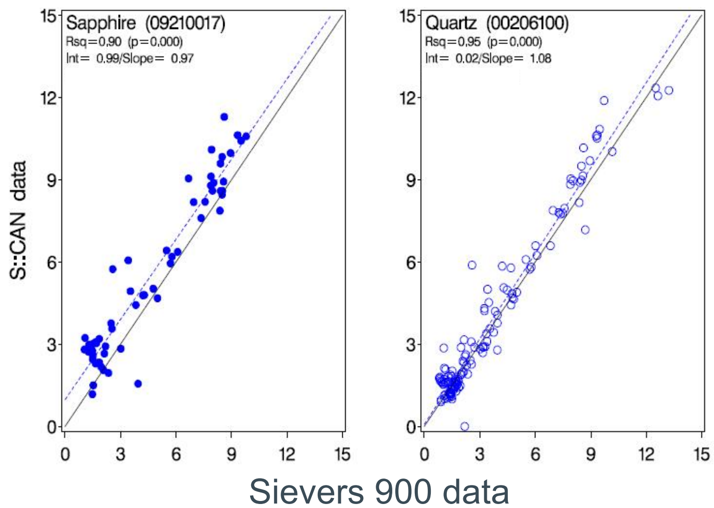
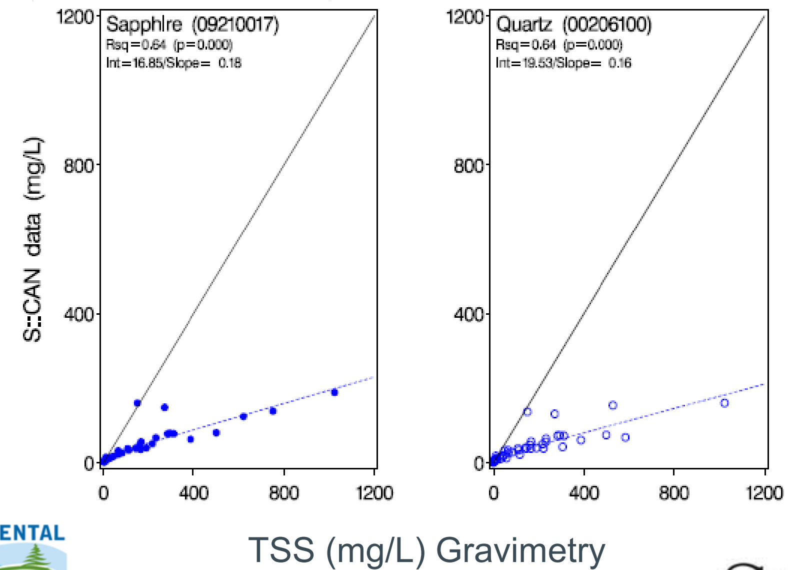
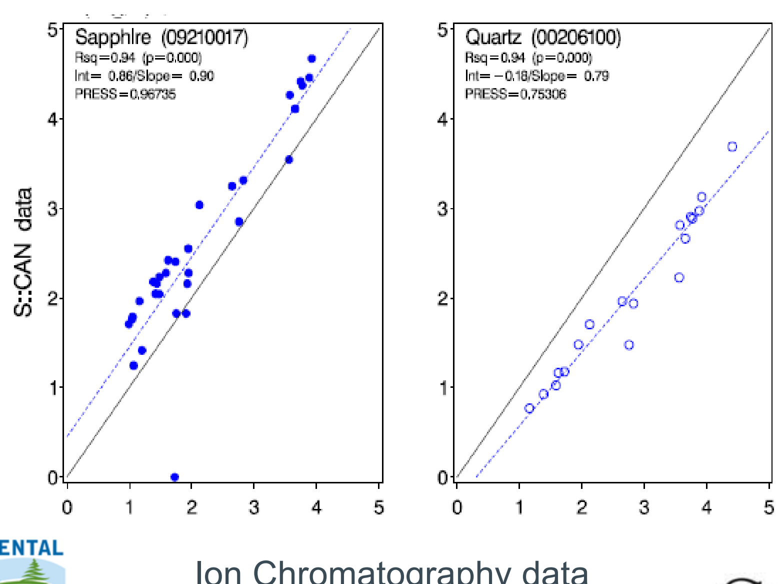
# DOC (mg/L)




# Total Suspended Solids




# $NO_3$-N (mg/L)

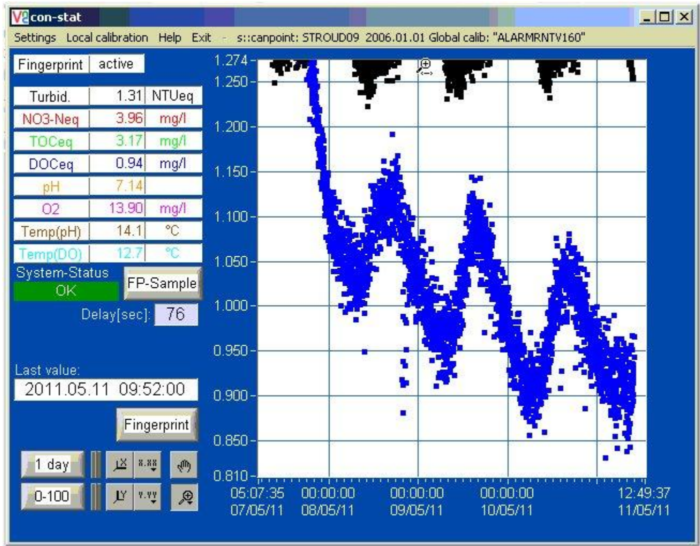



# Challenges Ahead

- Remote cleaning
- Remote diagnosis of window fouling
- Energy consumption
- Additional parameters

  Biodegradable DOC
  Suspended solids particle size

# DOC Pulse from Vernal Algal Bloom





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# Characterization and source determination of stream suspended particulate material in White Clay Creek, USA

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ABSTRACT

The material exported from a watershed reflects its origin and the processes it undergoes during downhill and downstream transport. Due to its nature as a complex mixture of material, the composition of suspended particulate material (SPM) integrates the physical, biological and chemical processes effecting watershed material. This study will (1) use a sediment fingerprinting approach to quantify the composition and sources of SPM in the White Clay Creek Watershed in SE Pennsylvania and Delaware, USA, (2) examine longitudinal trends in SPM composition and source in first to fourth reaches of the White Clay Creek, (3) quantify the differences in composition and source with hydrologic variations produced by storms and seasonality.



## 1. Introduction

The material exported from a watershed is the product of its origin and the processes it undergoes during downstream transport. Due to its nature as a complex mixture of material, the composition of suspended particulate material (SPM) provides an example of integrated physical, biological, and chemical processes effecting watershed material. SPM is comprised of mineral and organic material originating from the watershed landscape as well as from within the stream channel. In streams, the mineral and organic materials are often found within the same particle, for example as clay particles with adsorbed organic material (Aufdenkampe et al., 2001), or as flocculates of organic C and mineral particles (Droppo, 2001).

The composition of SPM differs with time and stream location based on the source of the material as well as processes it has undergone. For example, the sorption of organic material onto a clay mineral particle occurs only if these two materials come into contact with each other in an environment that favors attachment. Ultimately, the source and transport of SPM must be understood in order to quantify the sources and sinks of mineral and organic material within the watershed.

In order to determine if watershed erosion and stream suspended sediment transport comprise a net source or sink of watershed material, it is necessary to quantify the amount of SPM and its origin. However, it is often difficult to determine the fraction of total material coming from within channel versus landscape sources. Sediment fingerprinting techniques use the chemical composition of SPM and potential source materials in order to determine the origin of suspended particles (Walling, 2005). For example, variations in mineral composition can identify suspended material from areas of different surficial geology or different urban land uses within the same watershed (Irvine et al., 2009). Fallout radioisotopes, such as $^{7}$Be, $^{210}$Pb and $^{137}$Cs can distinguish between recent landscape surface erosion and erosion lower in the soil profile (Mambit et al., 2008) as well as quantify resuspension of previously settled sediments (Jweda et al., 2008). Stable isotopes of C ($^{13}$C) and N ($^{15}$N) indicate erosion from areas covered by different vegetation communities and those that undergo different vegetation management, such as crop tillage (Fox and Papanicolaou, 2007). Combinations of different fingerprints can describe the source of stream suspended material. For example, $^{137}$Cs and $^{15}$N concentrations were used to determine that 60% of the suspended load in a Georgia piedmont stream resulted from bank erosion, 23–30% from subsoil in the upland portion of the watershed and 10–15% from pastures (Mukundan et al., 2010).

This study will (1) quantify the composition and sources of suspended material to the White Clay Creek Watershed, (2) examine longitudinal trends in SPM composition and source in the 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. This study is designed to integrate geochemical, soil science, and ecological research conducted within the Christina River Basin Critical Zone Observatory at the watershed scale.

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## 2. Methodology

### 2.1. Study site

This study will be conducted in the 277 km$^2$ White Clay Creek (WCC) Watershed (Fig. 1). Located in southeastern Pennsylvania and northern Delaware, the WCC lies within the piedmont and Atlantic Coastal Plain physiographic provinces. The WCC flows into the Christiana River, a tidal river which drains to the Delaware River. Over the past several decades, the WCC has been the site of several stream ecological and hydrologic studies (Newbold et al., 1997; Kaplan et al., 2008; Richardson et al., 2009). The SPM has been shown to consist of both mineral-core organic-coated particles and organic core particles (Richardson et al., 2009). As a whole, more SPM transport occurs during storms than during baseflow (Newbold et al., 1997), however, the nature of the particles has not been compared between these flow conditions nor has it been evaluated for source contribution. Understanding the SPM sources and transport dynamics is of particular importance in the WCC because the entire Christiana River Basin has been listed as impaired for sediment by the United States Environmental Protection Agency.

### 2.2. Sample collection and analysis

SPM will be collected at four locations in WCC ranging from first- to fourth-order stream reaches. Bulk water samples of approximately 200–400 L will be collected during storm and baseflow stream condition in each of four seasons throughout 1 year. Suspended particles will be isolated from stream water using a continuous flow centrifuge. During one storm per season, multiple samples will be taken throughout the storm event hydrograph in order to assess changes in SPM source within a single event. Upon isolation, bulk sediments will be characterized for several compositional fingerprints. Mineral composition will be determined by inductively coupled plasma mass spectrometry (ICP-MS) following digestion of a subsample of the solid sediments. Fallout radioisotope activity of $^{137}$Cs, $^{7}$Be, and $^{210}$Pb will be evaluated by gamma decay.

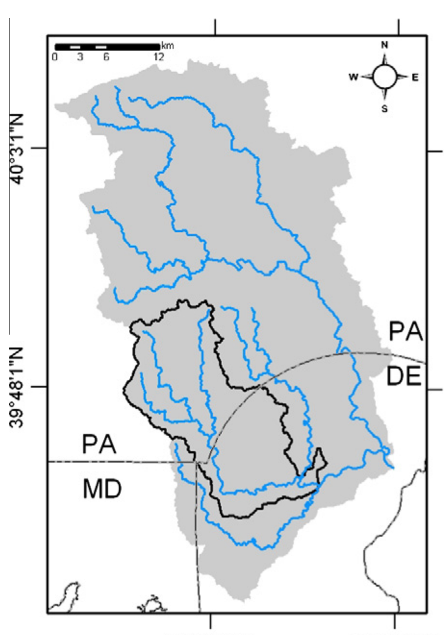


**Fig. 1.** Boundaries of the White Clay Creek Watershed is outlined on the shaded area of the Christina River Watershed with the major stream network of the entire Christina River Watershed.

Lead-210 activity will also be counted by alpha decay following the methods of (Aalto et al., 2003, 2008). Elemental and stable isotope analysis of C and N will be conducted on an Elemental analyzer (Costech ECS 4010) interfaced with an Isotope Ratio Mass Spectrometer (Thermo DeltaPlus XP). Radiocarbon ($^{14}$C) will be quantified based on published methods (Raymond and Bauer, 2001). Organic material will be further characterized with measurements of chlorophyll-a by absorbance and respiration quantified (Richardson, 2008). Particle specific surface area will be measured using Brunauer–Emmett–Teller isotherms of $N_2$ adsorbtion with a Micromeritics Tristar Surface Area and Porosity Analyzer.

In addition to the bulk water sample, separate water will be collected for the isolation and subsequent analysis of particles less than 1 μm to approximately 10 μm in diameter. Aquatic colloids will be separated into size fractions using a Split-Flow Lateral-Transport Thin Due to their small size, colloids have a large surface area and can comprise a large fraction of suspended organo–mineral complexes. Like SPM isolated from the bulk collection, colloids will be analyzed for mineral and organic composition, stable isotopes of C and N, surface area, chlorophyll-a, and organic material lability, as described above.

Probable sources of SPM will be collected and analyzed for geochemical and organic fingerprints by the same methods as suspended sediment described above. Sampling will take place upstream and upslope of the SPM sample locations and will include hillslope surface materials and 1–2 m deep cores collected from locations stratified by hillslope position and land use (forest, agriculture, urban/suburban). Additional materials from exposed surfaces, such as stream cut banks, gully walls, near stream soil aggregate deposits, road ditches and mountain bike and bridle paths will be collected.

Sediment fingerprint data (radioisotope activity, organic composition and stable isotope abundance, mineral composition, etc.) from the potential sources will be used as end members in a multivariate mixing model (Motha et al., 2003). This mixing model will describe the relative contribution from each of the two contributing sources (hillslope and channel) to the SPM at each reach.

## 3. Discussion

In this study, sediment fingerprinting analyses, common in geomorphological studies of mineral SPM, are integrated with biological and ecological characterizations of particulate organic C. Through this combination, quantifiable budgets of particulate organic C and mineral material will be produced, together with integration of the calculations of C and mineral cycling in a complex, human-influenced watershed. This interdisciplinary project will be conducted as one of many studies in the Christina River Basin Critical Zone Observatory (CZO) and will directly contribute to the overall research focus of this CZO: to quantify the net C sink or source due to mineral production, weathering, erosion and deposition as materials are transported and transformed across geophysical boundaries within a dynamic watershed.

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# Hydrologic alterations of stream water dissolved organic carbon (DOC) and its constituent lability classes

Chris McLaughlin and Louis A. Kaplan
University of Pennsylvania, Philadelphia PA and Stroud Water Research Center, Avondale PA

## Introduction

- DOC is the largest pool of organic matter in streams with the majority of DOC coming from multiple terrestrial sources.
- The contribution of terrestrial sources is altered during storms as different flow paths are activated
- As such, hydrology influences a vital source of energy for stream ecosystems
- The quantity & quality of DOC delivered to the stream are altered by processes that occur in transit
- DOC is a mixture of molecules with a continuous array of biological lability classes
- The amount of biodegradable DOC (BDOC) regulates both microbial biomass as well as nutrient cycling
- The objective our of our work was to measure quality of DOC in watershed sources and determine how changes in flow paths during storms influence the lability of in-stream DOC

## Questions

- How does the biological liability of DOC differ among terrestrial sources?
- What are the temporal patterns in the DOC constituent lability classes during storms?

## Study Site

- East Branch of White Clay Creek (WCC)
- southeastern Pennsylvania Piedmont
- catchment area of 7.25 km$^2$
- deciduous woodlands, pastures, & agricultural land


## Field methods


*Terrestrial source water BDOC:*
- measured labile DOC

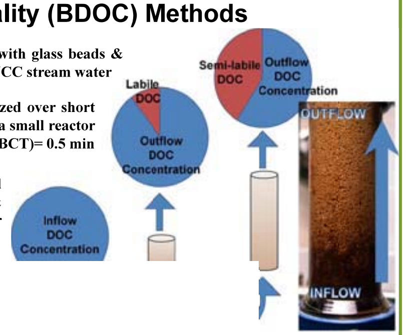
*Storm water BDOC:*
- separate into labile & semi-labile classes
- diluted high DOC samples with biologically stable bioreactor effluent to normalize for concentration.

DOC:
- Sievers 800 or 900 organic carbon analyzer

## DOC Quality (BDOC) Methods

*Plug-flow biofilm reactors:*
- chromatography columns filled with glass beads & colonized by microorganisms in WCC stream water
- the most labile DOC is metabolized over short exposure times & measured using a small reactor with an empty bed contact time (EBCT)= 0.5 min
- semi-labile DOC is metabolized after longer exposures & measured using a large reactor with an EBCT = 150 min.

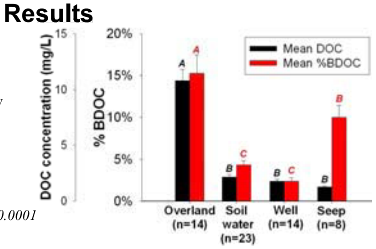
$$\%BDOC = \frac{DOC_{inflow} - DOC_{outflow}}{DOC_{inflow}}$$




## Results

*Terrestrial source water BDOC:*

- DOC lability differenced significantly among sources
*(ANOVA, F(3,577)=24.6066, p<0.0001)*
- Overland & seep water had higher %BDOC than both soil & well water
*Tukey post-hoc comparisons:*
*overland: $\bar{x}$ =15%, 95% CI [13, 18], p <0.0001*
*seep water: $\bar{x}$ =10%, 95% CI[6.9, 13], p[well]=0.0014, p[lys]=0.0138*
- %BDOC for soil & well water was not different
*soil water: $\bar{x}$ =4.3%, 95% CI[2.5, 6.2]*
*well water: $\bar{x}$ =2.4%, 95% CI [0.0, 4.7], p=0.5530*




*Storm water BDOC*

- The large fall storm represents an extreme hydrologic condition composed of two discharge peaks: a small first peak (427 L/s) followed approximately 18 hours later by a much larger second peak (5039 L/s).
- The smaller winter storm was a quarter of the size with only one distinct discharge peak.

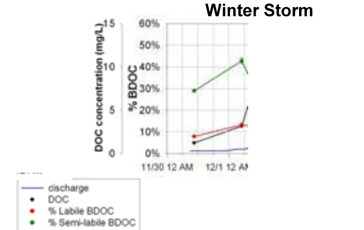
Storm Event Parameters

| Storm | n | Min Q (L/s) | Max Q (L/s) | Precipitation (cm) | API$_7$* (cm) | API$_{30}$* (cm) |
|---|---|---|---|---|---|---|
| Fall Storm (Sept 30, 2010) | 11 | 44 | 5210 | 16.1 | 2.0 | 3.9 |
| Winter Storm (Nov 30, 2010) | 10 | 30 | 1444 | 4.2 | 0.5 | 5.2 |

* Antecedent moisture conditions computed using the antecedent precipitation index (API$_X$) which is the summation of the precipitation amounts for *X* days prior to the event

Fall Storm

Winter Storm




- Both DOC quantity & quality increased during storms
- However, the temporal dynamics between and among the 2 storms differed substantially
- Both DOC lability classes were significantly different across time
*Fall Storm:*
*Labile class ANOVA, F(10,20)=29.5637, p<0.0001,*
*Semi-labile class: REML fixed effects test, F(10) = 74.2422, p< 0.0001*
*Winter storm:*
*Labile class ANOVA, F(9,20)=52.7215, p<0.0001,*
*Semi-labile class: REML fixed effects test, F(9) = 102.1602, p<0.0001*
- A comparison of the two lability classes over time showed significant differences through an interactive effect between lability class & time
*Fall Storm:ANOVA, F(10, 22) = 21.9208, p<0.0001*
*Winter Storm: ANOVA, F(9,20) = 10.4836, p<0.0001*

## Discussion

*Terrestrial source water BDOC*
- BDOC in terrestrial source water decreased with soil depth due to increased residence time and different conditions for degradation.
- The lability of seep water DOC was greater than the lability of unsaturated soil water suggesting that these deep groundwater sources are mixing with near surface sources of labile C before being released into the channel.
- The large variation in BDOC among terrestrial sources means that the composition of DOC exported from the watershed will depend on the flow path taken by the water that is discharged into the stream.

*Storm water BDOC*
- Storm flow bypasses soil control mechanisms resulting in dynamic changes in both DOC and BDOC.
- Increases in BDOC observed during storms suggest increased discharge from shallow pathways through C-rich soil horizons.
- Multiple flow paths contributing both increased and decreased BDOC to the stream during storms could be leading to differences in BDOC among storms.
- The different temporal patterns observed in the 2 lability classes indicate differences in the source pools for each lability class.

## Broader Impacts

The quality of DOC in stream water has important implications for ecological processes because of its regulatory role in stream metabolism and nutrient cycling. Since the majority of DOC in WCC is terrestrially derived, stream export of DOC has important consequences for the global carbon cycle.

Because stream heterotrophs are dependent on the supply of bioavailable DOC, stream ecosystem metabolism is influenced by changes in hydrologic flow paths that result in variations in BDOC. Interactions between water, soil, and microorganisms determine the lability of DOC exported from the terrestrial environment. Linking the water cycle to biogeochemical cycles is critical for integrating stream ecosystem models into a catchment framework.

## Future Research

Rates of N transformations are tightly linked to C cycling and are hypothesized to be influenced by C quality. Although the main factors that regulate rates of denitrification and nitrification are known, there is a lack of understanding about how C from different hydrologic flow paths might influence in-stream N transformation rates. Understanding the effect of C delivered from different flow paths on in-stream N cycling is critical to regulating water quality and effectively managing freshwater ecosystems.

Our future work will be aimed at testing the effect of different source water DOC quality on in-stream denitrification and nitrification rates. Denitrification, the reduction of $NO_3$ to $N_2$, is a heterotrophic process that can be limited by the availability of organic C, but organic C can have a negative effect on nitrification, the oxidation of $NH_4$ to $NO_3$, which is believed to be the result of heterotrophic bacteria out-competing the less abundant slower-growing nitrifying bacteria.

*Question:*
What effect do changes in DOC lability have on in-stream nitrification and denitrification?

*Experiment:*
Stream sediment perfusion cores will be exposed to different terrestrial sources of water amended with $^{15}NO_3$, and denitrification and nitrification rates will be measured using the nitrogen isotope pairing and isotope dilution techniques.

**Acknowledgements:**

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# A $^{13}$C DOC tracer approach to estimate the contribution of semi-labile dissolved organic carbon to stream ecosystem metabolism

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## Introduction

In streams and rivers, dissolved organic carbon (DOC) supplies energy and carbon (C) to heterotrophic bacteria. The complexity of the DOC pool combined with simultaneous processes that continually produce, transform and consume DOC molecules in transport, makes in situ measurements of DOC uptake challenging. We used a tracer approach and prepared a $^{13}$C tracer of semi-labile DOC from soil-aged $^{13}$C-labeled *Liriodendron tulipifera* tissues for use in bioreactors and whole stream releases.

Fig. 1. Stream DOC is mixture of > 10,000 molecules with various biological labilities. A central question in stream ecology is **does DOC contribute to stream ecosystem metabolism?**

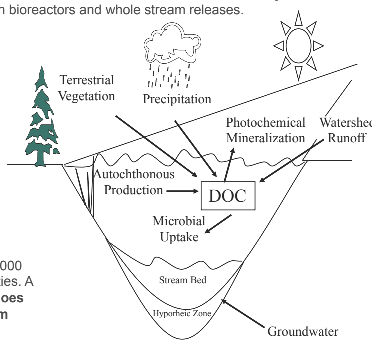


Fig. 2. Processes altering DOC concentrations and quality

## Laboratory Methods

(A) Bioreactor with density, activity, and species gradients

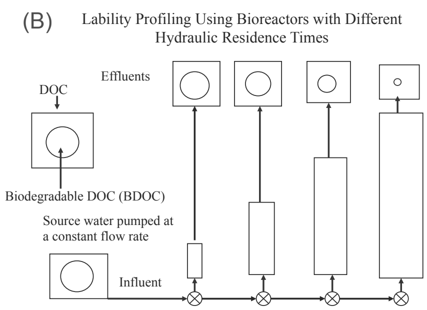


Fig. 3. (A) Bioreactors kept in the dark and fed stream water in the upflow mode develop gradients of bacterial densities, activity, and species composition. (B) Residence time influences the amount of DOC metabolized. Uptake of BDOC of lower lability increases in larger bioreactors with increasing empty bed contact time (EBCT) and leads to effluents that are increasingly refractory. A series of bioreactors with increasing residence times from 0.5 min to 74 min. were used to separate the stream water DOC and the $^{13}$C -DOC tracer into different biological lability classes.

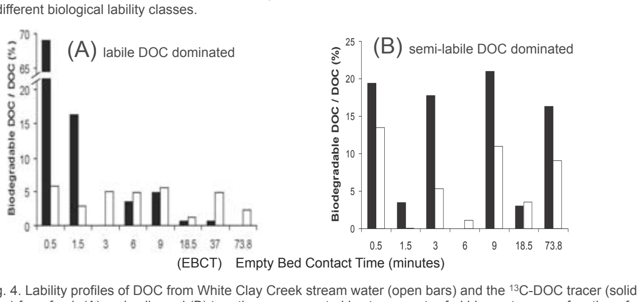


Fig. 4. Lability profiles of DOC from White Clay Creek stream water (open bars) and the $^{13}$C-DOC tracer (solid bars) from fresh (A) and soil-aged (B) tree tissues generated in stream water-fed bioreactors as a function of residence time or EBCT. Labile DOC (≤ 1.5 min. EBCT ) accounted for 85% of the fresh tracer and 22% of the soil-aged tracer while the semi-labile class (≥3 min. EBCT) accounted for 15% of the fresh tracer and 78% of the soil-aged tracer. Bioreactor lability profiling was calibrated with glucose and arabinose. Glucose was completely removed in the bioreactors after EBCT of 0.5 min. while arabinose was completely removed after EBCT of 6 min. In whole stream releases of glucose and arabinose, the uptake length of arabinose was ~ 3 times longer than that of glucose (2.9 ± 0.7, n = 59; mean, s.d.).

The stream water BDOC data from the bioreactors provide concentrations of the labile and semi-labile BDOC classes. These concentrations are used along with mass transfer coefficients derived from the whole stream additions to estimate fluxes of DOC uptake in the stream ecosystem.

## Field Methods: $^{13}$C Release and Metabolism

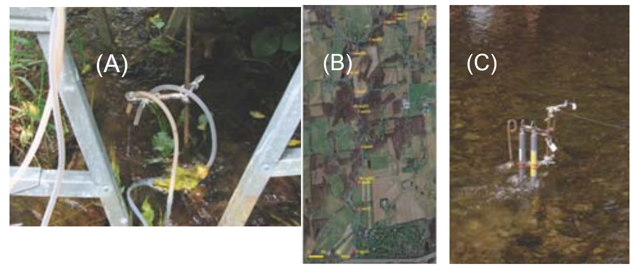


Fig. 6. (A) The $^{13}$C tracer and $Br^-$ conservative tracer were injected into a 2nd –order reach of White Clay Creek. (B) The 2-h injection was followed at 12 stations extending downstream for 5.4 km over the next 20 hr. (C) Dissolved oxygen was measured with sondes and corrected for reaeration by propane evasion measurements for the estimates of stream ecosystem metabolism.

## $^{13}$C DOC Uptake

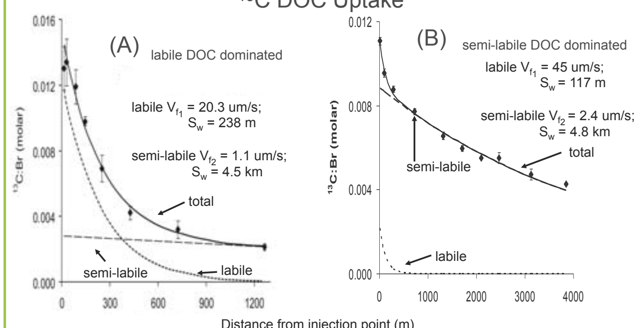


Fig. 7. Longitudinal uptake of fresh (A) and soil-aged (B) $^{13}$C-DOC tracer during whole-stream additions dominated by labile and semi-labile lability classes, respectively. Mass transfer coefficients ( $V_f$ ) or uptake velocities are calculated from the inverse of the longitudinal uptake rate coefficients of each lability class.

## $O_2$ Dynamics

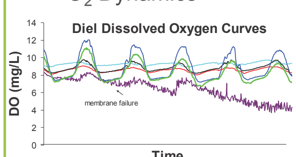


Fig. 8. Diel oxygen curves for the 5 stations used to calculate metabolism. Ecosystem metabolism generated from $O_2$ uptake in the dark, corrected for algal respiration to approximate heterotrophic respiration ($H_r$), and converted to units of C. $H_r$ rates ranged from 0.05 to 4.8 $gO_2/m^2/d$ and averaged 3.2 ± 1.6 $gO_2/m^2/d$ (mean, s.d.)

## Calculations with Field and Laboratory Data

Average heterotrophic metabolism: **1.22 g C/m²/d**

Uptake of stream DOC:
(mass transfer coefficient) x (lability class concentration) = flux

Labile = (45 μm/s) (250 μg C/L) = **0.97 g C/m²/d**

Semi-labile = (2.4 μm/s) (804 μgC/L) = **0.19 g C/m²/d**

**DOC uptake (1.16 g C/m²/d) can support 95% of the stream metabolism with the semi-labile constituents supporting 15% of the metabolism.**

## Conclusions

Soil-aging of the $^{13}$C tree tissue tracer increased our ability to measure the uptake of semi-labile DOC classes in whole-stream releases. The bioreactors are laboratory tools that facilitate measurements of DOC uptake without the confounding issues of algal excretion, photolysis, inputs from groundwater, and leaching of benthic organic matter, permitting measurements that can not be made *in situ*. Increasing bioreactor residence time, EBCT, becomes a surrogate for DOC biological lability. The $^{13}$C-DOC tracer, derived from tulip poplar trees, is a natural product present in White Clay Creek. However, our goal was not to assess the importance of tulip poplar molecules to stream respiration, but rather the role of the natural, complex mixture of DOC molecules in the stream. The validity of our DOC lability profiling scheme rests on a primary assumption regarding the fidelity of the bioreactors as models of stream processes, i.e., that organic molecules of similar lability at the bioreactor scale will have similar lability in the stream. We assert that the ordering of DOC lability is preserved across systems with different spatial and temporal scales. This method can be used with molecular-level analyses to begin to provide lability information for individual molecules within the >10,000 molecule DOC pool in freshwaters.

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# Role of Fe- and Mn- Redox Coupling on the Carbon Cycle in a Mixed Land Use Watershed: Christina River Basin Critical Zone Observatory

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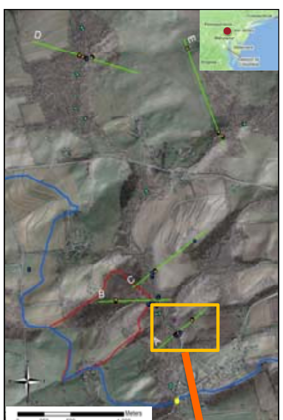
## INTRODUCTION

A multitude of scientific publications have emphasized the importance of an organic carbon (C) - mineral complexation mechanism as a crucial factor in C stabilization and sequestration. Carbon-mineral complexation is strongly controlled by mineral surface area, mineralogy, pH, redox, polyvalent cations, ionic strength, and the chemical composition of organic matter. These factors vary spatially as a function of geomorphologic, hydrologic, and microbiological processes. Soil horizons and sediments with abundant Fe and Mn oxides/hydroxides have high mineral surface area and thus a high capacity to complex C, reducing its susceptibility to microbial degradation. Additionally, both sediment and hydrological fluxes transport mineral surface area in both solid and dissolved phases (i.e., Fe can be hydrologically transported in its reduced state and then oxidized to iron oxides with high mineral surface area).

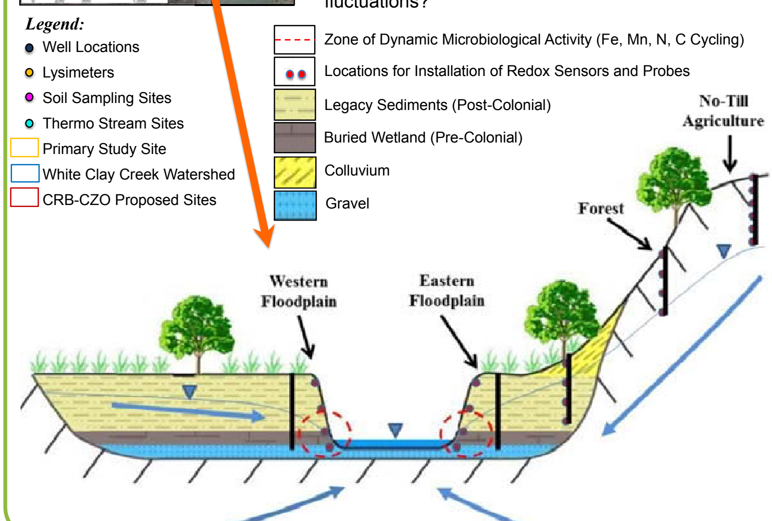
At the Christina River Basin-Critical Zone Observatory (CRB-CZO), one of six observatories located in the Piedmont region of Southeastern Pennsylvania and northern Delaware and funded by the National Science Foundation, we investigate how Fe- and Mn-redox coupling affects the C cycle under varying redox conditions across a wide range of landscape positions and uses, such as floodplain forest, upland forest, and agriculture.

## STUDY AREA



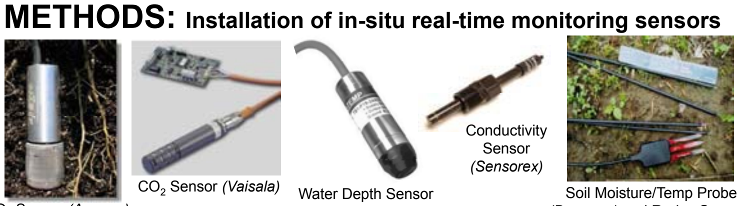
## Proposed Research Questions:

- How do redox conditions in soils affect the transport of mineral surface area via the dissolved phase?
- How deep and fast does $O_2$ penetrate through soils under different land use types and landscape positions?
- Does $O_2$ diffusion back into riparian soil/sediments facilitate complexation between C and newly-precipitated Fe- and Mn-oxides in the pore water?
- 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?
- 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 the C cycling under these redox fluctuations?



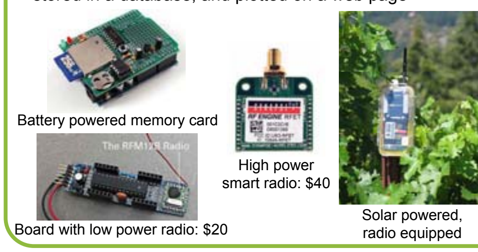

Modified from Walter and Merritts, 2008

## METHODS: Installation of in-situ real-time monitoring sensors




## METHODS (continued)

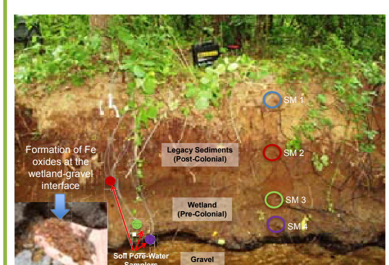
- **Wireless Datalogging and Sensor Communication (www.arduino.cc):**
  - Based on open-source hardware and software platforms keeping development and costs low
  - Live streaming data can be displayed on a computer, stored in a database, and plotted on a web page

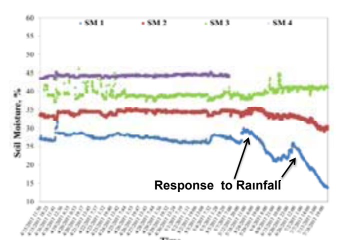


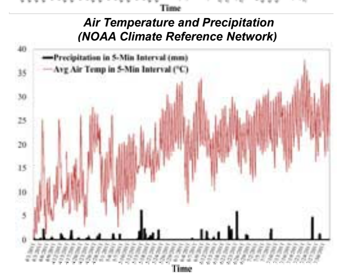

- Sampling of soil cores, soil pore waters, stream water, and groundwater
- Water sample analysis: pH, T, DO, $Fe^{2+}$, conductivity, alkalinity, TDS, DOC, TOC, stable isotopes of water, major anions, major cations, and metals
- Soils sample analysis: total chemical composition, OC%, isotopes of N, C, and mineral surface area
- Selected samples will be analyzed by XRD, SEM, EPR, Mossbauer Spectroscopy, and molecular analysis on microbial communities

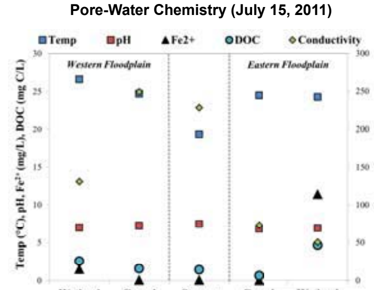
## PRELIMINARY RESULTS:

### *Western Floodplain*

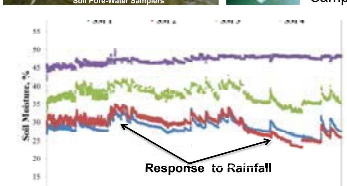


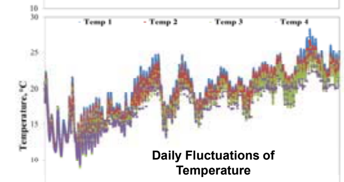



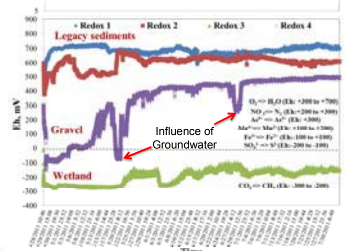




### *Eastern Floodplain*


- Eastern floodplain is affected by high hillslope morphology where the groundwater discharge into the stream after heavy rainfall creates a substantial redox gradient.
- Higher DOC and $Fe^{2+}$ at the buried wetland of the eastern floodplain compared to the western side.
- As expected, very low DOC and $Fe^{2+}$ within gravel deposits due to the formation of Fe oxides along a redox gradient.
- What is the fate of DOC within the gravel during reductive dissolution of Fe oxides?

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