Water Resources Research Center
Annual Technical Report
FY 2006

Introduction

The major water science issue in Maryland is the recovery of the Chesapeake Bay. It is the largest economic asset in the State and is estimated to contribute millions of dollars annually to Maryland's fiscal resources. Four of the 5 projects funded by the Maryland Water Resources Research Center deal with the Bay. These projects are directed at streams and rivers that flow directly into the Bay. The Center tries to keep abreast with the other Federal and State agencies involved in problems in the Bay. A good example of this cooperation revolves around the annual fall conference cosponsored by our Center.

One issue that is receiving a great amount of research is being devoted to the impact of road salts in streams and wetlands. Nitrogen cycles in streams are being disrupted as the salt concentrations increase. The impact of denitrification on nitrates could increase the amounts of nutrients that reach the Bay. One of the major problems in monitoring nitrogen has been time and expenses. Maryland scientists have developed a system whereby they can measure nitrogen levels in wetlands using hyperspectral radiometry to measure reflection from leaf surfaces. These measurements could tell us if salts are causing increased nitrate levels in wetlands.

The impact of sea level rise on coastal wetlands in the Chesapeake bay is also under investigation. Sea level rise is likely to result in increases in salinity and soil waterlogging in low-salinity marshes, causing stress and mortality of salt intolerant species and altering vegetation diversity and species composition.

Research Program

Investigation of the effects of increased salinization from deicer use on increased transport of nitrogen in streams of the Chesapeake Bay Watershed

Basic Information

Title:	Investigation of the effects of increased salinization from deicer use on increased transport of nitrogen in streams of the Chesapeake Bay Watershed
Project Number:	2006MD116B
Start Date:	3/1/2006
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Descriptors:	None
Principal Investigators:	Sujay Kaushal, Keith N. Eshleman, Gary Thomas Fisher, Peter Groffman, Paul M Mayer, Ray Morgan

Publication

Investigation of the effects of increased salinization from road deicer use on increased transport of nitrogen in streams of the Chesapeake Bay watershed

Published Abstracts

Kaushal, S.S. 2006. Increased salinization of fresh water in the northeastern U.S. Annual Report of the Freshwater Society. St. Cloud, MN.

Kaushal, S.S., P. Groffman, P. Mayer, E. Striz, E. Doheny, A. Gold. 2006. Successes and challenges in removing nitrogen from coastal streams of the Chesapeake Bay. Long-term Ecological Research All Scientists Meeting. Estes Park, CO.

Kaushal, S.S. 2006. Successes and challenges in removing nitrogen from coastal streams of the Chesapeake Bay. Integrated Application Network Chesapeake Bay Seminar Series. http://ian.umces.edu/mp3s/kaushal_cbss_feb_2006.mp3. Annapolis, MD.

Mayer, P., E. Doheny, S. Kaushal, P. Groffman, and E. Striz. 2006. Ground water is a chronic source of chloride to surface water of an urban stream exposed to road salt in a Chesapeake Bay watershed. American Geophysical Union, Spring Meeting. Baltimore, MD.

Groffman, P.M., L.E. Band, R.V. Pouyat, K.T. Belt, G.T. Fisher, M. Grove, S. Kaushal, P.M. Mayer. 2006. The Bio-Geo-Socio-Chemistry of urban watershed ecosystems. American Geophysical Union, Spring Meeting. Baltimore, MD.

Kaushal, S., K. Belt, W. Stack. R. Pouyat, P. Groffman, and S. Findlay. 2006. Variations in Heavy Metals Across Urban Streams. American Geophysical Union, Spring Meeting. Baltimore, MD.

Kaushal, S., K. Belt, W. Stack, R. Pouyat, P. Groffman, and S. Findlay. 2006. Variations in heavy metals across urbanizing watersheds. Ecological Society of America Meeting 89th Annual Meeting. Memphis, TN.

Bogush, P.M., S.S. Kaushal, and C.M. Swan. 2007. The interaction of road salt deicer and dissolved organic carbon on microbial respiration in stream sediments. Ecological Society of America Meeting. San Jose, CA.

Mayer, P.M., E. Striz, E. Doheny, S.S. Kaushal, and P.M. Groffman. 2007. Chloride dynamics in the hyporheic zone of a flashy urban stream in the Chesapeake Bay watershed. Ecological Society of America Meeting. San Jose, CA.

Statement of Problem

Previous research has documented sharp increases in concentrations of sodium and chloride in aquatic systems of the rural and urban mid-Atlantic and northeastern U.S. over decades due to use of road salt, fertilizers, operation of water softeners, and discharges from septic systems and wastewater treatment plants (e.g. Bubeck et al. 1971, Peters and Turk 1981, Herlihy et al. 1998, Rosenberry et al. 1999, Godwin et al. 2003). Due to unprecedented rates of increasing suburban and urban development and large increases in coverage by impervious surfaces in Maryland over the last several decades (Jantz et al. 2003), baseline salinity is now increasing at a regional scale in certain streams and rivers of the Chesapeake Bay watershed toward thresholds beyond which significant changes in ecological communities and ecosystem functions may be expected (Kaushal et al. 2005). We studied the potential effects of increased salinization on impairment of removal of nitrogen via denitrification in streams, and subsequent implications for increased downstream transport of nitrogen to coastal ecosystems. Increased sodium and chloride concentrations in surface waters can be propagated a substantial distance from roadways leading to widespread effects on water quality (Environment Canada 2001). Increases in salinity up to 1000 mg/L can have lethal and sublethal effects on aquatic plants and invertebrates (Hart et al. 1991), and chronic concentrations of chloride as low as 250 mg/L have been recognized as harmful to sensitive freshwater life and not potable for human consumption (Environment Canada 2001, U.S. EPA 1988). Other ecological effects of increased salinization on the quality of surface waters include acidification of streams (Lofgren 2001), mobilization of toxic metals through ion exchange or impurities in road salt (Lewis 1999), facilitation of invasion of saltwater species into previously freshwater ecosystems (Richburg et al. 2001), and interference with the natural mixing of reservoirs and lakes (Bubeck et al. 1971). In particular, high chloride concentrations may potentially inhibit denitrification, a microbial process that is critical for removal of nitrate and maintainenance of water quality in many streams and rivers (Groffman et al. 1995, Hale and Groffman 2006).

Maintaining and restoring the capacity for denitrification, which is the microbial conversion of nitrate dissolved in water to gaseous forms such as dinitrogen, nitric oxide, or nitrous oxide, may be particularly important in streams and rivers of Maryland (Groffman et al. 2005), where elevated amounts of nitrogen transported to running waters from human-dominated landscapes has stimulated eutrophication and the formation of "dead zones" within the Chesapeake Bay (Kemp et al. 2005). Debris dams and hyporheic zones are "hot spots" of denitrification (Groffman et al. 2005, Kaushal et al. Submitted), but the ability of benthic habitats in streams and rivers to process and remove nitrogen may be severely impaired in suburban and urban landscapes (e.g. Groffman et al. 2002, Kaushal et al. In Press) due to altered hyrologic flowpaths, increased nitrogen loading, and the presence of contaminants. Previous work has shown that that high chloride concentrations may inhibit microbial activity and N cycling in soils (Hahn et al. 1942, Rosenberg et al. 1986), and increased levels of salinity due to long-term deicer may have the potential to alter denitrification rates in streams (Hale and Groffman 2006). The effects of road salt on denitrification may be different in streams draining watersheds of different land use.

Objectives

We studied the potential effects of increased salinization on impairment of denitrification in streams, and the subsequent implications for increased downstream transport of nitrogen to receiving waters. The specific objectives of this project were:

(1) Characterize seasonal changes in levels and sources of salinity in streams across a land use gradient by measuring concentrations and ratios of Na and Cl ions.

(2) Investigate the effects of increased salinity on denitrification rates in sediments in streams and rivers with surrounded by different land use and geomorphic status (e.g. forest, degraded, and geomorphically restored).

(3) Investigate other potential factors (organic carbon quality and stormflow and baseflow) influencing denitrification rates in sediments in streams across watershed land use.

Our original goal was to conduct measurements in streams across the entire state of Maryland, but because of an abnormally low snow year during 2005-2006 and shorter sampling period during winter, we focused our efforts across a gradient of watershed land use and restoration status in Baltimore, MD. The project supported the research projects of 3 students: Peter Bogush (UMBC), Tammy Newcomer (UMBC) and Carolyn Klocker (UMCES AL).

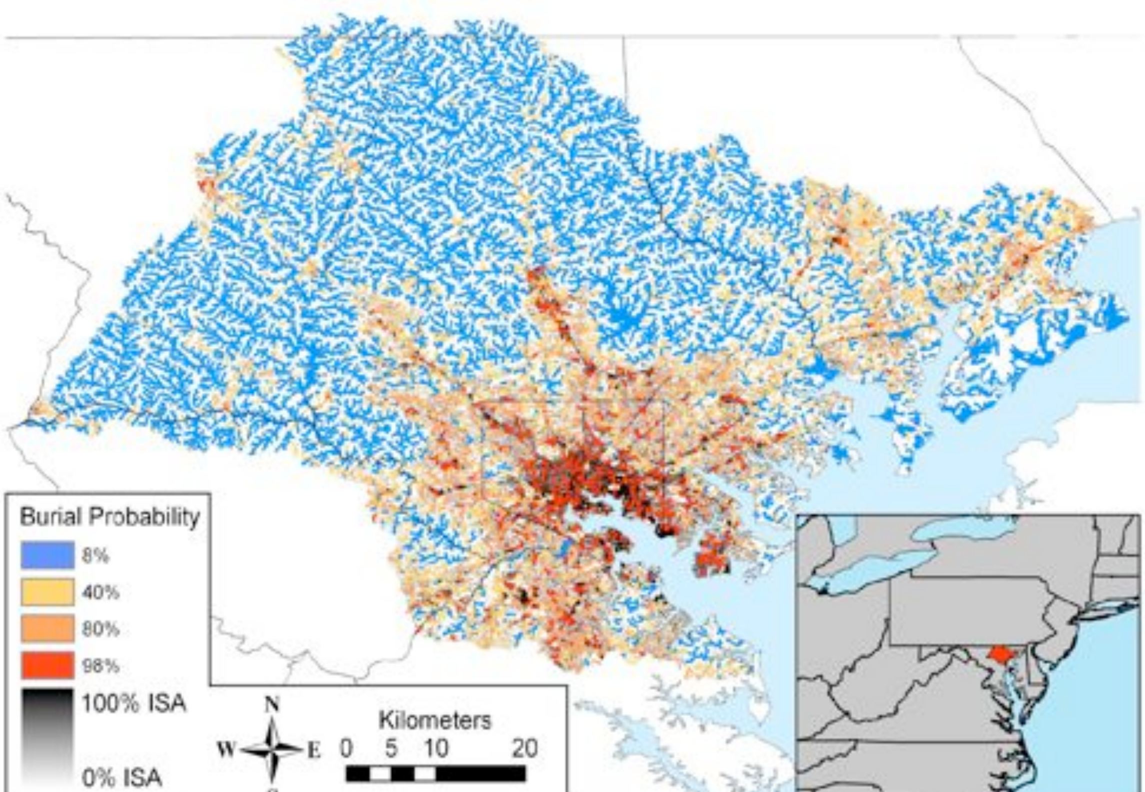
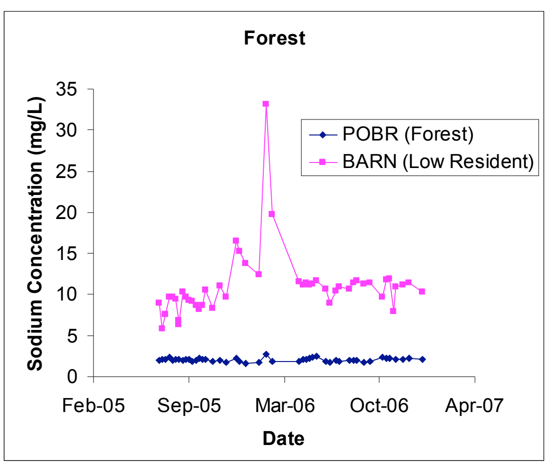


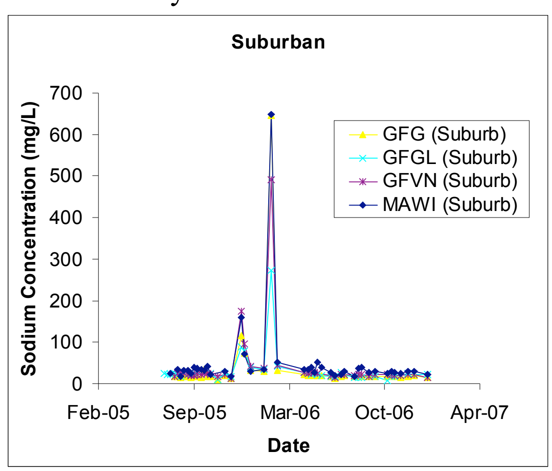
Figure 1: Stream burial extent for the Gunpowder-Patapsco watershed in Maryland expressed as a probability of burial based on the distribution of impervious surface (shown in shades of gray) in the vicinity of each stream reach. Networks of buried streams connected to impervious surfaces that increase transport of road salt and roadways chemicals to surface waters. From Elmore and Kaushal (Submitted); Funding from Maryland Water Resources Research Center acknowledged in paper.

Objective 1: Seasonal Changes in Sources and Levels of Salinity

Site Description

Within the Baltimore metropolitan area, we explored intrannual changes in sodium and chloride concentrations across a gradient of land use to determine relationships between concentrations and sources of salinity and increasing coverage by impervious surface. The Baltimore metropolitan watersheds drain into the Chesapeake Bay and represent one of the most rapidly developing areas of the northeastern U.S. In this region, coverage by impervious surface increased by approximately 39% from 1986 to 2000 (Jantz et al. 2005). In addition to increasing coverage by impervious surfaces, there have also been increasing artificial hydrologic "connections" between roadways and surface waters accelerating the transmission of roadway chemicals. Recent work using aerial photography calibrated remote sensing shows that the spatial distribution of stream burial (predominantly conversion to storm drains) in the Gunpowder-Patapsco watershed broadly follows patterns of urbanization with most of the streams in Baltimore City having the highest probability of burial (Elmore and Kaushal Submitted) (Figure 1). Overall, in Baltimore City 66% of streams have been detected as buried across catchments spanning 10 to 10^4 ha in size and are likely "connected" directly to impervious surfaces. Burial extent was reduced to 19% in the counties outside of Baltimore City, and to 21% for the Gunpowder-Patapsco watershed as a whole (Elmore and Kaushal Submitted). While much of the heavy development follows the main transportation corridors between rural areas and the center of Baltimore City, stream burial is apparent in most regions of the watershed (Elmore and Kaushal Submitted). For example, across the upper watershed 8% burial probabilities were found in areas with just 4% impervious surface area (Elmore and Kaushal Submitted). Conversion of many streams in drainage networks to storm drains may greatly accelerate the transport of road salt and other contaminants to streams and rivers in Maryland.





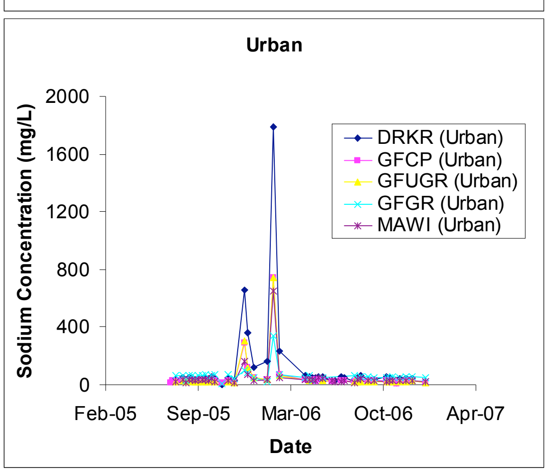


Figure 2. Seasonal patterns in sodium concentrations analyzed from MWRRC funds. Concentrations of sodium in streams draining developed watersheds peaked strongly during winter months. A low residential watershed (BARN) with 1% impervious surface coverage had approximately 10 times greater sodium

Methods
In order to examine how concentrations and sources of salinity change across land use, streams draining forest, agricultural, suburban, and urban watersheds were sampled in sites of the NSF supported Baltimore long-term ecological research (LTER) project. Samples were collected bi-weekly from 2005 - 2006 without regard to flow conditions (no bias towards storm versus base flow), filtered in the field (47-µm GF/A and 0.45-µm pore size nylon filters). Samples were analyzed for chloride using a Dionex LC20 series ion chromatograph and analyzed for sodium using a flame atomic absorption spectrophotometer at the University of Maryland Center for Environmental Science Appalachian Laboratory in Frostburg, Maryland. Detailed site descriptions and sampling protocols are described elsewhere (Kaushal et al. 2005). Baltimore LTER sites were not downstream of any wastewater treatment plants, which could release chloride or sodium.

Results
Seasonal peaks in sodium concentrations in streams coincided with winter months (Figure 2), reflecting applications of road salt in response to predicted snowfall (which typically has an annual mean of 18.2 inches), and freezing rain events. Sodium remained elevated throughout the winter, with peak concentrations of sodium approaching 2 g/L. Interestingly, concentrations of sodium also remained elevated throughout spring, summer, and autumn up to 100 times greater than concentrations found in streams draining forested watersheds without impervious surfaces (Figure 2). Concentrations of sodium during the growing season in some urban streams were almost 100 mg/L. We observed a 10-fold increase in baseline concentrations of sodium in a mostly forested watershed (BARN) with approximately 1% impervious surface relative to an adjacent forested reference with no impervious surface (POBR) (Figure 2). Results for sodium patterns are similar to a previous study examining chloride concentrations

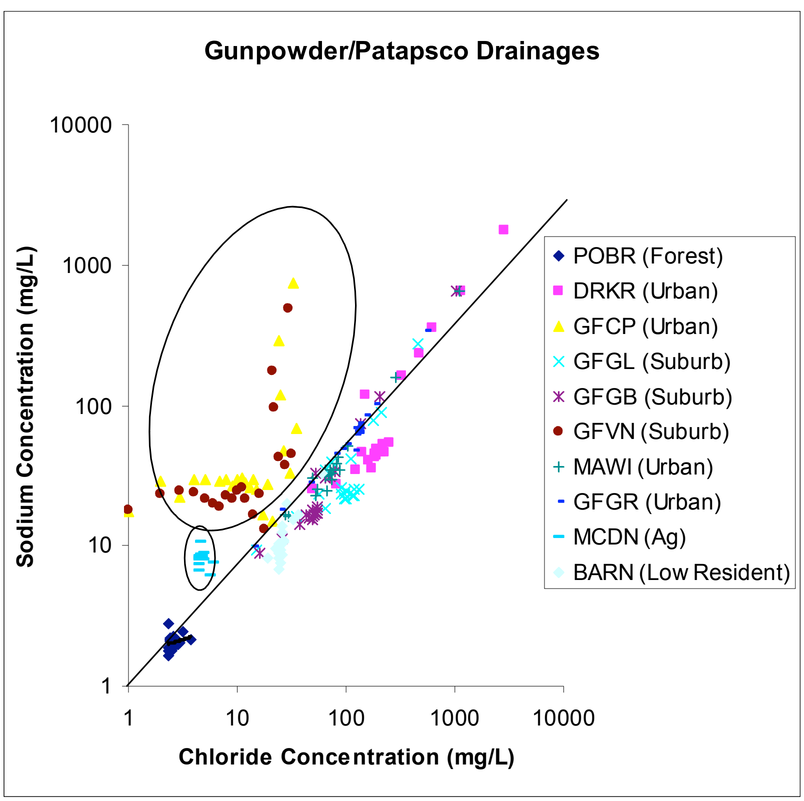


Figure 3. Comparison of Cl^- concentrations vs. Na^+ concentrations in Baltimore streams during 2005 - 2006. The ratio of Na/Cl remained constant in the same proportion as rock salt (halite). An agricultural site (MCDN) showed very little variation in Na/Cl ratios seasonally, and 2 of the largest suburban and urban watersheds (GFVN) and (GFCP) showed elevated Na/Cl ratios above halite suggesting a mixture of salt sources or differential transport of ions at larger spatial scales

(Kaushal et al. 2005). In addition to road salt, sodium contamination in these watersheds may also have resulted from other sources in developing landscapes, such as septic field effluent, which includes water softeners which have high sodium and chloride concentrations). This was investigated by comparing Na/Cl ratios in streams across differing watershed land use and catchment size.

We found that almost all sites had a nearly consistent linear relationship between Na and Cl in stream water from 2005 – 2006, and the Na/Cl ratio was similar to that of rock salt (halite). There were some marked deviations in the Na/Cl ratios for the two suburban and urban sites, GFVN and GFCP, that were the largest study watersheds located along the mainstem of the Gwynns Falls watershed. Both GFVN and GFCP both still showed strong seasonal peaks of sodium and chloride coinciding with snow events suggesting that salt from deicer was a major source. It is possible, however, that different forms of road salt were used as deicers in across larger watersheds of the metropolitan area of Baltimore, MD. Another alternative is that the mobility and transport of Na^{+} and Cl^{-} ions differed in soils and streams leading to differential patterns in the smaller study watersheds vs. larger study watersheds. Nonetheless, our results suggest that road salt may be a major source of sodium and chloride in many watersheds in the Baltimore metropolitan area, and concentrations can remain elevated in streams year round.

Objective 2: Effects of Increased Salinity on Denitrification in Streams
The effects of increased salinity on denitrification rates was investigated in debris dams in streams that represented forested, urban, and restored conditions. Previous work has shown that increased chloride can inhibit denitrification in streams, particularly debris dams, which are "hot spots" of denitrification (Hale and Groffman 2006). All streams were located in Baltimore County, MD and represented a gradient of land use and geomorphic restoration status.

Land Use/Land Cover Classifications

In order to present land use data using uniform methods, land use characteristics were determined for the 12 digit watersheds of each study site from a 2002 GIS layer of Land Use and Land Cover data of Baltimore County, MD, created by the Maryland Department of Planning. A series of layers were also created from a digital elevation model (DEM) of the Baltimore County area to determine the area of each watershed that was upstream of and contributed directly to the stream segment sampled. These layers were then used with the Land Use Land Cover data to determine the land use of the contributing portion of the watershed. The digital elevation map was obtained from the National Elevation Dataset.

The Land Use/Land Cover data obtained was classified using a modified Anderson Level 2 classification. A more general classification was also applied that grouped low density residential and open urban land into a Suburban land use category. Medium-density and High-density residential were grouped along with Commercial, Industrial, Institutional, Extractive and Transportation land uses into an Urban land use category. All agriculture land uses were grouped into one category, as were all forested land covers into another category. All other land covers, water, wetlands level, and bare ground were classified as other.

Forest Sites

Pond Branch

Pond Branch is a completely forested “reference”watershed that has an area of 41 ha, it is located in Oregon Ridge Park managed by Baltimore County. It is sampled routinely as part of the National Science Foundation funded Baltimore Ecosystem Study Long-term Ecological Research (LTER) project (Groffman et al. 2004, Kaushal et al. 2005).

Patapsco River Tributary

Patapsco River tributary is a completely forested small ‘reference” watershed that is part of Patapsco State Park in Baltimore County, MD. Routine water chemistry sampling and invertebrate sampling began there during 2006, it is a candidate site for a whole stream salinization experiment in 2007 funded by the Maryland Water Resources Research Center (C. Swan, personal communication).

Degraded Sites

Gwynns Falls at Glyndon

Glyndon is the1st order watershed of the 19,000 ha many Gwynns Falls watershed that is part of the National Science Foundation funded Baltimore Ecosystem Study Long-term Ecological Research (LTER) project (Groffman et al. 2004, Kaushal et al. 2005). The 12 digit Upper Gwynn Falls watershed that Glyndon is within consists of 7% agriculture, 24% forested, 50% urban, 17% suburban and 1% other land cover. Land cover for the 79ha of the contributing portion of the watershed was 6% forested, 70% urban, and 24% suburban. The particular reach of the Glyndon stream studied here had visible channel incision and riparian zones consisted largely of mowed lawns extending to the edge of the stream bank.

Tributary of Dead Run (DR 5)

DR 5 is a headwater tributary of the larger 3rd order Dead Run stream located in the Gwynns Falls watershed of Baltimore County, MD. Land use for the 12233ha of the Lower Gwynn Falls watershed in which DR5 is located is 2% agriculture, 14% forested, 75% urban, 8% suburban, and 1% other. Land use for the 189 ha of the contributing portion of the watershed was 6% forested, 85% urban and 8 % suburban. DR5 was similar to Glyndon as there was visible channel incision and little remaining of the riparian buffer.

Restored Sites

Minebank Run

Minebank run is a 2nd order stream located in a predominantly suburban watershed within Baltimore County, Maryland. The 12 digit Lower Gunpowder watershed is approximately 11828 ha with 30% agricultural, 32% forested, and 18% urban ,19% surburban land cover and 1% other. Land cover for the 113ha of the contributing portion of the watershed was 13% forested, 83% urban, and 4% suburban. The section of Minebank run chosen for this study was restored in 1998 and 1999 (Mayer et al 2004). The goal of the restoration was to improve the geomorphic stability of the stream bed and reduce channel incision (Mayer et al 2003). The restoration included techniques such as installing step-pool structures designed to reduce erosion, reshaping the stream banks to reconnect the stream channel to the flood plain, armoring stream banks against erosion with large boulders, reconstructing stream meander features and riffle zones, and re-establishing riparian vegetation (Mayer et al 2003).

Spring Branch

Spring Branch, a restored 1st order stream in Baltimore County, MD, drains the suburban Loch Raven watershed eventually emptying into the Loch Raven Reservoir, a major drinking supply for the Baltimore Metropolitan area. Land use for the 12 digit Loch Raven 9437 ha watershed was 12% agriculture, 36% forested, 14% urban, 29% suburban and 9% other. Land use of the 188ha contributing portion of the watershed was 2% forested, 77 % urban and 20% suburban. The Spring Branch Stream Restoration project began in 1994 and was completed in 1997 (US EPA River Corridor and Wetland Restoration 2002). The goal of this restoration was to manage the flow of the stream to control for erosion and floods (US EPA River Corridor and Wetland Restoration 2002). Restoration features used included step pools at the outfall channel, plunge pools below pipe outfalls, rip rap in outfall channels and downstream of culverts, catch basins to attenuate flow, and floodplain access for bankfull discharges (US EPA River Corridor and Wetland Restoration 2002). Stabilization of stream banks and enhancement of aquatic habitats were also attempted through the construction of features such as vortex rock weirs, root wad revetments, gravel riffles, step pools, meander bend pools, live brush mattresses, live fascines, live branch layering, as well as live joint planting (US EPA River Corridor and Wetland Restoration 2002).

Methods: Denitrification Bioassays

Three replicate stream features (i.e. organic debris dams), separated by at least 10 m were sampled from each stream during January of 2007. Large sticks and insects were removed from sediments, and the samples were then homogenized in a blender with small quantities of ambient stream water. Sediment moisture was determined by drying at 60°C for 24 hours and organic carbon and nitrogen content were analyzed with a Carlo-Erba NC 2100 CHN elemental autoanalyzer. Ambient stream chloride and nitrate concentrations were determined by ion chromatography as described above.

To establish laboratory mesocosms, ~150 g of debris dam material was incubated in sealed mason jars with 40 ml of stream water (Groffman et al. 1999). Samples from each stream were incubated with native, ambient water as well as with native water with different amendments (similar to Hale and Groffman 2006). In amendments, debris dams were incubated with: (1) stream water amended with 5,000 mg Cl^-/L to determine the effects of chloride present in urban environments during winters (2) stream water amended with leaf leachate to determine the effects of elevated dissolved organic carbon (DOC) associated with storm drain inputs, and (3) stream water amended with both 5,000 mg Cl^-/L and leaf leachate to investigate potential interactive effects. All treatments were replicated in triplicate.

Mesocosms were sampled after 10-day incubations and analyzed for rates of denitrification. Denitrification enzyme assay (DEA) was measured using a method similar to Groffman *et al.* (1999, 2002) to characterize denitrification potential following the incubation with differing amendments. Briefly for DEA, sediment samples were amended with NO_3^-, dextrose, chloramphenicol and acetylene, and incubated in anaerobic conditions for 90 minutes to measure maximum potential rates of denitrification for sediments in incubations. Chloramphenicol acts as an inhibitor blocking complete conversion of nitrate to N_2 gas so that the intermediate N_2O is produced, which can be measured more easily than N_2 production due to less contamination from the atmosphere. Gas samples were taken at 30 and 90 minutes and analyzed for N_20 by electron capture gas chromatography.

<u>*Results*</u>

Statistical analysis of the data was completed using SAS utilizing a full factorial design. The two forested sites, Pond Branch and Patapsco, were found to have the lowest rates of denitrification across all sites. Treatments containing a chloride addition showed lower rates of denitrification compared to treatments without an addition of chloride. This effect was independent of site and was marginally significant (a= .05, p=.058). Denitrification rates without salt amendments were approximately 280 ng N/g dry soil/hr (+/- 25) whereas denitrification rates with salt amendments were approximately 230 ng

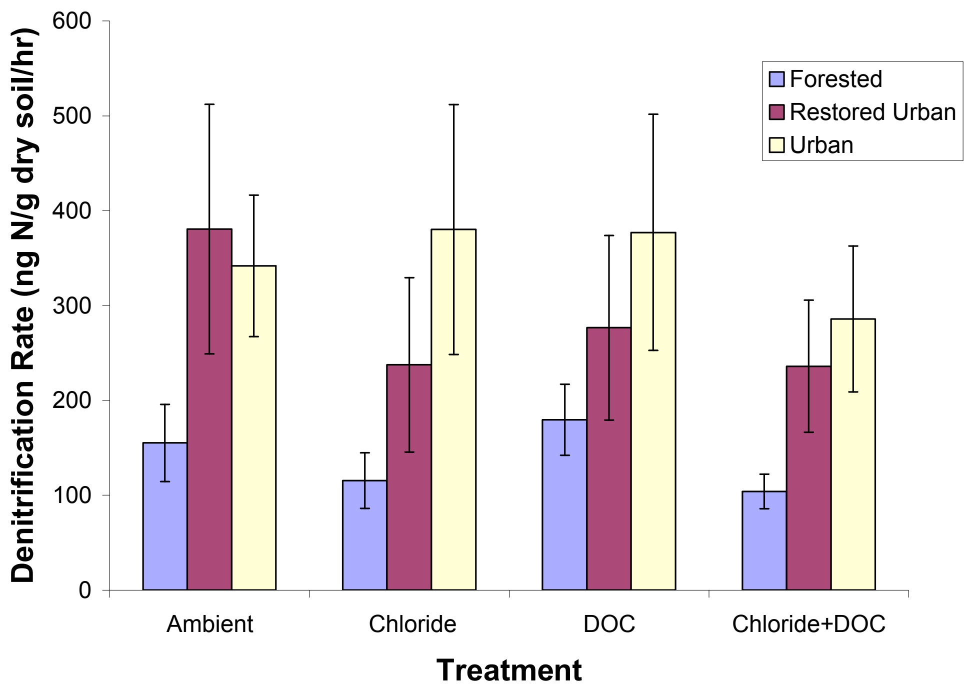


Figure 4. Mean denitrification rates for all sites and treatments. There were 3 replicate debris dams (n=3) analyzed at each stream and 2 streams per category (forest, restored urban, urban). Error bars represent the standard error for each treatment. Chloride amendment produced a marginally significant decrease in denitrification rates across all sites ($p = 0.058$) with consistent decreases in forest and restored sites, but not urban sites routinely exposed to high chloride concentrations

N/g dry soil/hr (+/- 25). Increased replication in future studies or ecosystem manipulation may help to further identify the significance of this effect associated with increased chloride concentrations. Results were consistent with previous work, which has shown that elevated chloride concentrations can inhibit denitrification rates in other Maryland streams (Hale and Groffman 2006). We are currently investigating the effects of increased salinization at the whole stream reach scale on N processing in the Patpasco River tributary where increased salinity has shown significant effects on microbial respiration (P. Bogush, data not included).

Treatments containing an addition of dissolved organic carbon leachate from leaves did not show significant differences in denitrification rates across all sites (a=.05, p=.7004), suggesting that dissolved organic carbon from leaf leachate may not be a limiting for denitrification in debris dams at any of the sites (forested, restored urban, or urban).

Objective 3: Other Factors Influencing Stream Denitrification: DOC Quality
Although we observed a marginally significant effect of chloride on denitrification rates at all sites (with consistent decreases in forest and restored sites), we also conducted experiments to investigate whether other potential factors could be influencing denitrification rates in the streams, such as DOC quality and stormwater and baseflow conditions. We conducted a similar incubation experiment (as described above) incubating hyporheic sediments with ambient water with carbon leachate amendments of differing quality (leaves, grass from lawns, and algae) and stormflow water.

Sample Collection

Hyporheic sediments were collected from each stream using a 5hp Gas Powered Earth Auger to drill down to a depth of a half meter below the stream level. At Pond Branch the Earth Auger was not used due to transportation difficulties. When the desired depth was greater than that achieved with the Earth Auger, manual shovels and posthole diggers were implemented. Two samples were taken from each stream on opposite banks at a distance of one meter from the main channel (except for at Spring Branch where both holes were on the same bank due to armoring on opposite side). Samples were refrigerated until analyzed (<2 wk).

Allochthonous and autochthonous organic carbon sources (algae, leaves, and grass clippings) were collected from each site and refrigerated in zip-lock bags (<2 wk). Grass samples were cut from as near the stream as possible. Leaves were collected from undecomposed debris dams within the stream channel at each site. Algae was scraped off of rocks within the stream channel at each site. Additionally base flow and storm flow samples were also collected from each site to compare the potential importance of baseflow and stormflow conditions on denitrification.

Denitrification Bioassays

The dry mass equivalent of 0.2 gram of the selected carbon source treatment (grass, algae, or leaves) was added along with 5 grams of site specific sediment and 10 mL of site specific stream water were shaken together in mason jars. For unamended controls there were also jars that contained only 5 grams of site specific sediment and 10 mL of site specific base flow stream water or storm flow stream water in half-pint mason jars. The loosely covered jars were agitated twice daily for 58 hours. There were 60 jars total (6 stream sites x 2 samples x 5 treatments).

Denitrification potentials for hyporheic sediments from each site were determined using denitrification enzyme activity (DEA) assays for wetlands (e.g Groffman et al. 2005) (as described earlier for salt amendment experiments in debris dams). Media was prepared from 1.44 g KNO_3, 0.25 g chloramphenicol, and1 L deionized water and glucose was omitted due to use of endemic carbon sources from each stream. Mason jar mixtures were amended with this media and incubated for an additional 90 minutes in sealed flasks under anaerobic conditions. Flasks were set on a shaker table and samples were taken from flask air spaces at thirty and ninety minutes. Samples were stored in evacuated glass tubes and analyzed by electron gas chromatography for N_2O concentrations.

Results

Across the five different carbon treatments, the degraded streams exhibited significantly greater denitrification rates for all DOC treatments except for leaves (Fig. 4). Denitrification rates associated with the grass leachate in the degraded streams was an order of magnitude greater than both other stream types, and denitrification rates associated with the grass leachate in the restored streams were almost double the rates in the forested streams. The denitrification rates from the algal leachate decreased from

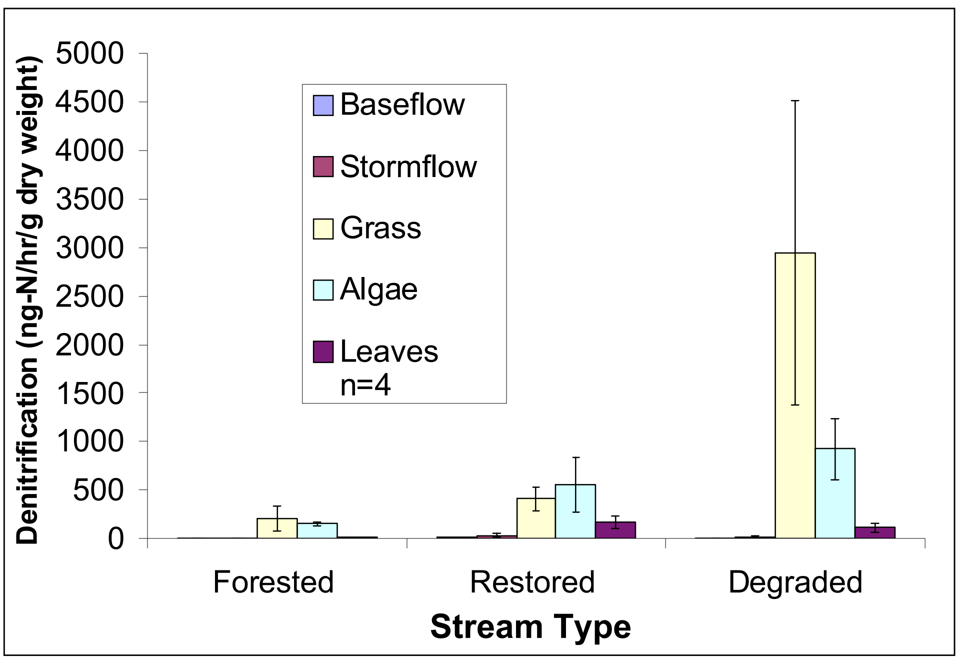


Figure 5. Comparison of denitrification rates produced from natural, degraded, and restored streams in Baltimore County, MD using leachates from algae, leaves, and grass clippings. The degraded stream produced denitrification rates that were an order of magnitude greater than the other streams. The grass leachate in degraded streams stimulated denitrification the most. The denitrification response of restored streams to different DOC leachates closely resembled that of the forested stream suggesting that microbial communities in forested and restored streams may be more similar.

degraded to restored to forested streams. Overall, patterns in denitrification rates associated with different DOC sources in the restored stream appeared to more closely resemble the forested stream suggesting that microbial communities in restored streams may become more similar to forest streams than urban streams. Microbial community dynamics may be an important indicator of stream restoration success, although less work has focused on using microbes as bioindicators of stream restoration success. Finally, lawn clippings may represent labile sources of DOC in suburban/urban streams, which have shown strong peaks in DOC concentration relative to forest sites (Kaushal, unpublished results).

Expected Publications and Products

The work has already led to submission of 1 paper, Elmore and Kaushal (Submitted), and several other papers that are in progress such as Klocker et al. (In preparation), Newcomer et al. (In preparation), Bogush et al. (In Preparation), and Kaushal et al. (In preparation). We will inform the Maryland Water Resources Research Center regarding publication of papers that result from the project. In addition, funding from the Maryland Water Resources Research Center was instrumental in providing pilot data for acquisition of the following new grants:

Investigation of stream restoration as a means of reducing nitrogen pollution from rapidly urbanizing coastal watersheds of the Chesapeake Bay. National Oceanic and Atmospheric Administration, Maryland Sea Grant. 2007 – 2009. $155,315.

Maryland Sea Grant Graduate Fellowship. 2007 –2009. $35,000.

Collaborative Research: The effects of watershed urbanization on in-stream transformation of organic nutrients within running waters. National Science Foundation. 2007 – 2010. $613,620

Training of Undergraduates and Graduates in the Project

Funds from MWRRC supported the research of 3 students (2 graduate and 1 undergraduate). They supported one MS student, Mr. Peter Bogush, during the 2006-2007 academic year. Mr. Bogush is currently enrolled in the Marine, Estuarine, Environmental Science (MEES) Program at the University of Maryland, College Park, but is taking coursework and located at the University of Maryland Baltimore County. Funds were also used to support the research of an undergraduate student, Ms. Tamara Newcomer. Ms. Newcomer was an undergraduate at the University of Maryland at Baltimore County during the 2006 – 2007 academic year and received matching funds for her summer project supported by MWRRC from a National Science Foundation supported Research Experience for Undergraduates (REU) grant. Finally, funds from MWRRC were used to support the research of Ms. Carolyn Klocker, an M.S. student in the MEES graduate program based at the Appalachian Laboratory in Frostburg, MD. The 3 students obtained unique perspectives from working with academic, non-profit, and state and federal agency researchers from the University of Maryland Center for Environmental Science, Institute of Ecosystem Studies, U.S. Geological Survey, and Environmental Protection Agency with projects directly related to predicting the effects of land use change and salinity on N transport in streams and rivers of Maryland to the Chesapeake Bay.

Conclusions

The work provided a survey of sodium and chloride dynamics and denitrification rates in streams draining a land use gradient in Maryland. Results also contributed to further elucidating how rates of N cycling can be potentially altered by increased salinization and surrounding changes in land use. Elucidation of factors affecting nitrogen transport in streams and rivers is critical to protection of water quality in the Chesapeake Bay. According to statewide surveys, there are over 50 stream sites in the Maryland Biological Stream Survey with spring chloride concentrations greater than 100 mg/L where background concentrations in completely forested watersheds are typically < 4 mg/L (Kaushal et al. 2005, Morgan et al. 2007). There are also many other streams in Baltimore that also exceed limits of 250 mg/L established by the U.S. EPA and Environment Canada for chronic toxicity to sensitive freshwater life on a seasonal basis. This work can be used to further elucidate factors inhibiting or limiting nitrogen transformations in a variety of streams experiencing urbanization and geomorphic restoration, and also contributes to our understanding of microbial responses to salinity and dissolved organic carbon as potential bioindicators of stream integrity and/or restoration success.

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Salinity effects on using hyperspectral radiometry to determine leaf nitrogen of emergent wetland macrophytes

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Salinity effects on using hyperspectral radiometry to determine leaf nitrogen of emergent wetland macrophytes

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Statement of Problem

The Clean Water Act (CWA) stipulates that States report the health and quality of all water bodies, including wetlands, in a National Water Quality Inventory Report, but only 4% of wetlands were included in the most recent edition (USEPA 2002a). By 2012 the USEPA's leniency will end and States will be required to report wetland water quality and ecological health (USEPA 2001). The lack of reporting stems from technical difficulties associated with sampling wetlands and unresolved issues in defining wetland health. In Maryland, water quality monitoring and reporting is conducted by the Maryland Department of the Environment (MDE) and the Maryland Department of Natural Resources (DNR). Recently, MDE has received an EPA grant to develop guidelines for programs to monitor wetland water quality (Denise Clearwater, MDE, pers. comm.).

The low monitoring rate of wetlands is due largely to the time and expense of intensive direct sampling in areas that are difficult to access. Presently, the U.S. EPA National Health and Environmental Research Lab is working directly with seven states to test less intensive sampling methods, such as rapid biological assessment and GIS analysis of land use (e.g., Landscape Development Intensity Index), in an effort to fully develop wetland assessment tools (Richard Sumner, USEPA, pers. comm.). However, it is clear that more tools need to be developed and tested to increase the nation's capability for assessing wetland water quality and ecological health and to meet statutory requirements of the CWA.

Nitrogen is a ubiquitous pollutant that shifts wetland plant composition, lowers diversity and increases productivity ((DiTommaso and Aarssen 1989; Morris 1991; Baldwin unpublished). Agricultural and urban runoff and atmospheric deposition are sources of excess nitrogen to wetlands and open-water systems, such as Chesapeake Bay. In general anthropogenic inputs of nutrients to the biosphere is increasingly viewed as a global threat to ecosystem integrity (Vitousek et al. 1997; Fenn et al. 1998). Although Maryland's load of total nitrogen to Chesapeake Bay decreased by 28% from 1986 to 2001 nitrogen loading remains a priority concern for achieving the 2000 Chesapeake Bay Agreement (MDNCWG 2001). Statewide, point source nitrogen loads have decreased from 14,300 MT to 7710 MT (46%) and agricultural loads have dropped from 14,600 MT to 9590 MT (34%). Urban loads, on the other hand, have grown 19%, from 5370 MT to 6390 MT.

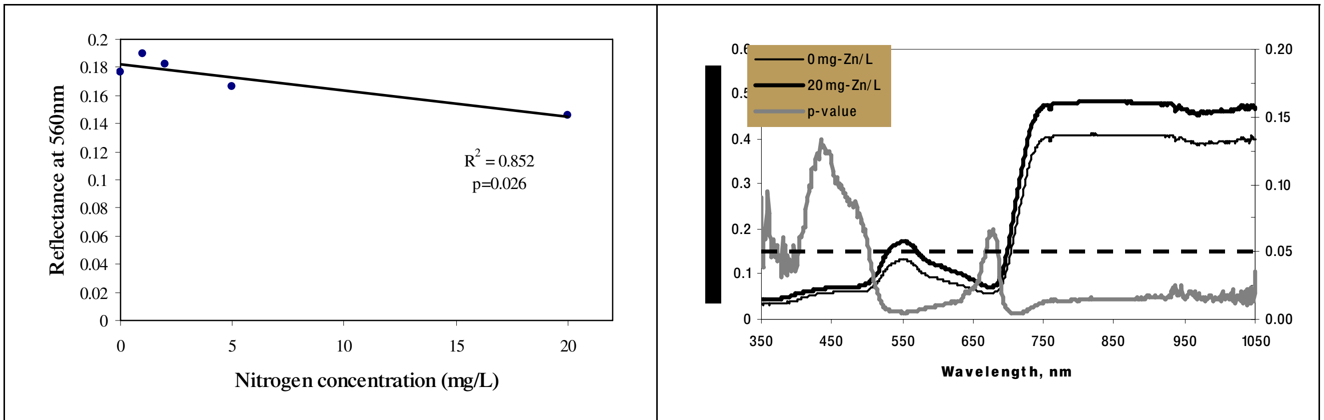
Hyperspectral Radiometry for Ecosystem Assessment

Hyperspectral radiometry measures the electro-magnetic energy reflected from a surface in hundreds of narrow (1—10 nm) spectral bands in the ultraviolet (UV), visible (VIS), near-infrared (NIR) and shortwave-infrared (SWIR) portions of the spectrum. Hyperspectral radiometric imaging can be conducted on the ground with commercially available equipment or from above with airborne (e.g., AVIRIS) and satellite (e.g., Hyperion) systems. In ecosystem radiometry, hyperspectral reflectance is affected by the vegetation's photopigments (e.g., chlorophylls and carotenoids; Hader and Tevini 1987), other leaf biochemicals (e.g., cellulose, lignin; Curran and Kupiec, 1995), inorganic elements (e.g., water, nitrogen, metals), plant morphology, ground cover, soil properties, incident irradiance quality and other environmental factors. When using hyperspectral radiometry to assess the nitrogen levels of leaves or whole ecosystem canopies, much of the effect is due to the strong relationship between reflectance, chlorophyll and nitrogen, although other indirectly associated nitrogen effects (e.g., higher leaf water content) may be partially responsible for the response.

Historically, radiometric remote sensing techniques have been employed to delineate wetland types and track their quantity and location, but recently the techniques have been employed to assess wetland quality and stress levels based on nutrients, metals, salinity, and invasive species (Anderson and Perry 1996; Penuelas et al. 1997; Tilley et al. 2003; Tilley et al. 2004; Wilson and Ustin 2004; Xue et al. 2004; Poynter-Jenkins et al. 2005; Tilley et al. in press). Of course, hyperspectral radiometry has been widely used to assess the condition of open-water aquatic ecosystems--classifying the trophic status of lakes (Koponen et al. 2002, Thiemann and Kaufmann 2000) and estuaries (Froidefond et al. 2002), characterizing algal and red tide blooms (Stumpf 2001, Kahru and Mitchell 1998), and identifying and classifying submerged aquatic vegetation (Williams et al. 2003). Research on applying the techniques to assess the health of emergent wetlands needs acceleration.

Our most recent wetland radiometric studies (Tilley et al. 2005b; Tilley et al. 2005c) have, for example, used partial least squares (PLS) regression (described below) to predict sub-surface water total nitrogen levels in the absence of salinity (R^2=70%). These findings supported our earlier efforts that found leaf reflectance indices [e.g., Photochemical Reflectance Index: $(R_{531}-R_{570})/(R_{531}+R_{570})$; red-edge (wavelength of maximum slope at red—near-infrared transition); and simple ratios (e.g., R_{493}/R_{678}) responsive to water column ammonia in a brackish treatment marsh (Ahmed 2001; Tilley et al. 2003). The PRI was found by others (Gamon et al. 1997) to be positively related to nitrogen, phosphorus, and potassium fertilization rates for annual, deciduous and evergreen upland species. The red-edge is responsive to leaf chlorophyll concentration, which is strongly influenced by nitrogen availability (Carter and Miller 1994). Strachan et al. (2002) included PRI along with the red-edge as necessary members of a multi-index reflectance model developed for classifying nitrogen application rates in corn (*Zea mays*). Read et al. (2002) found a simple blue to red reflectance ratio (R_{415}/R_{710}) as a strong indicator (R^2 = 0.70) of leaf nitrogen in cotton (*Gossypium hirsutum*). We have also found that the normalized difference vegetation index (NDVI) and floating water-band index (fWBI) were responsive to small (1 part per thousand) changes in salinity (Tilley et al., in review).

Figure 1 provides an example of the findings we made during the first MWRRC funded project. High nitrogen availability decreased reflectance in the green waveband (Figure 1a) and blue and red wavebands (data not shown), which indicated that more photosynthetically active radiation was absorbed when more nitrogen was available. Preliminary results from our newest, on-going experiment (Tilley and Baldwin 2005) revealed that heavy metal (Zn) stress in common marsh macrophytes significantly increased reflectance in the green, red and near-infrared wavebands (Figure 1b), which supports our notion that wetland hyperspectral radiometry can be used to assess heavy metal stress in wetlands.



(A) (B)

Fig. 1. (A) Effect of elevated nitrogen on greenband reflectance (560 nm) and (B) effect of elevated Zinc on visible (400-700 nm) and near-infrared (700 –1050 nm) reflectance of *Spartina* and *Typha*.

The large amount of spectral data gathered with hyperspectral radiometry presents a strong case for employing multivariate data analysis techniques that can handle multicollinearity (i.e., the correlation among spectral bands). Partial least squares (PLS) regression is a type of eigenvector analysis that can reduce full-spectrum data to a small set of independent latent factors (i.e., PLS-components) that explain the most about dependent variable response (Esbensen 2002). PLS regression is related to principal components analysis (PCA), which decomposes the independent spectral data (matrix **X**) to its principal components (latent factors) to ascertain which spectral bands are related and possibly important in explaining dependent variable response. Whereas PCA decomposes the X matrix while completely ignoring the Y matrix, PLS regression exploits information contained in the response matrix (**Y)** to decompose the spectral data (**X)** to latent factors that are used to build a regression model that explains the most about **Y**. Thus, PLS overcomes the multicollinearity problem, which is a concern with a method such as stepwise multiple linear regression (MLR) (Grossman et al. 1996) that has been used extensively in analyzing hyperspectral images. PLS has a proven history in chemometrics and is becoming a preferred method for relating hyperspectral reflectance to ecosystem properties as shown by Smith et al. (2003) and Townsend et al. (2003) who used it to develop highly predictive reflectance models of temperate forest canopy nitrogen concentration from airborne and satellite hyperspectral images, respectively. More recently Wilson and Ustin (2004) used PLS discriminant analysis (PLS-DA) of leaf hyperspectral reflectance to classify the Cu and Cd exposure levels of three salt marsh species (*Frankenia* spp., *Salicornia* spp*., and Scirpus* spp.), finding relatively low prediction errors (4.4 to 8.8%). Kooistra et al. (2003) used PLS to relate the reflectance of a facultative upland grass species (*Lolium perenne*) growing in a restored Dutch floodplain to the Zn concentration of the soil. Preliminary results from our wetland imaging (Poynter-Jenkins et al. 2005b) suggested that PLS-DA could detect the presence of invasive

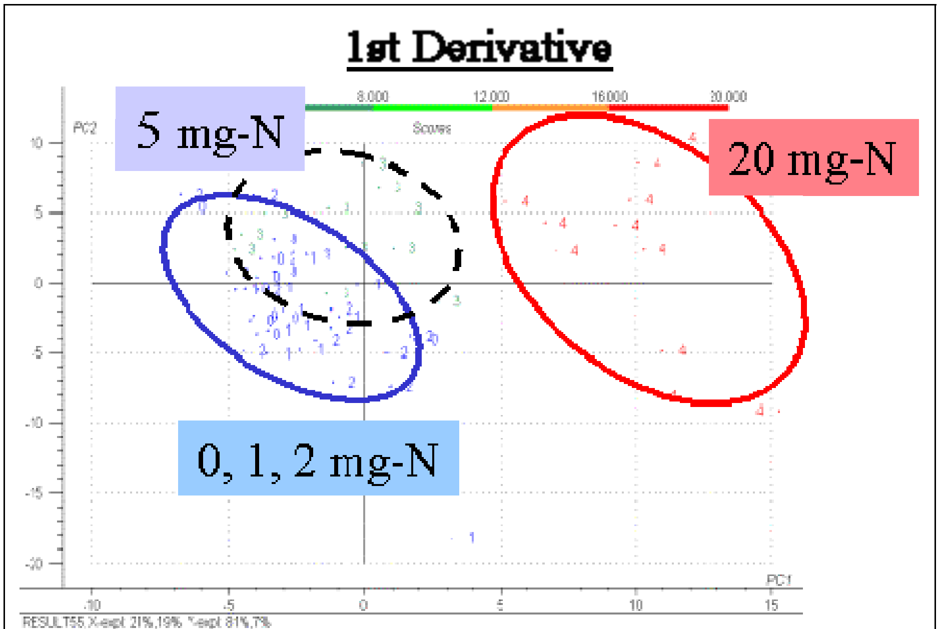


Fig. 2. Partial Least Squares (PLS) regression modeling of 1st Wavelength Derivative of Reflectance classified nitrogen treatment. The 20 mg-N/L treatment was clearly distinguished by the first PLS-component (abscissa) while the second PLS-component (ordinate) indicated some separation of the 5 mg-N treatment. The first PLS-component used 21% of spectral variation to explain 81% of nitrogen treatment. In contrast, the first PLS-component of the model that used the untransformed reflectance used 98% of the spectral variation to explain only 3% of the nitrogen treatment, while the second PLS-component used an additional 1% to explain 37% of nitrogen treatment. Thus, spectral derivative transforms improve predictive efficacy of nitrogen.

species like *Phragmites australis* (88% accuracy) and classify the cover of dominant species like *Polygonum arifolium* (62% accuracy). We have also found success using PLS to build hyperspectral models predictive of nitrogen availability based on (1) individual leaf reflectance in pot-studies (Fig. 2) and (2) field-based canopy reflectance of two tidal freshwater marshes with distinctly different species compositions (Poynter-Jenkins et al. 2005a). As mentioned above, we have a funded project to assess whether we can build a PLS/hyperspectral model predictive of leaf Zn concentration in three common coastal marsh macrophytes (*Phragmites, Typha,* and *Spartina*; Tilley and Baldwin 2005).

Therefore, there is mounting evidence that the combination of PLS and hyperspectral imaging can create an effective tool for assessing many features of wetlands including N availability, species composition and heavy metal-induced stress. One major question about applying the technique to assess nitrogen levels in coastal wetlands located at the freshwater/brackish fringe is whether salinity produces a strong counteractive effect on the nitrogen signal because salinity has been found to increase visible reflectance and reduce near-infrared (Wang et al. 2002), which is opposite of nitrogen. This is the major question we propose to address in the Md. Water Resources funded project. Clarification of this question will continue to advance wetland hyperspectral radiometry as a practical tool for assessing wetland water quality and ecological health.

Long-term Goals for Wetland Radiometry Research

Our research efforts are focused on developing wetland hyperspectral radiometry as an assessment tool complimentary to existing techniques, which will quantify nitrogen (Tilley et al. 2004) and metals (Tilley et al. 2006) in marsh plant tissue, and distinguish which marshes have high nitrogen availability (Tilley et al. 2004), whether they are freshwater or brackish systems. Development of these fundamental capabilities would eventually lead to the ability to remotely sense which wetlands were under stress from high nutrient or metal loading in coastal environments. Thus, our work will assist the States and US EPA in meeting the statutory requirements, which will lead to improved management of the nation's wetlands.

Our proposed research project supports the program objectives of the MWRRC by exploring new ideas in wetland remote sensing for water quality monitoring, fostering the research of a junior faculty (Tilley has completed 4 y at UMCP, receiving his Ph.D. in 1999), and training students in a new technology. In general, our research develops information necessary to protect and enhance water quality and habitats supporting natural ecosystem function and to translate new research knowledge and technologies to decision makers and citizens of the Chesapeake Bay, Mid-Atlantic region and the nation.

Table 1 indicates how MWRRC funding fits into our long-term research and development efforts to develop a wetland hyperspectral radiometry as a tool that can assess the water quality and stress of wetlands. Our earliest in brackish treatment marshes demonstrated that leaf reflectance was affected by nitrogen and salinity. Our more recent work confirmed this capability and indicated species had a strong effect on reflectance, especially in response to elevated nitrogen (Tilley et al., in review). Funding from Md. Sea Grant College supported field-based experimentation that confirmed our greenhouse results (Tilley et al. 2004). Currently, we are testing whether we can detect metal stress (Zn) in common marsh macrophytes with the radiometer. We have submitted proposals to NOAA's CICEET program over the last 3 years to conduct an experiment that would be the field-scale compliment to the project proposed here. Once we obtain funding to complete field-based experimentation, we plan to test the developed algorithms on imagery gathered from satellite (Hyperion) or airborne (e.g., AVIRIS) platforms. If that is successful wetland hyperspectral radiometry should be ready for end-users to pilot-test in real applications of wetland water quality monitoring in support of National Water Quality Inventory Reports (303b).

Table 1. Tasks required to develop wetland hyperspectral radiometry as a tool for wetland assessment.

Tasks	Status	Comments
Proof-of-Concept	Completed 2002	Tilley et al. 2003; Tilley et al. 2007
Leaf-scale nitrogen modelling	2003-2005	Tilley et al. (in review)
Field-scale nitrogen fertilization	2004-2005	Tilley et al. 2004; Poynter-Jenkins et al. 2005a.
Leaf-scale detection of zinc stress	2005-2006	Tilley et al. 2006
Leaf-scale nitrogen with salinity effects	2006-2008	MWRRC (this project)
Field-scale nitrogen w/ salinity effects	2008-2010	Planned
Satellite/airborne testing	2008-2010	Planned
Public application	2011	Planned

In addition to meeting a statutory need for monitoring wetlands, wetland hyperspectral radiometry would help environmental managers screen large expanses of wetlands to identify which ones are nitrogen "hot-spots"; that is potential sites receiving excessive amounts of non-point source runoff. Identifying these major sources of NPS runoff, which has traditionally been very difficult, would allow for directed application of environmental management techniques to reduce nitrogen in runoff and groundwater. This capability will benefit society by improving science-based management of agricultural operations and urban stormwater management to reduce impacts on coastal resources. Locally, this is important since agriculture and urban runoff are two of the predominant causes of eutrophication in the Chesapeake Bay (Jaworski et al. 1992; Chesapeake Bay Program 1995).

By 2012 States will be required by the U.S. EPA to report on the water quality conditions and ecological health of wetlands. Thus, development of wetland hyperspectral radiometry is timely and will have a significant impact on state monitoring strategies and capabilities.

The emerging field of precision agriculture, whereby satellite, airborne, and handheld spectroradiometers are employed to measure nitrogen status of crops, demonstrates the potential of employing remote sensing technologies to understand the nutrient status of wetland ecosystems. Advancing the capability of wetland remote sensing to quantify the nitrogen status of wetlands can (1) provide a tool for the large scale monitoring of water quality in difficult-to-access wetlands, (2) offer a rapid screening method for identifying nitrogen "hot-spots" in a watershed, (3) enable near real-time monitoring in areas suspected of producing significant quantities of non-point source (NPS) pollution, and (4) be used to monitor wetlands used as treatment filters.

Project Objectives

Having developed proof-of-concept that elevated availability of nitrogen changes the visible and near-infrared reflectance of common wetland macrophytes (Tilley et al. 2003; Tilley et al. 2005a), that low level salinity changes in the brackish range alter visible and near-infrared reflectance of marsh macrophytes (Tilley et al. in review), and that partial least squares (PLS) regression modeling can predict nitrogen effects on leaf reflectance of common marsh macrophytes and the availability of sub-surface nitrogen in tidal freshwater marshes (Tilley et al. 2004), an important next step is to investigate the effects of salinity and its interactive effects with nitrogen on the reflectance of emergent marsh macrophytes. This can lead to the development of PLS/hyperspectral models that are predictive of marsh nitrogen and salinity across the fresh/brackish coastal gradient. This ability will be especially useful where coastal marshes are periodically inundated with brackish water during drought years (Baldwin, personal observation) or are gradually shifting to brackish conditions due to relative sea level rise. Also, our previous experiments never evaluated a salt marsh species like *Spartina alterniflora* or *Spartina patens* so the proposed research will include these species.

Specific objectives are:

1. Determine whether salinity decreases near-infrared and increases visible reflectance of freshwater and salt/brackish marsh macrophytes;
2. Determine whether there is an interaction effect between nitrogen and salinity on near-infrared and visible reflectance of freshwater and salt/brackish marsh macrophytes;
3. Determine whether species has a significant effect on hyperspectral reflectance.
4. Determine whether PLS models that use hyperspectral reflectance can distinguish the nitrogen levels of leaf tissue across a gradient of salinity expected at the tidal freshwater/brackish interface.
5. Determine whether PLS models that use hyperspectral reflectance can distinguish the salinity of the water column across a gradient of salinity expected at the tidal freshwater/brackish interface.

<u>Timeline</u>. Originally, this was planned to be a one year project that started March 1, 2006 and ended February 28, 2007. However, we were not able to hire a graduate research assistant, which precluded us from completing the project by the original deadline. We were granted a no-cost extension to February 28, 2008. With the hiring of Mr. Aaron Lewis from the MEES

program we are on target to complete the project by the new deadline. We will collect plant samples from local marshes in July and August of this year and transplant to the greenhouse microcosms where they will be used for the experiment. By end of August plants should be established so nitrogen and salinity treatments may begin. Treatments will be conducted during August and September. Data will be analyzed from September until January, and the final report will be written in February.

Methods, Procedures, and Facilities

Procedures

Experimental Design. Greenhouse marsh microcosms containing one each of six common marsh species (*Acorus calamus*, *Phragmites australis, Typha latifolia, Spartina patens* and *Spartina alterniflora*) will be treated with four levels of salinity and four levels of N in a 5x4x4 factorial treatment arrangement in a randomized block design with four replicates of each treatment, resulting in 4 blocks of 16 microcosms (i.e., 64 microcosms in total) and 320 individual plants. A microcosm will consist of a black plastic tub with five pots each containing a different species. The randomized block design removes variation due to gradients of light, temperature, humidity, and other greenhouse variables. Target salinity levels will be 0, 1, 3, and 7 ppt while N levels will be background, 1, 5, 20 mg-N l^{-1} (Table 2). Seedlings will be collected from marshes on the Patuxent River and propagated in plastic pots containing a peat-perlite mixture at the UMCP Research Greenhouse Complex, which offers state-of-the-art control over lighting, humidity, temperature, irrigation, and pests (UMCP 2003). Previously we have successfully collected plants for use in greenhouse studies using this method from Patuxent River (Baldwin et al. 2001; Tilley et al. in press) and Louisiana delta plain coastal marshes (Baldwin and Mendelssohn 1998). Plants will be supplied weekly with Hoagland's solution minus any N (Mendelssohn et al. 2001). Treatments will be prepared by combining Instant Ocean® synthetic sea salt (Aquarium Systems, Mentor, OH) and ammonium chloride in de-chlorinated municipal water. Because ammonium is the dominant form of available N in wetlands, ammonium chloride has been used by us (Clarke and Baldwin 2002) and others (e.g., Wang 1991) in ammonia toxicity studies. Resulting chloride concentrations will be far below levels toxic to aquatic plants (230 mg L^{-1}, USEPA 2002b). Treatments will be initiated by flushing and filling tubs with treatment solutions. Pots will be kept saturated by maintaining water levels 5-10 cm below surface. The experiment will last 4-6 weeks.

Table 2. Nitrogen and salinity treatments for marsh microcosms will be replicated four times with each microcosm containing one potted individual of each of five plant species (total microcosms = 64).

		Salinity (parts per thousand, ppt)			
		0 (S0)	1 (S1)	3 (S2)	7 (S3)
Nitrogen (mg-N L^{-1})	Nominal (N0)	N0×S0	N0×S1	N0×S2	N0×S3
	1 (N1)	N1×S0	N1×S1	N1×S2	N1×S3
	5 (N2)	N2×S0	N2×S1	N2×S2	N2×S3
	20 (N3)	N3×S0	N3×S1	N3×S2	N3×S3

The levels of salinity chosen were based on ranges that we have observed at tidal freshwater marshes on the Nanticoke River (Baldwin, unpublished data). Normally, salinity levels are <0.5 ppt, but during the late summer months or drought years salinity can increase to several ppt due to decreased freshwater flow. Nitrogen levels were selected to bracket levels measured in Nanticoke tidal freshwater wetlands (1-2 mg/L, Tilley et al. 2004) to an upper bound level (20 mg-N/L) that could reasonably be expected to occur in wetlands receiving agricultural non-point source runoff or wastewater treatment discharge (some forms of agriculture such as confined animal operations can generate even higher ammonium concentrations that are toxic to wetland plants; Clarke and Baldwin 2002).

Data Collection. Measurements of leaf photosynthesis, transpiration and hyperspectral reflectance will be made prior to application of treatments, near the mid-point of the experiment, and at the end of the 4 week period. Photosynthesis and transpiration (net CO_2 and H_2O exchange, respectively) will be measured with a portable infrared gas analyzer (Analytical Development Company, Herts, England: model LCA-2). Leaves will be clamped with the LCA-2, ambient air pulled through at constant flow rate, and CO_2 and H_2O inlet and outlet concentrations measured. Leaf reflectance will be measured with a hyperspectral radiometer (Analytical Spectral Devices, Boulder, CO: model ASD Handheld 325-1075 nm). Percent reflectance will be found by dividing leaf reflectance by the reflectance of a calibrated white panel (LabSphere, North Sutton, NH: Spectralon). The plants, located in black tubs, will be placed in full sun outside the greenhouse while photosynthesis, transpiration and reflectance are measured between 1000 to 1500 h with a 1° field-of-view foreoptic attached to the ASD. Leaf samples will be harvested from each plant at the end of the treatment period to analyze for N concentration at an independent lab.

Data Analysis. A full factorial mixed effects analysis of variance (ANOVA) will be conducted to examine the effects of N, salinity, and species on leaf photosynthesis, transpiration, spectral band reflectance, reflectance indices, and N concentration using SPSS for Windows 12.0 (SPSS Inc., Chicago, IL). Differences among means will be distinguished with Tukey's honestly significant difference procedure. Significant differences will be defined at the 0.05 probability level. Partial Least Squares (described below) regression will be used to develop predictive models of N and salinity treatment levels and leaf N concentrations. We will use Unscrambler 9.0 (Camo Process, Oslo, Norway) to conduct PLS. Sample data will be split into training and test sets to perform calibration and validation, respectively. The number of PLS components to include in the final model will be chosen for the model with the minimum root mean square error of prediction (RMSEP) based on the independent test set. The coefficient of determination of the final model will also indicate model efficacy. Various pre-processing transformations will be tested including normalization, first and second derivatives, and multiplicative scatter correction which can reduce scatter and non-linear effects.

Facilities

Our proposed research will be carried out using the Ecosystem Engineering Design Laboratory, Wetland Ecology and Engineering Laboratory, and University of Maryland Research Greenhouse Complex. Both laboratories are housed within the Department of Environmental Science & Technology at the University of Maryland, and are well-stocked with standard and advanced equipment and materials for ecological and environmental research including spectrophotometers, light meters, a portable photosynthesis system, a digital canopy LAI meter, hip and chest waders, soil augers, drying ovens, a muffle furnace, refrigerators, a grinding mill, balances, glassware, and safety equipment. Specific equipment used in the proposed research includes an ASD Handheld Hyperspectral Radiometer and a Spectralon Calibrated White Panel. Additionally, we have a 24-ft pontoon boat, a 17-ft single hull craft and a jon boat, all with trailers, that can be used to visit marsh sites for collecting donor plant material. The Biological Resources Engineering department also has several trucks and vans for towing the boats to collect plants.

Results

At this time we do not have any results to report. Data will be collected this summer.

Personnel

We have hired a Marine-Estuarine-Environmental Science (MEES) masters student as our graduate research assistant. He will begin work in July 2007. We also have employed 5 undergraduate research assistants to assist with the study during the last year. We have demonstrated the wetland radiometric assessment technique to students enrolled in Restoration Ecology (NRMT 444), which has an enrollment of 15-25 students. We also plan to demonstrate our methods to state and federal wetland managers.

Dr. David Tilley, an associate professor of ecological engineering in the Department of Environmental Science & Technology at the University of Maryland, is the lead investigator. His responsibilities include project oversight, supervision of student assistants, collection and analysis of radiometric data. Dr. Andy Baldwin, associate professor of wetland plant ecology in the Department of Environmental Science & Technology at the University of Maryl will assist with experimental design, plant identification, and inferential statistical analysis.

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Chemical and Biological Impacts of Zinc and Road Salt from Road Runoff Entering Stormwater Retention Ponds

Basic Information

Title:	Chemical and Biological Impacts of Zinc and Road Salt from Road Runoff Entering Stormwater Retention Ponds
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Principal Investigators:	Ryan E. Casey, Edward R Landa, Steven Lev, Joel Wade Snodgrass

Publication

Problem and Research Objective

Highway runoff has the potential to negatively impact receiving systems due to elevated levels of constituents such as deicing salts, metals, organic compounds and nutrients. As part of the Federal Highway Administration - U.S. Geological Survey (USGS) National Highway Runoff Data and Methodology Synthesis, Buckler and Granato (1999) reviewed assessment strategies for the biological effects of highway runoff constituents and indicated that changes in individual organisms and in community structure have been reported. Recent work by Greenstein et al. (2004) showed that dissolved Zn likely caused observed toxicity (assessed using USEPA's marine toxicity, sea urchin fertilization test) in parking lot runoff after simulated rainfall, with tire wear particles and motor oil being suspected Zn sources. Previous estimates of Zn loading from motor oil leakage by Davis et al. (2001) suggested contributions of only 1-2% of the total Zn load in urban runoff. In contrast, tire wear particles, which contain about 1% Zn, make up approximately one-third of the vehicle derived particulates in highway runoff (Breault and Granato 2000). Davis et al. (2001) estimated that about 15 to 60% of the Zn in urban stormwater runoff comes from tire wear. Recent work from the USGS (Councell et al. 2004) has shown that tire wear particles constitute a significant source of Zn to the environment, with release inventories similar to waste incineration; during 1999 approximately 10,000 tons of Zn was released to roadways in the U.S.

Because these and other metal-bearing vehicular wear particles continuously form and collect on roadway surfaces, stormwater retention ponds become a focusing environment for their deposition. Retention ponds attract and are utilized by a wide range of wildlife species (Campbell 1994; Bishop et al. 2000), therefore deposition of metal-bearing vehicular wear particles may result in significant exposures of biota to elevated levels of Zn. Additionally, accumulation of Zn by biota inhabiting ponds (e.g., larval amphibians and fish) may result in trophic transfer of Zn out of ponds as semiaquatic wildlife (e.g., wading birds, waterfowl) feed on pond organisms that accumulate significant quantities of Zn. At this point, neither the magnitude nor the effects of such exposures are clearly known.

In addition to trace element loading, the transportation infrastructure in Maryland contributes large quantities of road salt into receiving waters. A study recently conducted in Central Maryland indicated that the increasing salinity of streams in the northeastern United States poses a threat to potable water sources and habitat for freshwater wildlife (Kaushal et al. 2005). At our study site in Owings Mills, Maryland, we have observed chloride concentrations exceeding the chloride level of seawater persisting in a stormwater retention pond through mid-summer (July 2005). While levels in the pond decreased after August, shallow groundwater immediately adjacent to the pond discharges into an adjacent wetland resulting in surface water chloride levels approximately 10% that of seawater. Shallow groundwater remains at this level year round. While trace elements such as Zn or Cu are effectively retained in stormwater pond sediments, road salt has little to no affinity for sediment particulate matter and can be easily leached into groundwater and subsequently transported into adjacent surface waters. Little is known about the magnitude of this contamination or the contribution of stormwater ponds to long-term salinization of surface waters via shallow groundwater inputs.

Study Objectives

In this study we pursued three objectives.

1. We assessed the magnitude of long-term Zn storage in sediments from multiple retention ponds and related that storage to the magnitude of Zn transport in the surface water of a tributary

of Red Run. We used soil cores from retention ponds to determine the storage of Zn in pond sediments. Cores above the high water line of the ponds were used to determine Zn background in these soils. Zinc background was subtracted from the total Zn in the cores to provide an estimate of anthropogenic Zn that had been stored in the ponds. Zinc storage in the subwatershed was compared to the load of Zn that was measured in surface water flow. We used these data to determine whether the scale of Zn storage in pond sediments was significant in comparison with the magnitude of Zn transport out of the watershed through surface water flow.

2. We used these same retention pond sites to quantify the annual pattern of salt concentrations in two retention ponds and in adjacent shallow groundwater to determine whether stormwater retention ponds were contributing to the long-term increases in salinization previously observed in this region (Kaushal et al. 2005). We monitored surface water and shallow groundwater inside two adjacent retention ponds and in a network of shallow groundwater wells immediately downgradient of the ponds. We also measured salt levels in first order streams originating in this floodplain to determine the spatial and temporal extent of elevated salinity resulting from proximity to the retention ponds.

3. Because roadway-derived Zn originates in large part from tire wear particles, we conducted a bioassay to measure the impacts of tire debris on the development of larval amphibians. We determined the toxicological effects of Zn and tire debris on amphibian eggs and larvae in saturated sediments simulating the sediment environment of stormwater ponds and wetlands where many of these particulates accumulate due to roadway runoff

Materials and Methods

Metal Storage in Retention Pond Cores

Sediment cores were collected from within stormwater ponds using a grid system of approximately 10 x 10 m. Cores were obtained by inserting a soil probe to refusal which generally occurred near 30 cm depth. At least three samples representing background soil conditions were taken above the high water line at each pond. Sediment cores were capped and remained in their plastic sleeves for transport and storage.

The wet mass of each core was determined to allow for subsequent estimates of metal storage in each area of the pond and a sub-sample was then used for dry weight determination. For ICP-MS analysis, approximately 60 mg dry sample was placed into a clean Teflon vial. Samples were acidified using 1 ml of HF and 3 ml of HNO3 and placed on a hot plate overnight. Both acids were of trace metal grade. The samples were dried and 3 mL of hydrogen peroxide was added to the vessels and placed onto the hot plate. The samples were again dried and HF and HNO3 was added in the same proportions as before and placed onto the hot plate. This extra digestion step was to ensure that the samples were completely digested. Finally samples were dried and an internal standard solution of 2% HNO3 containing 10 ppb of germanium and 1 ppb of indium was added to each vial and samples were put back onto the hotplate for re-digestion. Samples were then analyzed by ICP-MS for total metal concentrations. The NIST standard reference material 2709 (San Joaquin Soil) was also analyzed with the sediment samples to monitor external reproducibility.

For samples analyzed by X-Ray fluorescence spectrometry (XRF), a portion of each dried soil sample was ground using a SPECS Mixer/Mill 2500. The mixer/mill was cleaned between each sample using DI water and methanol. Ground samples were pressed into pellets using the SPEC X-Press. Approximately 7 g of sample and 0.7 g of a cellulose binder were mixed together and placed into the pressing die. Each pellet was then kept in a desiccator until analyzed by the XRF. NIST SRM 2709 (San Joaquin Soil) was used during XRF analysis for QA/QC. Using the mass of the sediment cores, the surface area of the sampler, and the area of the sampling grid, total pond storage was estimated for Cu and Zn.

Stream Discharge and Load Determinations

Stream discharge measurements of a second order tributary of Red Run were made periodically over 10 months in 2006-2007 just above the confluence with Red Run at the bottom of the watershed in this investigation to establish a rating curve. The monitoring location was selected in order to characterize the total suspended and dissolved load leaving the watershed. USGS protocols for current meter measurement of discharge were followed and an average discharge was calculated for each sampling event. Over the same time period a levelogger was placed in the stream at the same location and depth measurements were collected every 3 minutes. A curve was fitted to the field discharge vs. depth measurements and a rating curve was established ($r^2 = 0.75$). Based on the rating curve equation, depth measurements from the levelogger were converted to discharge.

In order to make accurate estimates of both the particulate and dissolved Zn load leaving the watershed, a series of equations were developed to estimate the Zn load from the levelogger data using the relationship between field measurements for discharge and suspended sediment, Zn particulate concentration and dissolved Zn. While there are a series of assumptions that must be made in order to relate these parameters to one another, this is the only reasonable approach to estimate the elemental load from a small watershed without continuously sampling dissolved and suspended sediment from the stream.

Monitoring of Salinization Due to Retention Ponds

Two stormwater retention ponds were chosen for detailed monitoring of chloride and conductivity to determine the temporal and spatial extent of elevated salinity due to road salt application. Surface water in each stormwater pond was periodically monitored, along with shallow groundwater approximately 1 m below ground surface. A network of shallow groundwater wells (~ 1 m below ground surface) was deployed in the floodplain between the retention ponds and an unnamed second order tributary of Red Run. Three first order streams originate in this floodplain between the ponds and the tributary. Conductivity and chloride levels were determined for the first order streams, the second order tributary and the groundwater in the floodplain. Conductivity was determined using a hand-held field probe (YSI, Inc.) and chloride was determined using a Dionex IC 20 ion chromatograph.

Tire Debris Bioassay

The bioassay was performed using soils obtained adjacent to a retention pond. These soils represent the background material in pond sediments prior to mixture with road debris. Soil was collected and placed into three 5 gallon plastic containers. One treatment contained soil amended with approximately 8380 mg kg^{-1} of tire material, the second contained soil that had been amended with approximately 1000 mg kg^{-1} of Zn^{2+} in the form of $ZnCl_2$, while the final treatment was unamended soil. The tire material was obtained from a scrap tire facility in Baltimore, MD and contained 1.26% Zn by mass (Councell et al. 2005). Particle size was less than 590 μm and steel belt debris had been removed. Enough $ZnCl_2$ and tire debris were added to their respective containers to yield approximately equal amounts of total Zn at a target concentration of 1000 mg kg^{-1}, with the $ZnCl_2$ serving as a positive control representing completely bioavailable Zn. Enough aged tap water was mixed with each treatment to saturate the soils and soils were homogenized mechanically using a mortar mixing attachment on a hand-held drill. All treatments were sealed and allowed to age for 8 months to simulate conditions occurring after deposition of roadway debris in a stormwater retention pond. Although continual mixing of surface sediments in retention ponds with standing water can occur, this usually takes place most often in the flow path of runoff entering the pond and leaving the pond over the spillway. In deeper sections of retention ponds sediments can settle for longer periods of time, similar to the conditions that are represented in this study.

Three pairs of wood frogs (*Rana sylvatica)* in amplexus were collected in the beginning of March 2006 from a reference site in Baltimore County, MD and allowed to deposit eggs in the laboratory. Approximately 1 cm of the aged sediment treatments was placed into the bottom of clean acid-washed plastic containers with approximately 3 L of aerated tap water. Exposure bins were set up in a randomized block design with a total of ten replicates for each treatment. Eggs were placed into exposure bins 3 days after set-up of the bins to allow sediments to settle. Between 5 and 6 eggs from each clutch were placed into each bin, and the hatching success of each clutch was recorded. Once all tadpoles had hatched, all but one from each container was removed and euthanized using MS-222. The one that remained in each bin was randomly selected and these remaining organisms were maintained until metamorphosis.

Each tadpole was fed Tetramin® fish food every 1-2 days. The starting mass of food was 10 mg per ration; however every 2-3 feedings the ration was increased to account for increased growth in the tadpoles with a final ration of 65 mg per feeding. Half of the water in each container was removed and replaced with fresh aerated tap water once per week. Temperature, pH, and conductivity were also measured once per week. Filtered water samples were collected randomly from 3 bins in each treatment once per week. Water samples were acidified to 0.2 N with trace metal HNO_3 and stored until analysis. The first water sample was collected 2 days after exposure bin set-up, prior to egg addition. The mass of each organism was measured on day 36 when organisms were between Gosner stages 33-35. Tadpoles were removed from the water, blotted to decrease the transfer of water, then place into a tared beaker of water to obtain their mass.

Once organisms developed front limbs, they were removed from the treatment bins and placed into a separate clean container with moist towels until metamorphosis was completed. Once organisms had developed to Gosner stage 46 they were euthanized using MS-222 and frozen until further analysis. Time to metamorphosis was recorded for all organisms.

Acidified water samples were spiked with an internal standard solution containing indium and germanium and analyzed using inductively coupled mass spectrometry (ICP-MS). A previously digested NIST SRM 2976 (mussel tissue) was analyzed along with the water samples for quality assurance. All samples were analyzed for Cu, Zn, Ni, Cr, As, Se, Cd and Pb. Average recovery for each of the metals was: Cr = 125%, Ni = 103%, Cu = 90%, Zn = 105%, As = 88%, Se = 80%, Cd = 137% and Pb = 97%. All elements except for Cd were within in the certified confidence ranges. Cd recovery was 115% of the upper limit of the certified confidence range.

The froglets were placed into a drying oven at 70°C and then weighed to obtain dry mass. Organisms were then placed into clean Teflon vessels digested overnight with 5 mL of 6N HNO_3

on a hotplate at 150ºC. Samples were dried and 3 mL of trace metal grade H_2O_2 (Ultrex II, J.T. Baker) was added to each vial then digested overnight on the hotplate again. Samples were diluted to 40 mL using 0.2N HNO_3 and analyzed on the ICP-MS for the same analytes as the water samples.

Sediment samples collected from the treatment bins were leached overnight using 6 M HNO_3 at 150ºC then analyzed using ICP-MS. All results are reported in terms of dry weight.

An ANCOVA was used to assess significance of size at metamorphosis between treatments with time to metamorphosis as a covariate. A repeated measure ANOVA was used to compare pH, conductivity, Zn concentrations in water samples, and temperature over the course of the experiment for each treatment. An ANOVA followed by Tukey's HSD test for *post hoc* determination was used to assess significance between treatments for Zn in sediments, Zn concentrations in tissues, size at mid experiment, and time to metamorphosis. All data were log transformed in order to meet the assumptions of a normal distribution.

Results

Storage and Transport of Zn in a Small Watershed

The results presented here are preliminary. Data acquisition is still under way, as per the no cost extension agreement that we obtained.

Of the ten retention ponds in the watershed being investigated, we have sampled and determined Zn storage for three. Subtracting soil background Zn from the sediments in the retention ponds these three ponds stored 3.4, 8.6 and 0.8 kg of anthropogenic Zn, respectively. If we consider these ponds to be typical of others in the watershed and extrapolate this storage throughout the watershed, we estimate that the ten retention ponds are storing a total of 42.6 kg of anthropogenic Zn. This storage has occurred over approximately 6 years in these ponds.

The annual background corrected Zn transport out of the catchment area is estimated at 6.9 kg yr^{-1}. This estimate is based on the calculated particulate and dissolved Zn load derived from field measurement. This annual Zn load estimate is approximately equal to the annualized total anthropogenic Zn storage in storm water retention ponds from the watershed being investigated. Based on this comparison, the storm water retention basins in this catchment are storing approximately 50% of the total anthropogenic Zn load and are in fact acting as a significant sink for roadway derived Zn.

Salinization in Stormwater Ponds and Surroundings

The results presented here are preliminary. Data acquisition is still under way, as per the no cost extension agreement that we obtained.

Conductivity measurements from three ponds within the Red Run watershed are presented in figures 1 and 2. The data in figure 1 was collected every 12 hours continuously between March, 2005 and June, 2007. The points in black represent conductivity measurements from shallow groundwater directly beneath the deepest portion of the retention pond. Open symbols are bottom water conductivity measurements from the deepest point in the pond. Also plotted are a field, marking the observed range of down-gradient groundwater conductivities and dashed lines that represent the conductivity of seawater and the adjacent portion of Red Run which will ultimately receive groundwater discharged from the retention pond.

This pond is perennially wet and is receiving direct highway runoff from an adjacent 6 lane primary roadway. The conductivity of the surface water in the pond is highly seasonal with the highest conductivities directly related to road salt events during winter storms. Over the monitoring period, there were only 2 major snow fall events one in December 2005 and the second in January 2007. As the snow from the winter storms melted salt applied to the roadway before, during and after the snow fall was washed into the retention pond increasing the conductivity by 2 orders of magnitude. This elevated conductivity remains for up to 10 months before returning to background surface water levels. The conductivity of groundwater directly beneath the pond lags behind surface water demonstrating the connection between the surface water and groundwater. This slow infiltration rate dramatically limits this systems ability to flush roadway derived salt and creates a continuing source of salt to groundwater and ultimately surface waters. Groundwater directly beneath the pond is constantly elevated and fluctuates, depending on the amount of salt free recharge, between 10 and 200 times the conductivity of fresh water in Red Run. Groundwater down-gradient of the pond, between the pond and the main branch of Red Run, is elevated year round and has a relatively constant conductivity that is 2 – 20 times the conductivity of Red Run. This large plume of salt is migrating towards Red Run and will provide a significant continuing source of salt to Red Run once it begins to discharge.

In order to evaluate the relevance this perennially wet pond, 2 adjacent rapid infiltration ponds in a more suburban portion of the watershed were also investigated. The results of this part of the investigation are on-going however; it has become clear that rapid infiltration ponds can also act as a continuing source of salt groundwater and ultimately Red Run. Figure 2 is a plot of conductivity along a transect from the input of one of the ponds through the flood plain to a 1st order tributary of Red Run which represents a discharge point for groundwater in this system. This pond is representative of the behavior of both ponds. Results from 4 sampling events beginning in January 2007 immediately following a major storm event are plotted at each point along the transect. Note the movement of roadway salt through the system over time and more significantly the sustained elevated conductivities at the point labeled "well" which represents groundwater beneath the retention pond. Despite the rapid infiltration design of this pond, groundwater conductivities remain up to 100 times that of surface water for more than 5 months after a major salting event. These ponds are demonstrating the same dynamics as the perennially wet highway pond and are similar with respect to the range of conductivities found in groundwater year round. These ponds will be continually monitored until spring 2008 in order to document range of conductivities over a calendar year.

Toxicity of Tire Debris Amended Sediments to Larval Amphibians

Conductivity, pH, and temperature values were similar through all treatments (Table 1). Conductivity and pH were significantly different between treatments, but in terms of environmental conditions they were most likely not a controlling factor in the experiment. Aqueous Zn concentrations decreased dramatically after the first two weeks of the experiment for both the $ZnCl_2$ and tire treatments (Figure 3). During the first week the $ZnCl_2$ treatment had a concentration of 300 $\mu g\ L^{-1}$ Zn which dropped to 80 $\mu g\ L^{-1}$ by the second week and 21 $\mu g\ L^{-1}$ by the third week. A similar trend was seen in the tire treatment with week one concentrations approximately 25 $\mu g/L$ Zn and week three concentrations approximately 7 $\mu g/L$. These changes reflect dilution of water column Zn by the weekly water changes in the bioassay containers.

The presence of Zn in the water column of the tire treatment indicated that the aging period did in fact leach some of the Zn out of the tire material, making it potentially available for uptake by larvae. Sediment Zn concentrations between treatments were significant ($F_{3, 15}$=154.11, $P < 0.0001$) with the tire and $ZnCl_2$ treatments having significantly higher Zn concentrations than the soil treatment as measured by 6M HNO_3 leach. However, sediment Zn levels were statistically similar between the $ZnCl_2$ and tire treatments. All other metal concentrations were substantially lower than Zn in both the water and sediment (Table 2) and were generally similar between all three treatments.

Eggs from three clutches were placed into separate corners of each exposure bin in order to determine hatching success of each clutch. Differences in hatching success were significant between clutches ($F_{1, 27} = 24.74$, $P < 0.0001$) and moderately significant between treatments ($F_{2, 27} = 3.51$, $P = 0.0442$). Of the three clutches, one had a 0% success rate due to lack of fertilization of the eggs; this clutch was not included in the statistical analyses. The mean success rate for eggs from the soil, $ZnCl_2$ and tire treatments were 86%, 68% and 80%, respectively.

Zn concentrations in anuran tissues were significantly different between treatments ($F_{3, 33} = 99.23$, $P < 0.0001$). Organisms in the $ZnCl_2$ and tire treatments had statistically higher accumulations of Zn than those from the unamended soil. Additionally, tissue Zn accumulation in the $ZnCl_2$ treatment was statistically higher than the accumulation in organisms from the tire treatment (Figure 4). There was little accumulation of other metals in the organisms (Table 2). Organisms weighed at day 37 of the experiment showed no significant difference between the size of the organism and the exposure treatment ($F_{3, 36}$=2.00, p=0.1322).

The number of days to complete metamorphosis was significantly different depending on the treatment ($F_{3, 27} = 4.83$, $P = 0.0081$). The tire treatment and the $ZnCl_2$ treatment were significantly slower to reach metamorphosis than the control soil treatment. There was no significant difference in time to metamorphosis between the tire and $ZnCl_2$ treatments.

An ANCOVA with day as the covariate showed that exposure to Zn had no effect on the mass of the organisms at metamorphosis ($F_{5, 15}$ =1.41, $P = 0.4344$). Although the differences were not significant, there was a relationship between days to metamorphosis and size at metamorphosis. Larvae that were exposed to control soils had a positive relationship between days to metamorphosis and size at metamorphosis, however larvae exposed to tire treatments had a negative relationship (Figure 5).

Only one larval amphibian died during the exposure period. The organism died 15 days after hatching and was in the $ZnCl_2$ treatment. Since there were no other mortalities during this time, the single mortality cannot be attributed to the exposure conditions. After organisms developed front legs they were removed from exposure bins and placed into containers with only wet paper towels to ensure high moisture. Eight organisms died during metamorphosis, but mortality during metamorphosis was not related to Zn exposure. Out of the eight organisms that died, 2 were from the tire treatment, 3 from the soil treatment, and 3 from the Zn treatment. Even though these organisms did not complete metamorphosis, they were saved and analyzed for total metal accumulation along with all other organisms. They were not used for time to metamorphosis or size at metamorphosis calculations.

The most substantial difference between exposure conditions was the concentration of Zn in the sediment as well as the water column. Zn was present in the water column in tire exposures showing that a portion of the total Zn in the tire rubber leached out of the tire material and entered the water column. Decreases in water column Zn were due to the water changes that occurred once per week. During the first week, substantial Zn that was dissolved in the pore water or loosely attached to the sediment surface was released into the water column. The first water change and subsequent water changes removed approximately half of the Zn in the water column. The highest concentrations of Zn were present during the hatching period and may have affected the hatching success of eggs. This pulse of high aqueous Zn is similar to what is seen during a storm event with the first half of the stormwater runoff having higher concentrations of metals. This indicates that it is possible for organisms to be exposed to very high concentrations of metals for a very short amount of time. Different life stages of anurans could exhibit varying susceptibility to metals, so the stage at which these organisms are exposed to these high metal pulses in the environment could affect the magnitude of their response.

Accumulation of Zn in the tissues of the adult anurans was seen in both the tire and $ZnCl_2$ amended treatments in comparison with the unamended soil treatment; however no significant larval mortality occurred in any of these treatments. Tissue Zn concentrations in the tire-exposed organisms are similar to concentrations in organisms found in a stormwater management pond (Casey et al. 2005) but lower then tissue concentrations found in organisms from a river system in Greece (Loumbourdis and Wray 1998). A study by Snodgrass et al. (2003) indicated that Zn is one of several elements that are retained in anuran tissues through metamorphosis.

Water column data as well as accumulation data show that Zn is leaching out of the tire material and becoming available to the larvae. Both the tire and $ZnCl_2$ amended soils showed slowed rates of development when compared to the unamended soil treatment, however there was no difference in the metamorphosis rate between the $ZnCl_2$ treatment and the tire treatment. The delayed metamorphosis of organisms exposed to Zn indicates that there is a sublethal effect of the metal on *R. sylvatica* larvae. The $ZnCl_2$ treatment should have more available Zn than the tire treatments and it would have been expected that the tire treatment would have reached metamorphosis faster based solely on Zn concentrations. However, Zn is not the only component of tire material that could be causing a sublethal effect. In addition to Zn, tires may also contain a variety of other pollutants including PAHs, various organic chemicals, and other metals (Wik and Dave 2005) which could have contributed to the slowed time to metamorphosis. The amended soils reached metamorphosis approximately 7 days after those from the unamended soil treatment. It may be that this 7 day difference is not large enough to have a major impact on survival in the environment; however, this is only one measure of stress and may be indicative of other sublethal stresses occurring as a result of the exposure. The negative relationship of days to metamorphosis and size at metamorphosis for tire treatments indicates the length of time that larvae are exposed to tire debris adversely affects their size. This negative relationship has also been observed in larvae exposed to coal combustion wastes (Snodgrass et al. 2004).

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	Soil	$ZnCl_2$	Tire	P values		
				Treatment	Day	T x D
Zn (μg/L)	bdl (bdl-3.7)	65.89 (2.5-374.3)	10.06 (1.15-32.93)	<0.001	<0.001	<0.001
pH	8.51 (7.90-9.49)	8.14 (7.43-9.79)	8.17 (7.60-9.24)	<0.001	<0.001	<0.001
Conductivity (μS/cm)	373 (338-386)	491 (364-627)	387 (369-488)	0.0265	0.6822	0.0793
Temperature (Celsius)	18.4 (14.9-21.9)	18.4 (15.1-21.9)	18.2 (15.0-22.4)	0.3168	<0.001	0.2343

Table 1: Arithmetic means of experimental water conditions (ranges in parentheses) and repeated measure ANOVA results.

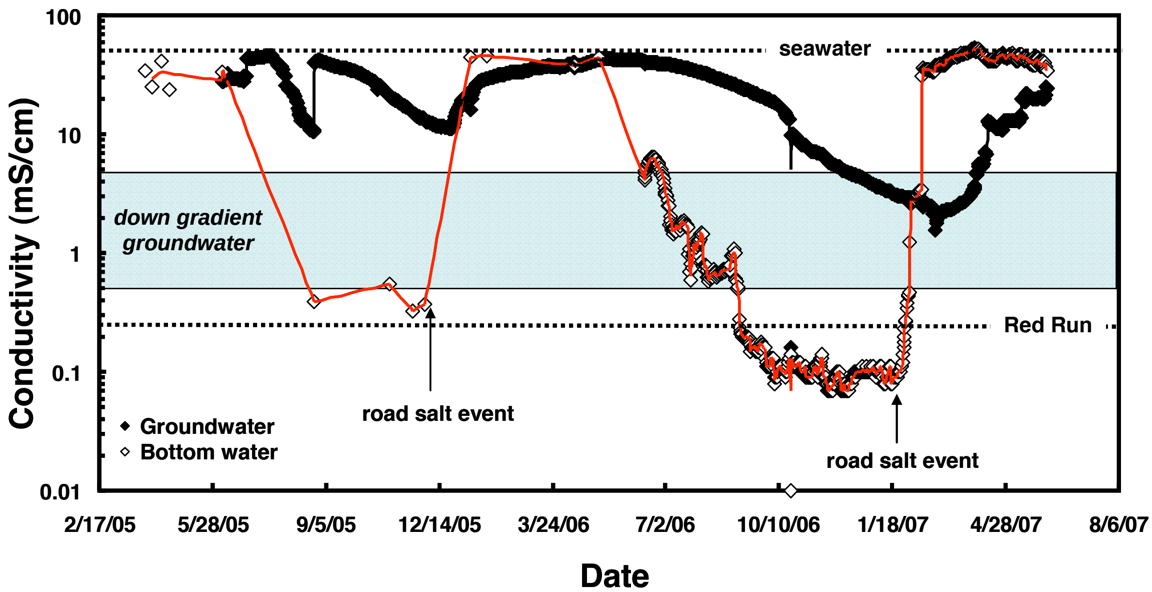

Figure 1. Continuous record of surface and ground water conductivity from a perennially wet highway pond in the Red Run watershed.

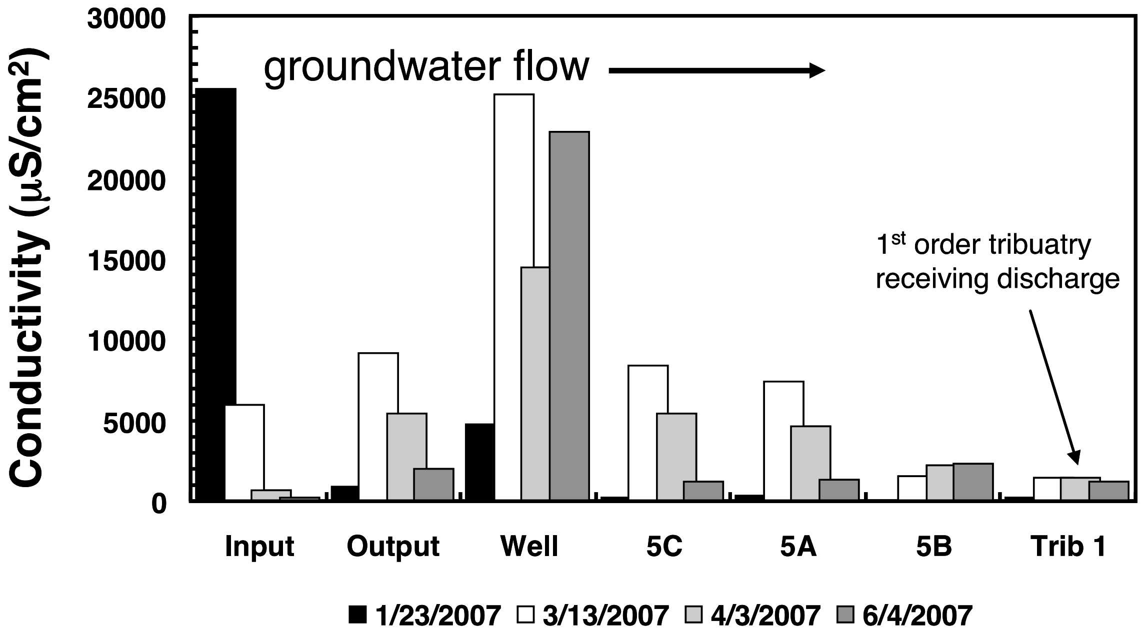

Figure 2. Plot of conductivity along a transect between the storm water input point of a rapid drainage suburban pond and a 1st order tributary of Red Run receiving discharge for groundwater connected to the pond. Input and Output are surface water measurements while Well (inside the pond), 5C, 5A and 5B (in the flood plain) are shallow groundwater wells in the pond adjacent flood plain.

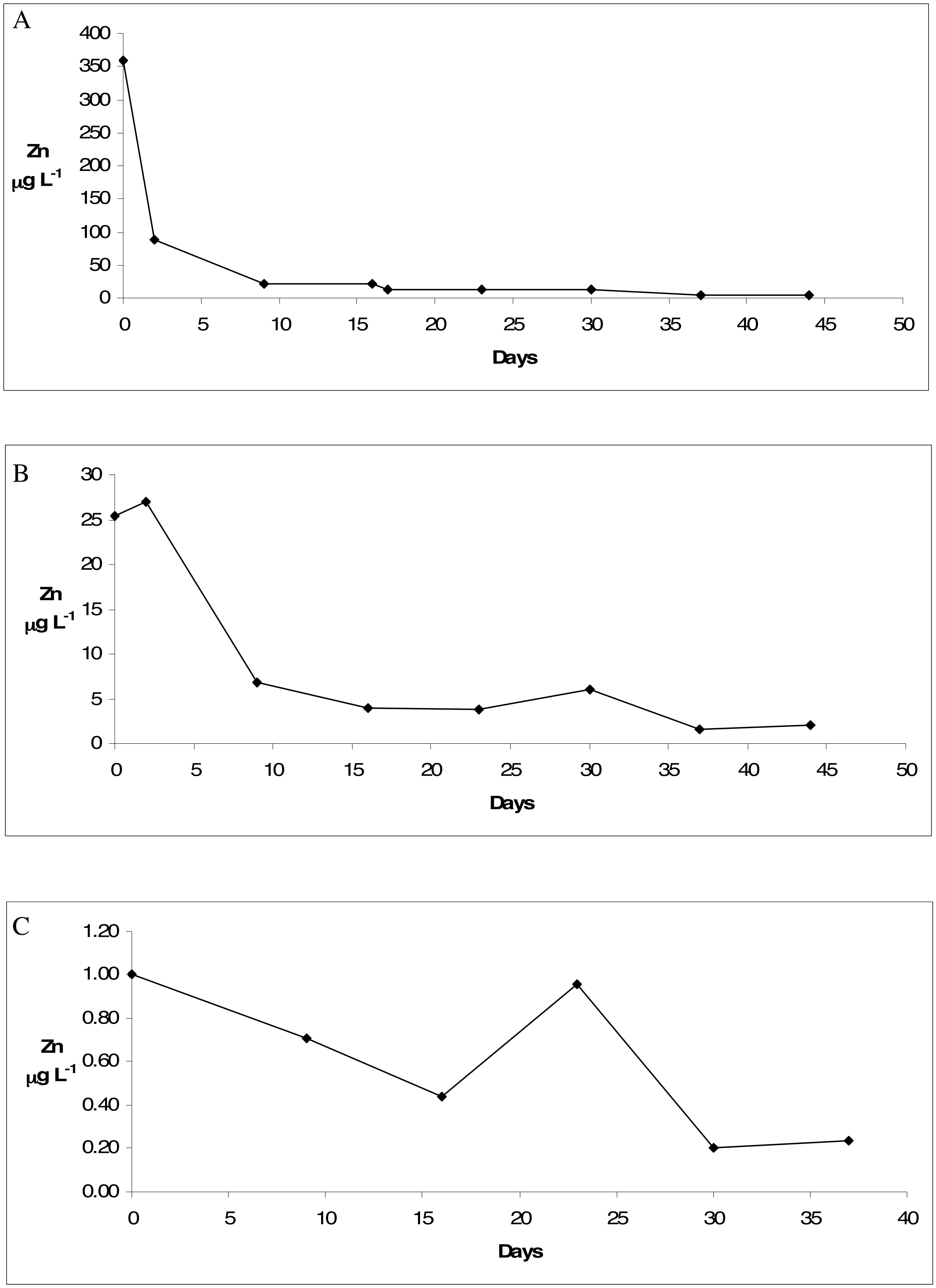

Figure 3: Mean Zn concentration in the water column over the course of larval exposure (day 0 is day eggs were added) for the treatments; A) $ZnCl_2$ B) Tire C) Soil

	Sediment (mg/kg)			Tissues (mg/kg)			Water (μg/L)		
	Soil	Tire	ZnCl2	Soil	Tire	ZnCl2	Soil	Tire	ZnCl2
Cr	52.5	37.2	40.1	0.40	0.29	0.41	bdl	bdl	bdl
Ni	45.4	35.4	42.0	0.96	0.59	0.86	bdl	bdl	bdl
Cu	19.1	19.4	22.9	4.53	8.9	3.9	3.5	3.2	3.4
Zn	62.0	1155	1187	81.7	212	324	bdl	12.6	32.8
As	0.13	bdl	bdl	bdl	bdl	Bdl	bdl	bdl	bdl
Se	bdl	bdl	bdl	1.0	0.76	1.2	bdl	2.1	bdl
Cd	0.15	0.43	bdl	0.15	0.11	0.11	bdl	bdl	bdl
Pb	26.1	41.5	24.8	0.04	0.38	0.04	bdl	bdl	bdl

Table 2: Arithmetic means of metal concentrations in sediment, tissues, and water. The detection limit (bdl) for water is 1 μg L^{-1}.

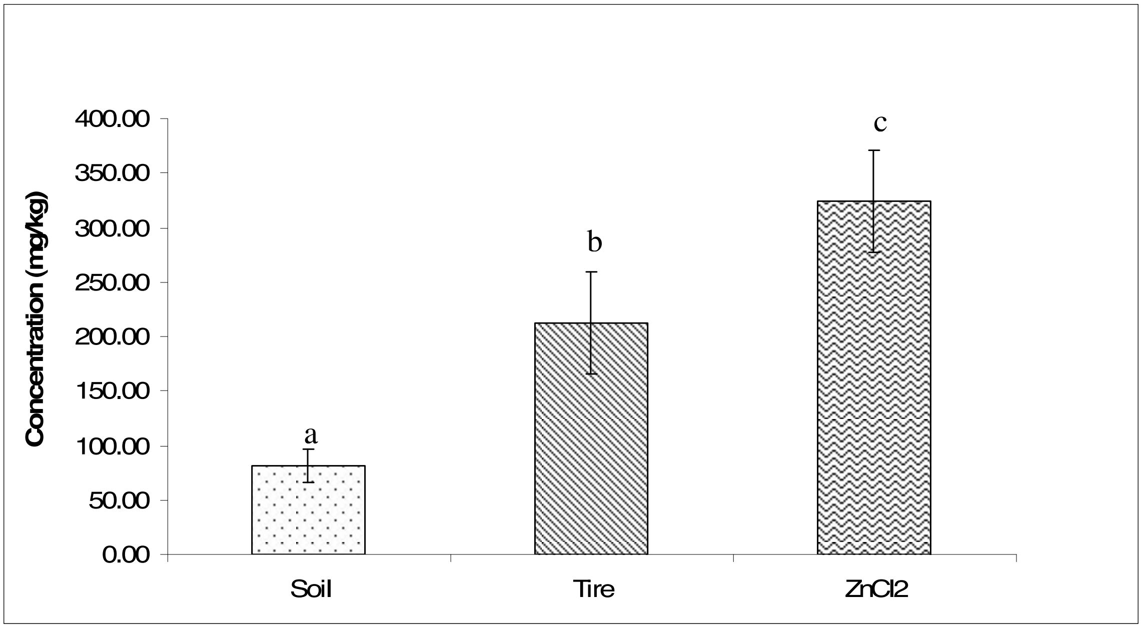

Figure 4: Concentration of Zn accumulation in tissues of *R. sylvatica* for the three treatments; soil, tire, and $ZnCl_2$. Error bars are ± 1 S.D. Letters indicate significant differences ($P < 0.05$) between treatments for Zn accumulation based on Tukey's post hoc test

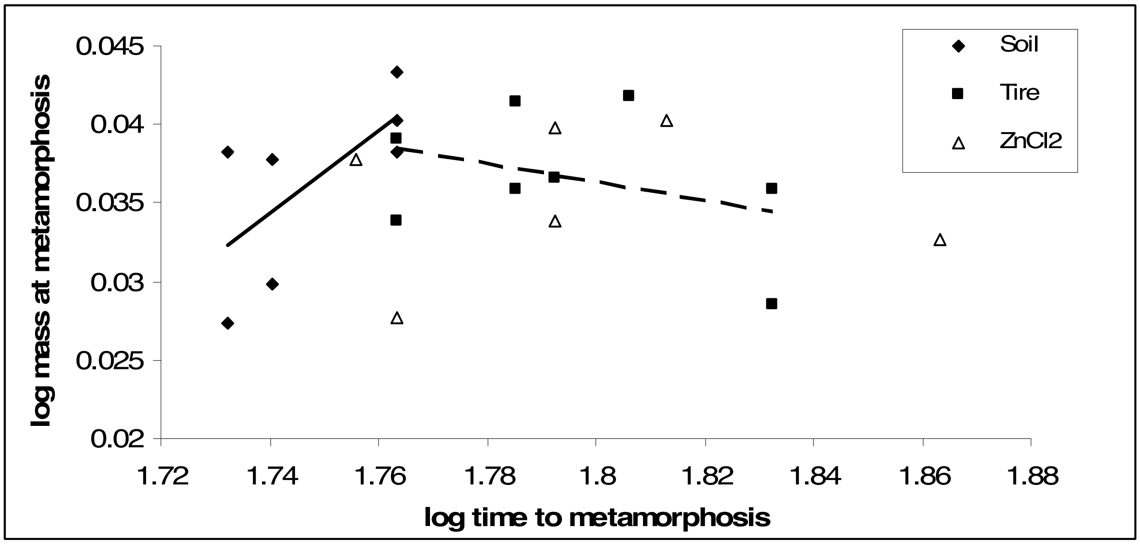

Figure 5: Relationship between days to metamorphosis and size at metamorphosis. Solid line is a linear regression for soil treatment ($y = 0.2631x - 0.4234$; $R^2 = 0.4624$; $P = 0.006$). The dotted line is a linear regression for the tire treatment ($y = -0.0585x + 0.1416$; $R^2 = 0.1358$; $P = 0.055$) No line is given for the $ZnCl_2$ treatment because the relationship was not significant ($P = 0.886$).

2006 Summer Research Fellow

Basic Information

Title:	2006 Summer Research Fellow
Project Number:	2006MD139B
Start Date:	3/1/2006
End Date:	1/1/2007
Funding Source:	104B
Congressional District:	5
Research Category:	Biological Sciences
Focus Category:	Ecology, Water Quality, Conservation
Descriptors:	None
Principal Investigators:	Allen Davis

Publication

Summer 2006 Graduate Summer Fellowship Project Summary for NIWR Annual Report

Brian Laub
Doctoral Candidate
Department of Biology
University of Maryland

Introduction

In 2006, I received a fellowship from the Maryland Water Resources Research Center for summer support. For my summer work, I asked whether geomorphic restoration projects facilitated nutrient reduction in streams and why they were or were not effective at reducing nutrient loads. I worked on 10 streams, all located in Anne Arundel County, Maryland. The streams included 6 restored streams, 3 urbanized non-restored streams (control streams), and 1 forested stream (reference stream).

To investigate the potential for restored streams to reduce nutrient loads, I measured the concentration of nitrate (NO_3^-) and ammonium (NH_4^+) upstream and downstream of each restoration reach and over similar distances on control and reference streams. I also attempted to explain any reductions in nutrient concentrations or lack thereof by measuring community metabolism and channel complexity in each stream. If community metabolism is low, there may be a lack of biological activity to reduce nutrient concentrations substantially. If complexity is low, this indicates that water moves through the stream rapidly, leaving insufficient time for biotic nutrient uptake.

Summary of Results

Although streams differed substantially in N concentration, metabolism, and complexity, there was no consistent trend of decreased N concentrations from upstream to downstream at any stream. Thus, community metabolism and channel complexity did not appear to influence N concentrations. It is possible that at some streams, N concentrations were so high that they overwhelmed the ability of biota to uptake nutrients by a detectable amount. However, it is more likely that concentration data taken at two points was not a good measure of the N uptake capability of each stream. Groundwater inputs of N were not accounted for, and substantial inputs could mask reductions through uptake. More sophisticated procedures, such as a budgeting approach would better characterize N removal potential in each stream.

Variation in N concentration, metabolism, and complexity was as great between restored streams as between restored streams and control and reference streams. Thus, restoration does not seem to have altered stream environments substantially. However, the high variation observed suggests that even within a small geographic area, differences between streams can be great. With such a large range of natural variability, quick, general assessments of stream restoration projects are unlikely to uncover effects of restoration unless the effects are dramatic.

Future Research

For my future PhD work, I will examine how geomprphic restoration projects change channel complexity of river channels and how these changes affect the ability of algal communities to recover from floods. The work performed this summer provides important data that will help frame future work. Most importantly, I have shown that the study streams differ widely in complexity and nutrient concentrations, which are both likely to constrain algal community growth and composition.

Information Transfer Program

Extreme Water in Maryland

Basic Information

Title:	Extreme Water in Maryland
Project Number:	2006MD163B
Start Date:	10/27/2006
End Date:	10/27/2006
Funding Source:	104B
Congressional District:	MD 5th
Research Category:	Climate and Hydrologic Processes
Focus Category:	Climatological Processes, Education, Floods
Descriptors:	
Principal Investigators:	Allen Davis

Publication

Extreme Water in Maryland

A one-day symposium entitled "Extreme Water in Maryland" was held Friday, October 27, 2006 at the University of Maryland, sponsored by the *Maryland Water Resources Research Center* and *Maryland Sea Grant*

Maryland has suffered severe damage in recent years from several extreme water events. There was keen interest in lessons learned from two past hurricanes and projected problems in the future. Over 75 participants from across the State attended the symposium.

Highlights

Below are some of the highlights presented by several speakers.

Gerry Galloway, CEE, University of Maryland, College Park, MD.

The US faces many water resource challenges including dealing with the consequences of extreme water events such as floods and droughts. Unfortunately the nation does not have any coherent policy that describes how these water challenges should be addressed. As a result the nation deals with hazards as well as other water issues on an ad-hoc basis. Water Professionals must become involved in educating the public about wise use of these resources and influence decision makers to deal with water on a comprehensive, sustainable basis.

Wilson Shaffer, National Weather Service, Silver Spring, MD.

The National Weather Service (NWS) uses its Sea, Lake, and Overland Surges from Hurricanes (SLOSH) model for generating storm surge forecasts. This model is run in three modes – for simulation studies, for real-time, operational surge guidance, and for new, experimental probabilistic storm surge forecast guidance. For simulation studies to support hurricane evacuation planning, approximately 50,000 hypothetical hurricanes were run through the Chesapeake Bay. These hurricanes vary in track direction and landfall location, intensity, size, forward speed, size, and tide level. Composites depicting the possible flooding in the Bay were presented for various categories of hurricanes. As operational forecast guidance to NWS forecasters and emergency managers, SLOSH is run in a deterministic mode, beginning 24 hours before forecast landfall, based on the forecast track and hurricane parameters. The NWS has recently embarked on generating probabilities of storm surge exceeding various threshold levels.

Michael S. Scott, Salisbury University, Salisbury, MD.

To analyze the vulnerability of Maryland's environment to a 100-year flood we used the HAZUS-MH modeling software. Developed by FEMA, HAZUS-MH consists of several stochastic flood models operating within ArcGIS that create damage estimates from both coastal and riverine flooding. A generalized HAZUS-MH model was created for each county (and Baltimore City) in Maryland. Results from the study (available at www.esrgc.org/hazus.htm) show that Maryland has almost $8 billion in buildings potential exposed to a flood hazard. In the event of a 100-year flood, the predicted building damage could equal over 109 million square feet. The direct economic losses from a 100-year flood could exceed $8.1 billion. Researchers are now examining identified vulnerable areas, like Ocean City, Maryland, in more detail in order to refine the results.

Kevin G. Sellner
Chesapeake Research Consortium, Edgewater, MD.

Hurricanes have impacted the mid-Atlantic region for recorded time and recent storms have resulted in tremendous losses of property, human and animal life, and staggering economic consequences. Hurricane Agnes of 1972 and Hurricane Isabel of 2003 are examples of differences in impacts associated with storms traveling up the east and western sides of the Bay, respectively. Agnes devastated Bay residents, land and the Susquehanna Basin. Impacts were largely a function of rains with river discharge and associated flooding damage in most of the tributaries flowing to the south into the Bay. Huge losses occurred in PA and NY State. Sediments and nutrient deliveries were huge, eliminating many submerged grasses and some benthos in the Bay. Excessive discharges displaced fish populations and their prey in freshwater rivers and creeks. Nutrient levels lead to elevated algal production and in the following year, high summer productive from nutrients remineralized from the loads and algal production form Agnes. Isabel on the other hand had its major impacts through storm surges mediated through counter-clockwise winds blowing northwards up the Bay, thereby piling up more saline coastal or southern bay waters up the estuary and tributaries. Rains and discharge were modest relative to Agnes impacts. This surge, coupled with wind waves and tides resulted in massive coastal damage in low-lying areas along the Bay. Even with considerable ‘forecasts of surges in the region. The northward flowing, more oceanic waters brought in coastal species, increasing some fish populations and larvae higher than seen in non-storm conditions. Some SAV were lost in tidal waters. The differences between the storm tracks, relative to the axis of the Bay and Susquehanna, indicate that future hurricane forecasts and potential emergency responses must account for storm location.

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	10	0	0	0	10
Masters	3	0	0	0	3
Ph.D.	1	0	0	2	3
Post-Doc.	0	0	0	1	1
Total	14	0	0	3	17

Notable Awards and Achievements

Grant 2006MD116B to Dr. Sujay Kaushal ("Investigation of the effects of increased salinization from road deicer use on increased transport of nitrogen in streams of the Chesapeake Bay watershed") was used to collect pilot data that was instrumental in obtaining new funding from an NSF grant ($613,620) and MD Sea Grant ($155,315).

Publications from Prior Projects