Report as of FY2007 for 2006MD116B: "Investigation of the effects of increased salinization from deicer use on increased transport of nitrogen in streams of the Chesapeake Bay Watershed"

Publications

Project 2006MD116B has resulted in no reported publications as of FY2007.

Report Follows

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).

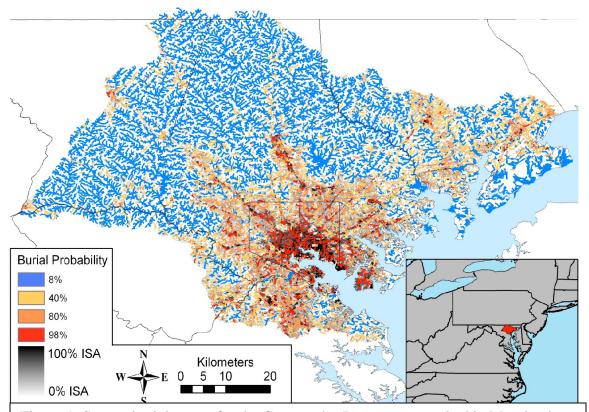
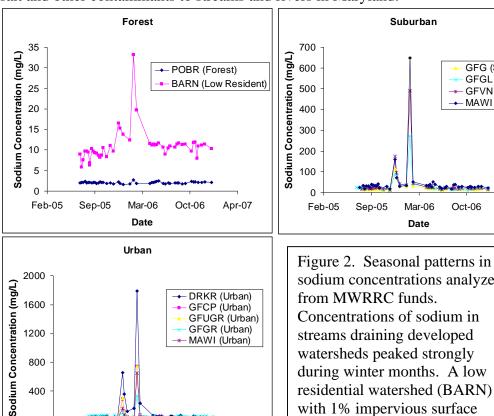


Figure 1: Stream burial extent for the Gunpowder-Patapsco watershed in Maryland expressed as a probability of burial based on the distribution of impervious surface (shown in shades of gray) in the vicinity of each stream reach. Networks of buried streams connected to impervious surfaces that increase 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 10⁴ 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.



1200

800

400

Feb-05

Sep-05

Mar-06

Date

Oct-06

GFUGR (Urbán) GFGR (Urban) MAWI (Urban) Apr-07

sodium concentrations analyzed 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

GFG (Suburb)

GFGL (Suburb)

GFVN (Suburb) MAWI (Suburb)

Apr-07

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

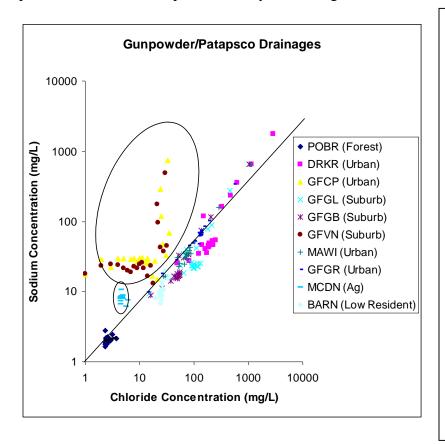


Figure 3. Comparison of Cl⁻ concentrations vs. Na⁺ concentrations in Baltimore streams during 2005 - 2006. The ratio of Na/Cl remained constant in the same proportion as rock salt (halite). An agricultural site (MCDN) showed very little variation in Na/Cl ratios seasonally, and 2 of the largest suburban 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 the 1st 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 NO₃-, 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 N₂ gas so that the intermediate N₂O is produced, which can be measured more easily than N₂ production due to less contamination from the atmosphere. Gas samples were taken at 30 and 90 minutes and analyzed for N₂O by electron capture gas chromatography.

Results

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

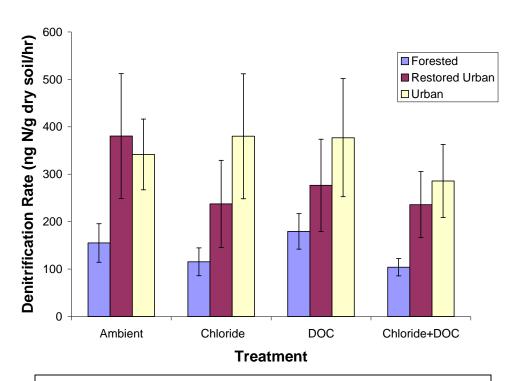


Figure 4. Mean denitrification rates for all sites and treatments. There were 3 replicate debris dams (n=3) analyzed at each stream and 2 streams per category (forest, restored urban, urban). Error bars represent the standard error for each treatment. Chloride amendment produced a marginally significant 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 KNO₃, 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 N₂O 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

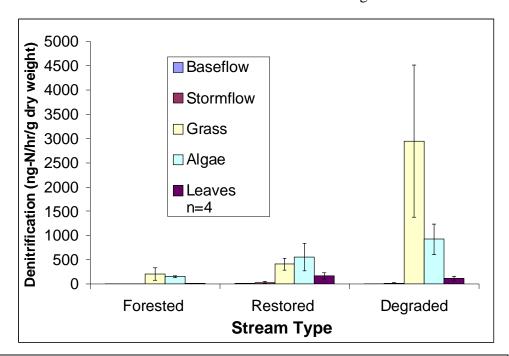


Figure 5. Comparison of denitrification rates produced from natural, degraded, and restored streams in Baltimore County, MD using leachates from algae, leaves, and grass clippings. The degraded stream produced denitrification rates that were an order of magnitude greater than the other streams. The grass 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.

References

- Bubeck, RC, WH Diment, BL Deck, AL Baldwin, SD Lipton. 1971. Runoff of deicing salt effect on Irondequoit Bay, Rochester, New York. Science 172: 1128-1971.
- Elmore, AJ and SS Kaushal. Patterns of stream burial due to increasing urbanization in the mid-Atlantic U.S. *Frontiers in Ecology and the Environment* (Submitted)
- Environment Canada. Assessment Report Road Salts. 2001
- Godwin, KS, SD Hafner, and MF Buff. 2003. Long-term trends in sodium and chloride in the Mohawk River, New York: the effect of fifty years of road-salt application. Environmental Pollution 124: 273-281.
- Groffman, PM, AJ Gold, and G Howard. 1995. Hydraulic tracer effects on soil microbial activities. Soil Science Society of America Journal 59: 478-481.
- Groffman, P.M., E. Holland, D.D. Myrold, G.P. Robertson and X. Zou. 1999.

 Denitrification. Pages 272-288 *In* Standard Soil Methods for Long Term

 Ecological Research (G.P. Robertson, C.S. Bledsoe, D.C. Coleman and P. Sollins, editors). Oxford University Press, New York.
- Groffman, PM, NJ Boulware, WC Zipperer, RV Pouyat, LE Band, and MF Colosimo. 2002. Environmental Science and Technology 36: 4547-4552.
- Groffman, P.M., N.L. Law, K.T. Belt, L.E. Band and G.T. Fisher. 2004.

- Nitrogen fluxes and retention in urban watershed ecosystems. Ecosystems 7:393-403.
- Groffman, PM AM Dorsey, and PM Mayer. 2005. Nitrogen processing within geomorphic features in urban streams. Journal of the North American Benthological Society 24: 613-625.
- Hahn, BE et al. 1942. Influence of KCl on nitrification in Bedford silt loam. Soil Science 54: 113-121.
- Hale, R and PM Groffman. 2005. Chloride and nitrogen dynamics in forested and urban stream debris dams. Biogeochemistry (submitted).
- Hart, BT, P Bailey, R Edwards, K Hortle, K James, A McMahon, C Meredith, and K Swadling. 1991. A review of the salt sensitivity of the Australian freshwater biota. Hydrobiologia 210: 105-144.
- Herlihy, AT, JL Stoddard, and CB Johnson. 1998. The relationship between stream chemistry and watershed land cover data in the Mid-Atlantic Region, U.S. Water, Air, and Soil Pollution 105: 377-386.
- Jantz, CA, SJ Goetz, and MA. 2003. Using the SLEUTH urban growth model to simulate the impacts of future policy scenarios on land use in the Baltimore-Washington metropolitan area. Environ. Plan. B 31: 251-271.
- Kaushal, SS, PM Groffman, GE Likens, KT Belt, WP Stack, VR Kelly, LE Band, and GT Fisher. 2005. Increased salinization of fresh water in the northeastern U.S. Proceedings of the National Academy of Sciences USA 102: 13517-13520.
- Kaushal, SS, PM Groffman, PM Mayer, E Striz, EJ Doheny, AJ Gold. Effects of stream restoration on denitrification at the riparian-stream interface of an urbanizing watershed of the mid-Atlantic U.S. *Ecological Applications* 16: 299-312.
- Kaushal et al. Interaction between climate and land use amplifies salinization of freshwater in the U.S. (In Preparation)
- Kemp, WM, WR Boynton, JE Adolf, DF Boesch, WC Boicourt, G Brush, JC
 Cornwell, TR Fisher, PM Glibert, JD Hagy, LW Harding, ED Houde, DG
 Kimmel, WD Miller, RIE Newell, MR Roman, EM Smith, and JC Stevenson.
 2005. Eutrophication of Chesapeake Bay: historical trends and ecological interactions. Marine Ecology Progress Series 303: 1-29.
- Klocker, CA, SS Kaushal, PM Groffman, and PM Mayer. Whole stream nitrogen uptake and denitrification in a restored stream of the Chesapeake Bay *Biogeochemistry* (In Preparation)

- Lewis, WM, Jr. 1999. Studies of environmental effects of magnesium chloride on deicer in Colorado (Colorado Department of Transportation, Denver), CDOT Report No. CDOT-DTD-R-99-10.
- Lofgren, S. 2001. The chemical effects of deicing salt on soil and stream water of five catchments in southeast Sweden. Water, Air, and Soil Pollution 130: 863-868.
- Mayer, P.M., E. Striz, R. Shedlock, E. Doheny, and P. Groffman. 2003. The effects of ecosystem restoration on nitrogen processing in an urban mid-Atlantic piedmont stream. Pp. 536-541 in Renard, Kenneth G., McElroy, Stephen A., Gburek, William J., Canfield, H. Evan and Scott, Russell L., eds. First Interagency Conference on Research in the Watersheds, October 27-30, 2003. U.S. Department of Agriculture, Agricultural Research Service.
- Morgan, RP, KM Kline, and SF Cushman. 2007. Relationships among nutrients, chloride and biological indices in urban Maryland streams. Urban Ecosystems 10: 153-166.
- Newcomer, TA, SS Kaushal, PM Groffman, and AJ Gold. Relative importance of carbon sources for denitrification in hyporheic zones as a potential indicator of stream restoration success *Freshwater Biology* (In Preparation)
- Peters, NE, and JT Turk. 1981. Increases in sodium and chloride in the Mohawk River, New York, from the 1950's to the 1970's attributed to road-salt. Water Resources Bulletin 17: 586-597.
- Richburg JA, WA Patterson III, F Lowenstein. 2001. Effects of road salt and *Phragmites australis* invasion on the vegetation of a western Massachusetts calcareous lake-basin fen. Wetlands 21: 247-255.
- Rosenberg, RJ, NW Christensen, and TL Jackson. 1986. Chloride, soil solution osmotic potential and soil pH effects on nitrification. Soil Society of America Journal. 50: 941-945.
- Rosenberry, DO, PA Bukaveckas, DC Buso, GE Likens, AM Shapiro, and TC Winter. 1999. Movement of road salt to a small New Hampshire lake. Water Air and Soil Pollution 109: 179-206.
- U.S. EPA. 1988. Ambient water quality criteria for chloride. Office of water, regulations, and standards. Criteria and standards division, Washington DC, 20460.