

**Maryland Water Resources Research Center
Annual Technical Report
FY 2013**

Introduction

During Funding Year 2013, the Maryland Water Resources Research Center (MWRRC) supported a variety of research and outreach activities that address the diversity of water issues in the State and the Chesapeake Bay Region. The Center's outreach/information transfer event focused on the response of coastal communities to floods and sea level rise. New research projects investigated toxic disinfection byproducts in drinking water, the environmental pathways and effects of road salt, and new methods to identify endocrine disruption (intersex) in freshwater fish. Three graduate students received summer fellowships: assessing the ability of management practices to restore natural hydro-ecological function in urban headwater streams; analyzing the water-holding capacity and evapotranspiration patterns of green roof soil/vegetation systems; and exploring denitrification, N₂O emissions and nutrient export from forest/agricultural headwater streams.

Funding cuts to the program were a challenge in FY 2013. The Federal portion of the budget was reduced to 60% after research projects and summer graduate fellowship recipients were selected. The MWRRC was able to preserve summer graduate fellowships and support three new research projects by taking cuts in administration and outreach expenditures, and by proportionate reductions in the research awards (including the reduction of two-year projects to a single year). The PIs whose projects were reduced from two years to one were assured special consideration – assuming reasonable progress – in the FY 2014 funding process.

Research Program Introduction

With 104B funding, the Maryland Water Resources Research Center supported three new research projects and three graduate student summer fellowships in Funding Year 2013:

- Bromide as a Precursor of Potent Brominating Agents During Drinking Water Chlorination (2013MD304B); PI: John Sivey (Chemistry, Towson University).
- Validation of non-lethal laparoscopic technique for detection of intersex in regional black bass populations (2013MD305B); PI: Lance Yonkos (Environmental Science & Technology, University of Maryland College Park).
- Tracing the rates of road salt runoff movement from impervious surface to stream and the effects on soil and aquifer geochemistry (2013MD306B); PIs: Joel Moore and Steven Lev (Physics, Astronomy & Geosciences, Towson University).
- Enhancing watershed infiltration to restore urban stream hydro-ecological function (Graduate Fellowship) (2013MD307B); Rosemary Fanelli (Ph.D. student, Marine Estuarine & Environmental Sciences, University of Maryland College Park; Advisor: M. Palmer)
- The role of streams in nitrogen fluxes from watersheds in the Choptank Basin (Graduate Fellowship) (2013MD308B); John Gardner (M.S. student, Marine Estuarine & Environmental Sciences, University of Maryland Center for Environmental Science – Horn Point Laboratory; Advisor: T. Fisher)
- Modeling the effects of green roof substrate organic matter on stormwater retention and plant-based water cycling (Graduate Fellowship) (2013MD309B); Whitney Griffin Gaches, Ph.D. student (Plant Science & Landscape Architecture, University of Maryland College Park; Advisors: S. Cohan and J. Lea-Cox)

A University of Maryland project selected for support under the IWR/NIWR program in 2012 continued during this performance period:

- The Effectiveness of a Computer-Assisted Decision Support System Using Realistic Interactive Visualization as a Learning Tool in Flood Risk Management (2012MD299S), Bahram Momen (Environmental Science & Technology, University of Maryland, College Park)

Three 104B projects begun in previous years were completed during this performance period:

- Relating pollutant and water quality parameters to landuse in a subwatershed of the Choptank River watershed (2011MD238B), Alba Torrents (Civil & Environmental Engineering, University of Maryland, College Park) and Cathleen Hapeman (USDA Agricultural Research Service, Beltsville, Md.).
- Quantifying remobilization rates of legacy sediment from Maryland Piedmont floodplains (2012MD262B), Andrew Miller (Geography & Environmental Systems, University of Maryland, Baltimore County).
- An Innovative Learning Tool in Communicating Flood Risk Management (2012MD270B), Bahram Momen (Environmental Science & Technology, University of Maryland, College Park) – a supplement to the IWR/NIWR award (2012MD299S).

Relating pollutant and water quality parameters to landuse in a subwatershed of the Choptank River watershed

Basic Information

Title:	Relating pollutant and water quality parameters to landuse in a subwatershed of the Choptank River watershed
Project Number:	2011MD238B
Start Date:	6/1/2011
End Date:	5/31/2013
Funding Source:	104B
Congressional District:	5th Congressional District
Research Category:	Water Quality
Focus Category:	Non Point Pollution, Surface Water, Water Quality
Descriptors:	
Principal Investigators:	Alba Torrents, Cathleen Hapeman

Publications

1. Nino de Guzman, Gabriela T., Cathleen J. Hapeman, Kusuma Prabhakara, Eton E. Codling, Daniel R. Shelton, Clifford P. Rice, W. Dean Hively, Gregory W. McCarty, Megan W. Lang, Alba Torrents, 2012, Potential pollutant sources in a Choptank River (USA) subwatershed and the influence of land use and watershed characteristics, Science of the Total Environment, 430, 270-279.
2. Nino de Guzman, Gabriela T., Cathleen J. Hapeman, Kusuma Prabhakara, Eton E. Codling, Daniel R. Shelton, Clifford P. Rice, W. Dean Hively, Gregory W. McCarty, Megan W. Lang, Alba Torrents, 2012, Potential pollutant sources in a Choptank River (USA) subwatershed and the influence of land use and watershed characteristics, Science of the Total Environment, 430, 270-279.

Completion Report for the period 3/01/13 through 5/31/13

Project: 2011MD238B

Project Title: Relating pollutant and water quality parameters to landuse in a subwatershed of the Choptank River watershed

Principal Investigator(s): Alba Torrents and Cathleen Hapeman

Problem and Research Objectives

The Choptank River, a tributary of the Chesapeake Bay, is surrounded by various agricultural practices and has been under scrutiny for impaired water quality. The majority contributor to the poor water quality of this river is speculated to be these agricultural facilities and farms, particularly the husbandry operations. According to the Environmental Protection Agency's Guidance for Federal Land Management in the Chesapeake Bay Watershed, agriculture is responsible for approximately 43% of nitrogen (N), 45% of phosphorus (P), and 60% of the sediment loads released into the Bay. Of this, approximately 17% of N and 19% of P load comes from chemical fertilizers, and 19% of N and 26% of P load comes from manure. About 60% of land use in the Choptank River watershed is devoted to agriculture, producing corn, soybean, wheat, and barley; much of this supports small- and medium-sized animal feeding operations, mostly poultry with some dairy and horse husbandry. Manure from poultry houses is routinely used as a fertilizer on agricultural fields. Though mitigation practices have been put in place to control runoff from the agricultural fields and husbandry lots, surface water pollution still occurs. Potential pollutants from these agricultural activities, especially poultry farming, include sediment, pesticides, nutrients, antibiotics, heavy metals, and non-indigenous microorganisms.

The main objective of this study was to survey a small section of a subwatershed in the Choptank River watershed and determine if a single poultry operation has a measurable effect on the surrounding environment. We are particularly interested in the impacts water quality. Water samples are tested for arsenic, nitrogen, phosphorus, *E. coli* and *Enterococcus* as bacterial indicators of contamination/natural reservoirs, antibiotics, and pesticides. Water quality parameters, such as pH, temperature, and conductivity are also measured at each site

The proposed tasks for the project were:

1. Address comments and revised a manuscript submitted for publication.
2. Evaluate the possible use of artificial sweeteners and MESA as nutrient and pollutant fate indicators in the Choptank River.
3. Develop analytical methods for the use markers and analysis of archival samples.

Graduate student Gabriela Nino de Guzman (Civil and Environmental Engineering, UMCP) completed manuscript revisions while being funded by another project. This work clearly illustrated the need to be able to identify and distinguish between urban and agricultural nutrient

sources and assess fate processes. Furthermore, our data suggested that N and P have different sources and/or presumably have different delivery mechanisms. Compounds that behave similarly to the nutrients and are unique to one source can be used to distinguish between the various anthropogenic aquatic inputs to the river; a manuscript was published based on this work.

MS student, Lucia Geis, conducted an in-depth literature review in the use of urban and agricultural chemical markers. We identified MESA {2-[2-ethyl-*N*-(1-methoxypropan-2-yl)-6-methylanilino]-2-oxoethanesulfonic acid}, a metabolite of the extensively-used herbicide metolachlor, as an ideal agricultural tracer. Sucralose is an artificial sweetener that is recalcitrant in the waste treatment process, and is an excellent source indicator of urban waste. We optimized a liquid chromatography - mass spectrometry (LC-MS) analysis to include MESA and sucralose, developed a high throughput analysis and improved identification by including more transitions and using ion ratios as qualifiers. Sample extraction techniques were optimized for sucralose and validated by determining sensitivity, dynamic ranges, accuracy, precision, limits of quantification and lowest calibration limits. An additional campaign was conducted in Fall-2013 to collect samples from 13 locations. With funding from another source, an additional sampling campaign was conducted at the Anacostia River to be able to compare to distinct watersheds. The newly developed method was used to analyze all samples and further discern sources and processes.

Choptank River results obtained were comparable to previous studies. Hence, the extended method proved to be effective and could substitute the two methods that were previously used for the analysis of river samples. Nutrients and herbicides followed previously described trends, except for the lack of biological degradation observed for nitrate. Sucralose was determined only in urbanized areas; however, its high LCL and variable ionization limited the evaluation of trends and comparisons with nutrient levels. MESA as expected showed to be a good tracer for agricultural nitrate loadings.

Anacostia River results were very interesting; to the best of our knowledge this is the first study that analyzed nutrients, herbicides and sucralose simultaneously in surface water, covering all the major subwatersheds. Nitrate and ortho phosphorus were lower than average at the USGS stations for the month of August. No trends were observed for nitrate and MESA. The results obtained for sucralose seemed promising even though the data collected was limited. In the case of ortho phosphorus a preliminary linear trend was observed when considering sucralose consumption per capita, but more sampling is needed in order to better support this observation. Overall, MESA was found at higher levels in agricultural areas and sucralose was found only in urbanized areas. This work provides proof of concept that sucralose and MESA could be used as tracers of urban and agricultural nutrient loadings.

Regarding other analytes under study, metolachlor findings in Anacostia River watershed were of concern, as the levels found were comparable to Choptank River, though Anacostia watershed is not a highly agricultural area. Hence, better management practices and education are necessary for metolachlor application by the general public to lawns and grass turf in recreational areas.

The authors recommends that in future works a new sampling site located in Northwest Branch, before its combination with Sligo Creek, could be added as this subwatershed has 9 percent of land used for agriculture, but contrary to Beaverdam it does not present any WWTP that discharge into the river. Also, the final method should be improved in order to include acesulfame because this compound is generally found at higher levels than sucralose and is more stable in groundwater. The addition of groundwater sampling would allow for a more comprehensive view of the nutrients fate in the watersheds. Moreover, sampling during storm events would be very interesting to better study possible relationships between runoff of pollutants and land use, and to evaluate the behavior of the WWTPs at the USDA in Beltsville and their impact on water quality.

The results of this work were presented at the 3rd Annual BA-UMD Fall Symposium Trends in Agriculture. Climate Change: Food and Environmental Security. Beltsville; a copy of the poster is included (below). Based on this work, a manuscript is under preparation.

Poster:

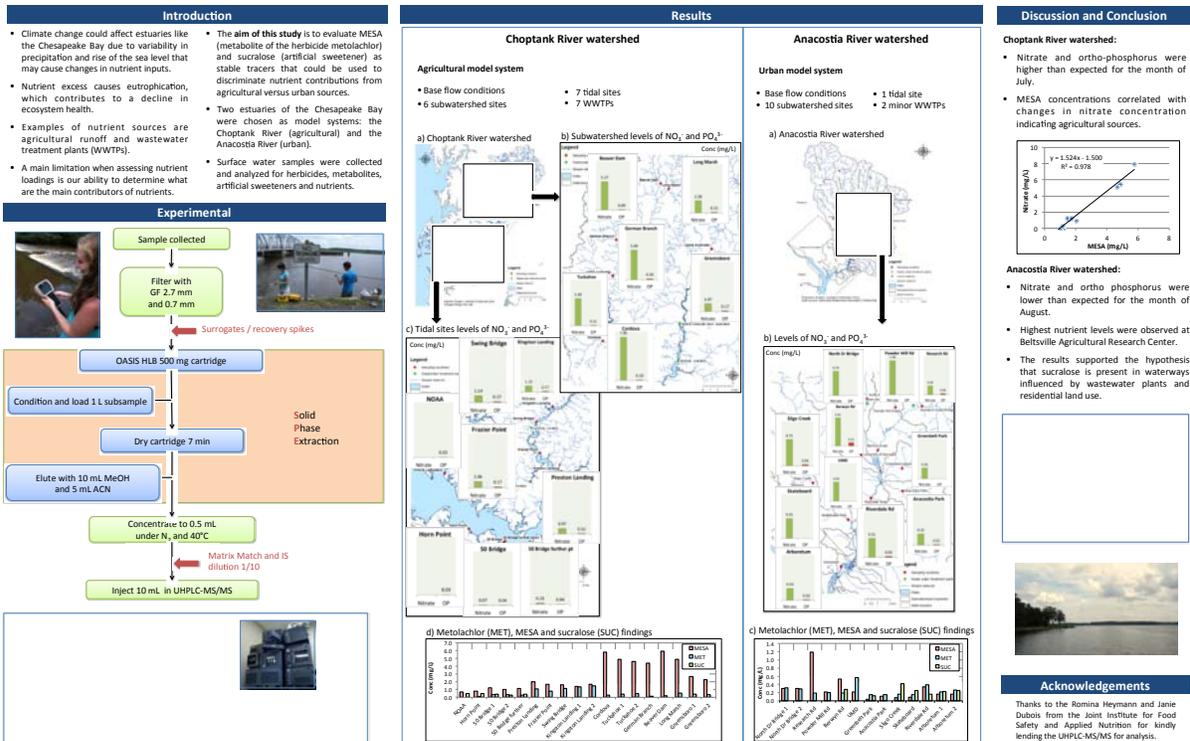


Developing unique tracers to distinguish nutrient contributions from agriculture and wastewater sources in the Choptank and Anacostia River watersheds

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Quantifying remobilization rates of legacy sediment from Maryland Piedmont floodplains

Basic Information

Title:	Quantifying remobilization rates of legacy sediment from Maryland Piedmont floodplains
Project Number:	2012MD262B
Start Date:	7/1/2012
End Date:	8/31/2013
Funding Source:	104B
Congressional District:	07
Research Category:	Climate and Hydrologic Processes
Focus Category:	Geomorphological Processes, Sediments, Non Point Pollution
Descriptors:	
Principal Investigators:	Andrew Miller

Publication

1. Donovan, M. and A.J. Miller. Quantifying remobilization rates of legacy sediments from Maryland Piedmont floodplains. Poster presentation, Amtrak Club (Mid-Atlantic Geomorphology Conference), Johns Hopkins University, May 17-18, 2013.

Completion Report:
2012MD262B

Quantifying remobilization rates of legacy sediment from Maryland Piedmont floodplains

Final title (ASSESSING THE CONTRIBUTION OF LEGACY SEDIMENT AND MILL DAM STORAGE TO SEDIMENT BUDGETS IN THE PIEDMONT OF MARYLAND)

1. Narrative Summary

a. Problem and Research Objectives

Sediment has long been recognized as a critical pollutant affecting water quality and habitat in Chesapeake Bay. Recently the U.S. EPA issued a “pollution diet” for the Bay in the form of a Total Maximum Daily Load (TMDL) document that includes a mandate for a 20 percent reduction in the mass of sediment reaching Chesapeake Bay (U.S. EPA, 2010). The TMDL document assigns 17 percent of the total sediment load reaching the Bay to sources in Maryland, many of which are closer to the Bay than more remote parts of the watershed. A key element of the TMDL involves the use of Watershed Implementation Plans that will involve state and local jurisdictions in decisions about how to limit sources and delivery of pollutants, including sediment. Thus every jurisdiction will need access to sound scientific understanding of the sources, transport and delivery of sediment in order to make appropriate decisions. As Smith et al. (2011) and Walter and Merritts (2011) point out, successful strategies for managing sediment delivery to downstream sources require a better understanding of sediment budgets and processes acting on key parts of the landscape than has generally been the case.

Numerous studies document that land use causing accelerated upland soil erosion leads to storage of sediment in the watershed both as colluvium and through aggradation of river valleys (Gilbert, 1917; Happ et al., 1940; Trimble, 1975, 1981; Costa, 1975; Knox, 1972, 2006; Phillips, 1991; James, 1991; Herman, 2001). The Piedmont physiographic province has the lowest natural long-term denudation rates among the provinces of the Chesapeake Bay watershed, accounting for the deep weathering profiles that have been preserved in much of the landscape, but also has the highest contemporary sediment yields as a result of historical land-use disturbance (Gellis et al., 2009). Much of the sediment mobilized by historical disturbance is currently stored in the form of “legacy” sediments as floodplain deposits dating from the period of intensive agriculture between the late 18th and the early 20th centuries (e.g. Jacobson and Coleman, 1986). A large fraction of the historical sediment stored in floodplains is in the silt and clay size ranges, which are considered more important contributors to degradation of habitat and water quality in Chesapeake Bay. There are major questions related to remobilization and delivery of stored sediment to receiving waters (Wolman, 1967, Meade 1982, Jacobson and Coleman 1986) and its effects on habitat loss and environmental degradation in Chesapeake Bay (Langland and Cronin, 2003; Merritts et al., 2011). Managers are concerned about whether a major part of their focus in meeting TMDL requirements should be devoted to managing streambank erosion to limit the remobilization of legacy sediments (Robert Summers, Secretary, Maryland Department of Environment, personal communication, April 2010).

Although the issue of legacy sediment has been familiar to geomorphologists for many years, recent interest in the topic has been spurred by a study suggesting that almost all of the historical alluvium stored in valley bottoms of the mid-Atlantic Piedmont region was trapped behind mill dams that were pervasive throughout this landscape (Walter and Merritts, 2008). The dams’ locations have been mapped and there are indeed a large number of them, as they formed the power grid of that time. Most of these dams were breached many years ago but their deposits remain mostly in place and they are considered a

major potential source of sediment. It has been argued that previous geomorphic understanding of the nature of Piedmont streams was almost entirely an artifact of the influence of mill dams; that under current circumstances the upland sources are largely decoupled from processes associated with streambank erosion and increased suspended sediment loads in streams; that entrenchment and remobilization of mill dam deposits is potentially a more important source of sediment than upstream sources including those associated with the impacts of urbanization on stormwater, soil erosion, and headwater channel enlargement; and that wetland restoration by removal of historic millpond sediment is a potentially effective strategy for ecosystem renewal (Walter and Merritts 2008; Merritts et al., 2011). These suggestions are intriguing and have policy implications but the ideas need to be tested further by other investigators. For example, recent evidence from a study in the Difficult Run watershed in the Virginia Piedmont (Hupp et al., 2013) suggests that historic mill dams are associated with some legacy sediment deposits but do not exert a controlling influence on the basin-scale balance of stored legacy sediment or on floodplain dynamics.

Research continues to refine approaches used to better understand sediment sources through field measurements (Hupp et al., 2013; Merritts et al., 2010; Wegmann et al., 2012), analysis of high-resolution digital topographic data (De Rose and Basher, 2011; Erwin et al., 2012; Kessler et al., 2012; Merritts et al., 2011), combined field and geospatial data (Lauer and Parker, 2008; Winterbottom and Gilvear, 2000), and geochemical tracers (Belmont et al., 2011; Gellis and Walling, 2011; Gellis et al., 2009; Smith et al., 2011).

Additional exploration is needed to understand the long-term contributions of remobilized floodplain and legacy sediments across stream networks. Differing conclusions about the relative importance of mill dam deposits as a sediment source (Hupp et al., 2013; Merritts et al., 2010; Rhoades et al., 2009; Wegmann et al., 2012) suggest there is a need for more systematic comparison of erosion rates from streams with and without mill dams (Bain et al., 2008). Finally, alternative hypotheses about the mechanisms governing the ongoing evolution of Piedmont streams- specifically, whether legacy sediments represent fill terraces or vertically-aggraded floodplains (Jacobson and Coleman, 1986; Walter and Merritts, 2008; Wolman and Leopold, 1957)- have yet to be settled.

This thesis project evaluated erosion from stream banks, legacy sediment, and mill dam deposits as sediment sources across the Piedmont stream network of Baltimore County by asking the following research questions:

1. How much sediment has been remobilized from Baltimore County floodplains by bank erosion over the last 50 years and how does this vary by stream order and drainage area?
2. What proportion of bank erosion is derived from legacy sediment?
3. Is mill dam presence a necessary requisite for the aggradation of legacy sediment, or are other factors important/necessary?
4. How important are mill dam deposits as a sediment source relative to total bank erosion?
5. Is remobilization of legacy sediments and mill dam deposits contributing substantial proportions to the high sediment yields of streams across the Piedmont physiographic province?

MWRRRC funds were used to support an M.S. thesis project by Mitchell Donovan, who defended his thesis at UMBC and graduated in May 2014. The project allowed collection of data sufficient to answer the questions mentioned above for a selection of floodplain sites in different watersheds, across a range of stream orders and drainage areas. The results include quantitative data on cumulative sediment derived from bank erosion over multiple decades, partitioned to account explicitly for legacy sediment and for differences between stream reaches with and without mill dam influence. Study sites were

limited to Baltimore County and to valleys with minimal impact from urbanization in order to avoid the confounding influence of urban development on watershed hydrology and sediment budgets, which was beyond the scope of this study

b. Methods

i. Site selection

Multiple criteria were considered when selecting a set of sites (Figure 1) suited to represent the distribution of streams across Baltimore County. Historical archives of dam locations were imported into ArcMap in order to determine whether a stream reach was under the influence of a dam. The distribution of stream orders was then determined for the streams containing mill dams, along with the entirety of streams across Baltimore County. Additional criteria such as lithology, land use, and slope characteristics were compiled as secondary traits to assist in determining which sites would be best suited for comparisons. Subsequent to determining whether stream reaches displayed characteristic geomorphic features of dam absence or presence, field examinations and documentation were used to confirm the suitability of each site.

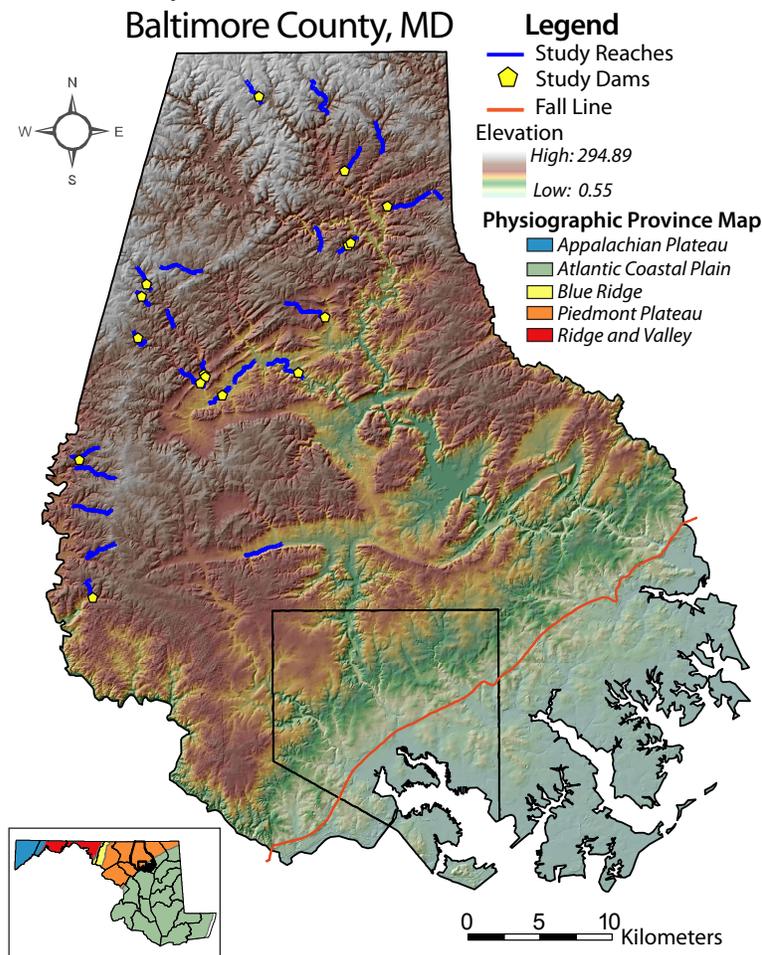


Figure 1: Study area of Baltimore County, Maryland. The inset map shows physiographic provinces. Blue lines and orange pentagons respectively represent stream reaches and mill-dam sites studied.

ii. Field reconnaissance

Field reconnaissance was used to determine (1) the absence/presence of a historic mill dam, (2) the location and depth of legacy material along streams, (3) the changes in bank height and stratigraphy along streams, especially near dam locations, (4) the diagnostic criteria for labeling stratigraphic layers as pre- or post-settlement (5) the suitable and representative locations for sampling material classified as pre- and post-settlement material. All potential sites were examined for these characteristics, and were discarded or selected as a site with or without a dam. Visual observations and sample data were recorded in a field notebook and backed up with photographs and GPS locations for the observations. Study reaches were selected to be representative, subject to constraints on accessibility, availability of both historic and contemporary data, presence of alluvial bottomland, and elimination of channel reaches affected by artificial structures. Upon establishing all of these characteristics and evaluating each site, 25 sites were chosen, 14 of which contained dams, while 11 were believed to be outside the influence of historic dams. The characteristics of our 25 sites are summarized in Table 1.

Table 1: General site characteristics and the site-averaged rates of erosion are provided, along with a legend at the bottom of the figure explaining the meaning of colors, abbreviations, and bold-faced results.

Summary of site characteristics												
Site	Mill Dam?	Stream Order	Shreve Magnitude	Area (km ²)	log(Drainage Area)	Study Length (km)	Slope (m/m)	Agriculture (%)	Forest (%)	Urban (%)	Quartz-Feldspar Schist (%)	Average Curvature
Bee Tree Run	No	4	102	23.23	3.15	4.25	0.0044	41.02	35.98	19.17	0	0.0017
Blackrock Run	No	4	37	5.81	1.76	3.51	0.0140	70.32	23.56	4.7	0	0.0047
Buffalo Run	Yes	3	42	7.53	2.02	3.46	0.0157	54.36	39.84	4.63	31.84	0.001
Chimney Branch	No	3	46	1.78	0.58	3.87	0.0247	8.15	57.17	14.37	0	0.0102
Cooks Branch	No	3	45	3.12	1.14	3.44	0.0210	19.74	67.95	5.62	77.4	0.0046
First Mine Branch	Yes	4	77	12.87	2.55	4.20	0.0103	51.31	42.85	4.22	64.24	0.0031
First MB Trib	No	3	11	3.35	1.21	0.91	0.0095	61.9	26.53	4.15	95.68	-0.004
Fourth Mine Branch	Yes	4	46	6.63	1.89	2.76	0.0099	37.56	42.23	12.55	0	0.0008
Jones Falls	No	5	217	33.06	3.50	3.20	0.0066	14.64	54.78	27.54	0	0.0057
Keyzers Run	Yes	3	25	3.10	1.13	3.40	0.0173	36.15	40.08	20.35	53.18	0.003
Little Falls	Yes	4	52	10.33	2.34	2.28	0.0098	66.11	27.25	6	0	0.0078
Little Piney Run	Yes	4	32	4.66	1.54	1.89	0.0230	64.47	30.79	5.28	0	0.0117
McGill Run (Butler)	Yes	4	321	16.20	2.79	3.39	0.0088	52.98	40.24	3.94	7.86	0.0053
McGill Run (Byerly)	Yes	3	24	4.60	1.53	2.10	0.0210	75.36	17.03	6.97	0	0.0083
Mingo Branch	No	3	15	2.05	0.72	2.10	0.0300	16.56	71.25	12.07	0	0.0055
Norris Run	No	3	38	5.61	1.72	4.10	0.0175	22.25	47.72	22.47	92.82	0.0083
Panther Branch	Yes	3	22	3.04	1.11	2.10	0.0330	16.27	20.28	20.65	35.95	0.0084
Piney Run (Mantua)	Yes	5	200	32.89	3.49	2.36	0.0065	59.06	32.63	6.75	3.6	0.0075
Piney Run (Mt. Zion)	No	5	146	21.16	3.05	1.43	0.0066	63.38	27.14	8	0	0.0016
Piney Run (Trenton)	Yes	4	41	7.95	2.07	2.11	0.0128	63.27	20.7	15.51	0	0.0107
Powells Run	Yes	3	12	1.82	0.60	2.00	0.0361	31.75	49.66	19.15	100	0.0042
Third Mine Branch	No	4	90	13.67	2.62	3.09	0.0103	50.76	40.88	5.46	0	0.0016
Western Run (Cuba)	Yes	6	1015	152.44	5.03	4.73	0.0026	51.83	37.55	8.08	17.87	0.0062
Western Run (Gadd)	No	6	664	99.46	4.60	3.12	0.0029	53.97	36.31	7.14	19.18	0.0038
Western Run (Mantua)	Yes	6	574	92.20	4.52	2.60	0.0032	47.59	35.46	5.82	19.99	0.0018

iii. Field sample collection

Stream bank sediment samples were taken from multiple transects throughout each site and were identified as presettlement sediment, legacy sediment, or recently deposited channel material using stratigraphic discontinuities in their color, grain size, and density, along with their location within the bank profile. Typical profiles exhibited a distinct contact between mineral rich layers of black to dark grey (Munsell system, 10YR2/1 to 7.5YR2.5/1) pre-settlement material, overlain by fine grained orange to brown (5YR4/6 to 7.5YR3/4) silty sands, typical of legacy sediments (Happ et al.,

1940; Jacobson and Coleman, 1986). For stratigraphic sequences not easily interpreted in the context of historic land patterns, we assigned samples to their “most probable” category in the field, and once in the lab, compiled their color, density, and bank position characteristics to confirm or re-assign their category.

Across all sites, we sampled 195 stream bank cores of known volume (100 – 200 cm³), of which 173 were used in determining characteristic bulk densities and 98 were wet sieved for particle size distributions. We converted the volume of eroded stream bank sediment into a mass using a bulk density of 1.13 Mg/m³, and the mass of deposition was determined using a bulk density of 1.42 Mg/m³. The number of samples per site ranged from 4 to 22, depending on the availability of clearly exposed streambanks. For each sample we recorded: (1) the height of the sample within the bank profile, (2) the primary color (using a Munsell chart), along with any interlaced colors, (3) the texture based on touch, (4) any potential compaction of sample, (5) a preliminary label of Presettlement, Legacy Sediment, or Point Bar, and (6) the thickness of pre- and post-European settlement material. Sampling error and uncertainty in density values arose from sediment packing, varying percent saturation and percent organic matter, presence of air pockets, and loss of sample in transportation, which was quantified by sample replicates from adjacent bank locations.



Figure 2. A field image of a stratigraphic profile and sample locations. A distinctive boundary is seen at the transition from pre- to post-settlement material at Western Run. The white tubes are samples before they were extracted.

Using the stratigraphic criteria established previously, we identified the presence of legacy sediment with reasonable confidence at all but one site and we measured the percent of bank material that could be classified as legacy sediment in 2 to 16 streambank exposures at each site. Because the proportion of legacy sediment fluctuated across exposures at each site, we calculated the site-average percent of bank material identified as legacy sediment. Continuous exposures along the downstream sites were counted as one sample because these exposures tended to contain higher than average proportions of legacy sediment and would lead to an overestimation of remobilized legacy sediment if counted as multiple measurements.

iv. GIS analysis of channel changes through time

In order to characterize the location of the historic stream channels, scanned images of Baltimore

County 1:2400-scale topographic maps were georeferenced in ArcMap and channel banklines were manually digitized from the channel edges depicted on the maps. In some cases, a single line was drawn on the historic maps, in which case the median channel width of the current channel was assigned as a buffer around the historic stream line. Current channels were delineated manually for each stream length using a combination of satellite imagery, hillshade, slope, and curvature grids. Local peaks and troughs in values of curvature, which is the derivative of slope, can be used to locate the edge of a channel or base of a streambank where other sources fail in doing so.

The delineations of the channels at each time period were overlaid and converted to discrete polygons of ‘Erosion’, ‘Deposition’, ‘EroDepo’ (indicating both erosion and deposition), or ‘No change’ (Figure 3). Concurrently, we generated DEMs of difference (DoDs) between the floodplain elevation raster (FER), channel elevation raster (CER), and lidar raster, which were clipped to the spatial extent of the Erosion, Deposition, or EroDepo layers and multiplied by bulk density to convert the volume to a mass of erosion or deposition. The DoD between the modern topography and CER represented the deposition and was therefore clipped to the Deposition and EroDepo layers. This deposition was usually in the form of lateral accretion deposits, or point bars, consisting of coarse sediment deposited as the channel migrated from its 1961 location. At the time of the historic maps’ delineation (1961), the EroDepo zone was occupied by a floodplain, which was eroded between 1961 and 2005 as the channel migrated laterally. Though this zone is partially occupied by a point bar deposit, the volume of sediment eroded from this area is the difference between the FER (red-dashed line) and CER (blue dashed-line). The area currently occupied by the channel has only been subject to erosion, so the volume missing between the FER and modern topography is equal to the volume of sediment eroded within this zone.

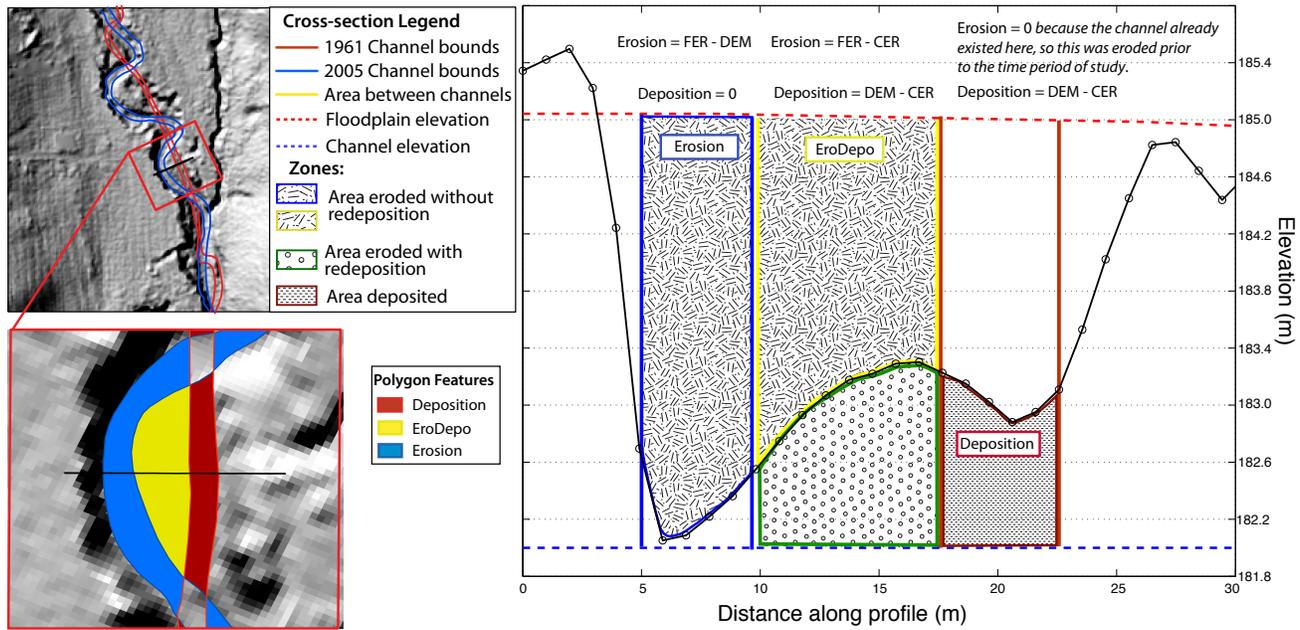


Figure 3. Planform and profile view of a channel illustrating the calculations of erosion and deposition. (Bottom left) An aerial view of the erosion, deposition, and erodepo zones found within the migrating channel of Piney Run (Top left). The black line indicates where the cross section (right) was extracted from. The different ‘geomorphic zones’ are expressed with unique hues and textures, illustrating how the volume of erosion/deposition was calculated within each.

The volumes of erosion and/or deposition were then multiplied by their respective densities to obtain a mass and then summed for each discrete zone (polygon) of Erosion, Deposition, or EroDepo.

The mass of erosion and deposition (Mg) were then summed for each entire site and divided by the length (0.94 – 4.73 km) and time elapsed (44 – 46 years) for each site to obtain the gross erosion and deposition rates (Mg/km/year). These rates will be described as the GER and GDR throughout the remainder of the paper. Subtracting the GDR from the GER obtained the net erosion rate (NER), which accounted for in-channel deposition along the site, but *not* deposition further downstream or on the floodplain. Finally, the site-specific average fraction of legacy sediment found in the stream banks was multiplied by the GER for each site to obtain the gross legacy sediment erosion rate (LSER).

v. Lateral migration calculations

In order to calculate lateral migration rate, the Channel Planform Statistics Tool (available from the National Center for Earth-Surface Dynamics Stream Restoration Toolbox, <http://www.nced.umn.edu/content/tools-and-data>) was used. The ‘Lateral Offset Measurement’ tool, (Lauer, 2006) estimates the mean lateral migration distance between two stream channel centerlines at equally spaced increments. For each point, the tool calculates the migration distance as the average length of four line segments extending to the adjacent stream channel centerline. The tool provided over 1000 measurements of migration for each stream, which were averaged for each site to look at general trends across the drainage network. The average rate of lateral migration (LM) was converted to the annual mass of stream bank sediment eroded per unit channel length (Mg/km/year), which were compared with the previous measurements of GERs to assess the *replicability* of the raster-based methods, but could not be used to validate the *accuracy* of our dataset.

vi. Statistics

Linear correlations were used as the primary exploratory statistic for assessing how remobilization rates varied in relation to independent watershed characteristics. The results of the correlations were useful for understanding patterns, but not for distinguishing causal relationships (McKillup, 2010). Regressions were used as inferential statistics when there was a good reason to hypothesize that the erosion rate may be predicted by a particular watershed characteristic. While we did not infer causation from the linear regression relationships, coefficients of determination provided a measure of strength for prediction of erosion rates using watershed characteristics.

vii. Extrapolations

The area selected for extrapolation covers a total of 1026 km² with 3624 km of total stream length outside the area of urban and suburban growth surrounding Baltimore City and has streams with drainage areas and land use patterns (primarily forested and agriculture) similar to our study sites (Table 2). Our streambank measurements covered a cumulative length of 72.4 km, which were used as a representative sample of basins draining a total of 267 km² within the area of extrapolation. An additional extrapolation was performed for the Western Run drainage basin (220 km²), which contained ten of our sites. Western Run drains into the Loch Raven Reservoir, which has TMDL requirements (MDE 2006) and long-term sedimentation records available (Dendy and Champion, 1978; Ortt et al., 2000; Wolman and Schick, 1967) for comparisons with our net stream bank sediment yields.

Table 2. The cumulative watershed and land use characteristics are compared for sites in this project and the area over which the results are extrapolated.

Characteristics of study basins and the areas of extrapolation					
	Characteristics		Land Use		
	Drainage Area (km ²)	Total Stream Length (km)	Agriculture (%)	Forested (%)	Urban (%)
Study area	267	828**	49.5%	37.2%	9.1%
N. Baltimore County Extrapolation Area	1026	3625	33.2%	46.6%	14.8%
Western Run Extrapolation Area	220	687	38.3%	38.9%	20.0%

***Represented by 72.4 km of channel length studied in this project.*

C. Principal results and discussion

i. Gross erosion, gross deposition, and net erosion rates

Gross streambank erosion rates ranged from 50.6 to 309.6 Mg/km/year and were strongly correlated with multiple variables, suggesting that the rate of streambank remobilization may be possible to predict with known watershed and channel characteristics. The regressions demonstrated strong correlations between GERs and independent variables including log-drainage area, log-Shreve magnitude, slope, lateral migration rate, bank height, and log-stream width (Figure 4). These variables are correlated with one another since they are all related to watershed contributing area, but each can still be used to understand relationships with erosion rates across the drainage network.

The magnitude of GDRs¹ generally increased more rapidly than GERs from smaller to larger streams, indicating there is increasing potential for in-channel deposition in downstream reaches. The ratio of channel bar deposition to gross erosion, ranged from 25 to 75%, was higher at sites with the largest drainage areas. However, field observations and sediment samples demonstrated differences in the grain sizes of in-channel deposits and stream banks indicating a maximum of half of the deposition found within channel deposits may be stream bank sediments.

The net erosion rates (NER), which accounted for both bank erosion and in-channel deposition, did not exhibit strong correlations with any independent variables excluding site averaged bank height ($r = 0.7$). Weak correlations are likely due to the multitude of factors that influence the net exchange of sediment within a stream, supporting previous research highlighting the complex nature of sediment erosion and storage across space and time (Gellis and Brakebill, 2012; Schumm and Lichty, 1965; Walling, 1983; Wolman and Schick, 1967).

¹ GDRs accounted for in-channel deposition along the site, not downstream or floodplain deposition.

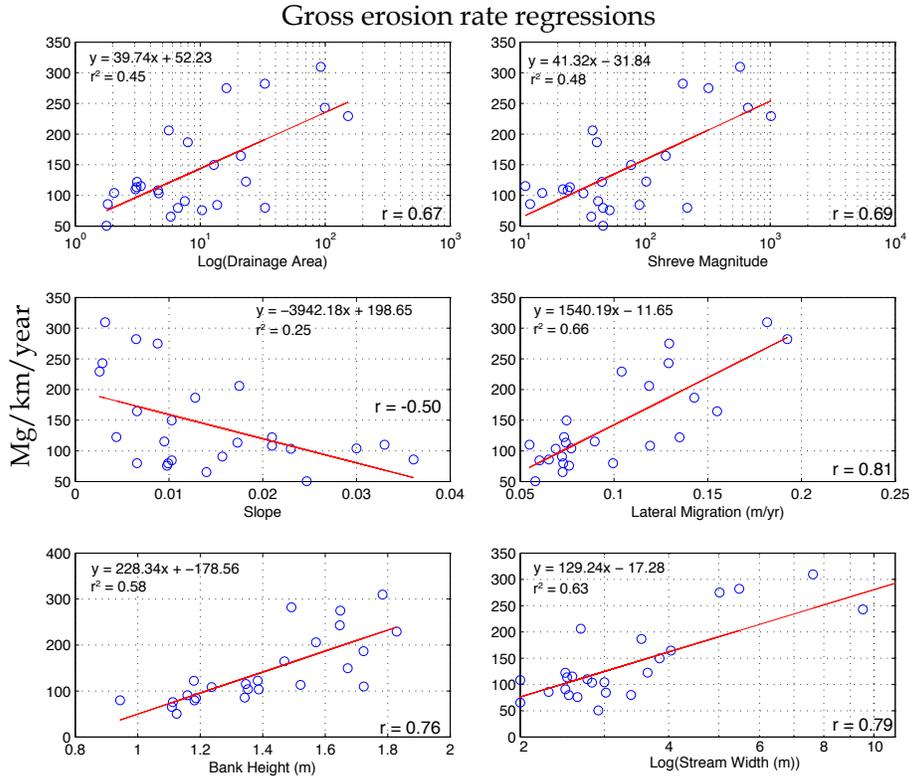


Figure 4. Linear regressions tested for variables that exhibited strong correlations with gross erosion rates. Within each graph, the linear regressions and r^2 -values are in the upper left, while the correlation coefficient is in the bottom right.

ii. Legacy sediment storage and erosion rates

Using the stratigraphic criteria established previously, we identified the presence of legacy sediment with reasonable confidence at all but one site and we measured the percent of bank material that could be classified as legacy sediment in 2 to 16 streambank exposures at each site. While there was a significant ($r^2 = 0.35$, $p = 0.002$) increasing trend in *average* legacy sediment thickness across our sites, reach-scale variability in legacy deposits demonstrated that local influences on legacy sediment storage are important and that the extent and thickness of legacy deposits is variable across a watershed.

The gross legacy sediment erosion rate (LSER) ranged from 3 – 220 Mg/km/year and represented 6 to 90% of the gross erosion across our sites. Multiple variables, such as log-drainage area, stream order, log-Shreve magnitude, slope, and average channel width, had strong correlations ($r^2 > 0.50$) with LSERs, indicating that a large amount of variability in LSERs can be attributed to location within the drainage network. Excluding the local variability, the strong correlations indicate that legacy sediment storage may be increased at large drainages due to the area available for storage in wide alluvial valleys.

iii. Lateral migration rates

The site-averaged lateral migration rates varied between 0.06 and 0.19 m/yr, with higher rates at larger drainage areas. Some watershed characteristics, such as log-drainage area, log-Shreve magnitude, log-stream width, and stream order, had moderately strong correlations with rates of lateral migration, but none were strong predictors of migration rates. Once the lateral migration rates were converted to estimates of bank erosion as Mg/km/yr, we compared them to the GER results described in Section i.

Differences expressed as a fraction of the gross erosion rate ranged between 0 and 52%; 16 of the 25 sites had differences less than 20% (Table 3).

Table 3. Comparison of two independent methods used to calculate gross erosion rates. The 'Estimated' values are those derived from the product of the lateral migration rates, site-averaged bank height, and site length.

Site	Lateral Migration	Average Bank	Site Length	Gross Erosion (Mg)		Gross erosion rate (Mg/km/yr)		Difference
	(m/year)	(m)	(km)	Estimated	Original	Estimated	Original	(%)
Bee Tree Run	0.073	1.37	4.25	21,213	22,889	113	122	7%
Blackrock Run	0.073	1.10	3.51	13,894	10,085	90	65	-38%
Buffalo Run	0.072	1.15	3.46	14,245	13,815	94	91	-3%
Chimney Branch	0.058	1.11	3.87	12,425	8,616	73	51	-44%
Cooks Branch	0.135	1.17	3.44	26,920	18,480	178	122	-46%
First Mine Branch	0.075	1.65	4.20	25,781	27,648	140	150	7%
First Mine Branch- Trib	0.090	1.33	0.91	5,428	4,634	135	115	-17%
Fourth Mine Branch	0.073	1.17	2.76	11,690	9,673	96	80	-21%
Jones Falls	0.100	0.93	2.90	13,381	10,186	105	80	-31%
Keyzers Run	0.067	1.50	1.28	6,686	6,682	114	113	0%
Little Falls	0.076	1.10	2.28	9,480	7,609	95	76	-25%
Little Piney Run	0.069	1.37	1.89	8,881	8,594	107	103	-3%
McGill Run at Butler Rd	0.129	1.63	3.39	35,554	41,009	238	275	13%
Mcgill Run at Byerly Rd	0.119	1.22	1.75	12,682	9,396	165	108	-52%
Mingo Branch	0.077	1.34	2.10	10,786	9,613	117	104	-12%
Norris Run	0.119	1.55	4.10	37,586	37,168	208	206	-1%
Panther Branch	0.055	1.70	2.10	9,694	10,162	105	110	5%
Piney Run at Mantua Rd	0.192	1.47	2.36	33,298	29,295	321	282	-14%
Piney Run at Mt. Zion Rd	0.155	1.45	1.43	16,008	10,354	254	165	-55%
Piney Run at Trenton Rd	0.143	1.70	2.11	26,678	18,113	275	187	-47%
Powells Run	0.065	1.33	2.00	8,618	7,552	98	86	-14%
Third Mine Branch	0.060	1.17	3.09	10,866	11,487	80	84	5%
Western Run at Cuba Rd	0.104	1.83	4.73	44,762	47,731	215	229	6%
Western Run at Gadd Rd	0.129	1.63	3.12	32,617	33,336	238	243	2%
Western Run at Mantua Mill Rd	0.182	1.76	2.60	41,411	35,418	362	310	-17%

iv. Extrapolated stream bank sediment yields

The extrapolated rates of gross stream bank erosion for 1026 km² of Northern Baltimore County were $2.62 \times 10^5 (\pm 7.28 \times 10^4)$ Mg/year over the past 44 years, a total of $1.15 \times 10^7 (\pm 3.20 \times 10^6)$ Mg. The largest sediment contributions (41%) of bank erosion were from first order streams, with decreasing inputs from each higher stream order (Figure 5). The sediment inputs of each stream order were similar to the cumulative stream length by stream order. However, with respect to the streambank sediment contributions, the first and second order streams are slightly underrepresented, while the proportion of sediment from third through sixth order streams is slightly greater than their fraction of cumulative channel length (Figure 5, upper right).

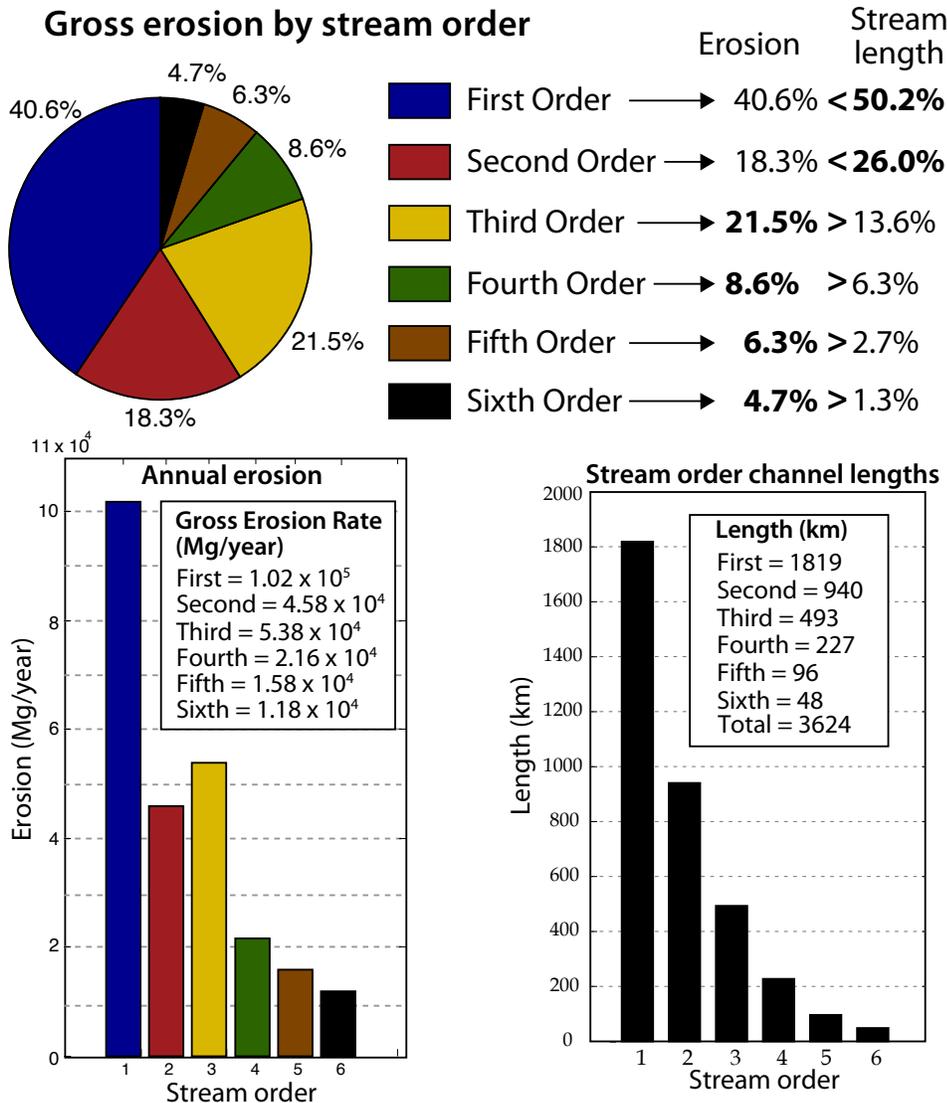


Figure 5. Graphs illustrating the proportion of sediment input from each stream order. (Top) A pie chart and table illustrate the percent of the gross erosion derived from each stream order, which are compared with the fraction of stream length. The bold-values illustrate whether the fraction of erosion or channel length is greater at each stream order. (Bottom) The bar charts illustrate reductions in sediment input and channel length at higher stream orders.

Legacy sediments comprise 49.3% of the total gross stream bank erosion and followed the same decreasing trend as gross sediment contributions with respect to increasing stream order- contributing 12.6%, 12.2%, 12.0%, 6.1%, 4.1%, and 3.9% of the total erosion. However, because legacy sediment deposits are thicker downstream, the trend of decreasing contributions is less pronounced than the trend in gross streambank erosion. Legacy sediment comprised 31.0% of the gross erosion from first order streams, but increased to 85.1% of the gross stream bank erosion derived from sixth order streams.

Table 4. Final estimates of net sediment yield and net sediment flux. The estimates account for in-channel and floodplain deposition.

Summary of extrapolated sediment flux and sediment yield								
	Northern Baltimore County (1026 km ²)				Western Run (222 km ²)			
	Stream bank sediment		Legacy sediment		Stream bank sediment		Legacy sediment	
	Gross	Net	Gross	Net	Gross	Net	Gross	Net
Annual Erosion (Mg/yr)	250,631	76,284	127,536	43,895	52,303	15,222	26,882	9,208
Sediment Yield (Mg/km²/year)	244	74	124	43	235	68	121	41

	Chimney Branch (1.78 km ²)				Powell's Run (1.82 km ²)			
	Stream bank sediment		Legacy sediment		Stream bank sediment		Legacy sediment	
	Gross	Net	Gross	Net	Gross	Net	Gross	Net
Annual Erosion (Mg/yr)	277	69	17	6	173	43	188	66
Sediment Yield (Mg/km²/year)	156	39	10	3	95	24	103	36

Although floodplain and downstream redeposition were not measured directly, their cumulative rates were estimated based on previously published results of floodplain sedimentation rates that range from 1.3 to 8.4 mm/yr in watersheds with similar land use history and/or physiographic traits (Happ 1945; Leopold et al. 2005; Allmendinger et al. 2007; Gellis et al. 2009; Trimble 2009). Using these rates, the annual deposition per unit length (Mg/km/yr) was estimated assuming a third of the valley is an active floodplain that traps sediment annually, 50% of the material trapped is from uplands, and that the deposited sediment has a similar density to the samples from this study (1.13 g/cm³).

Our estimates of net bank erosion are equivalent to 71% (47–95%) of long-term Piedmont sediment yields found in Gellis (2009). Similar estimates of stream bank sediment contributions (50 – 98%) are found in previous research published for Piedmont streams (Costa 1975; Trimble 1997; Schenk and Hupp 2009; Shilling 2009; Mukundan et al. 2011; Gellis and Noe 2013). Additionally, our legacy sediments yields were 41% (31-51%) of Piedmont sediment yield values cited by (Gellis et al. (2009). Similar results from Schenk and Hupp (2009) indicated 63% of the present sediment yield was likely coming from stored legacy sediments. Additionally, the results from Walter et al. (2007) indicated that legacy sediments accounted for 45 to 122% of the suspended sediment measured at the Conestoga River mouth.

The net stream bank sediment yields of Western Run (Figure 6) drainage basin (222 km²), were compared to estimates of sediment accumulation for the Loch Raven reservoir from 1917 to 1999 (Ortt et al. 2000). Although the Western Run watershed is 38% of the total area draining into the Loch Raven reservoir, its net stream bank erosion was equivalent to 34% of the reservoir's average accumulation rate. The net stream bank erosion currently represents 50% of the TMDL (28,925 Mg/year) established for the reservoir in MDE (2006).

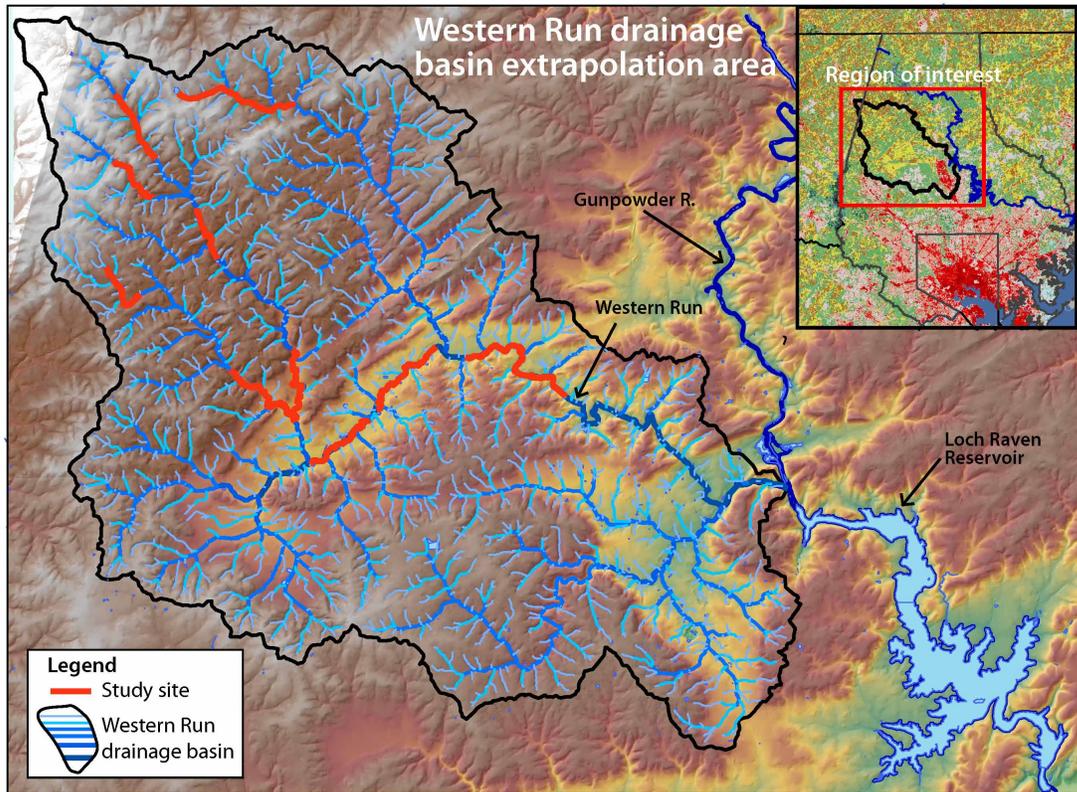


Figure 6. Western Run drainage basin, 220 km². The ten red portions of the stream network represent our study sites found within the drainage basin. Three sites were along the main stem of Western Run.

vi. Mill dams

Through field assessments and analysis of geospatial data, we demonstrated that legacy sediment is present along channels in our study area at sites with and without the influence of mill dams (Figure 7). Multiple tests at varying spatial scales were used to answer the fourth research question- How important are mill dams as a source of sediment relative to total bank erosion entering tributaries to the Chesapeake Bay? The evidence gathered from 14 mill dams indicates that on average, mill dam deposits will contribute 14.8% (± 5.4) more erosion than stream banks outside the influence of mill dams. Comparing the sediment inputs from mill dam deposits to stream bank erosion upstream and downstream of the channel reach influenced by mill dams demonstrated variable, but substantial, levels of excess erosion (0 – 34%) at the reach-scale. From seven site-specific comparisons of reach-scale rates of gross erosion, gross erosion was higher along five streams with mill dams, but the increased erosion also co-occurred with locally steeper slopes for six comparisons. While the data could not separate the influence of mill dams from the influence of channel gradient, the results support research indicating channel gradient is an important factor influencing bank erosion (Leopold and Bull, 1979) in addition to demonstrating that mill dams *may* be associated with higher rates of bank erosion.

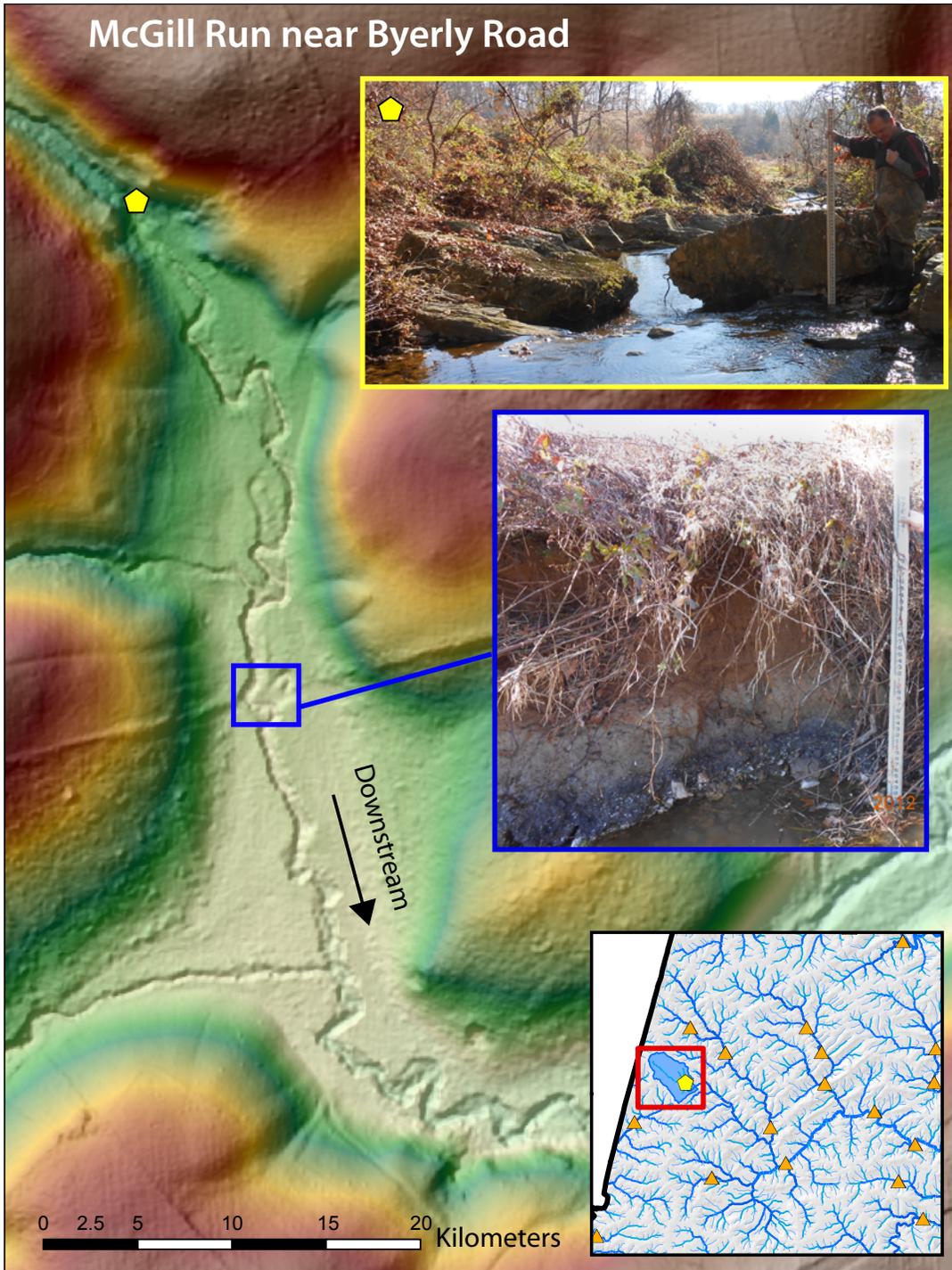


Figure 7. A hillshade map of McGill Run near Byerly Road (4.6 km²). The accompanying images illustrate the remnants of a breached dam (yellow pentagon) upstream of legacy sediment (blue inset figure) overlying a gleyed horizon and pre-settlement material.

There were no statistically significant differences in the distributions, medians, or trends of erosion when groups of sites with and without mill dams were compared across a range of drainage areas. Though a low sample size may have reduced the ability to detect significant differences with the

Wilcoxon Rank-Sum and Kolmogorov-Smirnov tests, the results suggest that statistically significant differences in rates of bank erosion are not likely to exist between samples of streams with and without mill dams. However, these statistics did not assess potential differences along portions of the drainage network, which was possible through comparison of LOESS regressions of erosion rates for streams with and without mill dams. The results of the comparison highlighted nonlinear increases in the rates of erosion along low- to mid-basin reaches (10 to 25 km²), along with significant differences in erosion rates (based on 95% confidence intervals) for streams from 20-40 km². These results suggest that mill dams may increase erosion rates along *portions* of the drainage network- distinct from the preceding results indicating no significant differences existed when drainage area was not considered.

d. Significance

i. Stream bank erosion and legacy sediments

From the collected data and measurements, it appears likely that channels are currently net exporters of sediment, but floodplains and channel margin deposits remain active storage sites of fine-grained streambank sediments, in agreement with previous results (Hupp et al., 2010; Skalak and Pizzuto, 2010; Walling et al., 1998). Additionally, the measurements and fieldwork indicated legacy sediments generally constituted a greater proportion of the stream banks along larger streams, and are therefore a larger fraction of the erosion along from such streams. Increasing proportions of legacy material along downstream reaches reflect the fact that storage capacities were greater along such wide valleys with low gradients during the period of heavy deforestation and increased agricultural land use, leading to increased legacy sediment aggradation from the late 1800s through the early 1900s.

Extrapolated bank erosion measurements were a large percent (47 – 95%) of long-term average sediment yields estimated by Gellis et al. (2009), which is in agreement with investigations across the Piedmont (Costa 1975; Trimble 1997; Schenk and Hupp 2009; Shilling 2009; Merritts et al. 2010b; Gellis and Noe 2013) indicating stream bank sediments are a large source of sediment. After accounting for potential downstream redeposition, our extrapolations also indicated that fine-grained legacy sediments may constitute a large proportion (31 - 51%) of suspended sediment yields, similar to previously reported values (Schenk and Hupp, 2009; Wegmann et al., 2012). Because Western Run drains only 38% of the contributing area to Loch Raven reservoir, our results suggest that stream bank sediments may represent a large fraction of sediment yields reaching the reservoir if our estimates of downstream deposition are considered reasonable. Although this study focuses on sediment contributions from remobilization of floodplain sediment by bank erosion, it is important to note that upland sources have also been cited with similar and even higher contributions to Piedmont watershed sediment yields (Allmendinger et al., 2007; Gellis and Noe, 2013; Gellis et al., 2009; Smith et al., 2011).

ii. Mill dams

The results of stream bank erosion were analyzed on multiple spatial scales in order to assess the local and regional impact of mill dams on bank erosion. Along individual study reaches, the excess sediment from each mill dam deposit was quantified and compared to the erosion from nearby stream banks unaffected by the dam. Our results suggest that on average mill dam deposits generate 14.8% more sediment than typical channel reaches along the same stream, comparable to the relative contributions described by Wegmann et al. (2012). Integrating our results from analyses at multiple spatial scales, it is reasonable to conclude that elevated erosion rates exist along reaches with mill dams (Walter and Merritts 2008; Pizzuto and O'Neal 2009; Wegmann et al. 2012), but that the additional

sediment is not a dominant fraction of the total erosion along the larger drainage network (Rhoades et al. 2009; Hupp et al. 2013). However, mill-dam deposits may serve as hotspots of erosion and may have the potential to impact an entire fluvial system in watersheds with a high density of mill dams, such as exists in Conestoga Creek.

Mill dams may lead to increased bank erosion along low- to mid-range channels (10 – 40 km²), where stream power (and therefore transport capacity) is rapidly increasing, but cannot typically provide sufficient capacity for sediment storage to match the transport capacity. When augmented with increased sediment storage behind mill dams, peaks in stream power along low- to mid-range streams with narrow valleys and steep gradients may experience the greatest increase in bank erosion as the result of mill dams. We hypothesize that the presence of mill dams may supplement the supply of stored alluvial sediment along lower-order streams to match the high transport capacity corresponding to peaks in stream power.

Our results demonstrate the importance of considering spatial and temporal scales when drawing conclusions about the importance of mill dams. Results that appear to differ in previous reports may be a reflection of the spatial scales considered in the research. In this project, we have addressed the call to compare watersheds with and without mill dams (Bain et al. 2008) and conclude that no single model can account for the role of mill dams in sediment transport. Though remains of mill ponds have the potential to contribute more sediment than typical streambanks, the evidence suggests they should not be universally regarded as dominant sources of sediment from Piedmont tributaries to the Chesapeake Bay.

2. Publication citations associated with the research project

There have been no publications associated with the work up to this point. A poster was presented in the Spring of 2013 at the Amtrak Conference held at John's Hopkins University for a group of geomorphologists from throughout the mid-Atlantic region. In addition Mitchell Donovan has attended two NSF funded workshops, including- *EarthCube Geochemistry, Biogeochemistry, and Fluvial Sedimentology Workshop*, and, *Critical Zone Research LIDAR Workshop*, which were both held in Boulder, CO. The project and methods were discussed and presented with an international group of earth scientists. He also presented a poster in San Francisco at the AGU 2013 Fall Meeting. This April, Mitchell formally presented his results in the "Peculiarities of Perviousness" session at the Chesapeake Bay Program's Scientific and Technical Advisory Committee (STAC) workshop, in order to aid managers and scientists developing Phase 6 of the Chesapeake Bay Watershed Model (CBWM). The workshop was held in Annapolis, and a PDF of the presentation has been posted to the STAC webpage (http://www.chesapeake.org/stac/presentations/230_Track%205%20Donovan.pdf). Recently, the USGS Maryland Water Science Center asked him to present his work in their ongoing Water Quality seminar series, which occurred in June 2014.

A manuscript is in preparation for submission to Geomorphology during summer 2014. Two additional publications are being planned for submission to journals selected from among the following: Geomorphology, Earth Surface Processes and Landforms, Journal of the American Water Resources Association, or Water Resources Research.

3. Number of students supported (with MWRRC funds and required matching funds)

MWRRC funds have provided support for one M.S. student and two undergraduate research assistants. Mitchell Donovan completed his M.S. thesis, defended it successfully in Spring 2014, and was awarded

the M.S. degree in Geography and Environmental Systems in May 2014. The first undergraduate research assistant, Andrew Bofto, is pursuing a career in environmental engineering. He has aided in all aspects of the project, including fieldwork, laboratory measurements, and ArcMap analyses. We also had a volunteer, part-time undergraduate assistant, who aided with the processing of sediment samples and GIS work during June and July 2013.

4. Notable achievements and awards resulting from the work.

Mitchell Donovan was awarded two NSF support grants to attend the EarthCube and Critical Zone Observatory (CZO) LiDAR workshops in Boulder, CO in April 2013 and May 2014. He also received support from UMBC to attend a Legacy Sediment workshop at Franklin and Marshall College in Spring 2012. In the course of attending the AGU conference, EarthCube workshop, CZO workshop, the Amtrak Club conference, the Southeastern Friends of the Pleistocene field conference, and a locally hosted trip visiting field sites associated with this project, colleagues from other research institutions have expressed interest in the results anticipated from this research. Researchers Dorothy Merritts, from Franklin & Marshall College and Milan Pavich of the U.S. Geological Survey in Reston have traveled to Baltimore County to visit the field sites with us and to exchange ideas and suggestions. Milan obtained radiocarbon dates of samples taken from multiple field sites to aid the interpretation of geomorphic features in the field. Allen Gellis of the U.S. Geological Survey MD-DE-DC Water Science Center is a member of Mitchell's thesis committee and a coauthor on the first manuscript currently being prepared for submission, and has also participated in multiple field trips and provided useful guidance on a range of technical topics. Verbal and written communication with other researchers provides ongoing feedback and suggestions to improve the work.

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An Innovative Learning Tool in Communicating Flood Risk Management

Basic Information

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Start Date:	1/12/2012
End Date:	8/31/2013
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Congressional District:	MD-005
Research Category:	Social Sciences
Focus Category:	Education, Management and Planning, Floods
Descriptors:	
Principal Investigators:	Bahram Momen

Publications

There are no publications.

Completion Report for MWRRC Project 2012MD270B
Reporting Period: 1 Mar 2013 – 28 Feb 2014; PI: B. Momen
An Innovative Learning Tool in Communicating Flood Risk Management

Prepared by: V. Beth K. Olsen and Bahram Momen

I. Summary

This grant supplemented and supported 2012MD299S (USGS Award no. G12AP20058) for the project entitled “The Effectiveness of a Computer-Assisted Decision Support System Using Realistic Interactive Visualization as a Learning Tool in Flood Risk Management,” in advancing the field of flood risk management by using technology to bridge the gap between science and decision-making.

Research Objectives, Methods, Findings and Significance

Reported in details in the 2014 Annual Progress Report for 2012MD299S (USGS Award No. G12AP20058).

II. Publications

None to date.

III. Students supported

Students supported by this project are the same as those supported under 2012MD299S. To avoid double-counting, they are not listed here.

IV. Notable achievements and awards resulting from the work

- The students supported by this grant completed extensive GIS training. The undergraduates, Masters and Ph.D. students completed three modules in the Environmental Science Research Institute (ESRI) ArcGIS 10™ (ESRI 2012) and eleven modules in ESRI™ HAZUS (ESRI 2012) online training. One Ph.D. student completed the FEMA Emergency Management Institute “HAZUS for Floods” course.
- Ph.D. candidate, V. Beth K. Olsen, successfully defended her dissertation, “Proposing a realistic interactive visualization model and testing its effectiveness in communicating flood risk.” Her dissertation project was funded by this grant.
- Several presentations have been given in scientific and professional conferences

Award--The Effectiveness of a Computer-Assisted Decision Support System Using Realistic Interactive Visualization as a Learning Tool in Flood Risk Management

Basic Information

Title:	Award--The Effectiveness of a Computer-Assisted Decision Support System Using Realistic Interactive Visualization as a Learning Tool in Flood Risk Management
Project Number:	2012MD299S
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Principal Investigators:	Bahram Momen, Kaye Lorraine Brubaker

Publications

1. Olsen, V. Beth Kuser, Cynthia McCoy, and Bahram Momen. "HAZUS Flood Risk Analysis: Regional vs Local Data," Poster Presentation, University of Maryland Bioscience Day, College Park: PS 35 Environmental Science: November 27, 2012.
2. Olsen, V. Beth Kuser, Cynthia McCoy, and Bahram Momen. "HAZUS Flood Risk Analysis: Regional vs Local Data," Poster Presentation, University of Maryland Marine, Estuarine, and Environmental Science Graduate Program 2012 Colloquium, Institute of Marine and Environmental Technology: PS 26: October 19, 2012.

**2014 MWRRC Annual Progress Report for Award No. 2012MD299S
Reporting Period: 1 Mar 2013 – 28 Feb 2014; PI: B. Momen**

**Effectiveness of a Computer-Assisted Decision Support System Using Realistic
Interactive Visualization as a Learning Tool in Flood Risk Management
(USGS Award No. G12AP20058)**

V. Beth Kuser Olsen and Bahram Momen

I. Research Summary

Results from this project will be useful in the field of flood risk management by using technology to bridge the gap between science and decision-making on the local community level. Those in coastal, tidal bay, and riverine communities have a history of flood risk that will likely increase in the future due to climate change and other factors. This requires more effective communication of flood risk and risk-reduction options, and methods of initiating action to reduce risk among stakeholders (those affected directly by flooding). Currently, flood risk and risk reduction options are communicated to the stakeholders by in flood risk management meetings using a set of dynamic models such as the Multi-hazard Loss Estimation Methodology (HAZUS) designed for the U.S. Federal Emergency Management Agency (FEMA). HAZUS is a computer-assisted decision support system (DSS) aided by geographic information system (GIS) to illustrate various flood scenarios during flood risk management meetings to facilitate collaborative discussions about risk and risk reduction options among meeting participants. Use of HAZUS requires expensive software and high-capacity laptop computers run by experienced technicians.

In this study, we propose a model with improved user interface capabilities, the Stakeholder-built DSS, in which meeting participants construct their own models. By doing so, stakeholders use realistic interactive visualization as a learning tool. Realistic visualization represents scientific information using virtual reality scenarios. The intent is to add drama to the scenarios while adhering to representation of accurate scientific information. This DSS method may trigger stakeholders' awareness of risk based primarily on emotional response to the images (Sheppard and Meitner 2005). Furthermore, direct participation of stakeholders in the construction and analysis of their models (referred to as interactive visualization) can lead to the stakeholders' increased understanding of the concepts and retention of the outcomes. This method allows the learner to match the visual representation of the activity to her/his mental representation through awareness, metacognition, and reflexive learning in order to improve the individual or group understanding of concepts. Awareness of the scenario being modeled is enhanced by the constant attention required of the model-builder during construction. Metacognition results from the accumulation of information about the scenarios within the memory of the model-builder as multiple steps are completed during model construction. Reflexive learning occurs as the model-builder repeatedly makes neurological connections between hand-eye coordinated motions and the cognitive information about the scenario being modeled.

In this research, the effectiveness of the HAZUS and Stakeholder-built DSS methods were examined by conducting FEMA-endorsed flood risk management meetings in ten randomly-selected communities in FEMA Region III, the mid-Atlantic area of the USA. Data were collected from participants through pre- and post-surveys and follow-up interviews.

Demographics of the ten communities studied were compared to those for the FEMA Region III population, and showed that the population was represented well by the ten communities

studied with the exception that the meeting participants were older, English-only speakers, better educated, from incomes above \$35,000 (2013 U.S. dollars), and more likely to own a home than the population. The Stakeholder-built DSS was as effective as the FEMA's HAZUS DSS in communicating flood risk and risk-reduction options. Both methods equally increased participants' intent to initiate action to reduce their risk. However, the cost of the HAZUS model was approximately six times higher and it was much less user friendly than the Stakeholder-built model.

Problem Statement and Research Objectives

This project tested the effectiveness of a computer-assisted decision support system (DSS) that uses realistic interactive visualization in combination with collaborative learning to (1) increase stakeholders' knowledge of risk, (2) increase stakeholders' knowledge of risk-reduction options, and (3) initiate action to reduce risk. The realistic interactive visualization DSS method was compared to the Multi-hazard Loss Estimation Methodology (HAZUS) developed and presently used by the Federal Emergency Management Agency (FEMA).

Objective I: Does a computer-assisted decision support system (DSS) using a realistic interactive visualization model, the Stakeholder-built DSS, significantly increase knowledge of flood risk communicated to stakeholders? How does that compare to the FEMA HAZUS DSS?

Objective II: Does the Stakeholder-built DSS that uses realistic interactive visualization significantly increase knowledge of flood risk-reduction options communicated to stakeholders? How does that compare to the FEMA HAZUS DSS?

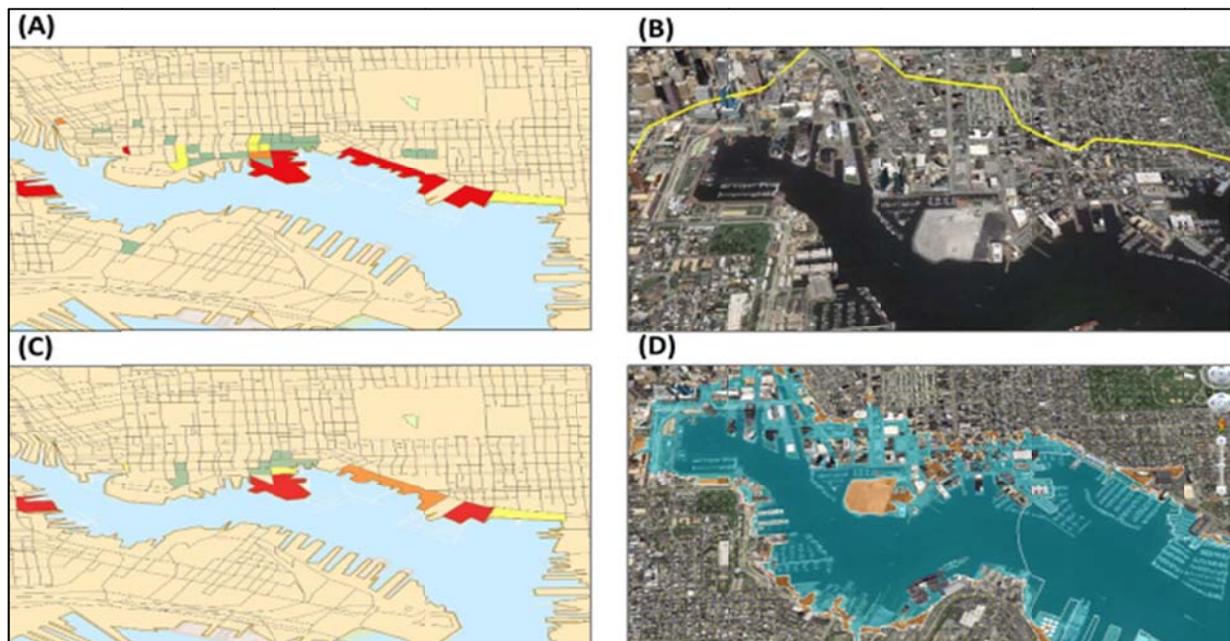
Objective III: Does the Stakeholder-built DSS, which uses realistic interactive visualization, significantly increase intent to take action to reduce flood risk among stakeholders? How does that compare to the FEMA HAZUS DSS?

Demographic Differences in Access to Flood Risk Communication: Do all demographic sectors of the population have access to information through participation in community-level flood risk management meetings?

Methods

Overview of Experimental Design for Quantitative Analyses: Objectives I, II, and III. The Stakeholder-built DSS method and the HAZUS DSS method were tested at local community flood risk management meetings in ten randomly-selected communities in FEMA Region III. Each flood risk management meeting was two hours in duration. At each, the research project was introduced and three scenarios, past, present, and future flood risk, were introduced. Following collaborative discussions among the participants about their flood risk, risk-reduction options were introduced and a discussion of the costs and benefits of implementing these options was facilitated by the researchers. In the meetings, past flood risk was represented by a recent flood event that exploratory interviews conducted prior to the meeting indicated most participants would remember (Figure 1: A and B). This scenario was designed to encourage confidence in the models. If the model illustrated flooding the participants remembered in the past, it was reasoned they would trust the model when probabilistic flood predictions for the future were introduced. Present flood risk was represented in both the HAZUS and Stakeholder-built DSS methods by the FEMA digital Flood Insurance Rate Map (DFIRM) flood hazard zone delineations for the 1% annual flood risk, previously known as the 100-year flood risk (Figure 1: C and D).

Figure 1: Model output illustrated historic (past) flooding scenario using (A) the Multi-hazard Loss Estimation Methodology (HAZUS) computer-assisted decision support system (DSS) method and (B) the Stakeholder-built DSS method. Model output illustrated present flood risk using (C) the HAZUS DSS method and (D) the Stakeholder-built DSS method.



In Figure 1A and C, red indicated greatest damage resulting from the flood scenario. Orange, yellow and green indicated decreasing levels of damage in that order. Tan indicated areas where data was not available. The Stakeholder-built DSS method showed (Figure 1B) historic (past) and (Figure 1D) present flood risk using Google Earth™ images presented to meeting participants. In (Figure 1B) the yellow line represented the estimated upper limit of flood waters during the historic storm event. The area between the yellow line and the image of water (black area) represented the area flooded during the historic event. In (Figure 1D) present flood risk was illustrated in the Google Earth™ image with a geographic information systems layer representing the U.S. Federal Emergency Management Agency National Flood Hazard Layer in blue (U.S. State Department Geographer, EuropaTechnologies, et.al. 2013).

Anticipated future flood risk was determined based on the best available data from multiple sources. Sources included in this determination were:

1. The Intergovernmental Panel on Climate Change Working Group II 2013 Report (IPCC 2013)
2. Report of the Maryland Commission on Climate Change, Adaptation and Response and Scientific and Technical Working Groups 2010 Phase II Report (Griffin, Boesch, et.al. 2010)
3. FEMA recommendation to raise structures to a two-foot freeboard above base flood elevation as a precautionary measure in addressing future flood risk (Bollinger 2013). Freeboard is the space between the expected flood height and the lowest horizontal component of the structure (FEMA 2010).
4. The opinion of the city or county planning department flood risk manager(s) based on their knowledge of flood risk within their jurisdiction.

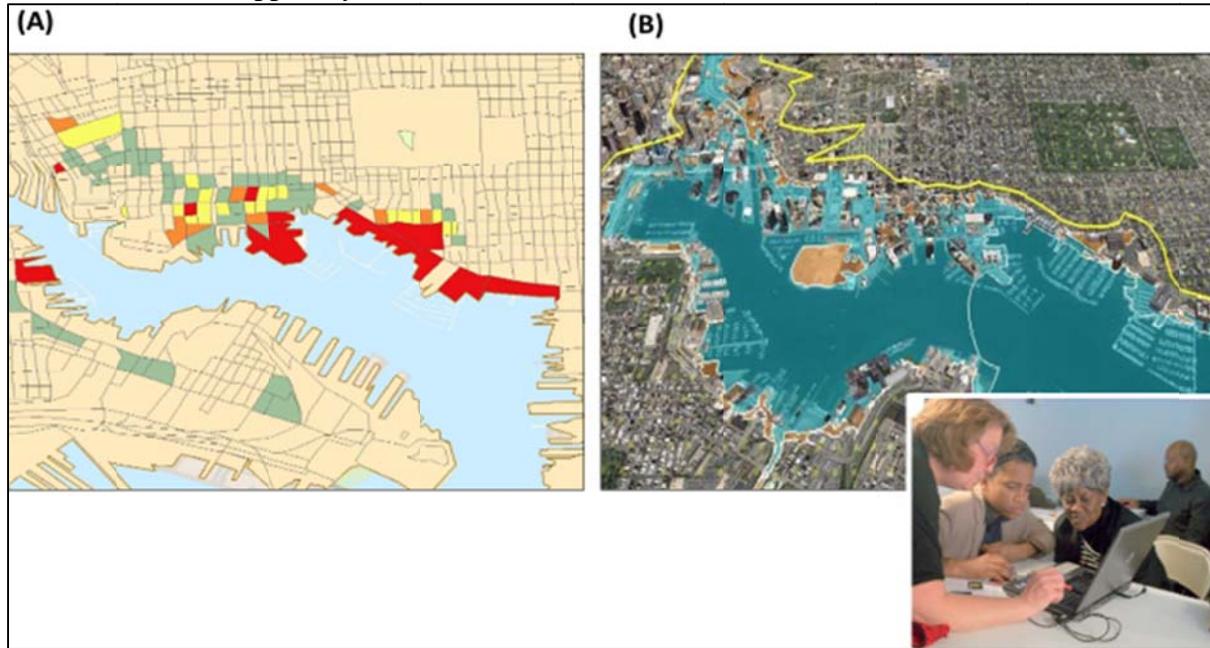
Information from all of the above sources (Table 1) was combined to determine the scenario that best illustrates the “anticipated future flood risk projected over the next 50 years” during the flood risk management meetings.

Table 1: Factors included in determining the best “anticipated future flood risk projected over the next 50 years”

Drivers of projected climate change-related flooding in U.S. Federal Emergency Management Agency Region III	Source
Sea level rise of 0.5 to 3 feet projected by 2050 in coastal waters due mainly to ocean warming	Intergovernmental Panel on Climate Change (IPCC 2013) Maryland Commission on Climate Change (MCCC) (Griffin, Boesch, et.al. 2010)
Higher storm surges due mainly to sea level rise	IPCC 2013 MCCC City/county flood risk manager(s)
Increase in high tides in the bays and tidal rivers due mainly to sea level rise	IPCC 2013 MCCC City/county flood risk manager(s)
Land subsidence due mainly to Greenland glacier melt and groundwater depletion	IPCC 2013 MCCC
Larger spring fresh-its (high velocity and volume of water in streams, rivers and bays due to run-off from snowmelt and rain during the first large rain storms in early spring)	MCCC
In the summer, more episodic tropical downpours occurring between periods of drought	IPCC 2013 MCCC
Increases in stormwater runoff due mainly to increases in intensity of winter rain events, spring fresh-its, summer tropical downpours, and changes in landuse resulting in increases in impermeable surfaces and decreases in vegetative riparian and coastal buffers.	IPCC 2013 MCCC City/county flood risk manager(s)

Anticipated future flood risk projected over the next 50 years was represented in the HAZUS DSS by the FEMA 0.2% annual flood risk, previously known as the 500 year flood risk (Figure 2A). In the Stakeholder-built DSS, future flood risk was represented by a two to three-foot increase in flood elevation above the FEMA DFIRM 1% annual flood hazard zone (Figure 2B). These choices were based on the opinions of the city/county planning department flood risk managers, the FEMA Region III Mitigation Outreach Coordinator, and the researcher leading this project.

Figure 2: Model output illustrated scenarios for the anticipated future flood risk projected over the next 50 years using (A) the Multi-hazard Loss Estimation Methodology (HAZUS) computer-assisted decision support system (DSS) method and (B) the Stakeholder-built DSS method.



In Figure 2A, red indicated greatest damage resulting from the flood scenario. Orange, yellow and green indicated decreasing levels of damage in that order. Tan indicated areas where data was not available. In Figure 2B, the Google Earth™ image showed the U.S. Federal Emergency Management Agency National Flood Hazard Layer 1% annual flood risk hazard area as a blue layer (U.S. State Department Geographer, EuropaTechnologies, et.al. 2013). The yellow line was added by the stakeholder using the Google Earth™ drawing tool guided by Google Earth™ elevation data and represented anticipated flood risk within the next 50 years. The area below the yellow line represented property anticipated to experience flooding.

When the HAZUS DSS method was used, all three scenarios were run prior to the community flood risk management meeting and displayed during the stakeholder discussions of flood risk. HAZUS produced maps of flooding (Figures 1A, 1C and 2A) and generated summary reports describing the extent of damage at the resolution of U.S. Census Bureau blocks. For the community flood risk management meetings, modeling of the damage was shown using the total residential economic loss (year 2000 U.S. dollars) measured by loss to residential structures and loss to their contents. Residential loss was chosen because, based on exploratory interview feedback collected prior to the meetings, most of the meeting participants were expected to be residents of the communities.

When the Stakeholder-built DSS method was used, flood information was limited to showing the areal extent of flooding, without information about inundation levels. Thus, the number of buildings subjected to ground-level flooding was illustrated, but the damage costs in dollars were not calculated. When the Stakeholder-built DSS method was used, the past and present flood risk scenarios (Figures 1B and 1D) were constructed in advance and displayed during the stakeholder discussions. Past flood risk of an historic event was constructed by the GIS technicians using the Google Earth™ drawing tool guided by Google Earth™ elevation data. Present flood risk was

constructed using a Google Earth™ image with the FEMA National Flood Hazard Layer (NFHL) applications in Keyhole Markup Language zipped files (KMZ) layer (U.S. State Department Geographer, EuropaTechnologies, et.al. 2011 and 2013). These were prepared in advance so that each meeting could be completed within the two hours allotted by community organizers.

The third scenario illustrating anticipated future flood risk projected over the next 50 years (Figure 2B) was built by the stakeholders during the meeting. Instructions for building the model were provided verbally by the meeting facilitator, illustrated on a large screen by the GIS technician, and provided in written format in each community. Available for use by meeting participants were six to seven laptops, pre-installed with Google Earth™ (2013) and the FEMA NFHL KMZ (U.S. State Department Geographer, EuropaTechnologies, et.al. 2011 or 2013). For participants who brought their own laptops, the meeting assistants and GIS technician installed the software, with permission from the laptop owner, on the day of the meeting.

Participants were asked to locate the FEMA NFHL “High Risk Area” nearest their property of interest, which was usually their home. The meeting facilitator gave instructions for opening and formatting a “new path” using the Google Earth™ drawing tool. Participants were then asked to place their computer cursor over the “High Risk Area” polygon edge nearest their property and read the elevation shown in the Google Earth™ window. Next they were asked to add either two or three feet to the elevation to simulate future flood risk and move their cursor so that the elevation window matched their calculation. Here they clicked to register their first point on their “anticipated future flood risk projected over the next 50 years” path. They were instructed to repeat the steps until they drew a path that delineated future flooding on all sides of their property.

Meeting assistants and the GIS technician were allowed to assist with re-installing the software and repeating the instructions to individual participants, but they were not allowed to move the cursor or draw the path for the participants. This restriction was in place because the interactive visualization requires the learner to build the model themselves. By the close of this exercise, all participants successfully drew a model showing their future anticipated flood risk that resembled the demonstration model completed by the GIS technician and shown at the close of the exercise on the projection screen.

Using the Stakeholder-built DSS method, the first two scenarios showing past and present flood risk tested the effectiveness of realistic visualization (Figures 1B and 1D). The third scenario showing future flood risk tested the effectiveness of realistic and interactive visualization combined (Figure 2B).

Table 2: Overview of the Multi-hazard Loss Estimation Methodology (HAZUS) and Stakeholder-built computer-assisted decision support system (DSS) methods within the context of the flood risk management meetings

Attributes	HAZUS DSS	Stakeholder-built DSS
Stakeholders completed a pre-survey describing their demographic characteristics	X	X
Stakeholders completed a pre-survey measuring their knowledge of flood risk prior to the meeting.	X	X
Stakeholders completed a pre-survey measuring their knowledge of flood risk-reduction options prior to the meeting.	X	X
Stakeholders completed a pre-survey measuring their intent to initiate flood risk-reduction action prior to the meeting.	X	X
Meeting facilitator introduced stakeholders to flood risk factors.	X	X
Stakeholders engaged in collaborative learning using a DSS.	X	X
Model-building required memory-intensive (expensive) hardware.	X	
To learn about past, present, and future flood risk, stakeholders viewed a pre-constructed model that used the HAZUS program. Model-building was performed by a geographic information system (GIS)-trained technician (expensive).	X	
Stakeholders used their own laptops or computer tablets to access free cloud-stored software (inexpensive).		X
To learn about past and present flood risk, stakeholders engaged in realistic visualization, viewing a pre-constructed model that used the Stakeholder-built technique (GoogleEarth™ and the FEMA NFHL constructed by GIS technicians).		X
To learn about anticipated future flood risk,		

stakeholders engaged in realistic interactive visualization, building their own model.		X
Lead researcher introduced stakeholders to risk-reduction options and facilitated a collaborative discussion of costs and benefits to implementing reductions.	X	X
Stakeholders completed a post-survey measuring their knowledge of flood risk at the close of the meeting.	X	X
Stakeholders completed a post-survey measuring their knowledge of flood risk-reduction options at the close of the meeting.	X	X
Stakeholders completed a post-survey measuring their intent to initiate flood risk-reduction action at the close of the meeting.	X	X
In each community, a randomly-selected group of three to six stakeholders were asked to complete a follow-up interview one to seven days after the meeting, measuring their intent to initiate flood risk-reduction action after a time lapse following the meeting.	X	X

Overview of Design for Qualitative Analyses: Demographic Differences in Access to Flood Risk Communication

Using demographic information supplied by participating stakeholders, patterns were identified that may indicate bias in flood risk management meeting representation. The following were included in the analyses:

1. Gender
2. Household yearly income
3. Ethnicity
4. Language spoken
5. Educational attainment
6. Age
7. Property ownership

To determine who had access to the flood risk information presented, U.S. Census Bureau information (USCB 2010) for FEMA Region III was compared to the demographics of the participants in the community flood risk management meetings. Univariate analyses described demographic comparisons between meeting participants and the FEMA Region III population by

examining each level within each demographic characteristic independently. A multivariate analysis was performed to describe all levels of all seven demographic characteristics simultaneously for each of the ten communities in which a flood risk management meeting was conducted, a unit representing the aggregate of all ten communities receiving meetings, and the population in FEMA Region III. The multivariate analysis grouped these in clusters based on their overall demographic similarity.

Principal Findings

The model using realistic interactive visualization performed as well as the Federal Emergency Management Agency (FEMA) Multi-hazard Loss Estimation Methodology (HAZUS) computer-assisted decision support system (DSS) in communicating flood risk. The results indicated that when realistic visualization was utilized independently and when it was combined with interactive visualization to illustrate flood risk in the Stakeholder-built DSS, both methods performed as well as the HAZUS DSS. All resulted in significant learning outcomes ($P < 0.04$ for learning about past and present flood risk and $P < 0.01$ for learning about anticipated future flood risk). Realistic visualization was implemented when GIS technicians produced pre-constructed models that were used to illustrate past and present flood scenarios during the flood risk management meetings. Realistic interactive visualization was engaged when participating stakeholders constructed their own models of anticipated future flood risk. Pre-survey knowledge was found to have a significant positive effect on the participants' knowledge of flood risk ($P < 0.01$) when analyzed as a covariate. In other words, although the flood risk management meetings resulted in significant learning about flood risk, there was not a sufficient amount of flood risk information presented at the meetings to close the gap between those with prior knowledge and those learning the information for the first time during the meetings.

When the effectiveness of the two DSS methods at communicating flood risk-reduction options were tested with the pre-survey as a covariate, both performed equally well and resulted in significant learning outcomes ($P < 0.01$). While these results indicated the flood risk management meetings using a DSS method were very effective at communicating flood risk-reduction options to stakeholders, neither DSS method could close the gap in knowledge between those entering the meeting with prior knowledge of risk-reduction options and those entering with little or no prior knowledge as shown by the significant effect ($P < 0.01$) of the pre-survey responses.

When the presence of municipal planning representatives at the meetings was analyzed as a covariate, the research indicated risk-reduction learning outcomes were significantly higher ($P < 0.03$) when municipal planning representatives were available during the flood risk management meetings to answer participants' questions about local flood risk-reduction options. With this covariate, both DSS methods performed equally well.

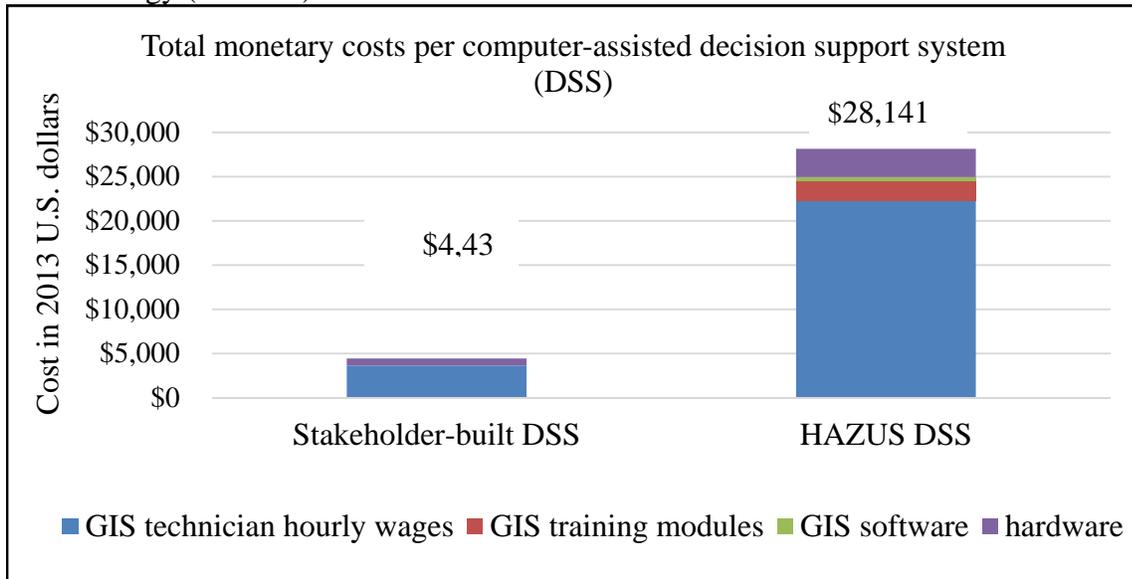
The study showed that following participation in the flood risk management meetings, significant increases occurred in the participants' intent to initiate actions to reduce risk ($P < 0.01$). When pre-survey responses to questions about intent to initiate risk-reduction action were used as a covariate, the results indicated the Stakeholder-built DSS method and the HAZUS DSS were equally effective. The effect of pre-survey participant intent to initiate risk-reduction actions differed in its significance, depending on the method used to collect post-meeting responses. Intent to initiate action prior to the meeting had a significant effect on responses on the survey completed following the meeting ($P < 0.01$). However, when asked the same question in an interview during the week following the meeting, the pre-survey responses did not have a

significant effect on follow-up interview responses ($P > 0.44$). On the written post-survey, participants listed fewer risk-reduction actions (mean increase of 0.9 actions from pre- to post-survey responses) than they did in the follow-up interviews (mean increase of 2.3 actions from pre-survey to follow-up interview responses). There are two possible explanations for this difference: (1) the interview format is more effective at encouraging responses from participants and/or (2) when participants were given a few days to process the information they gained from the flood risk management meeting, they added to the list of actions they planned to take. In summary, with pre-survey responses analyzed as a covariate, the flood risk management meetings using both DSS methods performed significantly well at increasing the participants' intent to take action to reduce flood risk.

The quality of the facilities had a significant effect on the intent of stakeholders to take action to reduce their risk following the flood risk management meeting ($P < 0.02$). The higher the quality of the facilities, the greater the intent to initiate risk-reduction action on the part of participants. The type of facility in which the flood risk management meetings were conducted varied widely. Some were located within well-maintained buildings where air conditioning was comfortable, visibility of the presentation was good for all participants, and acoustics were good for projecting the voice of the meeting facilitator throughout the room. Others were held in facilities where the wireless Internet connection was intermittent, there was no air conditioning and/or poor circulation with temperatures at 85 – 98° F, visibility of the presentation was poor for some or all participants, and the acoustics were poor for projecting the voice of the meeting facilitator throughout the room. When the quality of the facilities was analyzed as a covariate, there was a significant increase in the intent to take action to reduce flood risk following the meetings when the Stakeholder-built DSS method was used ($P < 0.01$) and a significant difference between the DSS methods utilized during the meetings ($P < 0.03$). When the HAZUS DSS was used with the quality of the facilities analyzed as a covariate, the increase in intent to take action to reduce flood risk following the meetings was not significant ($P > 0.07$). There was no significant interaction between the DSS method and the room quality ($P > 0.14$), indicating the Stakeholder-built DSS outperformed the HAZUS DSS in all three levels: high, medium and poor quality rooms. These results indicate the best combination for maximizing intent to initiate risk-reduction action is to hold the meeting in a high quality room using the Stakeholder-built DSS method.

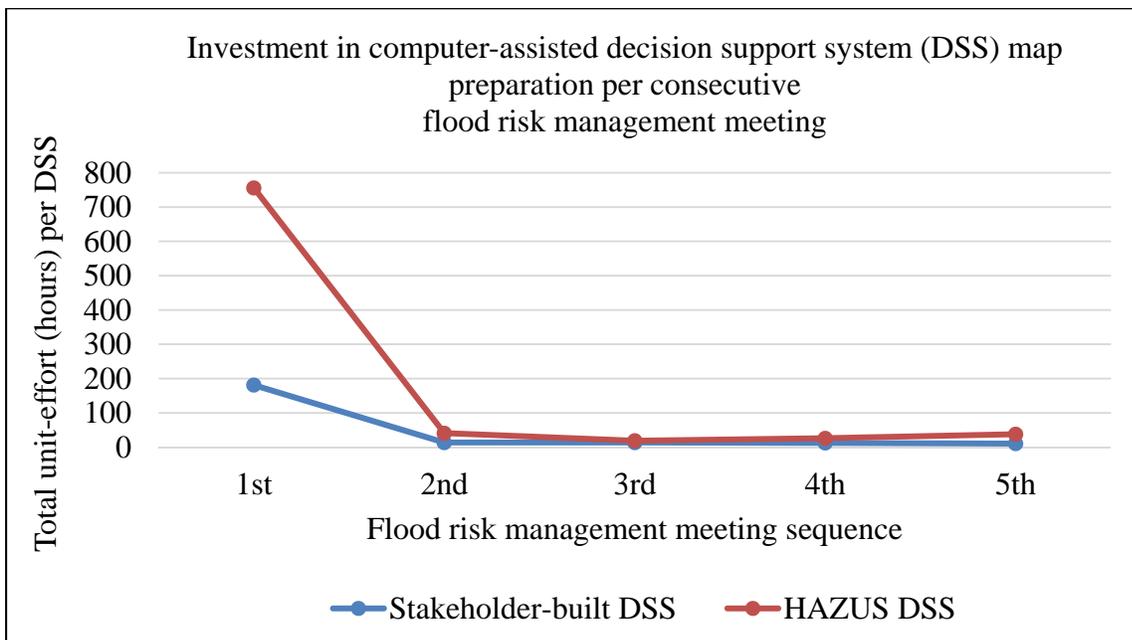
When the expense in time and money needed to train GIS technicians to perform the mapping in each of the two DSS methods was calculated, the HAZUS DSS method was found to require considerably more hours of training and, therefore, a much higher monetary investment, than did the Stakeholder-built method (Figure 3). The cost of hardware, software, and training modules also added to the cost of the HAZUS DSS training (Figure 3). The Stakeholder-built DSS training required minimal costs for hardware and no expenses for software or training modules.

Figure 3: Costs for geographic information system (GIS) training, software, and hardware per computer-assisted decision support system (DSS) method: the Multi-hazard Loss Estimation Methodology (HAZUS) and Stakeholder-built DSS Methods.



The greatest investment was in the early training for both DSS methods, with the HAZUS DSS requiring over six times the investment in time for initial training than the Stakeholder-built method (Figure 4).

Figure 4: Unit-effort by GIS technicians per consecutive flood risk management meeting map preparation for each computer-assisted decision support system method: the Multi-hazard Loss Estimation Methodology (HAZUS) and Stakeholder-built DSS Methods.

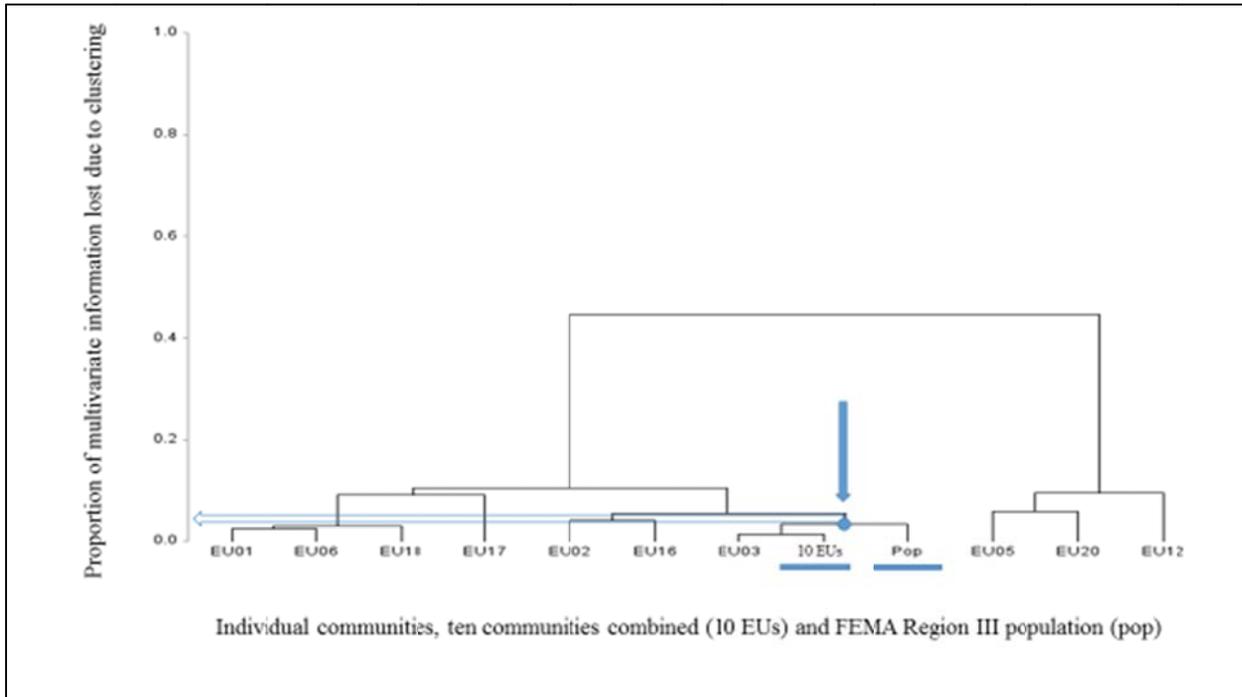


The research assistants trained as GIS technicians for this project were surveyed for feedback on their impressions of the differences between the two DSS methods. When asked about the capacity of their hardware to handle the software needed, all stated they were able to run the software required for both DSS models constructed on their computers, but there was a greater need to install additional software in order to run the HAZUS DSS than was needed to run the Stakeholder-built DSS. Most technicians experienced more error messages when working with the HAZUS program than with the Stakeholder-built and most found the Stakeholder-built to be a more user-friendly program. Overall, the Stakeholder-built DSS model was considered to require less prior GIS experience than the HAZUS DSS. Most technicians found both DSS models to be moderately difficult to teach others to use, with opinions leaning toward the Stakeholder-built model as easier to teach. While both the Stakeholder-built and HAZUS DSS resulted in significant learning outcomes, the lower cost of investment to run the Stakeholder-built DSS as compared to the HAZUS DSS, and the user-friendly aspects of the Stakeholder-built DSS, gave this method the advantage.

To address whether or not the participants were a true representation of the FEMA Region III population, the study compared U.S. Census Bureau (USCB) demographic data to self-reported demographics provided by participants in flood risk management meetings. Using univariate analyses that calculated differences between the meeting participants and the Region III population for each demographic characteristic independently, results indicated meeting participants were older, English-only speakers, better educated, from incomes above \$35,000, and more likely to own a home than data indicate for the general population. There was no significant difference in gender or race.

Cluster analysis showed similarities of the ten communities participated in flood risk management meetings and the FEMA Region III population based on simultaneous use of all demographics variables measured (Figure 5). A unit that represents the aggregate of all ten communities (Figure 5: “10EUs”) was included in the analysis. The analysis formed clusters of units with similar overall demographic characteristics. Results showed on a scale of 0 to 1.0 (Y axis in Figure 5), the proportion of multivariate information lost due to joining clusters. The cluster that includes the unit representing the ten-community aggregate and the FEMA Region III population lost approximately 0.025 of the original information about each unit in order to describe the cluster (Figure 5). When the scale of 0 to 1.0 is converted to a scale of 0 to 100, the results can be interpreted as the percent difference between the demographics of the units within a cluster. This indicates only a 2.5% loss of information when representing the population by the ten communities studied.

Figure 5: Demographic similarities the FEMA Region III population and ten communities participated in flood risk management meetings. The vertical blue arrow points to the node of the cluster that contains the unit representing all ten communities (10 EUs) combined and the Region III population (pop). The horizontal blue arrow points to the proportion of information lost (< 1%) assuming no difference between the ten-communities combined and the population.



Legend:

- EU(#) = demographic characteristics of participants at a single community flood risk management meeting
- “10 EUs” = demographic characteristics of participants in all ten communities combined
- “Pop” = demographic characteristics of the FEMA Region III population (USCB, 2010)

Additional findings

1. The FEMA Multi-hazard Loss Estimation Methodology (HAZUS) default information is compiled based upon best available National data sources and is accurate on a regional scale. HAZUS is designed to accept local, higher resolution, data. The City of Alexandria, Virginia was examined as a case study to answer the question: Is a model that uses local data, referred to as a Level 2 analysis, cost-effective as compared to a Level 1 analysis, which uses regional data, in terms of informed decision-making that will lower community costs during a flood? In most locations, the Level 2 analysis showed more precise 1% annual flood risk, a.k.a. the 100-year floodplain, delineations. Most calculated losses were very similar in both the Level 1 and Level 2 analyses. However, building repair and replacement costs were substantially higher, by approximately 33 ½ million dollars, in the Level 2 analysis as compared to the Level 1 analysis.
2. The use of each computer-assisted decision-support system (DSS), HAZUS and Stakeholder-built, were compared to determine how efficiently each modeled flood risk on the campus of

the University of Maryland in College Park, Maryland by training a team of five undergraduates with little or no GIS experience to use both DSS methods. The simplicity of the Stakeholder-built DSS was found by the team to be its best characteristic. The small learning curve allowed them to quickly delineate flood hazard zones. Elevation and coordinates allowed the users to map a floodplain using online U.S. Geological Survey stream gauge data and Google Earth™ accessed from inexpensive laptop computers. Training and use of HAZUS was found to be time consuming and difficult to master for the inexperienced users.

3. Climate change is likely increasing vulnerability of flooding in many wildlife conservation areas due to predicted sea-level rise and increases in extreme precipitation events. A user-friendly, inexpensive model based on the Stakeholder-built DSS method was designed for use by wildlife managers for initial assessment of lands to determine where they need to concentrate efforts to adapt to these changes. In this study, the model was used to assess predicted changes in the Maryland/DC Audubon Important Bird Areas (IBA). The preliminary findings showed some IBA will likely experience major shifts in patterns of flooding, while others are predicted to experience minor changes over the next 50 years.

Significance of Findings

The effectiveness of realistic interactive visualization in communicating flood risk, increasing knowledge of flood risk-reduction options, and intent on the part of stakeholders to initiate action to reduce their risk opens doors for flood risk management planners across the USA. The lower cost of investment in training GIS technicians to run the Stakeholder-built DSS as compared to the HAZUS DSS, and the greater ease in the acquisition and use of software for the Stakeholder-built DSS, gives this method the advantage. At one-sixth the cost of the HAZUS DSS method, the Stakeholder-built DSS is likely to be within the budgets of many municipal flood risk management planners that are financially unable to make use of the HAZUS DSS.

If a GIS technician is interested in seeing a basic visual outline of flood hazard zones and not a structural damage report and other economic losses, the Stakeholder-built method that allows users to map a floodplain using Google Earth™ and the FEMA National Flood Hazard layer (NFHL) available in conjunction with Google Earth™ is a quicker and simpler method than using the HAZUS models. However, the Stakeholder-built method does not provide information on economic losses.

Another potential application of the Stakeholder-built DSS method is that stakeholders, once instructed on its use, may decide to teach others in their community or beyond how to assess flood risk information, amplifying the spread of knowledge beyond the communities in this formal study.

Potential expansion of the application of the Stakeholder-built DSS

Use of applied methodology in communities outside the USA

There is potential for designing modifications of the Stakeholder-built DSS to accommodate flood-prone areas outside of the USA. The Stakeholder-built DSS model in this study made use of the FEMA NFHL, which is available only in the USA. However, Google Earth™ and its elevation data are available worldwide. A method for measuring anticipated flood risk that relies on other sources, such as present sea level elevation combined with the Intergovernmental Panel on Climate Change anticipated sea level rise in each country or region, could be developed to

replace the reliance of this model on the FEMA NFHL. This would open to vulnerable communities worldwide the field of effective communication of flood risk and flood risk-reduction options, and spur the initiation of action on the part of stakeholders to reduce their risk using an inexpensive, user-friendly DSS.

Use as a rapid assessment tool for evaluating flood risk

Assessing future flood risks and developing risk-reduction strategies should ideally be approached using a process in which new data can be incorporated as information becomes available. The Stakeholder-built model is ideal as a rapid assessment tool to quickly make initial decisions on areas that would benefit most from closer monitoring for future changes in flood patterns. Examples of situations where this would be useful is in conservation biology, where it is important to monitor such changes as wildlife habitat and migration routes that may result from changes in flooding patterns in the landscape. Another potential application is in flood hazard emergency preparedness for handling of domestic products such as livestock. The Stakeholder-built model can be used as a tool for locating potential emergency shelters and evacuation routes. These are a few examples of the broad array of possible applications for this model.

II. Publications

None as yet.

III. Number of students supported

Undergraduates: 7

Masters: 2

Ph.D.: 2

Post Doc: 0

IV. Notable achievements and awards resulting from the work

- The students supported by this grant completed extensive GIS training. The undergraduates, Masters and Ph.D. students completed three modules in the Environmental Science Research Institute (ESRI) ArcGIS 10™ (ESRI 2012) and eleven modules in ESRI™ HAZUS (ESRI 2012) online training. One Ph.D. student completed the FEMA Emergency Management Institute “HAZUS for Floods” course.
- Ph.D. candidate, V. Beth K. Olsen, successfully defended her dissertation, “Proposing a realistic interactive visualization model and testing its effectiveness in communicating flood risk.” Her dissertation project was funded by this grant.
- Several presentations were given in scientific and professional conferences.

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Bromide as a Precursor of Potent Brominating Agents During Drinking Water Chlorination

Basic Information

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Project Number:	2013MD304B
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End Date:	2/28/2014
Funding Source:	104B
Congressional District:	MD-3
Research Category:	Water Quality
Focus Category:	Treatment, Surface Water, Toxic Substances
Descriptors:	None
Principal Investigators:	John D Sivey

Publications

1. Victor, Daniel A., 2014, Reactivity of 4-bromoanisole towards inorganic brominating agents in solutions of sodium bromide and free available chlorine, Undergraduate Honors Thesis, Department of Chemistry, Fisher College of Science and Mathematics, Towson University, Towson, Maryland, 36 pp.
2. Sivey, John D.; Daniel A. Victor; Mark A. Bickley, 2014, Contributions of BrCl, BrOCl, and Br₂O toward bromination rates of aromatic compounds in solutions of aqueous free bromine: Implications for water disinfection, 247th American Chemical Society National Meeting and Exposition, Division of Inorganic Chemistry, Dallas, Texas.
3. Victor, Daniel A.; John D. Sivey, 2014, Reactivity of anisole and bromoanisole regioisomers toward brominating agents in solutions of NaBr + free available chlorine, 247th American Chemical Society National Meeting and Exposition, Division of Inorganic Chemistry, Dallas, Texas.

Bromide as a Precursor of Potent Brominating Agents During Drinking Water Chlorination

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1. Introduction

1.1 *Unintended consequences of water disinfection.* In 1902, for the first time in the United States, chlorine was added to drinking water (DW) to protect the public from water-borne diseases.¹ Since then, countless lives have been saved by this potent microbicidal agent. Not until the 1970s, however, was chlorine's "dark side" discovered.^{2,3} In addition to inactivating pathogens, chlorine can also react with natural organic matter⁴⁻⁷ to form potentially toxic disinfection by-products (DBPs).⁸

In water with low nitrogen levels, chlorine consists primarily of hypochlorous acid (HOCl, $pK_a = 7.58$)⁹ and OCl^- ; the sum of such species is termed *free chlorine*. In addition to reactions with organic DBP precursors, HOCl can rapidly oxidize bromide (eq 1).¹⁰



As with HOCl, HOBr is both a potent microbicide and a reactive electrophile capable of forming brominated DBPs,^{1,11-13} which are generally more toxic than their chlorinated analogues.¹⁴ Therefore, strategies for minimizing the formation of brominated DBPs are highly desirable. Such DBP-minimization strategies necessitate a comprehensive understanding of aqueous bromine chemistry.

1.2 *Natural and anthropogenic sources of bromide.* Bromide is a ubiquitous constituent of unpolluted natural waters (**Table 1**), with median concentrations ranging from low $\mu\text{g/L}$ levels in precipitation¹⁵ to 65 mg/L in seawater.¹⁶ Bromide concentrations in groundwater typically range from low $\mu\text{g/L}$ to low mg/L.^{17,18} Brackish-water or seawater intrusion can, however, increase bromide concentrations in aquifers near coasts.¹⁹ Bromide levels measured in DW¹⁷ and wastewater²⁰ influents (50 – 250 $\mu\text{g/L}$) align with the upper levels measured in fresh surface waters. Even higher levels (~ 75 mg/L) have been reported for "produced water" associated with natural gas fracking (**Table 1**).²¹ Fracking operations in western Pennsylvania, for example, have been blamed for increases in bromide levels in river water used as a DW source.^{22,23} The concern over bromide in rivers (and its possible conversion into brominated DBPs) recently prompted the Commonwealth of Pennsylvania to ask natural gas companies to stop disposing of produced water via treatment plants that discharge into rivers.²⁴ There is currently a moratorium on fracking in Maryland as the State studies the issue.²⁵

TABLE 1. Bromide Concentrations in Natural Waters, Drinking Water, and Wastewaters

Natural Waters	[Br ⁻], (µg/L)		Ref
	median	maximum	
Precipitation	~6	12	15
U.S. groundwater (potable waters only)	16	58	18
U.S. freshwater lakes	23	322	17
U.S. rivers	63	426	17
U.S. groundwater (includes non-potable waters)	62	2700	17
Seawater	65,000	n/a	16
Drinking Water and Wastewaters	[Br ⁻], (µg/L)		Ref
U.S. drinking water influent	50 – 200		17
Municipal wastewater influent	100 – 250		20
Produced water from fracking	75,000		21

1.3 *Chemistry of free bromine*. The oxidation state of bromine is +1 in species such as HOBr ($pK_a = 8.70$, ref 26) and OBr⁻; the sum of all Br(+1) species is referred to as *free bromine*. The direct application of free bromine as a disinfectant of DW is uncommon due to the increased costs, increased DBP formation, and difficulty in maintaining a disinfectant residual relative to free chlorine.¹ Free bromine is, however, employed as a disinfectant in some recreational waters (e.g., spas).¹ In waters disinfected with ozone (O₃), free bromine can also form via the incomplete oxidation of bromide (eq 2).²⁷⁻²⁹



With few exceptions,³⁰⁻³² the formation of brominated DBPs is attributed to reactions involving HOBr. Indeed, conventional wisdom in the environmental literature assumes HOBr is “the” reactive brominating agent of DBP precursors (such as phenols,^{33,34} pyrene,³⁵ and amino acid residues³⁶) and of organic micropollutants (including 17α-ethinylestradiol,³⁷ amoxicillin,³⁸ and chlorpyrifox³⁹). Although often overlooked in the literature, four additional brominating agents (BrCl, Br₂, BrOCl, and Br₂O) can also form when bromide-containing waters are chlorinated (**Figure 1**).

Despite their lower concentrations under typical DW chlorination conditions (**Figure 1**), recent research has demonstrated that these overlooked brominating agents are several orders of magnitude more inherently reactive than HOBr toward the herbicide dimethenamid.³² This work corroborates a previous examination of *p*-xylene bromination, which determined Br₂ and BrCl to be several orders of magnitude more reactive than HOBr. The greater inherent reactivity of brominating agents such as BrCl and Br₂ can be attributed to the increased nucleofugality (leaving group ability) of Cl⁻ (from BrCl) and Br⁻ (from Br₂) relative to OH⁻ (from HOBr). (OBr⁻ is anticipated to be a very poor brominating agent due to the exceptionally weak leaving group ability of O²⁻.) The high reactivities of BrCl, Br₂, BrOCl, and Br₂O can more than compensate for their low concentrations (relative to HOBr). Accordingly, these species can influence overall bromination rates (eq 3) under typical DW chlorination conditions.

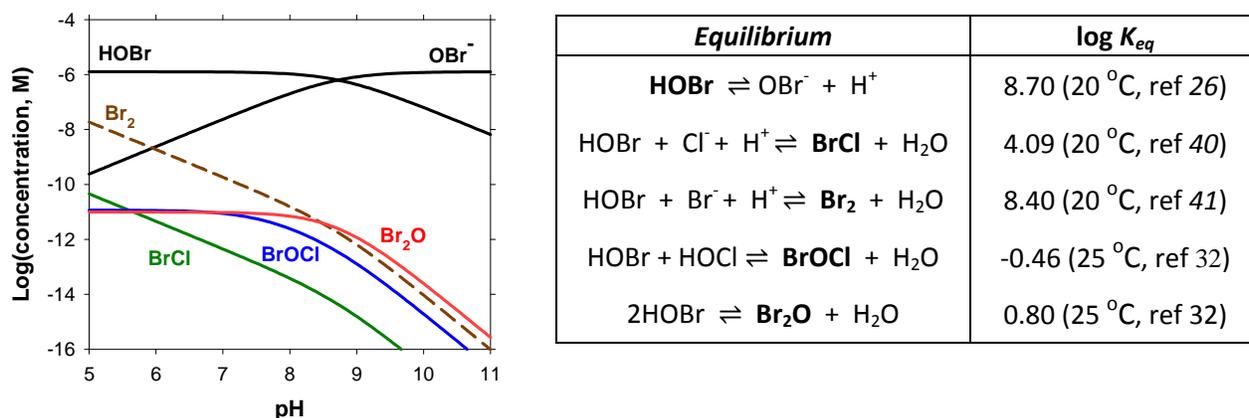


FIGURE 1. Speciation of aqueous free bromine under typical DW chlorination conditions (solid lines). Br_2 (broken line) requires that initial $[\text{Br}^-]$ exceed $[\text{HOCl}]_T$. Adapted from ref 32.

$$\text{rate} = [\text{organic compound}](k_{\text{BrCl}}[\text{BrCl}] + k_{\text{Br}_2}[\text{Br}_2] + k_{\text{BrOCl}}[\text{BrOCl}] + k_{\text{Br}_2\text{O}}[\text{Br}_2\text{O}] + k_{\text{HOBr}}[\text{HOBr}]) \quad [3]$$

The extent to which brominating agents other than HOBr influence (or control) rates of DBP precursor bromination is of practical importance. If, for example, BrCl makes a significant contribution to overall bromination rates, then the chloride concentration will also influence the bromination rate, noting from **Figure 1** that $[\text{BrCl}]$ is proportional to $[\text{Cl}^-]$. In this way, chloride can catalyze bromination reactions. Similarly, when BrOCl is an important brominating agent, HOCl functions as a bromination catalyst (noting that $[\text{BrOCl}]$ is proportional to $[\text{HOCl}]$). In models which assume HOBr as the only active brominating agent, the potential influences of chloride concentration and chlorine dose on bromination rates may be (incorrectly) deemed unimportant.

The extent to which brominating agents other than HOBr influence bromination rates of organic compounds other than dimethenamid and *p*-xylene is currently unknown. Also absent is an understanding of how organic compound structure influences the relative importance of each brominating agent.

2. Problem and Research Objectives

Geographic and anthropogenic factors make Maryland's drinking water (DW) sources susceptible to elevated levels of bromide. For example, Maryland's potable waters near coastal regions are susceptible to bromide augmentation via seawater intrusion¹⁸ and aerosol deposition.⁴² DW supplies in Maryland (and in neighboring states whose waterways flow through Maryland) are also susceptible to several anthropogenic sources of bromide, including municipal wastewater effluents,²⁰ discharges from hydraulic fracturing,⁴³ septic systems,⁴⁴ road de-icing salt,⁴⁵ flame retardants,⁴⁶ and pesticides.⁴⁷ Despite the common misconception of bromide as a "conservative" (i.e., unreactive) chemical in water bodies, during DW disinfection, bromide can be transformed into reactive bromine species capable of generating toxic disinfection by-products (DBPs). For several decades, the environmental chemistry literature

has focused almost exclusively on one oxidation product of bromide (HOBr) as “the” brominating agent responsible for the formation of brominated DBPs during DW disinfection.⁴⁸ Evidence presented herein suggests that this historical view is overly simplistic. In order to more accurately understand the behavior of bromide during drinking water treatment—and thereby minimize DBP formation—a more complete view of bromine chemistry is required.

The goal of this research is to explore the relationship between organic compound structure and bromination rates for the overlooked brominating agents (e.g., BrCl, BrOCl, and Br₂O) as well as for HOBr. Very few previous reports^{30,32} have quantified the inherent reactivities of these bromine species toward organic compounds. In this project, the reactivity of several overlooked brominating agents was determined for anisole and one of its bromination products (4-bromoanisole, 4-BA). Anisole was selected for study because methoxy-substituted benzenes likely represent important substructures within natural organic matter that are susceptible to electrophilic aromatic substitution reactions with brominating agents (**Figure 3**).

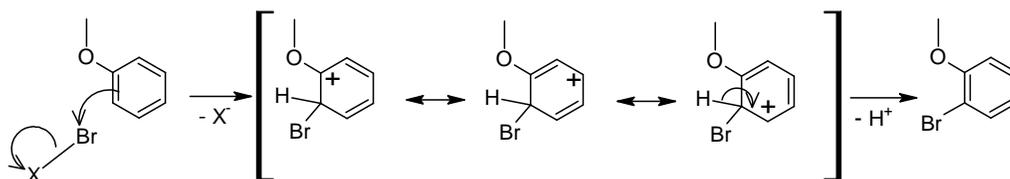


FIGURE 3. Postulated mechanism of anisole bromination by brominating agents of the form BrX (where X = Cl, Br, OBr, OCl, or OH). Resonance structures for the arenium ion intermediate are shown in brackets.

Objectives. This project investigated two main objectives:

- Elucidate the influence of solution conditions known to influence bromine speciation (e.g., pH, concentration of bromide, free chlorine, and chloride) on regiospecific bromination rates of anisole and 4-BA.
- Quantify second-order rate constants for reactions of anisole and 4-BA with individual brominating agents.
- Evaluate the selectivity among brominating agents for sequential bromination reactions of anisole (**Figure 4**), noting that selectivity is anticipated to increase (and the reactivity is anticipated to decrease) as the number of bromine substitutions increases (**Figure 5**).⁴⁹

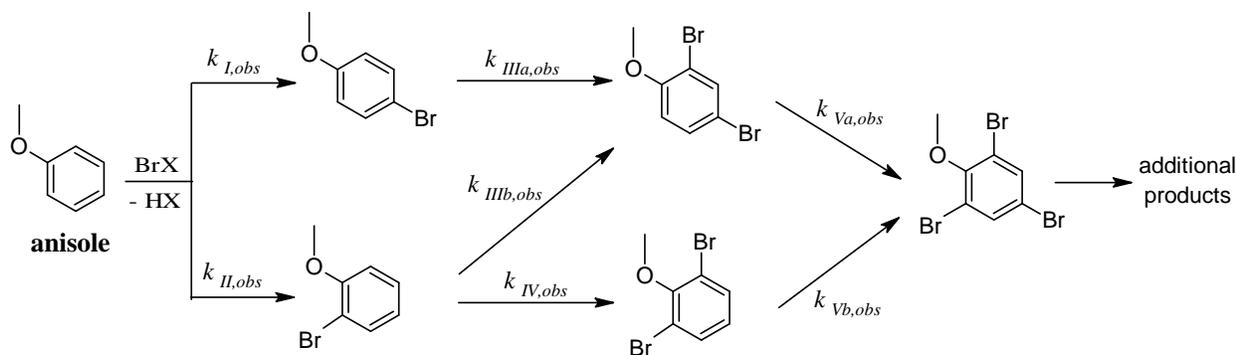


FIGURE 4. Postulated bromination pathways of anisole by brominating agents of the form BrX (where X = Cl, Br, OBr, OCl, or OH).

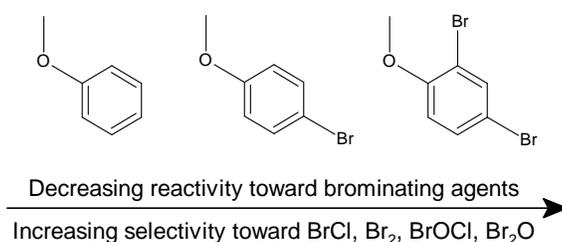


FIGURE 5. Reactivity-selectivity trend anticipated for the sequential bromination of anisole.

3. Methodology

3.1 Measurement of regiospecific bromination rates of anisole. Experimental measurements of bromination rates followed the method of Sivey et al.,^{32,50,51} with exceptions noted below. Briefly, reactions were performed in 40-mL amber glass vials with Teflon lined caps. Solutions (25 mL) were typically prepared with the following composition: $[\text{Br}]_0 = 120 \mu\text{M}$, total free chlorine ($[\text{HOCl}]_T = 570 \mu\text{M}$, $[\text{Cl}^-] = 10 \text{ mM}$, $[\text{NaNO}_3] = 90 \text{ mM}$, and [carbonate or borate pH buffer] = 20 mM. High purity NaBr (99.5%) and ultrahigh purity NaCl (99.999%) served as sources of bromide and chloride, respectively. Free chlorine was added as laboratory grade NaOCl (~6% w/w); NaOCl stock solutions were standardized spectrophotometrically.⁵² Following addition of NaOCl to solutions containing NaBr, NaCl, and a pH buffer, reactors were capped, shaken vigorously, and incubated at $20.00 \pm 0.02 \text{ }^\circ\text{C}$ in a circulating water bath for 4 minutes (for reactors with pH < 9) or 30 minutes (for reactors with pH between 9 and 10) to permit sufficient time for bromide to be oxidized into free bromine by free chlorine. At $t = 0$, anisole was added (as a methanolic spike) to achieve an initial concentration of $10 \mu\text{M}$; final methanol concentrations were < 0.6% (v/v). Aliquots (0.900 mL) of the reaction solution were transferred at selected time intervals to 4-mL amber glass vials pre-spiked with toluene (as an extraction solvent) and sodium thiosulfate ($[\text{thiosulfate}]/[\text{HOCl}]_T \approx 1.4$, to quench residual oxidants). The loss of anisole and formation of brominated products were concurrently monitored as a function of time using an Agilent 7890A gas chromatograph with an Agilent 5975C mass selective detector (GC/MS).

In selected reactors, pH was varied from 5.3 – 9.8 while holding other solution conditions constant (as specified above). In separate experiments, the effects of ionic strength ($[\text{NaNO}_3] = 60 - 120 \text{ mM}$ at pH 8.2), buffer concentration (10 – 40 mM at pH 7.2 (carbonate) and pH 9.0 (borate)), and initial anisole concentration (6 – 24 μM at pH 6.8 and 8.0) on bromination rates of anisole were evaluated.

3.2 Determination of selectivity trend for sequential bromination of anisole. Bromination rates of 4-bromoanisole to give 2,4-dibromoanisole were determined following the general method described in Section 3.1, with the following exceptions. Solutions (25 mL) were prepared with the following composition: $[\text{Br}^-]_0 = 400 \mu\text{M}$, total free chlorine ($[\text{HOCl}]_T = 500 \mu\text{M}$, $[\text{Cl}^-] = 10 \text{ mM}$, $[\text{NaNO}_3] = 90 \text{ mM}$, and [carbonate or borate pH buffer] = 20 mM. At $t = 0$, 4-bromoanisole was added (as a methanolic spike) to achieve an initial concentration of 10 μM ; final methanol concentrations were < 0.6% (v/v). Reaction rates for bromination of dibromo-anisoles to give 2,4,6-tribromoanisole are currently under investigation.

3.3 Modeling of kinetic data. For all experiments, $[\text{HOBr}]_T/[\text{anisole or 4-bromoanisole}]_0 > 50$. For reactions of anisole at $\text{pH} < 8$, the total bromination rate was calculated via eq 4:

$$\text{total bromination rate} = -\frac{d[\text{anisole}]}{dt} = k_{obs,tot}[\text{anisole}] \quad [4]$$

Pseudo-first-order rate constants for formation of 4-bromoanisole (4-BA) and 2-bromoanisole (2-BA) were calculated as fractions of k_{obs} based on measured product concentrations at the final sampling time (eqs 5 and 6).

$$k_{obs,4-BA} = k_{obs,tot} \frac{[4-BA]}{[4-BA]+[2-BA]} \quad [5]$$

$$k_{obs,2-BA} = k_{obs,tot} \frac{[2-BA]}{[4-BA]+[2-BA]} \quad [6]$$

For bromination of anisole at $\text{pH} > 8$ and for all reactions involving 4-BA as a reactant, bromination rates were measured via the initial rate method.⁴⁵ The reactivity of each brominating agent was delineated via nonlinear least squares regression analysis of eq 7:

$$k_{obs} = k_{BrCl}[\text{BrCl}] + k_{Br_2}[\text{Br}_2] + k_{BrOCl}[\text{BrOCl}] + k_{Br_2O}[\text{Br}_2\text{O}] + k_{HOBr}[\text{HOBr}] \quad [7]$$

where k_{obs} and calculated equilibrium concentrations served as model input and second-order rate constants (specific to each brominating agent) served as fitting parameters; for more details, see ref 32.

4. Principal Results

Reactions of anisole in solutions containing free chlorine + bromide gave 4-BA and 2-BA as the major and minor products, respectively (**Figure 6**). Mass balances (as [anisole] + [4-BA] + [2-BA]) were consistent with the initial concentration of anisole added (10 μM) and did not change significantly (at the 95% confidence level) throughout each experiment.

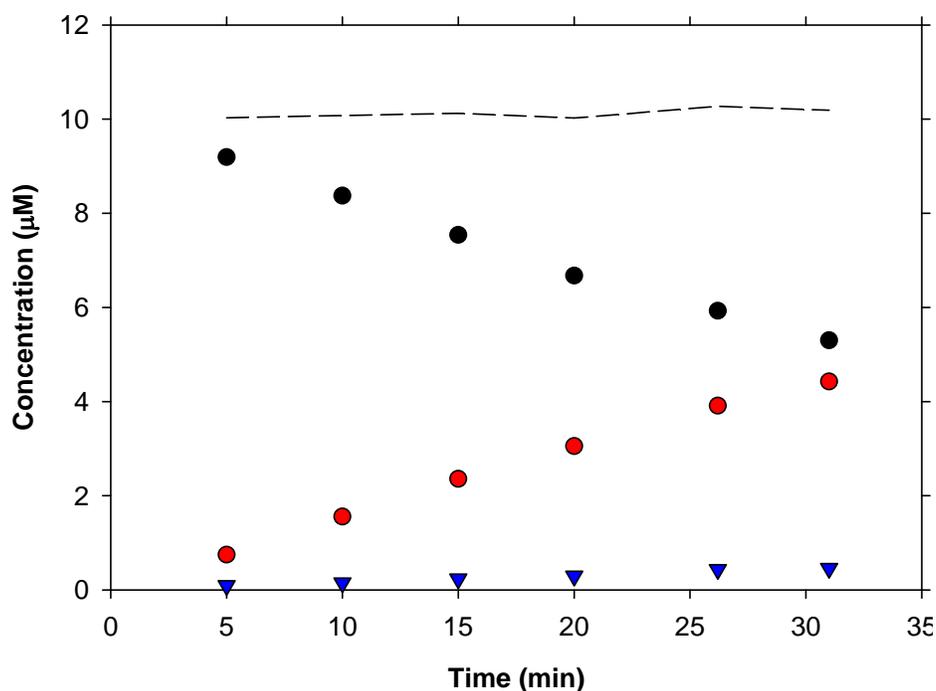


FIGURE 6. Example time course for the conversion of anisole (black circles) into 4-bromoanisole (4-BA, red circles) and 2-bromoanisole (2-BA, blue triangles). Broken line denotes the carbon mass balance ([anisole] + [4-BA] + [2-BA]). Conditions: pH = 7.87, $[\text{Br}^-]_0 = 120 \mu\text{M}$, $[\text{HOCl}]_T = 570 \mu\text{M}$, $[\text{NaCl}] = 10 \text{ mM}$, $[\text{anisole}]_0 = 10 \mu\text{M}$, $[\text{borate}] = 20 \text{ mM}$, $T = 20.00 \text{ }^\circ\text{C}$.

Initial rates of anisole bromination were examined as a function of initial anisole concentration at pH 6.83 and pH 8.02 (**Figure 7**). Log-log plots of initial rates of *para*- and *ortho*-bromination versus initial anisole concentration were linear with slopes not significantly different than 1.0, consistent with reactions first-order in anisole concentration. These findings suggest that formation of active brominating agents is not rate-determining under the examined conditions.

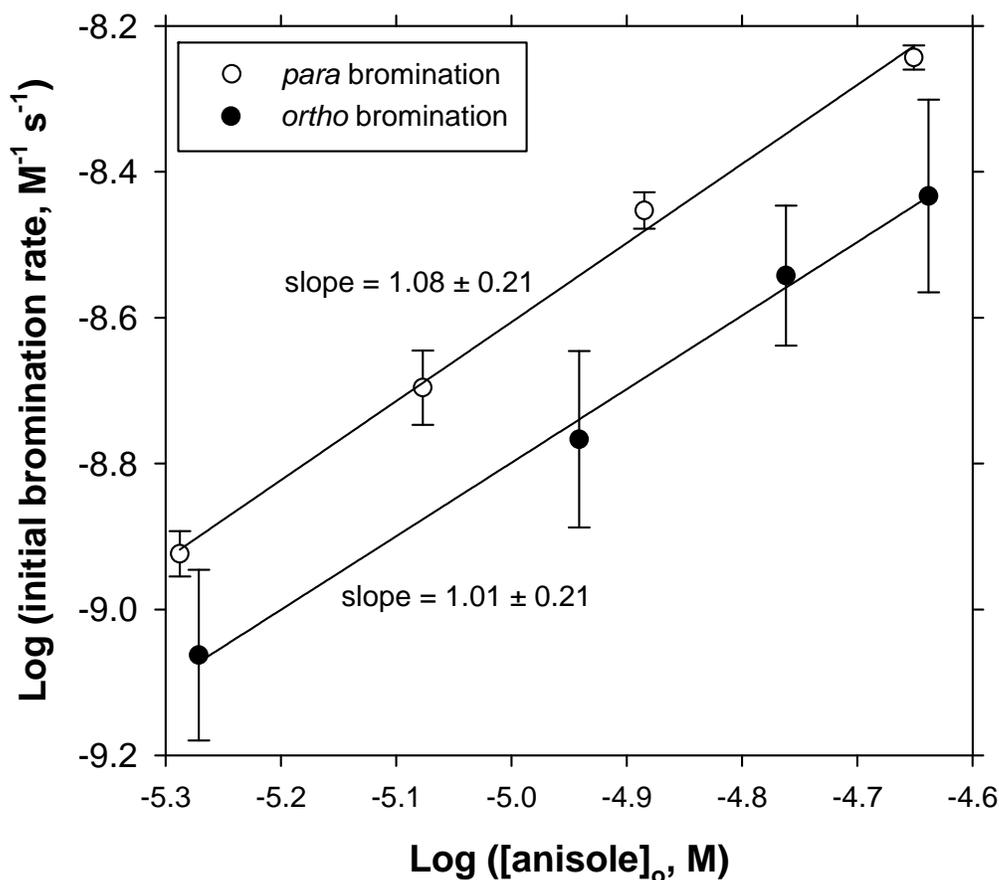


FIGURE 7. Initial rate of anisole bromination as a function of initial anisole concentration. Note log scale on both axes. Error estimates denote 95% confidence intervals. General conditions: $[\text{Br}]_0 = 117 \mu\text{M}$, $[\text{HOCl}]_T = 655 \mu\text{M}$, $[\text{NaCl}] = 10 \text{ mM}$, $T = 20.00 \text{ }^\circ\text{C}$; for *para*-bromination, $\text{pH} = 8.02$ and $[\text{borate buffer}] = 20 \text{ mM}$; for *ortho*-bromination, $\text{pH} = 6.83$ and $[\text{carbonate buffer}] = 20 \text{ mM}$.

Rates of anisole bromination to give 4-BA (**Figure 8**) and 2-BA (**Figure 9**) decreased with increasing pH. As anisole is not ionizable under the examined conditions, this trend suggests that changes in the speciation of free bromine (**Figure 1**) influence bromination rates of anisole as a function of pH. This finding is consistent with previous studies of electrophilic aromatic substitution, including bromination of *p*-xylene^{30,53} and of a substituted thiophene.³²

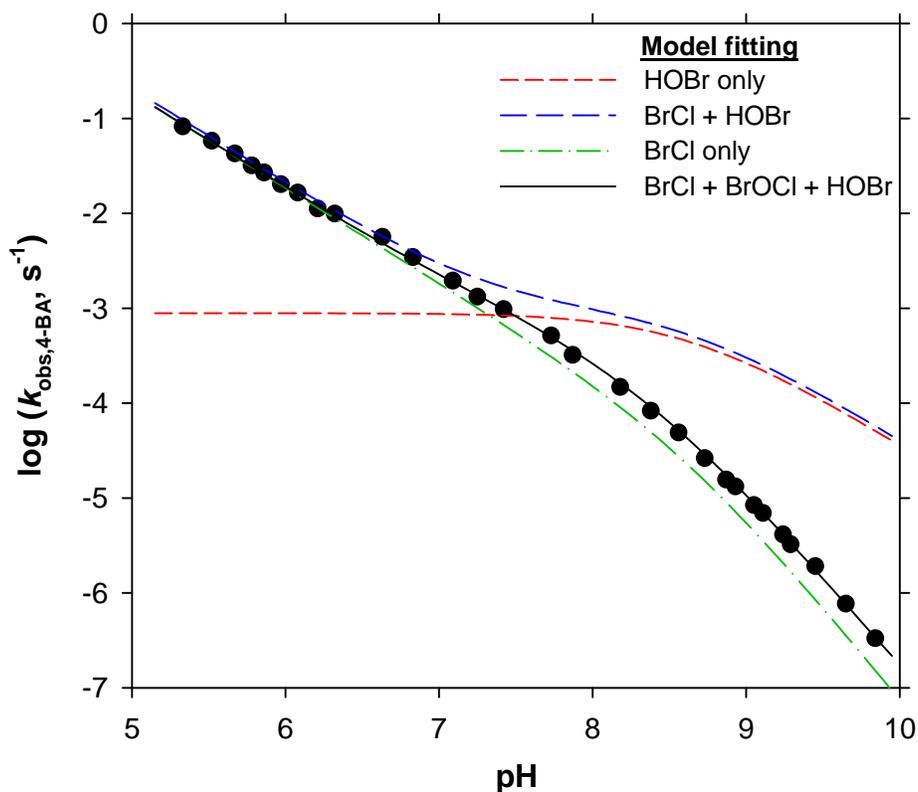


FIGURE 8. Pseudo-first-order rate constants (as $\log k_{\text{obs},4\text{-BA}}$) for regiospecific bromination of anisole to give 4-bromoanisole. Conditions: $[\text{Br}^-]_0 = 120 \mu\text{M}$, $[\text{HOCl}]_T = 570 \mu\text{M}$, $[\text{NaCl}] = 10 \text{ mM}$, $[\text{NaNO}_3] = 90 \text{ mM}$, $[\text{anisole}]_0 = 10 \mu\text{M}$, $[\text{carbonate or borate}] = 20 \text{ mM}$, $T = 20.00 \text{ }^\circ\text{C}$.

A kinetic model which assumes HOBr as the only active brominating agent yields poor fits for data associated with *para*-bromination of anisole (**Figure 8**). Inclusion of BrCl as a possible brominating agent improves model fits to the experimental data at $\text{pH} < 7$, but does not improve model fits at $\text{pH} > 7$. A model which assumes BrCl as the sole active brominating agent provides improved fits at all pH values. The best fit, however, was obtained when BrCl, BrOCl, and Br_2O were simultaneously considered to be active brominating agents. Additional examined models (including BrOCl only and Br_2O only) did not yield improved fits (data not shown). For *ortho*-bromination of anisole (**Figure 9**), the best model fit was obtained when BrCl and BrOCl were the only putative brominating agent.

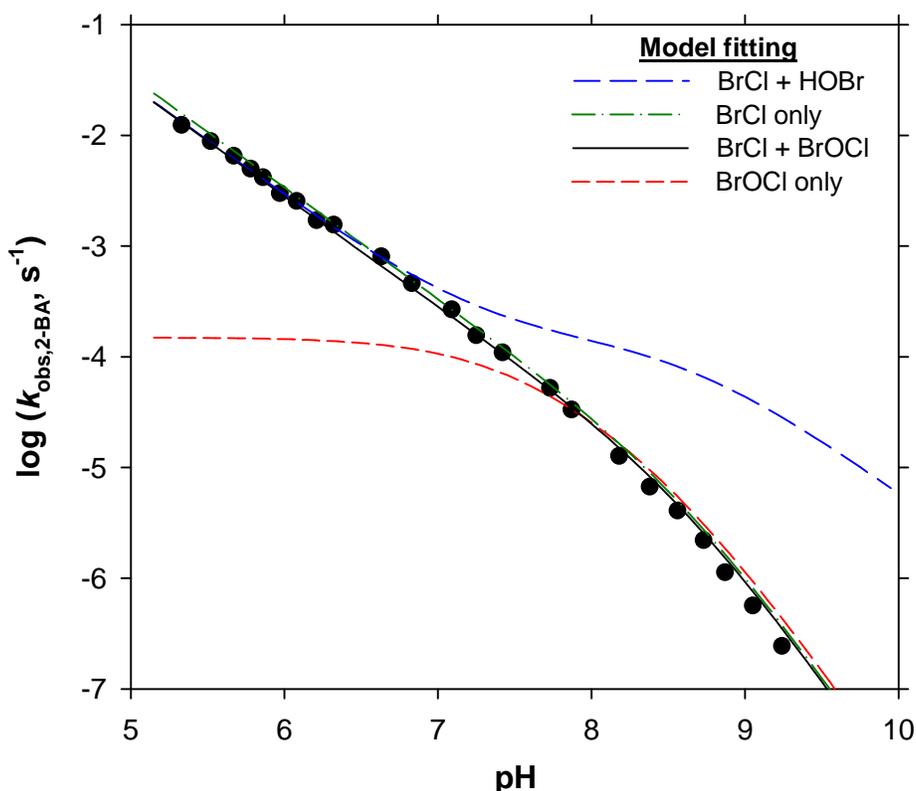


FIGURE 9. Pseudo-first-order rate constants (as $\log k_{\text{obs}}$) for regiospecific bromination of anisole to give 2-bromoanisole. Conditions: $[\text{Br}^-]_0 = 120 \mu\text{M}$, $[\text{HOCl}]_T = 570 \mu\text{M}$, $[\text{NaCl}] = 10 \text{ mM}$, $[\text{NaNO}_3] = 90 \text{ mM}$, $[\text{anisole}]_0 = 10 \mu\text{M}$, $[\text{carbonate or borate}] = 20 \text{ mM}$, $T = 20.00 \text{ }^\circ\text{C}$.

For all experiments with anisole, bromination *para* to the methoxy group (to give 4-BA) is favored over *ortho*-substitution (yielding 2-BA). Despite a 2:1 statistical prediction for the *ortho/para* ratio, preferential *para*-substitution can be explained by the increased stability of the arenium ion intermediate⁵⁴ and the lesser steric hindrance⁵⁵ relative to *ortho*-substitution.

That *para/ortho* selectivity increases from 7 (at pH 5.4) to 16 (at pH 9.4) under otherwise identical solution conditions suggests the predominant brominating agent is changing as a function of pH (Figure 10). Model fits (shown in Figure 8 for formation of the *para*-substituted product) indicate BrCl is the predominant brominating agent at $\text{pH} < 7$. At $\text{pH} > 7$, the less reactive BrOCl and HOBr also influence bromination rates. The corresponding increase in selectivity (Figure 10) as the predominant brominating agents become less reactive at $\text{pH} > 7$ is consistent with the reactivity-selectivity principle.^{56,57}

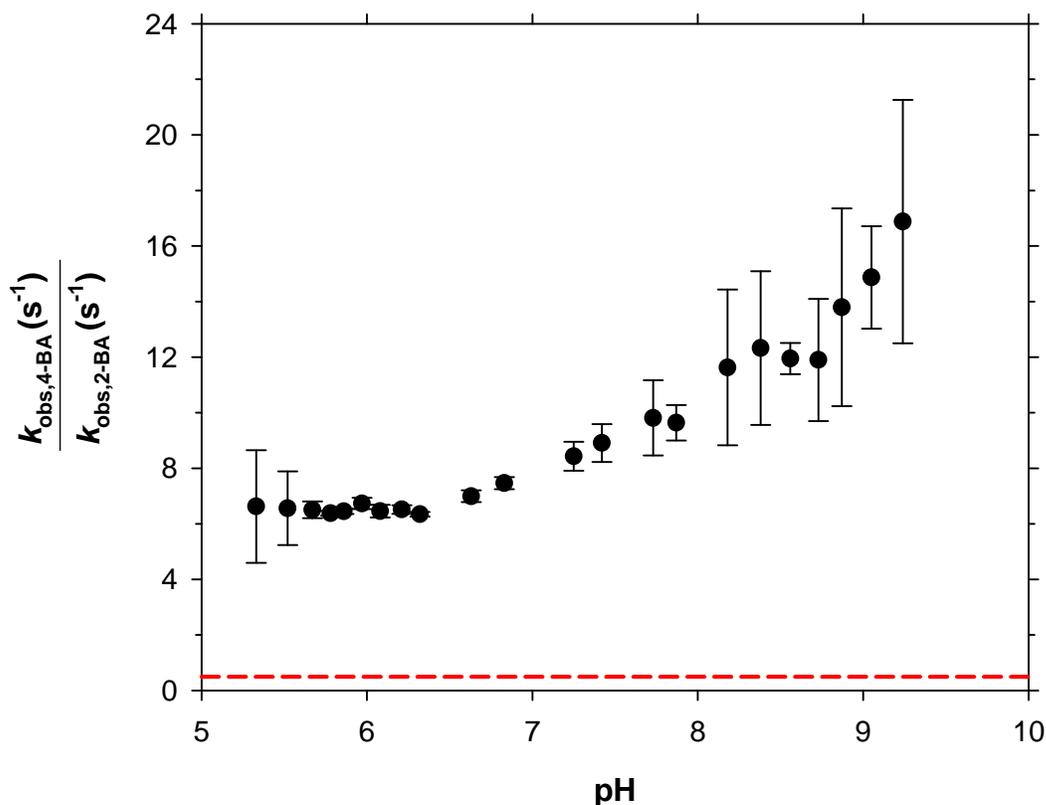


FIGURE 10. Regioselectivity of anisole bromination depicted as the ratio of k_{obs} values for formation of 4-bromoanisole (4-BA) and 2-bromoanisole (2-BA). Broken line denotes the theoretical regioselectivity (0.5) assuming the single *para* substitution site is equally nucleophilic relative to the two *ortho*-substitution sites. Error bars denote 95% confidence intervals.

Bromination rates of 4-BA were also measured as a function of pH (**Figure 11**); 2,4-dibromoanisole (2,4-DBA) was the only observed product. Despite a greater initial free bromine concentration (400 μM), rate constants for 4-BA bromination were more than 10-times smaller relative to those corresponding to *para*-bromination of anisole (employing 120 μM free bromine, **Figure 8**). The lesser nucleophilicity of 4-BA relative to anisole is consistent with the modestly deactivating properties of bromine substituents in aromatic systems. As bromination of 4-BA occurs *ortho* to the methoxy substituent, steric effects may also attenuate rates of 4-BA bromination relative to bromination rates of anisole.

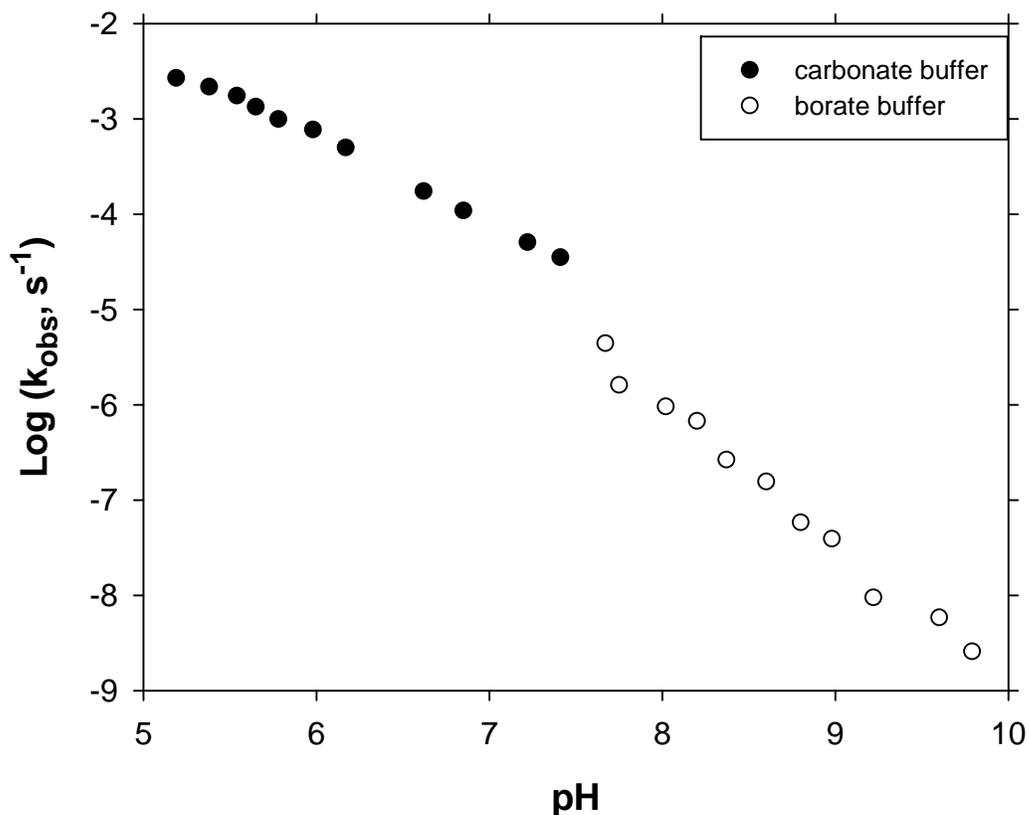
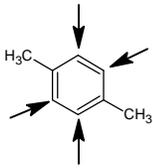
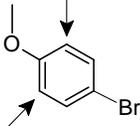
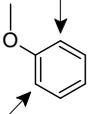
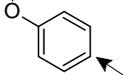
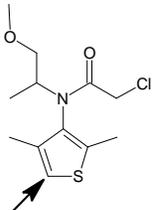


FIGURE 11. Pseudo-first-order rate constants (as $\log k_{\text{obs}}$) for bromination of 4-bromoanisole to give 2,4-dibromoanisole. Conditions: $[\text{Br}^-]_0 = 400 \mu\text{M}$, $[\text{HOCl}]_T = 500 \mu\text{M}$, $[\text{NaCl}] = 10 \text{ mM}$, $[\text{NaNO}_3] = 90 \text{ mM}$, $[\text{4-bromoanisole}]_0 = 8 \mu\text{M}$, $[\text{carbonate or borate}] = 20 \text{ mM}$, $T = 20.00 \text{ }^\circ\text{C}$.

Carbonate and borate buffer (10 – 40 mM) did not significantly influence rates of anisole bromination (data not shown). Rates of 4-BA bromination did, however, appear to be influenced by buffer identity, as indicated by the discontinuity of the data in **Figure 11** when the buffer changed from carbonate to borate near pH 7.5. Separate experiments indicated that rates of 4-BA bromination decreased as concentrations of carbonate and borate increased in the range of 10 – 40 mM (data not shown). Additional studies are underway to elucidate the effects of pH buffers on bromination rates of anisole and its brominated analogues.

Best-fit regioselective second-order rate constants for bromination of anisole and 4-BA are compiled in **Table 2**. The reactivity of brominating agents toward anisole and 4-BA increases in the order $\text{HOBr} < \text{BrOCl} < \text{BrCl}$. This trend is consistent with the previously reported second-order rate constants for bromination of *p*-xylene and dimethenamid (**Table 2**). Future experiments will be performed to quantify second-order rate constants for values listed as “not determined” in **Table 2**.

TABLE 2. Second-Order Rate Constants for Bromination of Aromatic Compounds

Brominating Agent	Second-order rate constants ($M^{-1} s^{-1}$) ^a				
	<i>p</i> -xylene ³⁰	4-bromo-anisole ^b	anisole ^b		dimethenamid ³²
			<i>ortho</i> -bromination 	<i>para</i> -bromination 	
BrCl	540 ± 9	(4.7 ± 0.6) × 10 ³	(9.4 ± 0.5) × 10 ⁴	(6.17 ± 0.28) × 10 ⁵	(2.1 ± 0.3) × 10 ⁸
Br ₂	0.251 ± 0.004	not determined	not determined	not determined	(3.8 ± 0.4) × 10 ⁶
BrOCl	not reported	260 ± 50	660 ± 230	(3.48 ± 0.28) × 10 ⁴	(3.7 ± 1.9) × 10 ⁵
Br ₂ O	not reported	not determined	not determined	not determined	(4.1 ± 2.2) × 10 ⁵
HOBr	(1.1 ± 0.7) × 10 ⁻⁴	(1.2 ± 0.5) × 10 ⁻⁴	not determined	0.007 ± 0.007	58 ± 15

^a Arrows denote sites of bromination.

^b Current work

The selectivity of aromatic compounds in **Table 2** toward brominating agents can be quantified as k_{BrCl}/k_{BrOCl} . For *ortho*- and *para*-bromination of anisole, $k_{BrCl}/k_{BrOCl} = 140$ and 18, respectively. That *ortho*-bromination of anisole is more selective for BrCl relative to *para*-bromination is consistent with the lower nucleophilicity of the *ortho* position.⁵⁴ In addition to these electronic effects, increased steric hindrance at the *ortho* position may also attenuate nucleophilicity (and increase selectivity) at this site.⁵⁵

5. Significance

This work provides a more comprehensive framework for understanding the reactivity of bromide during chlorination of bromide-containing waters, including DW, wastewater, and recreational waters (e.g., pools and spas). This project also provides insights into DBP minimization strategies. For example, this project demonstrated the important role of chloride and free chlorine as catalysts of DBP precursor bromination via formation of BrCl and BrOCl, respectively. This work may assist in the development of improved predictive models for DBP formation during field-scale DW treatment. Results from this project may also facilitate re-evaluations of previously published rate constants which relied on incomplete renderings of free bromine chemistry when describing bromination reactions.

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Publication Citations

Sivey, John D.; Daniel A. Victor; Mark A. Bickley, 2014, Contributions of BrCl, BrOCl, and Br₂O toward bromination rates of aromatic compounds in solutions of aqueous free bromine: Implications for water disinfection, 247th American Chemical Society National Meeting and Exposition, Division of Inorganic Chemistry, Dallas, Texas.

Victor, Daniel A.; John D. Sivey, 2014, Reactivity of anisole and bromoanisole regioisomers toward brominating agents in solutions of NaBr + free available chlorine, 247th American Chemical Society National Meeting and Exposition, Division of Inorganic Chemistry, Dallas, Texas.

Victor, Daniel A., 2014, Reactivity of 4-bromoanisole towards inorganic brominating agents in solutions of sodium bromide and free available chlorine, Undergraduate Honors Thesis, Department of Chemistry, Fisher College of Science and Mathematics, Towson University, Towson, Maryland, 36 pp.

Students Supported

*Undergraduate: 0**

Masters: 0

PhD: 0

Post-Doc: 0

* Two undergraduates worked on research related to this project, but neither was financially supported by this grant.

Achievements and Awards

This MD WRRRC grant yielded data which were central to the following grant proposal, which was recently selected for funding:

Sivey, John D. Kinetics of electrophilic aromatic substitution by aqueous BrCl, BrOCl, and Br₂O: Catalysis of alkylbenzene bromination. American Chemical Society Petroleum Research Foundation (Grant #54560-UNI4); \$55,000; Sept. 1, 2014 – Aug. 31, 2016.

During the period of this MD WRRRC grant, the PI was also inducted into the Towson University Academy of Scholars as a junior fellow. This award is presented annually to no more than three pre-tenure faculty members based on their excellence in research.

Validation of non-lethal laparoscopic technique for detection of intersex in regional black bass populations

Basic Information

Title:	Validation of non-lethal laparoscopic technique for detection of intersex in regional black bass populations
Project Number:	2013MD305B
Start Date:	7/1/2013
End Date:	6/30/2014
Funding Source:	104B
Congressional District:	MD-005
Research Category:	Water Quality
Focus Category:	Surface Water, Toxic Substances, Methods
Descriptors:	None
Principal Investigators:	Lance Yonkos, Lance Yonkos

Publications

There are no publications.

NIWR PROGRESS REPORT

PROJECT ID: MWRRRC PROJECT # 2013-MD-305B

**TITLE: VALIDATION OF NON-LETHAL LAPAROSCOPIC TECHNIQUE FOR
DETECTION OF INTERSEX IN REGIONAL BLACK BASS POPULATIONS**

DATE: June 6, 2014

PRINCIPAL INVESTIGATOR

Lance Yonkos, Assistant Professor
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College Park, MD 20742
TEL: 301-405-7871
Email: lyonkos@umd.edu

1. PROGRESS REPORT: SUMMARY

Regional Water Problem

Intersex in the form of testicular oocytes (TO) has been reported with high prevalence in regional smallmouth bass (*Micropterus dolomieu*) and largemouth bass (*Micropterus salmoides*) populations [Blazer et al 2007; 2011; Iwanowicz et al 2009; Yonkos et al 2014]. Prevalence in males from Potomac, Shenandoah, Susquehanna, and several Eastern Shore Watersheds often exceeds 80%. The presence of TO is generally accepted as evidence of exposure to endocrine disrupting compounds (EDCs) and suggestive of reproductive compromise and population level effects [Hinck et al 2009]. This raises concerns for the aquatic food web and for the quality of regional drinking water resources. Potential sources of estrogenic contaminants are numerous (e.g., WWTP effluent, agricultural and urban runoff, etc), but, as yet, no causal link to any particular source or contaminant has been identified that adequately explains the spatial heterogeneity of TO occurrence and severity [Blazer et al 2012]. Continued surveillance of resident fish populations is necessary to determine areas of particular concern and to employ a weight-of-evidence framework for identifying culprit contaminants/activities.

Black bass (largemouth and smallmouth) are climax predators within regional freshwater aquatic food webs. Because they appear uniquely sensitive to EDCs, they are the logical choice as sentinel species for monitoring contaminant effects. However, current methods for identification of TO in require field collection and sacrifice of fish for histological identification of oocytes within testis of male specimens. Generally a minimum of ten male fish is considered necessary to accurately assess TO prevalence and severity at a particular site. Because black bass are only minimally sexually dimorphic (and only during the spawning season), sampling efforts also involve collection and sacrifice of numerous females before achieving the requisite number of male fish. Where bass populations are already imperiled through over-exploitation, habitat modification, contaminant-impacts, and/or competition from invasive species, this level of experimental collection necessarily places an additional impact on population number. Thus, populations in regions where analysis of fish is most warranted are among those least able to accommodate this additional pressure. Employing a non-lethal means of determining TO prevalence will serve to alleviate this pressure while still allowing field assessment of endocrine disruption within impacted populations. Further, targeted regions can be re-sampled over multiple seasons or years to observe temporal shifts including recovery or further decline without undue influence to fish populations.

Project Objectives

Fish populations in many Chesapeake tributaries are sufficiently threatened that any additional burden of research-related collection is difficult to justify. This makes development of an effective non-lethal monitoring technique paramount. To that end, we are examining the efficacy of endoscopy via the genital pore (laparoscopy) as a non-lethal, minimally-invasive sampling technique for collection of largemouth bass (*Micropterus salmoides*) gonadal tissue for the detection of testicular oocytes (TO). Laparoscopic insertion into the body cavity allows testis

tissue collection via biopsy without penetration through the body wall. The method has been demonstrated previously to be effective for non-lethal gender identification in largemouth bass by allowing internal visualization and biopsy of gonadal tissue with high survival, rapid healing, and minimal infection [Matsche 2013]. Our research expands on previous efforts by collecting multiple testis biopsies (n=5) equidistant along a single testis lobe with the purpose of quantifying TO prevalence and severity. This is being accomplished in four non-sequential phases: (1) *Model Development*: determination of testis biopsy number and size necessary to quantitatively establish TO prevalence and severity; (2) *Recovery and Healing*: determination of post-operative survival and healing following multiple-biopsy tissue collection; (3) *Spawning Capability*: determination of post-operative spawning capability; and (4) *Field Validation*: comparison of non-lethal laparoscopic tissue collection and conventional tissue dissection for efficacy of detecting TO in native fish collected from regional waters with a history of high intersex prevalence.

Hypotheses

- H₁: Laparoscopic testicular tissue collection from mature male largemouth bass will heal rapidly and result in minimal mortality
- H₂: Laparoscopic testicular tissue collection will not interfere with natural spawning of mature male largemouth bass
- H_{3a}: Laparoscopic testicular tissue collection from mature male largemouth bass will allow non-lethal detection of testicular oocyte prevalence comparable to conventional methods that require sacrifice and dissection of specimens
- H_{3b}: Laparoscopic testicular tissue collection from mature male largemouth bass will allow non-lethal quantification of testicular oocyte severity comparable to conventional methods that require sacrifice and dissection of specimens

Methods

The proposed project uses a non-lethal laparoscopic technique (pioneered by fish pathologist Mark Matsche, MD DNR, Cooperative Oxford Laboratory, Oxford, MD) to collect testis biopsy samples prior to routine collection of tissue via dissection. Comparison of efficacy of TO detection by non-lethal laparoscopic tissue collection versus routine sacrifice and dissection is being used to determine the appropriateness of the method for field assessment of TO prevalence and severity. Post-laparoscopic survival, healing and spawning ability is being investigated to estimate the actual level of impact the procedure will have when employed on native bass populations. Research is ongoing with efforts toward satisfaction of the four individual objectives taking place concurrently. Hatchery-reared and field-collected largemouth bass are being used variously to ensure sufficient numbers of specimens for method comparison, model development, and/or post-laparoscopic of survival, healing, and spawning assessment. Field sampling is in coordination with on-going MD DNR, USGS, and US FWS population assessment efforts allowing use of already targeted-collections to minimize additional sampling

impacts. Processing of biopsied and dissected tissues is by routine histological processing and necessarily requires sacrifice of research fish. Briefly, tissue samples are dehydrated in alcohol, embedded in paraffin, sectioned at 6 μm , and stained with hematoxylin and eosin [Luna, 1992].

Laparoscopy – Refinement of non-lethal testis tissue collection

Methods for testis tissue collection have been adapted from Matsche [2013] to allow collection of multiple testis biopsies. Briefly, individual largemouth bass are anesthetized with tricaine methanesulfonate (Finquel®, Argent Laboratories, Redmond, WA) and placed dorsal side down between angled plastic positioning blocks with procedures initiated immediately after movement ceases. The urogenital opening is gently dilated using a blunt obturator with surgical lubricant (Surgilube®) followed by insertion of the examination sheath through the urogenital opening to the urinary bladder [Matsche 2013]. The exposed end of the examination sheath is then angled 30° towards the posterior of the fish (to direct the tip toward the head) and 30° toward the left body wall. The obturator is then removed and replaced with the laparoscope and biopsy forceps which are used to perforate the urinary bladder and access the body cavity. To assist with laparoscopic viewing the coelom is inflated using a low-pressure air supply connected to a stopcock on the examination sheath. Guided by the laparoscope, the examination sheath is advanced into the coelom caudally along the left dorsal region of the body wall until the gonad is encountered and gender determined. If determined to be female, procedures are discontinued and the fish is revived (or sacrificed) as necessary. If determined to be male, the five biopsies are collected along an approximately equidistant transect from the left gonad and placed in 10% neutral buffered formalin. The examination sheath remains in body cavity with only the flexible forceps removed during all five biopsies. If survival is to be assessed a passive integrated transponder (PIT) is inserted into the body cavity prior to removal of the examination sheath. If comparison with testis cross-sections is required, fish are sacrificed (via decapitation) and testis removed via routine dissection.

Phase I – Biopsy Validation

The primary goal of this project is to determine whether biopsies can detect TO with the same precision as existing methods using cross-sections from sacrificed fish and whether a severity index can be constructed to facilitate future research. The first step is to determine the instrument size and number of biopsies necessary to provide sufficient tissue for quantitative analysis of TO prevalence and severity, necessary to ascertain the utility and limitations of the laparoscopic technique as a non-lethal means of quantifying TO. The approach is to take multiple biopsies at discrete intervals along the testis using instruments of several sizes with cross-sections taken subsequently from regions between biopsies. Briefly, five biopsies are taken along the left testis lobe using forceps meant for small fish (1.7 mm diameter) and five biopsies are taken along the right testis lobe using forceps meant for larger fish (3.3 mm diameter). Routine histological processing of all biopsies and cross-sections allows comparison of the methods for detection and enumeration of TO. For each specimen, at least one histological section from each of the ten tissue segments and ten biopsies is examined via light microscopy for TO presence and other pathology. Establishment of TO prevalence involves observation of one or more discernible oocytes within preserved testis cross-sections and/or biopsies from an individual specimens. All tissue samples of adequate quality are examined for

the presence of oocytes under low and moderate magnification (4x and 10x objectives, respectively) with confirmation of potential oocytes determined under high magnification (40x objective). Determination of TO severity conforms as closely as possible to the ranking system described by Blazer et al [2007] for smallmouth bass (*Micropterus dolomieu*). Briefly, five cross-sections taken equidistant along the testis lobe are examined by light microscopy using a 10x objective (approx. 4 mm² of tissue) and scored for severity as follows: *Focal Distribution* (Score 1): single oocyte within a microscopic field; *Diffuse Distribution* (Score 2): more than one oocyte in a field of view without physical association with neighboring oocytes; *Cluster Distribution* (Score 3): more than one but less than five closely associated oocytes; *Zonal Distribution* (Score 4): more than five closely associated oocytes or numerous clusters in a field of view. Ranks for each section are averaged to determine a severity rank for the individual specimen. This system is being modified in an attempt to provide equivalent results for biopsy collected tissues. Issues to resolve include: (1) whether biopsies can collect tissues from appropriate regions of the testis and (2) how many biopsy sections need to be observed to provide quantitatively similar results to conventional methods.

Phase II – Survival Study

In order to be deemed effective post-laparoscopy survival must be high with minimal long-term compromises to fish health. Maintaining fish after the laparoscopic procedure allows for monitoring of infection and assessing post-operative healing and survival. Fish are anesthetized and, as described above, approximately five biopsies are taken equidistant along the length of the left testis. Post-operative survival has already been investigated as part of a dedicated “survival” study (March 2014) using hatchery-reared fish (SmartFish Farms, Auburn, KY). Additional survival data is being accrued on fish used in satisfaction of other project objectives. In the dedicated survival study a subset of fish was sacrificed immediately after the procedure (e.g., controls), another cohort was sacrificed at one week to investigate incidence of infection or other pathology, and the remainder were sacrificed at one month to investigate healing and establish long term survival. On sacrifice testis tissue was also collected for comparison of biopsy vs routine dissection. This serves to make more robust the sample size for method validation and model development.

Phase III – Reproduction Study

It is important to determine whether fish remain competent to spawn following laparoscopic biopsy of testis. Sterilizing and releasing a wild-caught mature male largemouth bass could potentially be more damaging to a population than actually sacrificing the fish on collection. He will continue to occupy a territory without contributing progeny. Therefore the third phase of the project is to perform laparoscopy on wild-caught largemouth bass to determine if biopsy collection of the testis affects reproductive capability of male fish. This process is currently underway. Field collected largemouth bass have been laparoscoped to definitively establish gender. Females received no additional treatment while males had five biopsies collected from the left testis. Fish were then segregated by gender and held for a prescribed recovery interval before being paired in spawning raceways at the Manning Hatchery (Cedarville, MD) and monitored for spawning activity. In the event females are induced to release eggs, fertilization success and milt quality will be assessed.

Phase IV – Field Validation Study

The final step of this study involves field validation of laparoscopic testis sampling as an effective tool for identifying TO prevalence and severity. This process is also ongoing. Largemouth bass have been collected via boat electrofishing from the Potomac and Anacostia Rivers. Additional collections are planned for these systems as well as the several watersheds in West Virginia, Pennsylvania, and Vermont. In each system an effort is made to collect testis via laparoscopic biopsy from approximately 10 mature male fish for assessment of TO prevalence and severity. Females are released once identified to minimize the number of fish removed from the system. Use of an electronarcosis system rather than MS222 avoids the need for quarantine allowing immediate release. Males are treated as described previously (i.e., after collection of biopsies fish are sacrificed, testis is removed and cross-sectioned, and all tissues are processed for histological examination).

Application to Other Species

At the request of MD DNR, US FWS, and USGS fisheries biologist, the laparoscopic method has been adapted for use with several other fish species of interest:

- First is the smallmouth bass which has been found in the Potomac and Shenandoah Rivers to have a high incidence of TO. This species has also suffered population declines in these regions as a result of fish kills over the past decade. While no causal link has been established, the possibility exists that TO induction and premature mortality are related to a common contaminant exposure occurring at some earlier life stage. Laparoscopic tissue collection will allow non-lethal investigation of TO prevalence in those regions where smallmouth bass populations are at particular risk. As this species is very similar to the largemouth bass, only minimal adaptation of the method is required. Also, since smallmouth bass generally occupy a distinct range from that of largemouth bass, this expands the inland surface waters systems that can be investigated for TO using this method.
- The northern snakehead (*Channa argus*) is a large fast-growing predatory fish species native to China but now invasive and established in many Chesapeake Bay tributary rivers. The species competes effectively with largemouth and smallmouth bass but grows faster so adds an additional stressor to systems where it is present. Currently very little is known about the reproductive biology of the snakehead including spawning frequency and other fecundity criteria. Even knowledge of whether females are single or multiple spawners is lacking. For this reason the laparoscopic method is being adapted to non-lethally investigate gonad development in female northern snakehead. The intent is to track gonad development in individual female fish over protracted periods to determine seasons of maturation and establish whether fish are single or multiple spawners. This information is considered paramount when devising management strategies. As the northern snakehead differs morphologically in significant ways from the largemouth bass, modification of the laparoscopic method will be more substantial and may require different instruments.

Preliminary Findings

While laparoscopic tissue collection does show promise for detecting testicular oocytes, all *Phases* of this project are ongoing; results are, therefore, incomplete and much work remains before endorsement of the method is justified. Preliminary results do indicate that laparoscopic imaging of the body cavity provides rapid, non-lethal gender identification. This allows release of females so minimizes population impacts of scientific sampling. Preliminary findings for individual objectives are as follows:

- *Model Development* — Determination of comparable amounts of tissue (i.e. cross-sectional area) between biopsies and conventional dissection is complete. However, determination of the ability of testis biopsies to detect TO requires a multitude of fish with the intersex condition, preferably demonstrating a range of severities. We have, thus far, encountered only one fish with TO which was detected both by conventional dissection and by biopsy (3.3 mm forceps). This is a promising start but very far from definitive. Further model development will require sampling of many more fish with TO. Field collections from sites with histories of high TO prevalence and severity will hopefully satisfy this need.
- *Survival* — Results from the dedicated “survival” study indicate post-surgery survival to 28 days is high ($\geq 80\%$) as is healing based on integrity of the urinary bladder ($\geq 90\%$). Survival of laparoscoped fish employed in satisfaction of other project *Phases* (e.g., spawning capability) indicate that this is a reasonable estimate of survival. Some caveats to be explored the implications of season and/or water temperature on survival and the health of the fish on collection. For example, fish with large parasite loads already have compromised immune function and I high likelihood of infection suggesting a greater
- *Spawning Capability* — Currently eight pairs of largemouth bass are being maintained in spawning raceways at the Manning Hatchery, Cedarville, MD. These fish were collected from regional waters (mostly the Potomac River) over approximately the past month. Unfortunately, unusually cold spring weather in the region has impeded normal spawning of largemouth bass, both in natural surface waters and in the hatchery ponds. Our fish are behaving in similar fashion with some evidence of male spawning behavior but no eggs released and therefore no milt release and fertilization. As largemouth bass spawning is seasonal and highly temperature dependent, this research *Phase* may not be suitably addressed during the period of project
- *Field Validation* — Largemouth bass have been successfully collected from regional waters and testis sampled via laparoscopic biopsy for identification of TO. Results are pending. Collection of fish from a region in Vermont with known history of high intersex is planned for the week of June 8 – 13. Additional collections in regions with historical detection of TO are planned for later in the summer and fall 2014. Smallmouth bass are also being collected where resident, allowing a multispecies comparison of method effectiveness. Results of all collections should be available by December 2014.

Significance

Preliminary results suggest laparoscopic tissue collection has promise as a non-lethal field sampling strategy. Since mortality is generally low (e.g., < 20%) the method appears especially well suited for use in regions where fish populations are already compromised. The method also shows significant adaptability for application to other species of interest, broadening the scope of potential studies. This procedure could provide fishery managers and scientists with an additional tool for monitoring fish populations for intersex both temporally (by repetitive sampling of individual fish) and spatially (by including compromised regions without causing undue impact). Field studies could be designed to correlate observed effects (i.e., TO prevalence and severity) with particular land use practices (e.g., non-point source agricultural runoff, WWTP effluent discharges) in an attempt to identify culprit contaminants and devise management strategies. There also exist the potential to use the method to non-lethally sample other tissues (e.g., liver) for contaminant analysis.

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2. PUBLICATIONS ASSOCIATED WITH THE RESEARCH PROJECT

As the work is on-going, no publications have yet been generated associated with this research. There have been numerous poster presentations including four related abstracts accepted at professional scientific meetings.

3. STUDENTS SUPPORTED BY RESEARCH PROJECT

One master's student in the University of Maryland - Department of Environmental Science and Technology, Alex MacLeod, is focusing the majority of his thesis research on validation of laparoscopic tissue collection as a viable means of non-lethal testicular oocyte detection and quantification. By adapting techniques and equipment to provide quality results, he is optimizing the method for rapid and reproducible biopsy collection on bass testis from fish of various ages/sizes. He is also adapting the method for use on other species including the invasive northern snakehead (*Channa argus*). Additionally, he is working with regional partners to demonstrate the utility of laparoscopy as a sound approach for field monitoring of fish condition. Included are fisheries biologists and environmental toxicologists from MD DNR, USGS Leetown Science Center, US FWS Chesapeake Bay Field Office, and elsewhere.

A Gemstone Undergraduate Research Team comprised of eight (8) undergraduate students from various University of Maryland academic departments has been supported in large part by this MWRRRC-funded project. They are investigating poultry litter-induced intersex in largemouth bass by exposing batches of fish at various ages to aqueous poultry litter mixtures and growing to maturity for Assessment of testis pathology. While they have not actually used the laparoscopic procedure on their test fish, they have been trained on the method and assisted Alex MacLeod in his efforts.

4. NOTABLE ACHIEVEMENTS AND AWARDS

Alex MacLeod was awarded a \$5,000 Dean's Fellowship from the College of Agriculture and Natural Resources largely in recognition of the quality of his laparoscopy validation research project.

Tracing the rates of road salt runoff movement from impervious surface to stream and the effects on soil and aquifer geochemistry

Basic Information

Title:	Tracing the rates of road salt runoff movement from impervious surface to stream and the effects on soil and aquifer geochemistry
Project Number:	2013MD306B
Start Date:	6/1/2013
End Date:	5/30/2014
Funding Source:	104B
Congressional District:	MD 3
Research Category:	Water Quality
Focus Category:	Geochemical Processes, Solute Transport, Water Quality
Descriptors:	None
Principal Investigators:	Joel Moore, Steven Lev

Publication

1. Moore J., S. M. Lev, R. E. Casey, 2013, Modeling the effects of road salt on soil, aquifer, and stream chemistry in 2013 MODFLOW and More Conference Proceedings, Integrated GroundWater Modeling Center, Golden, CO. 5 pp.

Progress Report

Tracing the rates of road salt runoff movement from impervious surfaces to stream and the effects on soil and aquifer geochemistry

2013-MD-306B

PI: J. Moore

March 1, 2013 – February 28, 2014

1) Narrative summary – Progress Report

Problem and Research Objectives

Runoff from impervious surface that contains dissolved road salt (NaCl) clearly affects the chemistry of soils, groundwater, and streams. However, effects on soils, groundwater, and streams typically have been studied in isolation from each other. Also, the effects of stormwater management basins on road salt movement from impervious surfaces to streams have not been investigated. The research funded by this grant has the goal of addressing the following questions about road salt movement from impervious surfaces to streams in a system with stormwater management basins.

- a) What are the rates of Na and Cl movement from impervious surface to stream?
- b) Where and how along the flow paths from road to stream are Na and Cl retained?
- c) What is the effect of Na retention on soil and shallow aquifer chemistry, particularly on pH and the concentrations of important plant macronutrients like calcium (Ca), magnesium (Mg), and potassium (K) in the cation exchange complex?

Methods

The methods employed include collection of

- Physical data such as stream discharge and water table levels
- Collection of water and soil/aquifer matrix samples at the field site
- Chemical analysis of those samples in the Urban Environmental Biogeochemistry Laboratory at Towson University including
 - Concentration of cations and anions in water via ion chromatography
 - Composition of the cation exchange complex via BaCl₂ extraction and then ion chromatography
 - Soil pH via 0.1M CaCl₂ suspension and pH probe
- Deployment of pressure and conductivity sensors to continuously monitor water level and the total dissolved content

Principal Findings

Stream discharge and water table levels increased from fall into winter as trees shed their leaves and evapotranspiration rates decreased. Na⁺ and Cl⁻ were loaded into groundwater via stormwater management basins (SMBs) and then moved via surface and groundwater flow into first- and second-order streams. In groundwater below the SMBs, Cl⁻ concentrations increased rapidly at the beginning of the 2013–14 winter and approached seawater concentrations (Fig. 1). Through early spring, Cl⁻ and Na⁺ concentrations decreased slowly. A similar, though smaller amplitude, Cl⁻ and Na⁺ concentration increase from fall into winter and then decline into early spring was seen in groundwater downgradient of the SMBs.

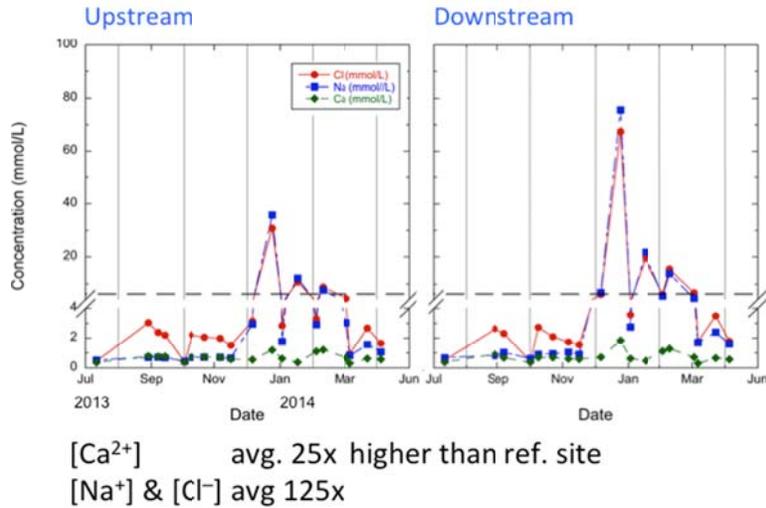


Fig. 1: Calcium, chloride, and sodium concentrations upstream and downstream where water from two stormwater management basins enters the stream via surface and groundwater. Concentrations are compared to a reference watershed ~15 km to the northeast with similar bedrock and a similar size.

The movement of high Na⁺ water through groundwater has increased the pH and Na⁺ concentrations in soils and aquifer matrix downgradient of the SMBs (Fig. 2). Compared to unaffected soils, soil pH increased from a value of ~4.5 to pH 6–7 and the Na⁺ fraction of the cation exchange complex increased from 0 to 20–40%. Measured Na⁺ fractions of the cation exchange complex in road salt-affected soils matched well with predictions from the PHREEQC geochemical model. Na⁺ replaced H⁺, Mg²⁺, and, to a lesser extent, Ca²⁺ in the cation exchange complex.

Significance

Preliminary results of this study increase understanding of how road salt affects the chemistry of soils/aquifer matrices, groundwater, and streams. Understanding groundwater and stream chemistry across seasons will provide information that will be useful in predictive models of road salt impacts in the future. Understanding of the effects of high Na⁺ water on

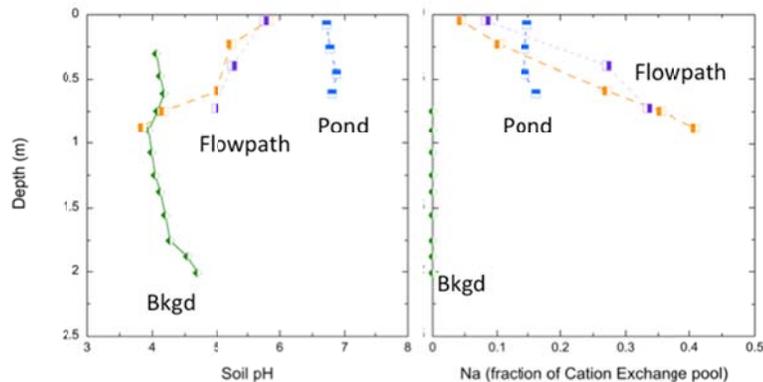


Fig. 2: Soil pH and Na as a fraction of total cation exchange pool versus depth in soils and aquifer materials from outside the road salt-affected area (background), within the flowpath from stormwater management basins (SMBs) to stream, and under the SMBs (pond). Soils and aquifer materials in road salt-affected areas exhibit a pH increase of 1–2.5 units and a Na increase from 0 to up to 0.4 of total cation exchange.

soil and aquifer matrix chemistry provides information that is important for assessment of the longer term impact of road salt.

2) Publication citations

Conference proceedings

Moore J., S. M. Lev, R. E. Casey, 2013, Modeling the effects of road salt on soil, aquifer, and stream chemistry in *2013 MODFLOW and More Conference Proceedings*, Integrated GroundWater Modeling Center, Golden, CO. 5 pp.

Abstracts

Moore J., Sandosky B.***, McGuire M., Casey R. E., Snodgrass J. W., Lev S. M. (2014) Alteration of Critical Zone chemistry due to addition of rapidly dissolving rock salt. *Goldschmidt Conference*, Sacramento, CA.

Sandosky B.***, Lev S. M., Casey R. E., Snodgrass J. W., McGuire M., **Moore J.** (2014) Increased Chemical Fluxes to the Critical Zone due to road salt (halite) addition. *Geological Society of America, Northeastern Section Meeting*, Lancaster, PA.

Moore J., Sandosky B.***, McGuire M., Casey R. E., Snodgrass J. W., Lev S. M. (2013) Salt overload: How quickly does road salt move from road to groundwater to stream in Baltimore County, MD and what are the effects on soil, groundwater, and stream chemistry? *Fall American Geophysical Union Meeting*, San Francisco, CA.

Moore J., Lev S. M., Casey R. E. (2013) Modeling the effects of road salt on soil, aquifer, and stream chemistry. *MODFLOW and More 2013: Translating Science into Practice*, Integrated GroundWater Modeling Center, Colorado School of Mines, Golden, CO.

3) Student Support

MWRRC and matching funds have supported stipends for 1 undergraduate student and 1 masters student. Research associated with this grant, including analytical costs, have supported 2 additional graduate students.

4) Notable achievements and awards

The sensor deployment originally proposed in this grant is being built upon through funds applied for, and received from, the School of Emerging Technology at Towson University. The \$31,725 in funds was used to purchase additional conductivity and pressure sensors as well as Isco instruments for measuring pipe flow in culverts. Joel Moore is collaborating with Michael McGuire, a computer scientist specializing in spatio-temporal data mining algorithms, on this project.

Joel Moore applied for, and was awarded, a three-year endowed chair position awarded to pre-tenure faculty (Jess and Mildred Fisher Endowed Chair of Geological Sciences) in part to expand on the work originally proposed in the MWRRC grant.

Enhancing watershed infiltration to restore urban stream hydro-ecological function (Graduate Fellowship)

Enhancing watershed infiltration to restore urban stream hydro-ecological function (Graduate Fellowship)

Basic Information

Title:	Enhancing watershed infiltration to restore urban stream hydro-ecological function (Graduate Fellowship)
Project Number:	2013MD307B
Start Date:	5/1/2013
End Date:	10/30/2013
Funding Source:	104B
Congressional District:	MD 3
Research Category:	Water Quality
Focus Category:	Methods, Non Point Pollution, Water Quality
Descriptors:	None
Principal Investigators:	Kaye Lorraine Brubaker, Margaret Palmer

Publications

There are no publications.

Maryland Water Resources Research Center
2013 Fellowship progress report for Rosemary Fanelli
Marine, Estuarine, and Environmental Science graduate program
University of Maryland, College Park
June 12, 2014

1. Summary of research objectives

The objectives of this research is to explore whether urban headwater stream hydro-ecological function may be restored by enhancing lost hydrological processes, such as stormwater infiltration and storage, through restoration activities within their watersheds. The proposed research for summer 2013 focused specifically on assessing the impacts of infiltration-based watershed restoration activities on stream water quantity and quality, and subsequently invertebrate community composition (in the following spring). Please see proposal for details on the experiment design.

2. Methods, preliminary results, and next steps

2.1. Hydrometric monitoring

I installed three tipping bucket rain gauges to record high-frequency rainfall patterns in the region (rainfall storm totals and average and maximum rainfall intensity). To monitor the hydrologic response to storm events in each of the nine streams, I established and maintained pressure transducers measuring water depth at 5-minute intervals in each stream. Next, I selected components of the flow regime (timing, magnitude, flashiness, duration, or frequency) that might be modified by urbanization and that could also be potentially quantified using stream stage data. For this study, I chose to use flashiness and timing metrics to compare the hydrologic responses in the urban degraded, urban restored and forested streams. I developed appropriate stage-based metrics that serve as proxies for these components. The first two are flashiness metrics, and are defined as the maximum rate-of-change for both rising and falling limb during a storm event. The third and fourth metrics describe the timing of the hydrologic response: the lag-to-peak and the rise time (see Figure 1 for more details). I used a 3-month test period from 4-13-13 to 7-26-13 to apply these metrics. During the test period, seven storms triggered runoff responses in all nine sites, and the stage hydrographs for these seven storms were used to quantify the four metrics for each stream.

Both overall flashiness metrics (average maximum rate-of-change in a 5-minute period for rising and falling limbs during the seven storms, respectively) were highly correlated with percent impervious of the watershed (Figure 2). Flashiness metrics for individual storm events were highly correlated to % impervious (R^2 ranged from 0.76-0.90), though regression slopes varied; variable regression slopes might originate from storm-specific characteristics (duration, rainfall intensity, etc.). In contrast, average timing metrics for the seven storm events were not sensitive to percent impervious cover (R^2 of 0.01 and 0.04 for rise-time and lag-to-peak metrics, respectively), and were instead more sensitive to catchment area. Lag times are a function of the storm event characteristics (including duration of the storm), watershed characteristics, and land cover, and are expected to decrease with increasing impervious cover. However, normalizing the timing metrics by storm characteristics (duration, rainfall intensity or rainfall total) for each event did not improve their correlation with percent impervious cover.

The next steps for this project are to expand the stage analysis to more storm events and to increase the temporal frequency of stage measurements. I've decreased the time intervals on all pressure transducers to three minutes in an effort to improve the accuracy of the timing metrics. Moreover, I'm also conducting additional analyses using a paired catchment approach to explore the application of these stage-based metrics to assess the effectiveness of infiltration-base water restoration. Two watersheds selected for further study: both CH1 (urban restored) and CH2 (urban degraded) have similar catchment size, shape, and percent impervious, and are located adjacent to each other. By using this approach, I can reduce the effect of some of the watershed characteristics that may co-vary with the timing metrics (namely, catchment area).

2.2. *Water quality*

I began baseflow sampling at eight of the nine sites in February 2013 and will continue to be collected until February 2015. Each month, a grab sample is collected and is filtered using a 70-um filter within 24 hours of sampling. After filtering, the sample is divided into three aliquots: one for anions, one for dissolved organic carbon and one for ammonium. I ran the samples for major anions (Cl^- , SO_4^{2-} and NO_3^-) for the first 6 months of the study and the results for this analysis are discussed below. While samples are taken at each site, in-situ water quality parameters (pH, temperature, dissolved oxygen, conductivity and specific conductance) are also measured in each stream using a YSI hand-held probe and are briefly discussed below as well. Samples for trace metals were also sampled during the months of March 2014 and April 2014 to coincide with the aquatic macroinvertebrate sampling (see section 2.3. for more details).

As expected, chloride concentrations were greatest in the three urban streams, followed by the two restored streams and the three forested streams (Figure 3). Impervious surfaces in watersheds with high levels of urban land cover are often sources of chloride due to de-icing activities in the winter time in the mid-Atlantic. Chloride concentrations were greatest in the winter and spring, when active road de-icing is likely occurring. Elevated concentrations persist into the summer months, however, and may indicate either an additional source of chloride in the watersheds or that groundwater contributing to baseflow in the summer was recharged during these winter months when chloride loading into the watershed was high. Nitrate-N concentrations were also greatest in the urban streams, intermediate in the restored streams, and lowest in the forested streams (Figure 3). When examining nitrate concentration dynamics at individual sites, a few sites consistently exhibited elevated concentrations throughout the time period (CH1, CH2, CC), while others sites had consistently low (or undetectable) concentrations (SW 1, 2, 3, ML, RR).

Next steps for understanding patterns in water quality across my sites is to analyze more samples for more constituents; for example, the trace metal sampling conducted this spring may reveal some factors driving community composition differences among sites. Limited storm event sampling of conducted, nutrients and trace metals may also be conducted this summer.

2.3. *Assessing macroinvertebrate community composition*

I followed the general Maryland Biological Stream Survey (MBSS) protocols for benthic macroinvertebrates sampling. Sampling of the aquatic community in each stream took place between April 21-28, 2014, and two additional suburban streams were sampled as well. Briefly, I selected a 50-meter reach that represented the overall geomorphology of the entire stream channel. In the selected reach, I used a 540 μm D-net and sieve bucket, I sampled approximately 20 ft^2 of favorable habitat. MBSS targets "favorable" habitats in their methodology, including

high-quality riffles (if present), stable leaf packs, roots wads, and woody debris. Each 1 ft² sample of habitat was disturbed and the habitat (if removable) was removed from the stream and processed in the field for 5 minutes or until all organisms had been removed from the sample. If the habitat was not mobile, it was disturbed (kicked, rubbed with hands or the net) and the D-net was placed downstream to capture organisms that were loosened in this process. The net contents were then processed in a similar manner as above. All organisms from the stream were placed in a composite bucket and fixed with 95% ethanol and stored until analysis. In the lab, biota from each composite sample will be identified to the lowest taxonomic level possible (genus or tribe), and a variety of metrics to describe community composition will be calculated (i.e., species richness, Shannon diversity index, percent EPT taxa, etc.).

Field sampling of the macroinvertebrate sampling took place between April 21 and April 28, 2014. Striking differences in both general taxa richness and overall organismal abundance was observed across the nine sites and both abundance and order-level richness are highly correlated with percent impervious (Figure 4). The restored sites (highlighted on Figure 4) show no improvement in either abundance or order-level richness for their given level of impervious, suggesting that the restorations may not be addressing the factors that are prohibiting more sensitive taxa from recolonizing these streams. Next steps for this project is to identify the organisms to their lowest taxonomic level (often genus), and to conduct multivariate statistical analyses with the community composition datasets as well as the stage-based metrics and the water quality datasets to determine what factors might be driving changes in community composition across the urbanization/restoration gradient.

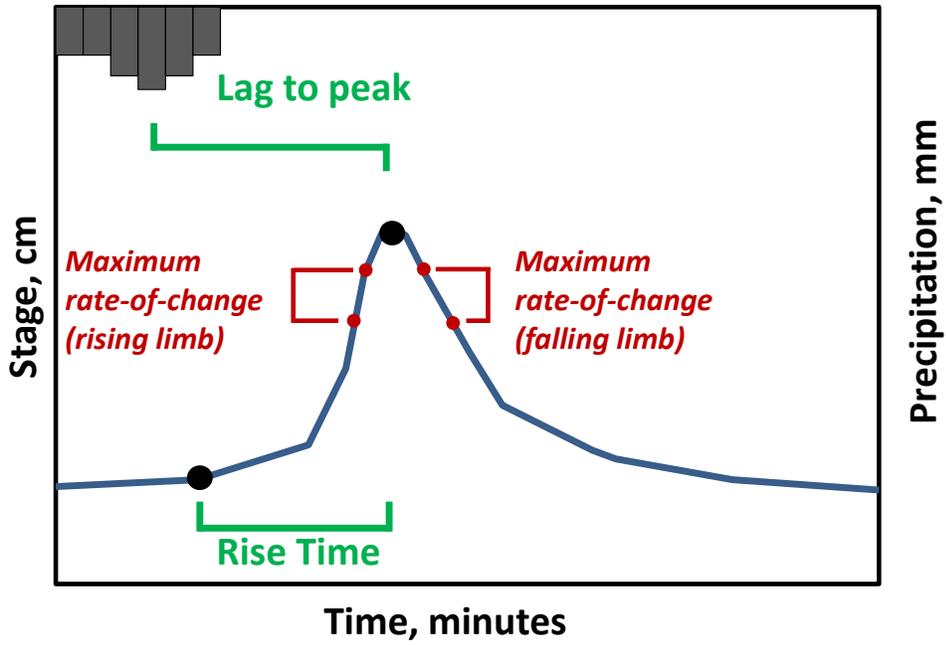


Figure 1: Conceptual diagram of the four stage-based metrics used in this study.

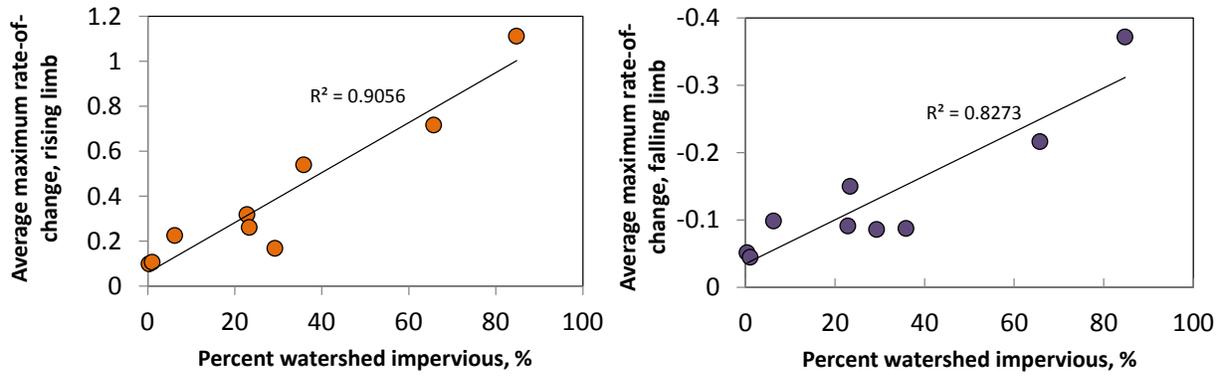


Figure 2. Relationship between catchment impervious cover and flashiness metrics averaged across the seven storm events for each watershed. Units of the rate-of-change metrics are the maximum change in stage during a 5-minute time period during either the rising or falling limbs, normalized by the average stage over the entire time period.

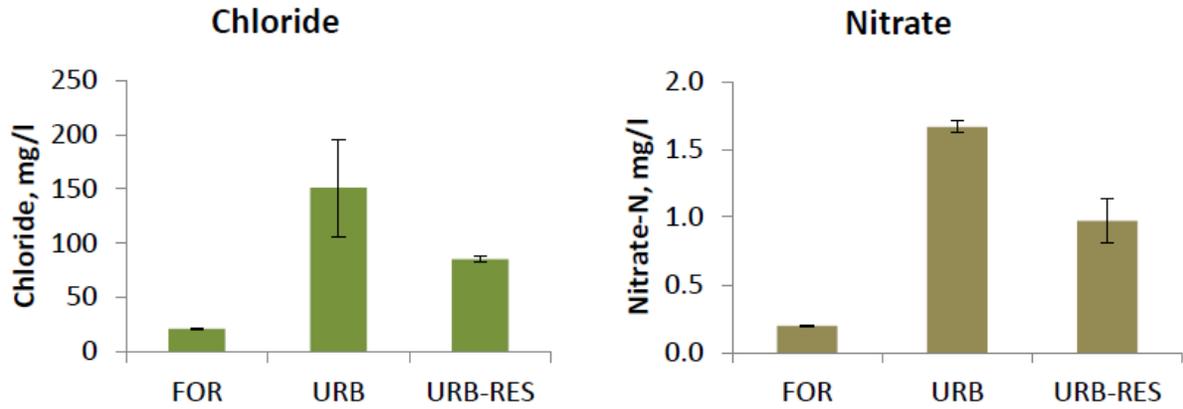


Figure 3: Average concentrations of chloride (left) and nitrate-N (right) for forested (n=3), urban degraded (n=3) and urban restored (n=2) streams. Saltworks, the third restored stream, was not sampled at points during this time period (February through August) due to restoration activities occurring in the steam channel.

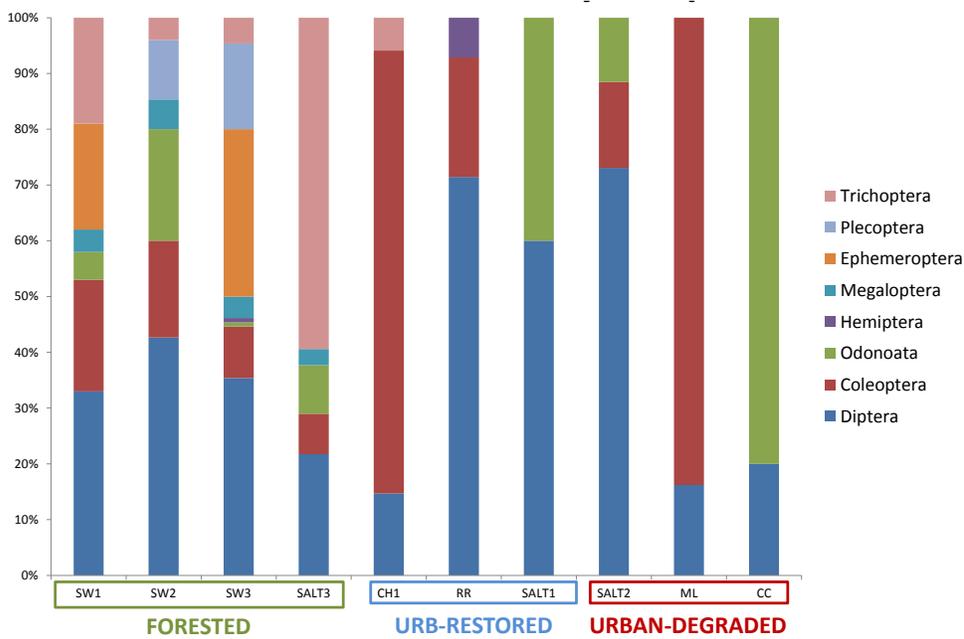
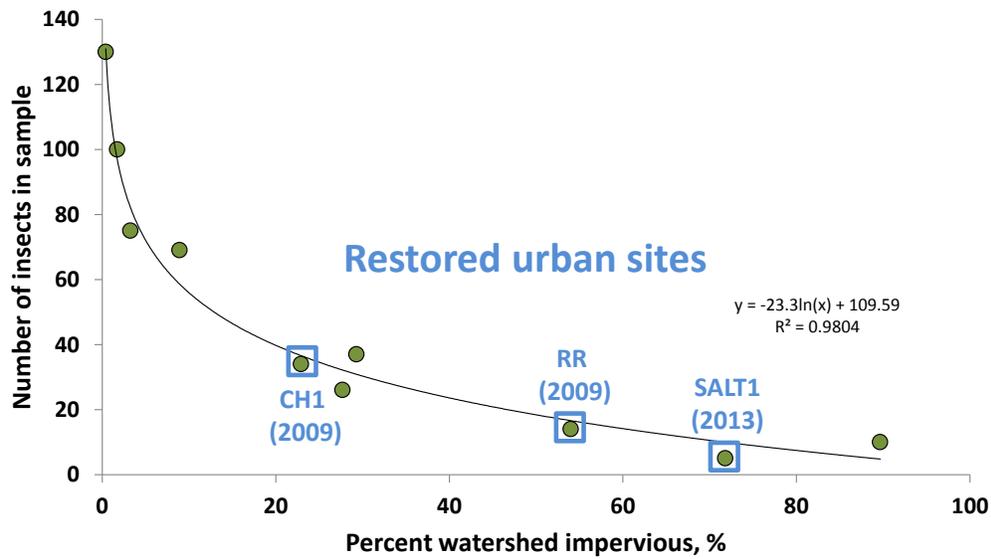


Figure 4: Preliminary results on the overall insect abundance and community composition in the 10 study streams. *Top panel:* relationship between watershed percent impervious and overall insect abundance. The blue boxes highlight the three urban restored streams; years below their name indicate the year in which they were restored. *Bottom panel:* Order-level community composition of each sample at each site, grouped by overall watershed status (forested, urban restored or urban degraded).



Photo 1: R. Fanelli conducting the macroinvertebrate sampling April 2014 at Riva Rd, one of the streams whose watershed received an infiltration-based restoration. Photo is looking upstream, toward the restored section.



Photo 2: R Fanelli's field assistant, C Mummert (undergraduate Biology major) sorting a sample for macroinvertebrate sampling in April 2014. Photo was taken at one of the forested sites (SW3), looking downstream.

The role of streams in nitrogen fluxes from watersheds in the Choptank Basin (Graduate Fellowship)

The role of streams in nitrogen fluxes from watersheds in the Choptank Basin (Graduate Fellowship)

Basic Information

Title:	The role of streams in nitrogen fluxes from watersheds in the Choptank Basin (Graduate Fellowship)
Project Number:	2013MD308B
Start Date:	5/1/2013
End Date:	10/31/2013
Funding Source:	104B
Congressional District:	MD 1
Research Category:	Water Quality
Focus Category:	Nitrate Contamination, Water Quality, Geochemical Processes
Descriptors:	None
Principal Investigators:	Kaye Lorraine Brubaker, Thomas Richard Fisher

Publications

There are no publications.

Denitrification, N₂O emissions, and nutrient export from coastal plain streams

John Gardner

MS in Marine, Estuarine, and Environmental Science (MEES)

University of Maryland Center for Environmental Science-Horn Point Laboratory
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Report to the Maryland Water Resources Research Center for the
Summer 2013 graduate research fellowship

Introduction

Denitrification remains the least understood transformation in the aquatic and terrestrial nitrogen (N) cycle. Among aquatic ecosystems, rivers have the highest areal rates of denitrification as well as the greatest spatial temporal variability, and could be a large source of N₂O to the atmosphere. However, most of our understanding is derived from laboratory studies with few reach scale measurements of denitrification and N₂O production. N₂O can be produced as a byproduct of nitrification and denitrification and is a powerful greenhouse gas and the dominant ozone depletor. It is often assumed N₂O and other biogenic gases found in headwater streams are a result of biogeochemical processes occurring along groundwater flowpaths prior to emerging in streams, but little empirical evidence exists. The open channel method was used to quantify denitrification and N₂O production as a result of in-stream production as well as the biogenic N₂ and N₂O delivered via emerging groundwater in three stream reaches within a small mixed-land use watershed.

Base and stormflow nutrient export were also measured from this watershed as well as two others representing a gradient of land use (0 to 66% agriculture or ~100-34% forest). Storms can account for a large fraction of N and phosphorus (P) export; however, hydrochemical storm response has varied depending on climate, geology, land use, and watershed features. It is important to measure stream chemistry during storms for nutrient budgeting as well as elucidating sources and transport mechanisms.

The overall objectives of this research were to 1) quantify biogenic N₂ and N₂O accumulation in streams from in-stream and groundwater sources, 2) evaluate a recently developed method for estimating gas transfer velocity (k) using ²²²Rn, 3) examine reach scale controls of N₂ production and N₂O emissions in one small stream network, 4) investigate patterns of nutrient concentrations during storm and baseflow to understand transport mechanisms and sources, and 5) compare base and stormflow nutrient export at the event and annual scale.

Results and Conclusions

During the summer of 2013, the final portion of field work was conducted for the 2012-2013 water year. Select results and conclusions are presented based on analysis of the entire water year. Watershed characteristics of the three study sites are presented in table 1. Baltimore Corner (BC) and South Forge (SF) have 26 and 66% agricultural land use while Marshy Hope

(MH) is 99% forested. Open channel studies of denitrification and N₂O emissions were focused in BC and conducted seasonally in three stream reaches.

Table 1. Area, land use, soils properties, and average baseflow nitrate, total nitrogen and total phosphorus concentrations for the South Forge, Baltimore Corner, and Marshy Hope watersheds.

Watershed	Area (km ²)	% Ag	% Forest	% Hydric Soils	NO ₃ ⁻	TN	TP
SF	8.49	66	28	35	325	354	1.32
BC	4.84	26	60	1.0	199	256	1.15
MH	1.36	1.0	99	55	1.11	33.3	0.41

Results demonstrated the one-station open channel method can be reduced to 6 hours (as opposed to the typical 12-24 hour duration) and used to simultaneously quantify biogenic N₂ and N₂O production from in-stream and groundwater sources. Also, ²²²Rn may provide a relatively simple and reliable method of empirically estimating gas exchange velocity in gaining streams. Biogenic N₂ from groundwater accounted for 38-100% (81% on average) of the total N₂ production in agricultural headwater streams and could be an important term loss term of watershed N budgets in coastal plain headwater areas. In-stream denitrification rates were significant (range: 0-7 mmol m⁻² h⁻¹), but varied greatly over time with less spatial variation between the three reaches. Denitrification was undetectable (negative rates were interpreted as undetectable) with this method during spring months due to the influence of high concentrations of physical and biogenic N₂ in emerging groundwater.

N₂O was largely produced in-stream while groundwater was a small source of N₂O emissions from streams (~13% of total emissions on average). N₂O emissions to the atmosphere were relatively high from the agricultural streams (mean 55 μmol m⁻² hr⁻¹), but with strong

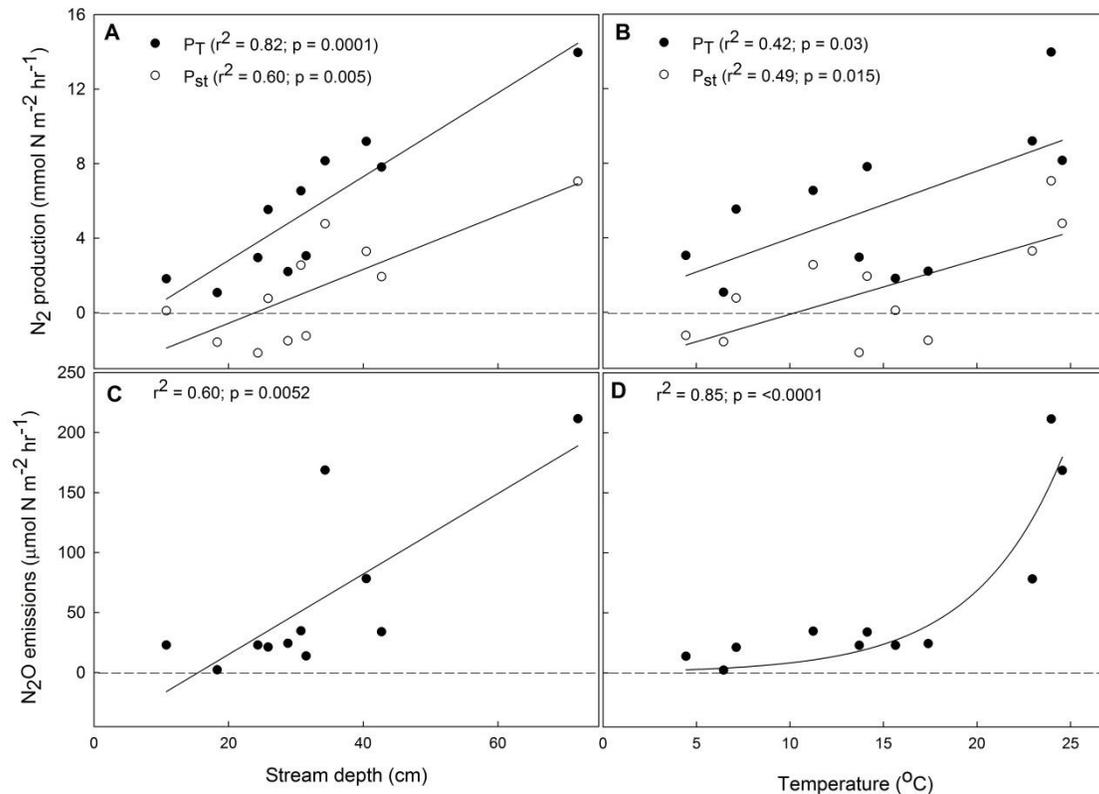


Figure 1. Relationships between antecedent stream depth (ASD) the week prior to each study and temperature with N_2O emissions, total N_2 production (P_T), and in-stream N_2 production (P_{st}).

seasonality. One study conducted in a low nutrient, forested stream indicated this stream was a small N_2O sink.

Antecedent stream depth (mean depth week prior to measurements) and temperature were significant reach-scale controls of N_2 production and N_2O emissions in the BC stream reaches (Fig. 1). Antecedent stream depth is control over short time scales that reflect hot moments occurring in stream sediments and riparian zones during baseflow recession induced by high flow events. Temperature accelerates microbial processes and may be a control over a longer (seasonal) time scale.

Large storm events were very important for transport of TP, PO_4^{3-} , and NH_4^+ in agricultural watersheds within the Maryland coastal plain. However, storms are relatively insignificant in a forested watershed where export of all N and P species was approximately proportionate to flow at the event and annual scale (Fig. 2)

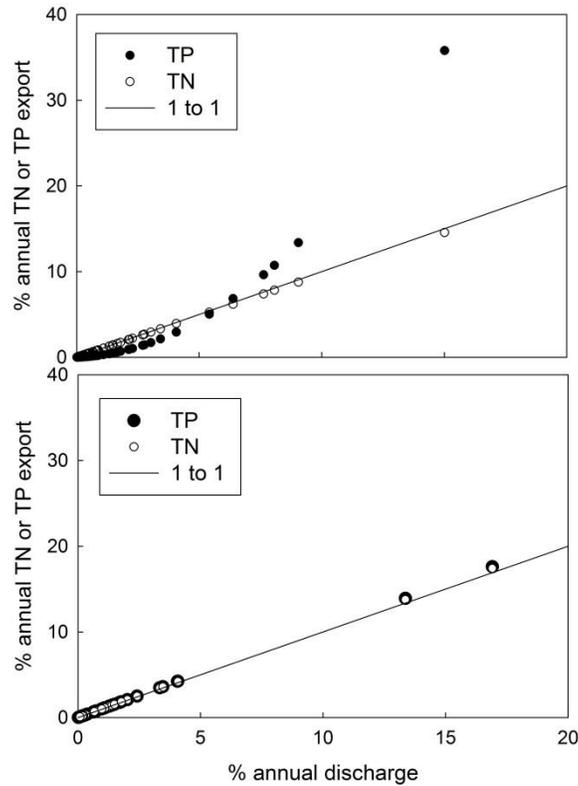


Figure 2. Relationship between % annual discharge and % annual export of TN and TP of individual storm events in the BC (top) and MH (bottom) watersheds. Sampled storm data was extrapolated to all unsampled events to estimate TN and TP export. TN follows the 1 to 1 line, however TP reaches a threshold storm size and export rapidly increases in BC. TP and TN export are approximately proportional to flow at MH with slopes slightly above 1.

Annual TN and TP export coefficients for the 2012-2013 water year in the BC (21 and 1.5 Kg ha⁻¹ y⁻¹ respectively) and SF (38 and 1.2 Kg ha⁻¹ y⁻¹) watersheds were relatively high given the amount of agricultural land use (26 and 65% respectively), reinforcing small streams can be important nutrient sources. However, there was substantial inter-annual variation due to differences in water yield as demonstrated by data from SF that dates back to 2004 (Fig. 3), and the 2012-2013 water yield was above average.

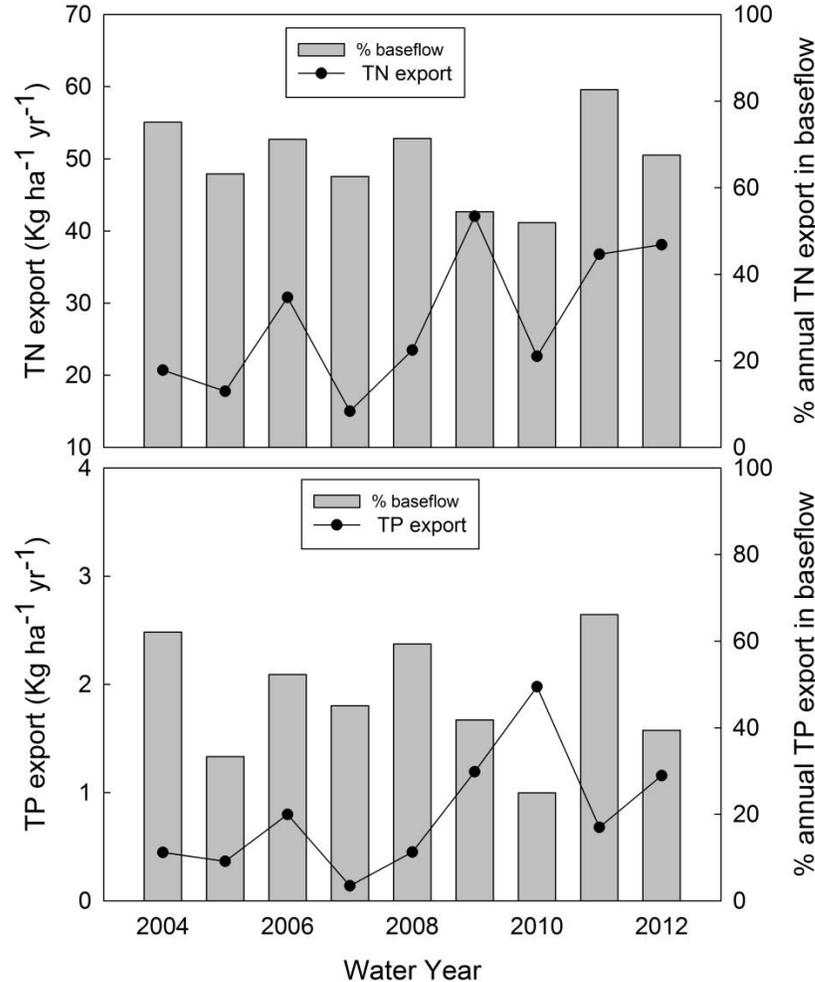


Figure 3. TN (top) and TP (bottom) annual export over water years 2004 to 2012 in the SF watershed as indicated by the line graph and left y-axis. Bar graphs (right y-axis) show the percent exported in baseflow, the remaining percent was due to stormflow.

Patterns in nutrient concentrations during storms suggested that in agricultural watersheds, groundwater was the dominant NO₃⁻ source, but NH₄⁺ and P were likely mobilized from in and near stream sources (Fig. 4). In the MH forested watershed, the NO₃⁻ and NH₄⁺ source during storms was atmospheric and the TP source was in-stream organic matter. Organic N and P fractions dominated base and stormflow at MH; however, large summer NH₄⁺ peaks in baseflow were observed.

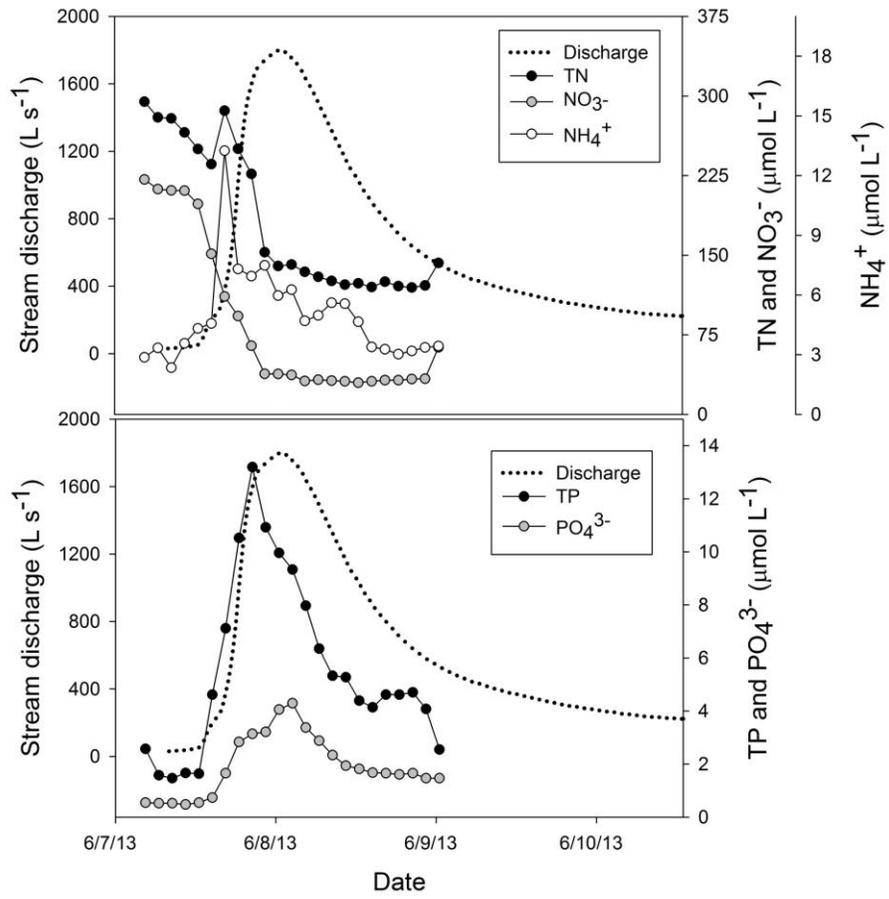


Figure 4. Hydrograph and chemographs for TN, NO_3^- , NH_4^+ (top), TP, and PO_4^{3-} (bottom) during the 6/6/2013 storm in the BC watershed.

Additional Figures

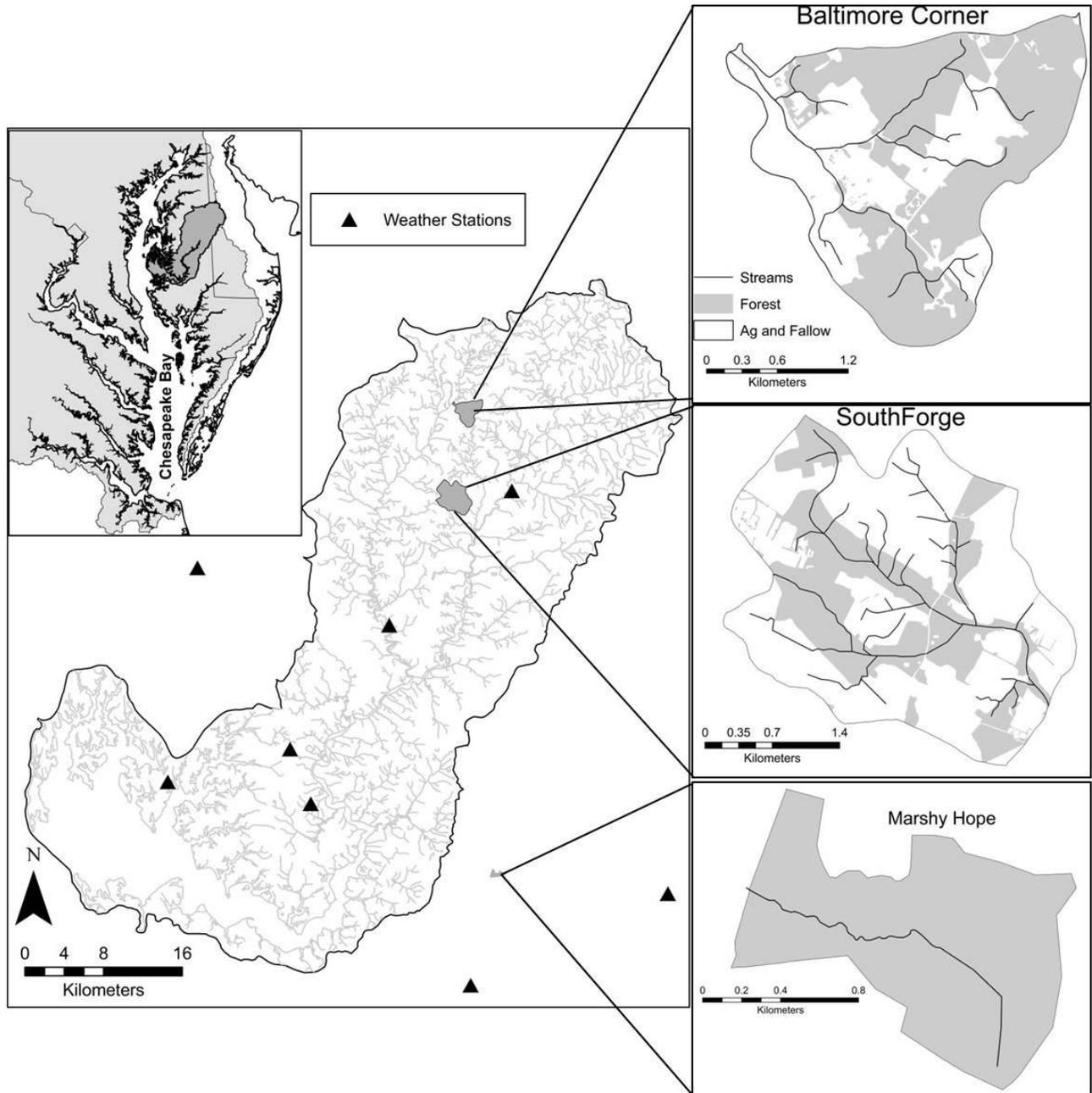


Figure 4. Map of the Choptank watershed with in inset of its location relative to the Chesapeake Bay. The three study watersheds are shaded in gray. Weather stations, both NOAA and Wye Research Center NADP site, are represented by black triangles. The three study watersheds are displayed on the right with land use (gray=forest, white=agriculture and fallow).



Top left: Sampling groundwater piezometers in BC watershed.

Top right: Setting up an ISCO autosampler for capturing storm events at the outlet of the BC watershed.

Bottom left: Measuring discharge in a small ditch in the BC watershed.



Top: Dr. Tom Fisher (and John Gardner) measuring storm discharge following Hurricane Sandy.

Bottom left: ISCO autosampler at the MH forested watershed.

Bottom right: Groundwater piezometer sampling for dissolved gases in a ditch in the BC watershed.



Modeling the effects of green roof substrate organic matter on stormwater retention and plant-based water cycling (Graduate Fellowship)

Basic Information

Title:	Modeling the effects of green roof substrate organic matter on stormwater retention and plant-based water cycling (Graduate Fellowship)
Project Number:	2013MD309B
Start Date:	5/1/2013
End Date:	10/31/2013
Funding Source:	104B
Congressional District:	MD 5
Research Category:	Climate and Hydrologic Processes
Focus Category:	Hydrology, Management and Planning, Models
Descriptors:	None
Principal Investigators:	Kaye Lorraine Brubaker, Steven M Cohan, John D. Lea-Cox

Publications

There are no publications.

Report on Summer 2013 Undergraduate Fellowship
Modeling the effects of green roof substrate organic matter on stormwater retention and plant-based water cycling
Whitney Griffin Gaches

Introduction

The Maryland Water Resources Research Center Summer Fellowship funded work relating to my dissertation, in which I investigated the effects of green roof substrate organic matter on water holding capacity, hydraulic conductivity, and matric potential as well as plant growth and the resultant stormwater retention performance. The objectives of my work were as follows:

1. I will relate substrate moisture data to the organic content and WHC of the various substrate treatments.
2. Thrice-yearly data on root density, leaf area, shoot and root biomass, and root length will be analyzed and compared to ET rates (rate of dry-down after rainfall events).
3. A substrate model subroutine will be developed that accounts for varying amounts of substrate organic matter in GRS. The model will account for varying ET rates and plant growth characteristics affected by organic content.

Overview of work

My project was completed in three segments – lab analysis of substrate physical properties, a growth chamber experiment to quantify *Sedum kamptschaticum* (a common green roof plant) growth during establishment (the first six months post-planting), and a 1.2 m² platform-scale field study to measure green roof stormwater retention. All studies used the same experimental green roof substrate blends with identical mineral components and increasing volumetric proportions (10%, 20%, and 40%) of organic matter (mushroom compost).

Results

The lab analysis failed to identify differences in hydraulic conductivity and matric potential of green roof substrates with increasing volumetric proportions of organic matter; however, this study identified for the first time the need for delineation between maximum water holding capacity (WHC) when determined via lab analysis and that which is attainable in the field. Most stormwater regulations that award credit for green roof systems use some combination of maximum WHC and substrate depth to estimate the stormwater retention potential. These predicted values are based on lab analysis of green roof media – which require an extended saturation period of the sample (24 or 48 hours). My results indicate that using saturated WHC may grossly overestimate predicted green roof retention. My lab analyses indicated maximum water holding capacity between 42-48% (volumetric water content after gravitational drainage); however, field study results indicate maximum substrate volumetric water content (VWC) of 30%. Furthermore, 30% VWC was only achieved when the substrate was above 10% VWC at the start of a rain event. When substrate VWC was below 10% at the

start of a rain event, maximum WHC was 22-25%. These results call into question the current methods for estimating green roof stormwater retention potential and point to the need for quantifying actual retention from real roof systems to better inform policies surrounding these systems.

The results of the growth chamber analysis indicated more aboveground and belowground biomass accumulation of *Sedum kamptschaticum* when grown in 40% organic matter compared to those grown in 10% or 20% organic matter. While these results were not unexpected, nutrient availability within each pot indicate that sedum growth was more sensitive to water availability than nutrient availability during establishment (the first six months following installation), as determined by three destructive harvests over the course of the experiment. At the end of the six month study, remaining replicates were dried down for ten days and weighed twice daily to quantify water loss due to evapotranspiration. Three consecutive dry downs were completed, with replicates hand-watered to mimic a 1.25 cm rain event occurring over one hour. Planted treatments lost more water ($p < 0.05$) than planted treatments but there were no differences in evapotranspirational water loss between any treatment. This is likely due to the limited pot volume – plants were grown in 500 mL pots, so substrate VWC fell below 5% by the tenth day of each dry down period.

There were no differences in substrate volumetric water content or rate of dry down between any treatments in the platform-scale field study. Although plant canopy coverage was greater ($p < 0.05$) for platforms with 40% organic matter, difference in growth did not result in differences stormwater retention. Runoff from each platform ($n=4$) was measured using a double tipping bucket rain gauge. No differences were identified in total volume retained nor in the rates of runoff from the platforms. I do not, however, believe that there is no effect of substrate organic content on stormwater retention. Instead, I believe that I was unable to identify differences because the platforms were in their first two years of growth. Because the plant-based effects of increased substrate organic content will compound over time, I expect that differences in stormwater retention based on substrate organic matter will be identifiable 3-5 years post-installation.

Due to a lack of identifiable differences in stormwater retention I was unable to contribute to our existing model; however, I am gainfully employed in Baltimore and plan to continue data collection and analysis of these experimental platforms. I expect that I will be able to identify differences in stormwater retention 3-5 years post-installation, or beginning approximately in 2015.

Figures

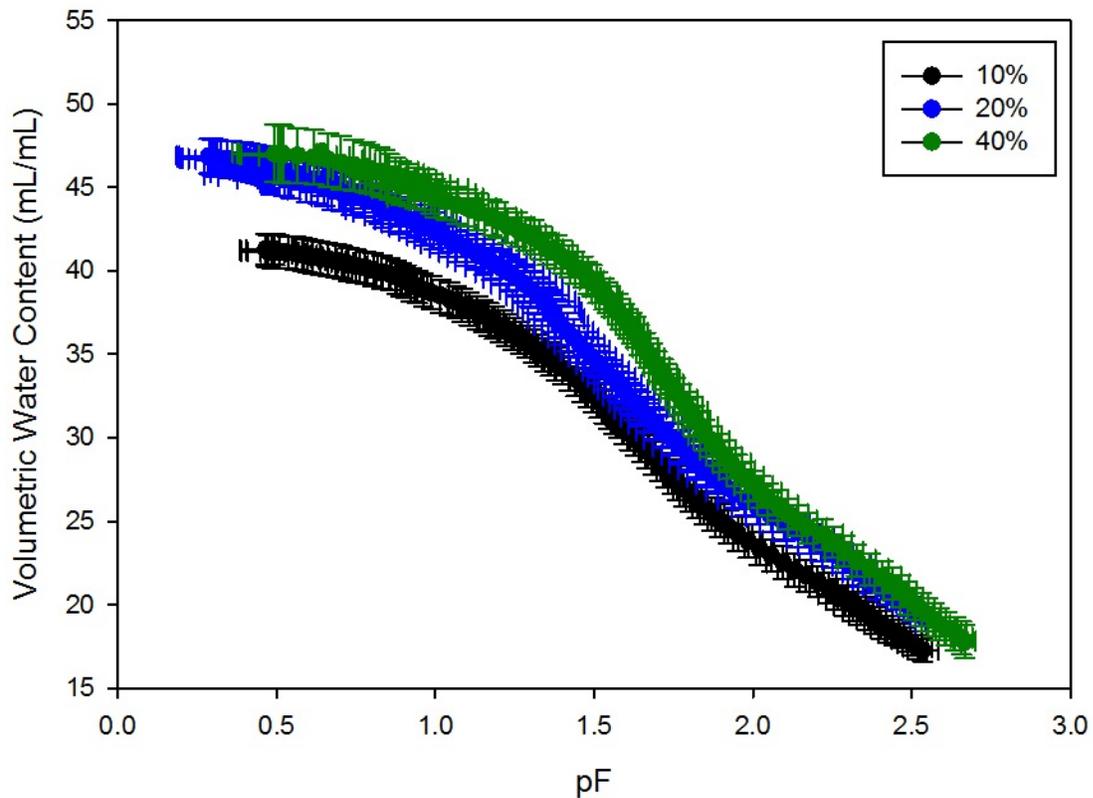


Figure 1. Matric potential of experimental green roof substrate blends with increasing (10%, 20%, and 40%) organic matter. There were no differences in matric potential; however, maximum water holding capacity ranged from 42-48% volumetric water content, far above any measured field values. These results point to the need for delineation between saturated maximum water holding capacity (i.e., lab based analysis) and unsaturated maximum water holding capacity (i.e. expected field performance).

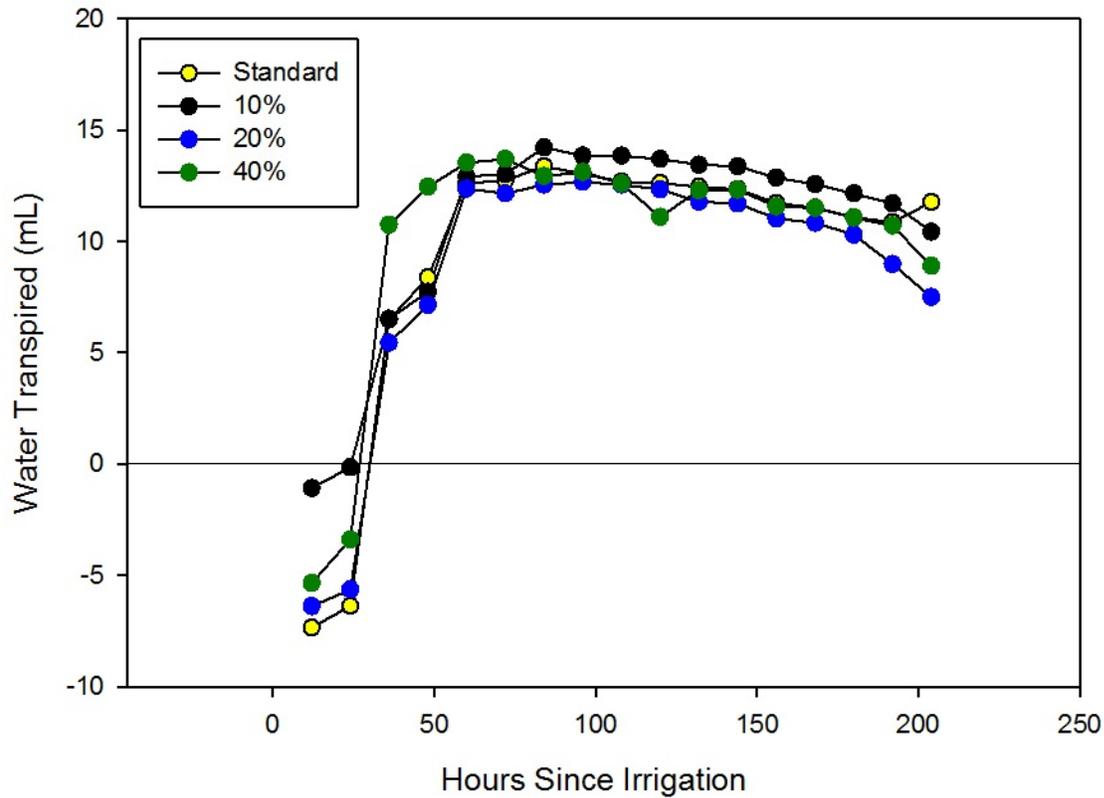


Figure 2. Water transpired from pots planted with *Sedum kamptschaticum* in substrate with increasing (10%, 20%, and 40%) volumetric proportions of organic matter compared to the industry standard blend Rooflite™. Values were extrapolated by subtracting averages of water loss of unplanted from planted pots (n = 6) during a 10 day dry down period following hand irrigation mimicking a 1.25 cm, one-hour rain event.



Figure 3. Experimental green roof platform and data logger, which is attached to 4 moisture sensors taking a substrate volumetric water content measurement every five minutes. Three experimental substrate blends with increasing (10%, 20%, and 40%) volumetric proportions of organic matter were installed in identical platforms (n=4). Substrate volumetric water content and runoff were measured for each platform.

Information Transfer Program Introduction

None.

Maryland Water 2013 - Symposium

Basic Information

Title:	Maryland Water 2013 - Symposium
Project Number:	2013MD303B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	MD 5
Research Category:	Not Applicable
Focus Category:	Education, None, None
Descriptors:	None
Principal Investigators:	Kaye Lorraine Brubaker

Publications

There are no publications.

Screening of Documentary on Coastal Communities Replaces Maryland Water Symposium 2013-14

In lieu of a Maryland Water Symposium in funding year 2013-14, the MWRRC sponsored a different mode of information transfer: screening of a new film, “Shored Up: A Documentary about Coastal Communities and Sea Level Rise,” with the movie’s producer, Ben Kalina, as special guest. The screening was scheduled to coincide with the Renewable Natural Resources Foundation (RNRF) Congress on Coastal Resilience and Risk, held on the University of Maryland campus. The MWRRC provided logistical support and publicity. The University of Maryland Department of Civil & Environmental Engineering endorsed the event; the Department’s student organizations helped with publicity and provided free popcorn at the event.

About 60 individuals from the University of Maryland, the RNRF Congress, and the community attended the screening. A variety of perspectives were expressed in the lively Q&A following the film.

The poster announcing the screening is included on the following page.

SCREENING OF

SHORED UP

A Documentary about Coastal Communities and Sea Level Rise

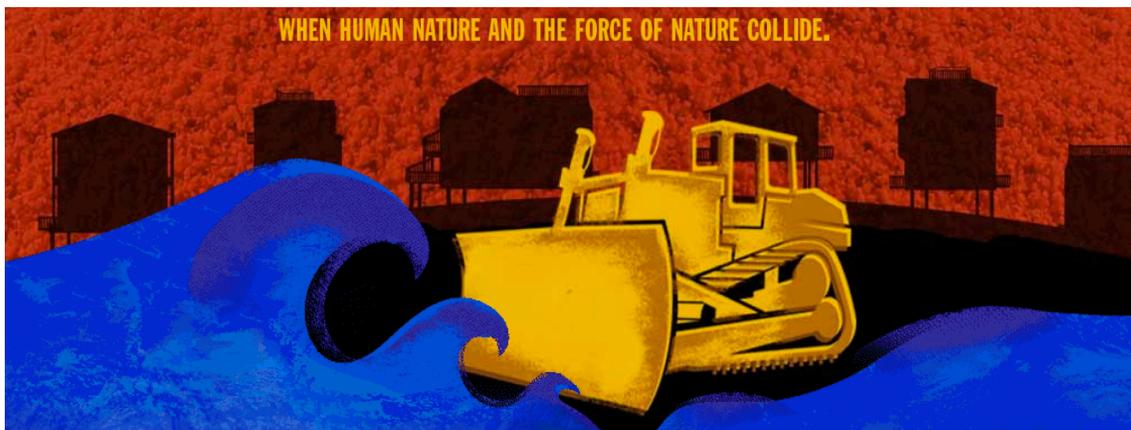
With Special Guest Director/Producer **BEN KALINA**

Wednesday, Dec. 11, 2013 • 7:30 p.m.

H.J. Patterson Hall* • Room 0226

University of Maryland, College Park

Free of Charge • Discussion/Q&A Following
Open to the University Community and the Public



Sponsored by:

Maryland Water Resources Research Center
Department of Civil & Environmental Engineering
American Society of Civil Engineers, UM Chapter
Chi Epsilon Civil Engineering Honor Society, UM Chapter

In Conjunction with:

RNRF Congress on Coastal Resilience and Risk (<http://rnrf.org/>)

*Across Campus Drive from Stamp Student Union
Location, Transit & Parking info: <http://waterresources.umd.edu/shoredup/>

For additional information about the film please visit: <http://outcast-films.com/>
<http://shoredupmovie.com/>

USGS Summer Intern Program

None.

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	11	0	0	7	18
Masters	5	0	0	2	7
Ph.D.	2	0	0	2	4
Post-Doc.	0	0	0	0	0
Total	18	0	0	11	29

Notable Awards and Achievements

Mitchell Donovan (MS student supported by **2012MD262B**) was awarded two NSF support grants to attend the EarthCube and Critical Zone Observatory (CZO) LiDAR workshops in Boulder, CO in April 2013 and May 2014.

Joel Moore applied for, and was awarded, a three-year endowed chair position awarded to pre-tenure faculty (Jess and Mildred Fisher Endowed Chair of Geological Sciences) in part to expand on the work originally proposed in **2013MD306B**. The MWRRC grant has been leveraged through funds applied for, and received from, the School of Emerging Technology at Towson University to extend the deployment of pressure and conductivity sensors to continuously monitor water level and the total dissolved content.

2013MD304B yielded data which were central to the following grant proposal, which was recently selected for funding:

Sivey, John D. Kinetics of electrophilic aromatic substitution by aqueous BrCl, BrOCl, and Br₂O: Catalysis of alkylbenzene bromination. American Chemical Society Petroleum Research Foundation (Grant #54560 UNI4); \$55,000; Sept. 1, 2014 – Aug. 31, 2016.

During the period of **2013MD304B**, PI John Sivey was inducted into the Towson University Academy of Scholars as a junior fellow. This award is presented annually to no more than three pre-tenure faculty members based on their excellence in research.

Alex MacLeod (MS student supported by **2013MD305B**) was awarded a \$5,000 Dean's Fellowship from the College of Agriculture and Natural Resources, University of Maryland, largely in recognition of the quality of his laparoscopy validation research project.

Publications from Prior Years

1. 2011MD247B ("Environmental Suitability of Fly Ash Use in Highway Structural Fills (Graduate Fellowship)") - Articles in Refereed Scientific Journals - Cetin, B., A.H. Aydilek, and L. Li, 2014, Trace Metal Leaching from Embankment Soils Amended with High-Carbon Fly Ash. *J. Geotechnical and Geoenvironmental Engineering* 140(1):1-13, DOI 10.1061/(ASCE)GT.1943-5606.0000996.
2. 2011MD247B ("Environmental Suitability of Fly Ash Use in Highway Structural Fills (Graduate Fellowship)") - Articles in Refereed Scientific Journals - Cetin, B., A.H. Aydilek, 2013, pH and fly ash type effect on trace metal leaching from embankment soils, *Resources Conservation and Recycling* 80: 107-117, DOI: 10.1016/j.resconrec.2013.09.006.
3. 2010MD229B ("Occupational and Community Exposure to Antimicrobial-Resistant Bacteria and Antimicrobials Present in Reclaimed Wastewater ") - Articles in Refereed Scientific Journals - Goldstein, R.E.R., S.A. Micallef, S.G. Gibbs, A. George, E. Claye, A. Sapkota, S.W. Joseph, and A.R. Sapkota, 2014, Detection of vancomycin-resistant enterococci (VRE) at four US wastewater treatment plants that provide effluent for reuse, *Science of the Total Environment* 466:404-411, DOI: 10.1016/j.scitotenv.2013.07.039.
4. 2009MD193B ("Low-cost Anaerobic Digesters for Dairy Manure Treatment and Renewable Energy Production") - Articles in Refereed Scientific Journals - Klavon, K.H., S.A. Lansing, W. Mulbry, A.R. Moss, and G. Felton, 2013, Economic analysis of small-scale agricultural digesters in the United States, *Biomass & Bioenergy* 54: 36-45 DOI: 10.1016/j.biombioe.2013.03.009.
5. 2006MD135B ("Chemical and Biological Impacts of Zinc and Road Salt from Road Runoff Entering Stormwater Retention Ponds") - Articles in Refereed Scientific Journals - Casey, R.E., S.M. Lev and J.W. Snodgrass, 2013, Stormwater ponds as a source of long-term surface and ground water salinisation, *Urban Water Journal* 10(3):145-1553, DOI: 10.1080/1573062X.2012.716070.