

Water Resources Research Center

Annual Technical Report

FY 1998

Introduction

Research Program

Basic Project Information

Basic Project Information	
Category	Data
Title	Development of a Systematic Approach for Channel Restoration Activities
Project Number	02-97
Start Date	09/01/1997
End Date	08/31/1999
Research Category	Engineering
Focus Category #1	Models
Focus Category #2	Geomorphological and Geochemical Processes
Focus Category #3	Methods
Lead Institution	University of Maryland

Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
Glenn E. Moglen	Assistant Professor	University of Maryland	01

Problem and Research Objectives

In response to erosion and other damage brought on by the urbanization of the landscape, the State of Maryland has become a leader in stream restoration activities. The goals of such activities are varied, but generally include "improvement" of the hydraulic and esthetic qualities of the channel and immediately adjacent areas. Anecdotal evidence exists that some completed restoration projects have not performed as designed or intended. The objectives of this research are threefold: 1. Quantify the hydraulic geometry of stable channels throughout Maryland. The crux of this description is the dependency of the channel size, shape, and extent as a function not only of drainage area, but of land

use as well. 2. Develop a scheme for ranking potential restoration sites and for optimal allocation of limited fiscal resources across these sites. 3. Report research activities and findings in a continuous and organized fashion using the world wide web.

Methodology

Methodology Channel Hydraulic Geometry: Efforts to quantitatively describe hydraulic geometry have evolved along a two-pronged approach: 1. Identify and survey stable cross-sections from around the state varying across a range of watershed sizes and composition. To date, we have surveyed approximately 35 cross-sections, focussing on the Piedmont geographic province within Montgomery County, Maryland. Survey information includes an x-y description of the channel and immediate floodplain, water depth, observed flow velocity, establishment of a benchmark elevation, and comments on any unique or peculiar properties of the cross-section. We have developed a MATLAB script, available at: <http://www.ence.umd.edu/~moglen/ChanRes/xsect.m> to analyze the surveyed x-y data and develop a three quantity (α , u , dbf) description of the channel cross-section. The cross-section size and shape is described by a power model relating channel width to depth: $w = \alpha d^u$ where w is the channel width, d is the channel depth, α is a scale parameter, and u is a shape parameter. The scale parameter is chosen such that the parameterized cross-section preserves the observed cross-sectional area at bankfull conditions: $\alpha = [aobs (u + 1)] / [dbf^{(u + 1)}]$ where $aobs$ is the actual observed cross-sectional area at bankfull depth, dbf . The shape parameter, u , is determined by observing that equation 1 can be derived from a Leopold and Maddock(1953) description of hydraulic geometry where: $w = aw Q^{cw} d = ad Q^{cd} v = av Q^{cv}$ where Q is discharge, v is velocity, and aw , ad , av , cw , cd , and cv are parameters calibrated from a log-log regression of the x-y survey data. Solving parametrically for w as a function of d in equations 3 and 4 yields: $u = cw / cd$ A calibrated fit is shown for some sample survey data is shown below where the blue line / dots indicate the actual surveyed cross-section and the black line indicates the calibrated cross-sectional approximation to this sample data. (contact PI for Figure) 2. Using a Geographical Information System (GIS), the location of each survey cross-section is determined. Using a combination of digital elevation models (DEMs) and digital line graphs (DLGs) (source: U.S.G.S.) and digital land use (source: Maryland Office of Planning) the watershed draining to the cross-section is automatically delineated and quantitative characteristics (drainage area, land use distribution, hydrologic soil composition, average curve number, basin relief, etc.) are determined.

Principal Findings and Significance

Findings and Conclusions Regression Equations: Regression equations for α , u , and dbf have been developed. These equations are: $\alpha = 0.62(DA)^{0.29} - 2.4(\%AG)^{0.078}$ $u = -5.8e-4(DA)^{0.57} - 7.2e-3(\%COM)^{1.1} + 7.6(\%FOR)^{0.023}$ $dbf = 1.3(DA)^{0.11} + 0.10(\%COM)^{0.74} - 1.4(\%AG)^{4.8e-5}$ Let us discuss the implications of each of these equations in turn. 1. α Equation: A positive correlation with drainage area and a negative correlation with percent agricultural land use is observed. These correlations are physically intuitive, indicating that all things being equal, the width of the channel will increase with increasing drainage area and decrease with increasing agricultural land use within the watershed. 2. u Equation: A negative correlation with drainage area, and percent commercial land use is observed, while a positive correlation is found with percent forest land use. This is again physically intuitive indicating that increases in both drainage area and percent commercial land use act to promote a more U-shaped cross-section while the forest land use favors a more V-shaped cross-section. 3. dbf Equation: A positive correlation with both drainage area and percent commercial land use is observed while a negative correlation is found with percent agricultural land use. This indicates that increases in drainage area and commercial land uses increase the bankfull depth of the channel while agricultural

land use tends to reduce this bankfull depth. Further, the very small exponent on the percent agricultural land use indicates a toggle-like behavior where there is a strong non-linearity between a basin with no agricultural content and a basin with some small agricultural content. In this fashion, the coefficient multiplying the percent agricultural content (-1.4) amounts to a constant which is subtracted from the alpha value in the event of there is some agricultural land use within the basin. By way of example, we will demonstrate a sample case study showing how the regression equations can be employed to predict channel size, shape, and extent in the face of two different urbanization scenarios. Consider a hypothetical watershed, 1.8 mi² in size. In its before condition, the watershed composition is 12% residential, 8% commercial, 46% agricultural, and 34% forest land use. We will illustrate two potential after conditions: Case 1: 65% residential, 15% commercial, 10% agricultural, and 10% forest Case 2: 75% residential, 15% commercial, 0% agricultural, and 10% forest The predicted before and after cross-sections are shown below. In both cases the before cross section is identical and is the upper section shown. The reader should note that the lack of any agricultural land use in the Case 2 scenario clearly has a profound effect on the predicted channel size for the reasons discussed earlier. (contact PI for figure) Sensitivity to land use classification scheme: Our land use classification comes from the 1994 Maryland Office of Planning data set. Alternatively, we also analyzed a coverage from the EROS data center which represents an essentially un-supervised land use classification over the same region from LANDSAT data. Further, we analyzed an experimental land use classification scheme obtained from the University of Maryland Geography department which was specifically developed to emphasize urban land uses within the region. We obtained different percent basin compositions for all three classification schemes but found both the magnitude of the correlations and the physical interpretations of these correlations to be strongest and most consistent with the Maryland Office of Planning data. While this may very well be the case, it does highlight the imperative need for land use data that is of high integrity, both in terms of the development of the regression equations and in their potential subsequent use in design scenarios. Characterization of the Basin Composition: Our regression equations clearly favor a description of the basin composition in terms of percent land use dedicated to various activities. We had actually initially attempted to describe the basin composition in terms of the NRCS curve number. Our findings however were that the curve number did not seem to adequately capture the very different compositions of the basins being studied. This is evidenced by the fact that our 35 basins produced average curve numbers ranging only from approximately 65 to 80 while the percent agricultural land use ranged from 0 to 80, percent residential land use also from 0 to 80, percent forest land use from 0 to 90, and percent commercial land use from 0 to 25. Both the separation of the basin description into four categories and the range of values observed for each category provide for a greater ability to differentiate amongst the basins studied and provide for more powerful quantitative equations to describe observed hydraulic geometry. Significance: It is possible to perform a study of synthetic sediment transport given a channel geometry described by the regression equations described above. By using actual discharge data at USGS gaging stations and allowing channel geometry to vary over a range of (alpha, u) descriptions, we can deduce the efficacy of channels in conveying sediment as a function of their hydraulic geometry. The figure below (contact PI for figure) shows contours of sediment transport for two different sized sediments transported in the Northwest Branch watershed. The relative slope of these contours in the (alpha, u) plane clearly varies as a function of sediment size. The nature of these contour lines is such that a more "V"-shaped cross-section is favored when the sediment load is of finer grain sizes and more "U" shaped when the sediment load is coarser grained. This finding is interesting in it's own right (the PI has integrated this into a graduate class) and is very consistent with the finding that agricultural land tends to result in smaller more, "V"-shaped cross-sections while more urbanized land tends to result in more "U"-shaped cross-sections. This result needs still further study and field verification beyond the scope of the current study. Summary: This project has resulted in a set of calibrated synthetic cross-section relationships that provide estimates for channel size, shape, and extent as a function of drainage area and percent land use composition for the watershed that the channel is draining. Findings show a strong dependency of channel size and shape on

agricultural land use which we postulate may be indicative of the sediment source these lands may present. Methods, findings, algorithms, and presentations are available at the provided web sites and several conference proceedings have already resulted from this project. One graduate student has successfully defended his masters on support from this project and the PI anticipates a refereed journal publication to ultimately result from this research as well. Based on these results a broader study cutting across all of Maryland's geographic provinces using a similar approach would help to quantify geographic differences across the state. At present, restoration designs currently being developed in the Maryland Piedmont could be compared against the estimates resulting from our regression results. Large discrepancies between our estimates and the proposed restoration design would suggest that the site location is outside of the bounds of applicability of our regression equations or that the proposed design merits further scrutiny and possibly needs modification for it to remain stable after construction.

Descriptors

channelization, geographic information systems, geomorphology, land use change, networks, numerical analysis, optimization, rivers, soil erosion, urbanization

Articles in Refereed Scientific Journals

Moglen, G.E. and S.P. Brown (in preparation) "Channel Hydraulic Geometry and Land Use in the Maryland Piedmont", to be submitted to the Journal of the American Water Resources Association.

Book Chapters

Dissertations

Brown, S.P., 1999. "Prediction of Stream Geometry in the Maryland Piedmont Based on Land Use and Urbanization. Masters Thesis, Department of Civil and Environmental Engineering, University of Maryland, College Park, Maryland. August, 1999.

Water Resources Research Institute Reports

Conference Proceedings

Moglen, G.E. and J.A. Berger, 1998. "Quantifying the Effect of Land Use Change on Channel Hydraulic Geometry" American Geophysical Union Spring Meeting, Boston, MA. Moglen, G.E. 1999. "Hydraulic Geometry of Streams in the Maryland Piedmont as a Function of Drainage Area and Land Use" Presented at the Stream Information Exchange (sponsored by Maryland Department of the Environment, U.S. Army Corps of Engineers, and NOAA), Laurel, MD. June 25, 1999.

Other Publications

See the following three web addresses for information on this project:

<http://www.ence.umd.edu/~sethb/project.html>

<http://www.ence.umd.edu/~moglen/conf/agusp98/sld001.htm>

<http://www.ence.umd.edu/~moglen/ChanRes/index.html>

Basic Project Information

Basic Project Information	
Category	Data
Title	Distribution and Biogeochemical Control of Mercury Methylation in the Florida Everglades
Project Number	01-98
Start Date	01/01/1998
End Date	12/31/1998
Research Category	Biological Sciences
Focus Category #1	Hydrogeochemistry
Focus Category #2	Ecology
Focus Category #3	Methods
Lead Institution	The Academy of Natural Sciences

Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
Cynthia C. Gilmour	Professional Staff	The Academy of Natural Sciences	01

Problem and Research Objectives

Mercury (Hg) in the Florida Everglades became an issue with the discovery of high levels of Hg in piscivorous fish and apparent Hg toxicity to fish-eaters, such as certain wading birds and the Florida Panther, in the later 1980's and early 1990's. Approximately 1 million acres of the Everglades system contains large mouth bass with mercury concentrations above 2 mg kg⁻¹, double the FDA the limit for human consumption. With regard to elevated levels of Hg in fish, Florida is not unique. Most US states have issued public health advisories for the consumption of fish due to Hg within the last decade. However, the Everglades ecosystem is substantially different from other ecosystems, mainly temperate lakes, where Hg bioaccumulation problems have been previously identified and studied. Increased deposition of mercury from the atmosphere to aquatic ecosystems is translated into human and wildlife health risks only after methylation and subsequent bioaccumulation in fish. Mercury methylation occurs in situ within watersheds, mediated by natural bacterial populations. The conditions under which high rates of net Hg methylation and MeHg accumulation occur have become much better defined during the last decade. Our work suggests that mercury methylation occurs predominantly under anaerobic, very mildly sulfidic conditions. As a result, aquatic sediments, saturated soils, and sometimes anoxic waters are the main locations for methylmercury (MeHg) production within watersheds. The rate of net MeHg production, and the accumulation of MeHg in sediments and saturated soils, varies over three or more orders of magnitude among, and sometimes within, ecosystems (Gilmour et al. 1998; Benoit et al. 1998;

Krabbenhoft et al. 1998a,b). This range appears to be larger than the range in atmospheric Hg deposition rates in the US (Mason et al. 1997). Detailed studies of Hg cycling in lakes have shown that changes in methylation rate, resulting in increased net MeHg production and subsequent bioaccumulation in fish (Wiener 1988; Wiener et al. 1990), can occur without increased Hg inputs (Bloom et al. 1991; Gilmour et al. 1992; Watras et al. 1994; Krabbenhoft et al. 1998a). Changes in methylation rate may be driven by sulfuric-acid deposition, reservoir formation and wetland creation (Bodaly et al. 1984; Kelly et al. 1996). Some types of ecosystems appear predisposed to high rates of methylation, including wetlands (St. Louis et al. 1994, 1996, Krabbenhoft et al. 1995; Branfireun et al. 1996), while other types of ecosystems, like estuaries and coastal waters, are less so (Benoit et al. 1998). We began work with the hypotheses that sulfate-reducing bacteria (SRB) mediate Hg methylation (Compeau and Bartha 1985; Gilmour et al. 1992; Krabbenhoft et al. 1998a) and that the primary site of methylation is at the oxic/anoxic interface, which is often near the sediment surface (Korthals and Winfrey 1987; Winfrey and Rudd 1990; Watras et al. 1995; Benoit et al. 1998; Krabbenhoft et al. 1998a). We have hypothesized that MeHg in sediments is related to the sulfate concentration. At the low sulfate concentrations found in oligotrophic freshwaters, additional sulfate stimulates microbial sulfate reduction and hence Hg methylation. However, sulfide inhibits Hg methylation. At higher surface water sulfate concentrations, sulfate appears to inhibit Hg methylation through microbial sulfide production. The most basic issue in managing Hg in the Everglades is whether Hg loading is the main control on Hg methylation and MeHg accumulation rates; or if other biogeochemical factors are more important. Our primary goal in this study is to identify the major biogeochemical controls on Hg methylation within the peat soils and sediments of the Everglades Stormwater Treatment Areas (STAs), Water Conservation Areas (WCAs) and Everglades National Park (ENP). The results of the study will provide a framework from which to ask questions about how future management practices may influence the existing mercury (Hg) bioaccumulation problem.

Objectives The objectives of this project were to: 1. To determine whether eutrophication of the Everglades has led to increased MeHg production. 2. To determine whether the Everglades are naturally high in MeHg production or sediment/water MeHg efflux. 3. To determine whether changes in MeHg bioaccumulation in the Everglades are not a function of MeHg production but depends on other factors such as biodilution, water chemistry and food chain structure. 4. To determine whether increases in the amount, or changes in the type of Hg deposition have lead to increased methylation regionally within the Everglades. 5. To determine the role of sulfate/sulfide concentration on MeHg production.

Methodology

Field Program Methylmercury (MeHg) concentrations and production rates were examined along with sulfur biogeochemistry by ANSERC in Everglades sediments during six field trips over the period 1995 to 1997. The 1995 trips were mainly exploratory. The majority of the data were collected on trips in June and December of 1996 and July of 1997. June and December 1996 and July 1997 were intensive studies of most of the ACME sites by all ACME groups. ACME sampling is highly coordinated among research groups. During these trips, a large suite of other parameters, including total and MeHg in the water column and in biota, and sediment parameters in addition to those measured by ANSERC, were examined by other groups within the ACME team. Samples taken during April 1997 were more limited in scope, designed to get a snapshot of concentrations during one of the few "dry" periods in the study time. The sites chosen by ACME for intensive biogeochemical study constitute a trophic gradient, generated in part from agricultural runoff, across the Everglades, from re-constructed wetlands in the north, through the Water Conservation Areas and into Everglades National Park. Additional "synoptic" sites were occasionally examined and experimental studies with sediments and periphyton were done throughout the field trips, but are not presented here. Analyses Analyses performed during the intensive examination of the six main field sites for 1995- 1997 include total Hg (T-Hg), MeHg, acid-volatile

sulfur (AVS) and chromium-reducible sulfur (CRS) in sediments; and sulfide, sulfate, T-Hg, MeHg, and iron concentrations in sediment pore waters. Hg methylation rates and sulfate reduction rates were measured by injecting cores with tracer levels of high specific activity ^{203}Hg and ^{35}S respectively. During the April 1997 trip, only solid phase sediment, surface water sulfate and sulfide water samples were collected. Total Hg and MeHg in sediments and T-Hg MeHg, SO_4 , HS^- and Fe in porewater are presented in this report. The methods for sample preparation and analysis of these parameters are described in the study proposal and RQUAPP. At intensive sites, all parameters were measured with depth in duplicate cores, and selected parameters were measured in three additional surface composites. Generally, 6 depth horizons were sampled, using the smallest horizon possible given analytical requirements. Most samples were taken at 2 to 4 cm intervals. At synoptic sites, parameters were measured in duplicate 0-4 cm surface composites only.

Principal Findings and Significance

In the areas examined to date by The Academy of Natural Sciences Estuarine Research Center (ACME), MeHg concentrations and %MeHg were lowest in the more eutrophic areas in the north Everglades National Park (ENR an northern WCA 2) and highest in the central Everglades (WCA 2BS and central WCA 3A). The relative distribution of Hg species and production rates, and sulfur cycling in the more pristine areas in the south (ENP) and in Loxahatchee NWR remains poorly understood. ACME focused on these areas in 1998. Of the variables examined, pore water sulfide appears to be the best predictor of soil MeHg content. Based on the data presented in this report, plus experimental work, we suggest that the MeHg production and bioaccumulation distribution gradient in the Everglades is controlled to a large extent by sulfide concentrations in sediments. Sulfide is a strong inhibitor of microbial methylmercury production. Nevertheless, sulfide-producing bacteria are important MeHg producers. The balance between stimulation of microbial activity by sulfate and inhibition by sulfide has been a focus of our the field and experimental work during this project, and will be primary part of data analysis efforts. Further, sulfide concentration is a function of not just sulfate supply, but also of primary production and macrophyte growth (and therefore nutrient loading) and of microbial and chemical sulfide reoxidation rates. There is a positive relationship between MeHg and total Hg in Everglades surface soils, but the relationship is weaker than with sulfide. These interactions will also be a part of data analysis. A more in depth discussion of the distribution of MeHg is given in the 1997 annual report to the SFWMD, including preliminary assessment of methylation rate and sulfur cycling data. The sources of sulfur to the Everglades and their magnitudes will be important in managing MeHg production in the ecosystem. Sulfur sources are currently being investigated within ACME, by W. Orem et al. (USGS, Reston) Modeling microbial S cycling in response to managed changes in nutrient and S loading will also be crucial to predicting the response in MeHg. References: Benoit, J., C.C. Gilmour, R.P. Mason, G.F. Riedel, G.S. Riedel and K. Sullivan. 1998. Mercury cycling in the Patuxent River and Estuary, MD, USA. *Biogeochemistry*. 40: 249-265. Bloom, N.S., C.J. Watras and J.P. Hurley. 1991. Impact of acidification on the MeHg cycling of remote seepage lakes. *Water, Air, Soil Poll.* 56:477. Bodaly, R.A., R.E. Hecky and R.J.P. Fudge. 1984. Increases in fish mercury levels in lakes flooded by the Churchill River diversion, northern Manitoba. *Can. J. fish. Aquat. Sci.* 41:682-691. Branfireun, B.A., A. Heyes and N.T. Roulet. 1996. The hydrology and methylmercury dynamics of a Precambrian Shield headwater peatland. *Water Res. Res.* 32:1785-1794. Compeau, G.C. and R. Bartha. 1985. Sulfate-Reducing Bacteria: Principal Methylators of Mercury in Anoxic Estuarine Sediment. *Applied Environ. Microb.* 50:498-502. Gilmour, C.C., E.A. Henry, and R. Mitchell. 1992. Sulfate Stimulation of Mercury Methylation in Freshwater Sediments. *Environ. Sci. Technol.* 26:2281-2287. Gilmour, C.C., G.S. Riedel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.A. Gill and M.C. Stordal. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry*. 40: 327-345. Kelly, C.A. J.W.M. Rudd., R.A. Bodaly, N.T. Roulet, V.L. St Louis, A.

Heyes, T.R. Moore, R. Aravena, B. Dyck, R. Harris, S.Schiff, B. Warner and G. Edwards. 1997. Increases in fluxes of greenhouse gases and methyl mercury following flooding of an experimental reservoir. *Environ. Sci. Technol.* 31:1334-1344. Korthals, E.T. and M.R. Winfrey. 1987. Seasonal and spatial variations in mercury methylation and demethylation in an oligotrophic lake. *Appl. Environ. Microbiol.* 53:2397-2404. Krabbenhoft, D.P., J.M. Benoit, C.L. Babiarz, J.P. Hurley and A.W. Andren. 1995. Mercury cycling in the Allequash Creek Watershed, Northern Wisconsin. *Wat. Air Soil Poll.* 80: 425-433. Krabbenhoft, D.P., C.C. Gilmour, J.M. Benoit, C.L. Babiarz, A.W. Andren and J.P. Hurley. 1998a. Methylmercury dynamics in littoral sediments of a temperate seepage lake. *Can. J. Fish. Aquat. Sci.* 55:835-844. Krabbenhoft, D.P., J.P. Hurley, M.L. Olson, and L.B. Cleckner. 1998. Diel variability of mercury phase and species distributions in the Florida Everglades. *Biogeochemistry* 40: 311-325. Mason, R.P., N.M. Lawson and K.A. Sullivan. 1997. Atmospheric deposition to the Chesapeake Bay watershed - regional and local sources. *Atmosph. Environ.* 31:3531-3540. St. Louis, V.L., J.W.M. Rudd, C.A. Kelly, K.G. Beaty, R.J. Flett, and N.T. Roulet. 1996. Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands. *Environ. Sci. Tech.* 30: 2719-2729. St. Louis, V.L., J.M.W. Rudd, C.A. Kelly, K.G. Beaty, N.S. Bloom and R.J. Flett. 1994. The importance of wetlands as sources of methyl mercury to boreal forest ecosystems. *Can. J. Fish. Aquat. Sci.* 51:1065-1076. Vaithyanathan, P. M.L. Barber, C.J. Richardson and T. Barkay. The effects of eutrophication on the distribution of mercury in the wetland soils of the Everglades (Florida, USA). Fourth International Conference on Mercury as Global Pollutant. Hamburg, Germany, August 1996. Watras, C.J. N.S. Bloom, R.J.M. Hudson, S.Gherini, R. Munson, S.A. Class, K.A. Morrison, J. Hurley, J.G. Wiener, W.F. Fitzgerald, R. Mason, G. Vandell, D. Powell, R. Rada, L. Rislov, M. Winfrey, J. Elder, D. Krabbenhoft, A. W. Andren, C. Babiarz, D.B. Porcella, and J.W. Huckabee. 1994. Sources and fates of mercury and methylmercury in Wisconsin Lakes. In: C.J. Watras and J.W. Huckabee, eds. "Mercury Pollution: Intergration and Synthesis." Lewis Publishers, Boca Raton. pp. 153-177. Watras, C.J., N.S. Bloom, S.A. Claas, K.A. Morrison, C.C. Gilmour and S.R. Craig. 1995. Methylmercury production in the anoxic hypolimnion of a dimictic seepage lake. *Wat. Air Soil Poll.* 80: 735-745. Wiener, J.G. 1988. Metal contamination of fish in low pH lakes. *Trans. 52nd N.A. Wildl. and Nat. Res. Conf.* pp. 645-657. Wiener, J.G., W.F. Fitzgerald, C.J. Watras and R.G. Rada. 1990. Partitioning and bioavailability of mercury in an experimentally acidified Wisconsin lake. *Environ. Tox. Chem.* 9: 909-918. Winfrey, M.R. and J.W.M. Rudd. 1990. Environmental factors affecting the formation of methylmercury in low pH lakes: A review. *Environ. Tox. Chem.* 9: 853-869.

Descriptors

Ecosystems, Geochemistry, Heavy Metals, Pollution Control, Water Quality Management

Articles in Refereed Scientific Journals

Benoit, J.M., R. P. Mason and C.C. Gilmour. (1998) Estimation of mercury-sulfide speciation and bioavailability in sediment pore waters using octanol-water partitioning. *Environ. Toxicol. Chem.* 18:2138-2141. Cleckner, L., C.C. Gilmour, D. Krabbenhoft, P. Garrison, and J. Hurley. (1998) Methylmercury production by periphyton in the Florida Everglades. *Limnol. Oceanogr.* 44:1815-1825. Benoit, J.M., C.C. Gilmour, R. P. Mason, and A. Heyes. (1998) Sulfide Controls on Mercury Speciation and Bioavailability in Sediment Pore Waters. *Environ. Sci. Technol.* 33:951-957. Gilmour, C.C., G.S. Riedel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.A. Gill and M.C. Stordal.(1998) Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry.*40:327-345.

Book Chapters

Dissertations

Water Resources Research Institute Reports

Conference Proceedings

1999 Presentations at the ASLO Aquatic Sciences Meeting, Santa Fe, NM, February, 1999: Heyes, A. and C.C. Gilmour. The biogeochemical controls on mercury methylation across ecosystems. Bell, J.T., G.S. Riedel, J.M. Benoit, A. Heyes and C.C. Gilmour. The influence of sulfur inputs on methylmercury production the Florida Everglades. Benoit, J.M., R.P. Mason, and C.C. Gilmour. Estimation of mercury-sulfide speciation and bioavailability in sediment pore waters using octanol-water partitioning. 1998 Gilmour, C.C. Methylmercury Production in the Florida Everglades. Mid-Atlantic SETAC, April 1998. Benoit, J.M., R.P. Mason and C.C. Gilmour. Octanol-water partitioning of Hg-sulfide complexes and the bioavailability of Hg for methylation. SETAC Europe, Bordeaux, April 1998. Heyes, A., C.C. Gilmour and J. Benoit. Controls on Mercury Methylation in the Florida Everglades. American Geophysical Union, Boston. May 1998. Invited. Cleckner, L.B., C.C. Gilmour, J.P. Hurley, and D.P. Krabbenhoft. Mercury methylation in periphyton of the Florida Everglades. American Geophysical Union, Boston. May 1998.

Other Publications

Basic Project Information

Basic Project Information	
Category	Data
Title	Multi-faceted Investigation of Arsenic Biogeochemistry
Project Number	02-98
Start Date	09/01/1998
End Date	08/31/2000
Research Category	Water Quality
Focus Category #1	Geomorphological and Geochemical Processes
Focus Category #2	Toxic Substances
Focus Category #3	Water Quality
Lead Institution	University of Maryland

Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
Allen P. Davis	Associate Professor	University of Maryland	01
Alba Torrents	Associate Professor	University of Maryland	02
Oliver J. Hao	Professor	University of Maryland	03

Problem and Research Objectives

Arsenic is present at nearly all the smelter sites in the U.S. and is listed as a major contaminant at approximately 150 sites on the National Priority List. Arsenic is found primarily in soils contaminated by arsenical pesticides, mine tailings, and metal-finishing and wood-preserving industries. A large portion of As in drinking water, however originates from geothermal sources, rocks and soils naturally containing high levels of As, which can further contaminate the groundwater surrounding them. Because of its high toxicity and persistence, EPA is considering lowering the MCL for As in drinking water from 0.05 mg/L. Therefore, new technologies will be needed in treatment facilities to reduce dissolved As levels. One potential new technology is microbial transformation, the use of bacterial metabolic processes to accomplish the transformation of As species. The chemical and biological processes which control the fate and mobility of As in contaminated soils and mine tailings are complex, due to transformations of numerous As species that occur under variable oxidation-reduction conditions. The predominant form of As in surface waters is usually arsenate, As(V), which is less toxic and more readily removed by sorption and sedimentation than arsenite, As(III). Aquatic microorganisms have the capability to reduce As(V) to As(III) and a variety of methylated arsenicals. Several studies have shown reduction of As(V) to As(III) by pure bacteria cultures. Additionally, a few recent studies have shown the reduction of selenium and uranium in mixed cultures (Spear et al., 1999; Rege et al., 1999). A mixed culture should more efficiently reduce metalloid oxyanions than pure cultures since there are different types of bacteria, many commonly found in nature, which can contribute to the reduction. Therefore, mixed cultures may be more suitable as an engineered solution for practical applications. The objectives of this research are to (i) evaluate As(III) reduction using the enrichment of As(III)-reducing bacteria provided by a mixed culture; (ii) determine rates and underlying mechanisms of the reduction of arsenite in model systems; and (iii) evaluate the role of reduction of As(III) on the mobility and transport of As in contaminated soils, mine tailings and aquifers by integrating the experimental data in a biochemical model that describes As(III) reduction. Results obtained from this study should improve the link between reactions controlling As speciation and processes such as mobility, transport, and bioavailability.

Methodology

To accomplish the above objectives, we have completed several complementary experiments. First, we have performed enrichments of As(III)-reducing cultures in 4-L anaerobic reactors fed with a medium containing As(III) and Na-lactate to acclimate the microbial population to toxic As(III). Two different input As(III) concentrations were tested given the well-known high toxicity of arsenic. Anaerobic sludge from the Blue Plains Wastewater Treatment Plant (Washington, DC) was used as the seeding biomass. For more than a month, a 2 L supernatant was replaced daily with a medium containing fresh municipal wastewater (Parkway Wastewater Treatment Plant, Laurel, MD), 1000 mg/L sodium lactate, 200 mg NaHCO₃, 20 mg As(III)/L in one enrichment, and 10 mg As(III)/L in the other. The As(III)-reducing ability of these cultures was confirmed by analyzing regularly 3 samples taken from the reactors: 1 sample is the input As(III) to the reactor, 1 sample is taken from the reactor immediately after input, and 1 sample is taken from the output of the reactor approximately 1 day after the As(III) input. Samples were centrifuged for 15 min, filtered (pore size, 0.2 μm), and analyzed for total As concentration. In order to check the performance of the reactors, COD and NH₄⁺-N data were collected together with pH and ORP measurements. The biomass grown inside the reactor was evaluated by measuring the MLVSS. Average temperature during growth in the reactors was 25 ± 3 °C. The 20 mg As(III)/L reactor was converted to uninterrupted cultivation in a chemostat fed with sodium lactate as the carbon source and containing a synthetic medium modified from Tomei et al. (1992). The

dilution rate was 0.08 day⁻¹ (a first trial at 0.2 day⁻¹ washed out cells after 20 days). During the continuous flow operation of the reactor, samples were daily withdrawn from the input and the output of the reactor and analyzed for total As reduction. Steady state was reached in 40 days. Using biomass from both reactors, batch tests were performed in 125 mL plastic bottles containing the mixed culture supplemented with additional Na-lactate and As(III). The small bottles were constantly shaken horizontally at 25°C. Several electron acceptors (sulfate, nitrate, and oxygen) were externally added from stock solutions. Two control reactors (one with no electron acceptor, and one with the addition of 20 mg/L HgCl₂) should ensure that the removal of As(III) is only biological. Samples were withdrawn periodically (every 2 hrs) and analyzed for total As reduction. Measurements of total soluble arsenic were performed using an atomic absorption spectrophotometer (Perkin Elmer 5100 ZL) using the hydride generator flame. Solution pH and ORP (oxidation/reduction potential) were measured by directly inserting probes into the reactor. COD (chemical oxygen demand), NH₄⁺ -N, and MLVSS (mixed liquid volatile suspended solids) were analyzed following the procedures presented in Standard Methods (APHA, 1995).

Principal Findings and Significance

An increase in pH was noted from 7.2 to 8.1 in the chemostat reactor; this is due to the microbial reduction. The mixed culture of As-reducing bacteria reduced As from an input of 20 mg/L to a steady state output of 12 mg/L after 40 days. The reduction in COD was from 1100 to 600 mg/L. After more than one month of operation, 560 mg MLVSS/L were measured. ORP inside the reactor reached as low as -221 mV. After 40 days cultivation period, the effluent cells from this As-reducing culture were used for batch tests. The chemostat capabilities were tested also by reducing the input to 10 mg As/L; after 33 days a constant output of 5 mg/L was measured. The effects on total As reduction of different As input concentrations and different carbon source (Na-lactate) concentrations were studied. Batch results performed over a period of 10 days show a reduction from a total As of 19 mg/L to 12, and from a total As of 16 mg/L to 9. However, prolonged exposure of the As(III)-reducing bacteria to this high As(III) concentration appeared to have a toxic effect on the cells. After 12 days, the total As concentration started to slightly increase. This may be due to release of As from cells after a long running time. To examine this, several batch tests using washed cells were performed. However, no significant difference (any improvement) in As reduction was observed. In other experiments, it was shown that a high carbon source concentration favors a higher As reduction. After 8 days, the As(III) concentration dropped from 20 mg As(III)/L to 17 mg/L with 25 mg Na-lactate/L added, and from 20 mg/L to 14 with 50 mg Na-lactate/L added. No As(III) reduction in the absence of Na-lactate suggested that As(III) reduction is associated with the microbial growth process. The effects of electron acceptors (sulfate, nitrate, and oxygen) on arsenite reduction are being tested now in batch reactors from the 10 mg/L As enrichment. Parameters such as pH, temperature, ORP, and biomass concentration are also evaluated in these batch tests. Preliminary results indicate that total As decreased from 8 mg/L to 1.8 mg/L in 10 hours in the presence of 50 mg/L SO₄²⁻ - S. A reduction in total As of 3 mg/L was found in the presence of 50 mg/L NO₃⁻ - N. Future experiments will test also the time course of As(III) concentrations utilizing different carbon sources (e.g., acetate, glucose, ethanol, citrate). Current work also involves the set-up of a similar continuous flow reactor with an input of 5 mg As(III)/L. Once a steady state is reached with this input concentration, an effective maximum As(III) loading condition at a constant dilution rate will be determined. Additionally, samples have been prepared for microscopy observations by transferring a drop of cells from the inside of the reactor (input As(III) = 10 mg/L) to a carbon grid. Serial dilutions were performed for the enumeration of microorganisms in the respective sample. The total cell number has been obtained (1.35x10⁸ cells/mL) and this value will be used in describing kinetic studies. Future work is directed towards evaluation of microbial community structure in cell enrichments. Enrichment culture experiments will be performed on agar plates in order to isolate and identify those cells

responsible for As(III) reduction. In order to obtain a mass balance in the microbial reduction system, experiments will be conducted to extract As from the biomass. These results should demonstrate which process is responsible for the removal of As(III) observed in the presence of bacterial cells: (a) As(III) binding to or inside the cell surface, (b) abiotic reduction of As(III) in conjunction with precipitation of As(0) species; or (c) bioreduction of As(III) to As(0) via enzymatic dissimilatory metal reduction. For practical purposes, further studies may employ the mixed As-reducing culture in conjunction with naturally occurring As containing waters or soils. These studies will observe to what extent As reduction is possible in natural soils by mixed cultures as reported for a pure culture such as *Sulfolobus acidocaldarius* strain BC (Sehlin and Lindstrom, 1992) or MIT-13 strain (Ahmann et al., 1994). Current work has shown that a mixed culture provided by an anaerobic sludge acclimated to arsenite can be used to reduce arsenic pollution. The capability of microbial arsenite reduction is dependent on the availability of organic carbon and on factors such as electron acceptors. These cultures may be used in engineered treatment systems, or may exist in nature, affecting As mobility. References: Ahmann, D.; Roberts, L. A.; Krumholz, L. R., and Morel, F. M. (1994) "Microbe grows by reducing bacteria," *Nature*, 371, p750. Rege, M. A.; Yonge, D. R.; Mendoza, D. P.; Peterson, J. N.; Bereded-Samuel, Y.; Johnstone, D. L.; Apel, W. A., and Barnes, J. M. (1999) "Selenium reduction by a denitrifying consortium," *Biotechnol. Bioengr.*, 62(4), 479-484. Sehlin, H. M., and Lindstrom, E. B. (1992) "Oxidation and reduction of arsenic by *Sulfolobus acidocaldarius* strain BC," *FEMS Microbiol. Lett.*, 93, 87-92. Spear, J.; Figueroa, L. A., and Honeyman, B. D. (1999) "Modeling the removal of uranium U(VI) from aqueous solutions in the presence of sulfate reducing bacteria," *Environ. Sci. Technol.*, 33 (15), 2667-2675. Tomei, A. F.; Barton, L. L.; Lemanski, C. L., and Zocco, T. G. (1992) "Reduction of selenate and selenite to elemental selenium by *Wolinella succinogenes*," *Canadian J. Microbiol.*, 38(12), 1328-1333. APHA (1995) "Standard Methods for the Examination of Water and Wastewater", 19th Edition, Washington, DC, (ed. A. D. Eaton, L. S. Clesceri, A. E. Greenberg).

Descriptors

Biological Treatment, Toxic Substances, Geochemistry, Biogeochemistry, Arsenic

Articles in Refereed Scientific Journals

Book Chapters

Dissertations

Water Resources Research Institute Reports

Conference Proceedings

Other Publications

Basic Project Information

Basic Project Information	
Category	Data
Title	Engineered Bioretention for Nitrogen from Urban Stormwater Runoff
Project Number	02-99
Start Date	03/01/1999
End Date	02/29/2000
Research Category	Engineering
Focus Category #1	Nitrate Contamination
Focus Category #2	Non Point Pollution
Focus Category #3	Surface Water
Lead Institution	University of Maryland

Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
Allen P. Davis	Associate Professor	University of Maryland	01
Eric Alan Seagren	Assistant Professor	University of Maryland	02

Problem and Research Objectives

Nitrogen-containing compounds are considered to be important pollutants and are responsible for rapidly growing environmental and human health problems. High nitrate and ammonia concentrations that are discharged to surface-water systems promote eutrophication, which can result in oxygen depletion and thereby stress aquatic organisms that depend on the supply of oxygen in the water. Reducing excess nitrogen and phosphorus that overstimulate algae growth (i.e., eutrophication) in the Chesapeake Bay is a primary goal in the Chesapeake Bay restoration program, with year 2000 goals of 40% removal from 1985 baseline levels. In addition, outbreaks of *Pfiesteria piscicida*, a toxic microorganism that can exert a neurotoxic effect on humans, may be triggered by excess nitrogen and phosphorus. Nitrate in drinking water also can cause serious health problems for humans, especially infants. Due to the associated environmental and human health problems, all water utilities are concerned with nitrogen species in their source water. Rather than focusing on treatment of nitrate in drinking water, a better alternative is to limit the input of nitrogen to the water supply. This means that watershed management activities by water utilities must keep nitrate levels below the MCL (10 mg/L as N) for drinking water. Because a major portion of Maryland water supply is from surface waters, especially in the populous central areas of the state, management of stormwater runoff in developed areas is an important part of watershed management. Half of the water in the Chesapeake Bay originates from about 150 major rivers and streams. Furthermore, 10% of the Chesapeake Bay watershed is made up of urban areas and 11% of its nitrogen load is contributed by urban areas. Therefore, removal of nitrogen from stormwater runoff, especially from developed areas is critical in minimizing the impacts of the development both on the local environment and further downstream. This research focuses on the fate of nitrogen in bioretention systems, which are simple, low impact runoff treatment/infiltration facilities for use in developed areas. The biological transformation and removal of nitrate is the focus of

this research because nitrate is the most difficult of the nitrogen species to address and it is not attenuated in a typical, conventional bioretention system. Therefore, modifications are required to engineer bioretention systems to remove nitrogen pollutants. Specifically, a modification to incorporate a continuously submerged anoxic zone with an overdrain is being evaluated for its capacity for nitrate removal via denitrification. In this evaluation, conditions that optimize the denitrification reaction will be determined so that design parameters can be established for use in bioretention systems that treat stormwater runoff. The result of these experimental evaluations will allow the specification of parameters such as the anoxic zone porous media and electron donor and carbon source type and content that will promote efficient denitrification as well as satisfy economic constraints. The key issues being addressed in this research include: 1) Determining (an) electron donor(s) and carbon source(s) that will be stable for a long period of time in the subsurface, but still not limit the denitrification process. This could be either an organic substrate for chemoorganotrophic denitrifying bacteria, or an inorganic substrate for chemolithotrophic denitrifying bacteria. 2) Optimizing the system with the electron donors that give the best nitrate removal efficiency and effluent quality (i.e., varying hydraulic retention time in terms of sizing of the anoxic zone in bioretention system and varying media by changing the sand and gravel mix and the ratio of the electron donor to the support media). 3) Evaluating the performance of the optimized system under conditions of intermittent loadings, such as are expected in the field and scaling up the optimized condition to a pilot scale bioretention system. The optimum compromises between rapid stormwater conveyance, degree of treatment and costs will be investigated.

Methodology

Our first task was to screen a variety of potential electron donors using a synthetic stormwater runoff and sand columns simulating the anoxic zone. Six organic substrates were selected as potential electron donors based on past related research (Michael et al 1996, Blowes et al 1994, Robertson and Cherry 1995, Schipper and Vojcodic-Vojvodic 1998, Vogan 1993): alfalfa, leaf mulch compost, newspaper, sawdust, wheat straw and wood chips. In the first experiment, the electron donors evaluated were alfalfa and newspaper, which were cut to >5 mm particles, and leaf mulch compost, which was passed through a 2 mm sieve. The total organic carbon (TOC) concentration was measured on a dry weight basis for each electron donor via a TOC analyzer (Shimadzu, Model 5000). Based on the analysis of TOC and a 2.2 mL/min synthetic runoff flow rate for a 60-day experiment duration, an estimate of the electron donor mass needed for denitrification was calculated using the reaction stoichiometry method of McCarty (McCarty, 1975). The estimated electron donor mass required was multiplied by safety factor of 20 and the calculated mass of material was uniformly mixed with silica sand that had been washed to minimize effects of residual organic carbon. The mixtures of electron donor and sand were then transferred into the experimental column reactors. The basic reactor design consisted of a 40 cm long by 6.4 cm inner diameter Plexiglas tube. Three sampling ports that penetrated into the center of the reactor were installed every 10 cm along the reactor to allow sampling from the center of the column. The media was tightly packed throughout the reactor. A total of 4 columns were set up including a control column, which was packed with washed silica sand only. The influent and effluent ports of the columns were separated from the packing material by two stainless steel screens. The influent screen was supported by a Plexiglas plate with 0.4 cm holes to promote even distribution of flow across the cross-sectional area of the column. The effluent screen was held in place by a rubber stopper. The columns were seeded with the supernatant of a secondary effluent sample from an activated sludge plant where denitrification was being performed, which had been allowed to settle at room temperature for 24 hours. For inoculation of the columns, the seed material was pumped into the column in an upflow mode and recycled through the column for 2 days to allow the microorganisms to attach and adopt. After the 2 day inoculation procedure, synthetic stormwater runoff was introduced into each column in

an upflow mode at a flow rate of 4cm/hr. The synthetic stormwater runoff was made using tap water with addition of about 2.0 mg/L nitrate as N, 120 mg/L CaCl₂, 0.6 mg/L Na₂HPO₄ as P, and the pH adjusted to 7. The water was dechlorinated and continuously purged with N₂ to remove residual chlorine and O₂ in the tapwater, respectively. All four columns were operated at room temperature (22±2°C). Samples were taken once per day. Nitrate concentration was quantified via ion chromatography (Dionex DX-100) and Total Kjeldahl nitrogen analysis was performed using procedures presented in Standard Method No. 4500 (APHA 1995). Organic carbon levels were quantified via TOC.

Principal Findings and Significance

The nitrate removal observed in the leaf mulch compost column and the control column was only about 60% and 7%, respectively. On the other hand, essentially 100% nitrate removal was observed from the alfalfa and newspaper columns through 38 days of operation. However, treated water from the alfalfa column showed some odor, turbidity and residual TKN, while that from the newspaper did not demonstrate any of these problems. Therefore, of the carbon sources studied so far, newspaper appears to be an efficient electron donor and carbon source for the removal of nitrogen from stormwater runoff. One significant result from this experiment is that the denitrification process in the newspaper column performed well just using an activated sludge inoculum, without selection of a cellulose-degrading bacteria inoculum. Thus, activated sludge has enough cellulose-degrading bacteria to permit use of newspaper as the ultimate electron donor and carbon source for denitrification of stormwater runoff. Using newspaper as the electron donor for removal of nitrogen from stormwater runoff has a number of economical and ecological benefits (Michael et. al, 1996). Currently, a second set of three organic substrates for chemoorganotrophic denitrifying bacteria - sawdust, wood chips and wheat straw - are being evaluated along with one control column packed with sand only. A third column study using a sulfur/limestone bed for chemolithotrophic denitrifying bacteria will follow this experiment to finish Task 1, the evaluation of an appropriate electron donor. Task 2, the optimization of the system, will be performed with the electron donor(s) that give the best nitrate removal efficiency and effluent quality in Task 1. The first step in this task is to vary hydraulic retention time to evaluate the required sizing of the anoxic zone in the bioretention system. The second step is to vary the media by changing the sand and gravel mix and varying the ratio of the electron donor to the support media. Analyses such as ammonia, nitrite, sulfate and biofilm thickness and density will be performed in this task as appropriate. The third task of the study is to evaluate the performance of the optimized system under conditions of intermittent loadings, such as are expected in the field. In this task, the viability of the system after long dormant periods will be investigated by examining nitrate removals and the concentration of functional denitrifying enzymes in columns that have been loaded and then allowed to stand for varying time periods. Using the information obtained from Tasks 1-3, scale up of the optimized conditions to a pilot scale bioretention system will be performed as a final task. Full scale bioretention design modifications and recommendations will be made based on the results obtained with the pilot scale system. References APHA, AWWA and WPCF (1995) Standard Methods for the Examination of Water and Wastewater, 19th Edition. Washington, D.C. Blowes, D.W., Robertson, W.D., Ptacek, C.J., and Merkley, C. (1994) Removal of agricultural nitrate from tile-drainage effluent water using in-line bioreactors. *J. Contaminant Hydrology*, 15, 207-221. McCarty, P.L. (1975) Stoichiometry of biological reactions. *Prog. Water Technol.*, 7(1), 157-172. Robertson, W.D. and Cherry, J.A. (1995) In situ dinitrification of septic-system nitrate using reactive porous media barriers: Field trials. *Ground water.*, 33(1), 99-111. Schipper, L. and Vojvodic-Vukovic, M. (1998) Nitrate removal from ground water using a denitrification wall amended with sawdust: field trial. *J. Environ. Qual.*, 27(3), 664-668. Vogan, J.L. (1993) The use of emplaced denitrification layers to promote nitrate removal from septic effluent. Master Thesis, University of Waterloo, Ontario, Canada Volokita, M., Belkin, S., Aberliovich, A. and

Soares, M.I.M (1996) Biological denitrification of drinking water using newspaper. Water Res., 30(4), 965-971.

Descriptors

Nitrogen, Biological Treatment, Urban Runoff, Denitrification

Articles in Refereed Scientific Journals

Book Chapters

Dissertations

Water Resources Research Institute Reports

Conference Proceedings

Other Publications

Basic Project Information

Basic Project Information	
Category	Data
Title	Atmospheric Deposition of Currently Used Pesticides to an Eastern Shore Watershed
Project Number	03-99
Start Date	06/01/1999
End Date	05/29/2000
Research Category	Water Quality
Focus Category #1	Non Point Pollution
Focus Category #2	Water Quantity
Focus Category #3	Models
Lead Institution	University of Maryland

Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
Alba Torrents	Associate Professor	University of Maryland	01
Laura Lee McConnell	Professional Staff	US Department of Agriculture	02

Problem and Research Objectives

The Chesapeake Bay estuarine drainage system contains 57,000 km² of harvested croplands and receives the highest pesticide application of any coastal area in the nation. Over 2.1 million kilograms per year are being applied. In order to protect sensitive ecosystems, there is a need to know the importance of atmospheric deposition on pesticide loading and to obtain degradation rate constants under conditions found in the Chesapeake Bay. This project will be the first comprehensive investigation of the environmental fate and transport of multiple currently used pesticides in both the air and surface waters of an Eastern Shore tributary and to provide site specific degradation rates for chlorpyrifos. This project is designed to use the Choptank River watershed as a model system in a first step towards testing the predictions of the Regional Transport model and to conduct actual measurements to determine the magnitude of atmospheric inputs of pesticides to the Eastern Shore region. Specific objectives are: 1. Directly determine the total air concentrations, vapor/particle partitioning and wet deposition flux of selected pesticides at a site within the Choptank River watershed to observe temporal trends and relate them to expected local and regional sources. 2. Determine pesticide concentrations in surface waters and soils at representative sites within the watershed to use in gas exchange calculations and to estimate the reservoir of pesticides in watershed at different times of the year. 3. Determine site-specific degradation rate constants and assess the influence of different water constituents on the overall fate of selected pesticides.

Methodology

In this study we will concentrate in the Choptank River Watershed located at the Maryland Eastern Shore. This ongoing study represents a comprehensive watershed study. We are conducting intensive, coordinated integrated sampling at special locations within the watershed, with wet deposition, dry deposition, and local catchments area characterizations. The proposed practical study will make a good contribution towards reducing the current uncertainty in estimates of the contribution of atmospheric deposition to declining aquatic ecosystem health. Results obtained will contribute to the body of information needed in decision-making processes used to assess pesticides inputs and risks. During the initial months, special efforts have been placed on developing extraction and highly sensitive analytical methods and to modify existing sampling equipment to automate it and facilitate sample collection at remote locations.

Principal Findings and Significance

In our objective of determining the contribution of atmospheric inputs of pesticides, Progress on this project has been made in two major areas. 1. We have developed a new, more efficient, in-line extraction method for rainwater sampling to be used at the Choptank River site. Kuang Zhihua, the University of Maryland graduate student working on this project, has been working with Dr. McConnell at USDA to modify existing rain sampling equipment to automatically pump rainwater through an adsorbent cartridge using a peristaltic pump whenever the rain sensor opens the sampler. A number of spike recovery experiments have been carried out at different flow rates and sample volumes to optimize the method, and results are very encouraging. The sampler will be ready for deployment in the field within a few weeks. The advantage of this system is two-fold. First, the water is extracted immediately before pesticide degradation can occur. Second, the equipment operator on-site can mail the small sample cartridges on ice into the USDA laboratory for analysis, saving time and transportation costs. 2. We have also identified an excellent location on the Horn Point campus to collect rain and air samples that is already equipped with a 10-m meteorological tower and is a very open area unaffected by any local sources of pesticides. Dr. Merritt of Horn Point Environmental Laboratory has a very reliable staff member on station that will be maintaining the sampler for us. A contract to upgrade the site with

electrical power is currently being negotiated. We are also in negotiations with scientists at NOAA's Air Resources Laboratory to synchronize our sampling with their NADP precipitation-monitoring network. Significant progress has been made on understanding the fate of chlorpyrifos in the Chesapeake Bay. The observed chlorpyrifos hydrolysis rates varied greatly from sample to sample. Hydrolytic rate constants ranged from 0.0055 to 0.0284 day⁻¹ (a 5 fold range), which correspond to hydrolysis half-lives of 126 and 24 days, respectively. The organic-carbon-free water hydrolytic degradation rate at pH 5.72, 0.0151 day⁻¹ (half-life is 46 days), fell between the range for natural waters and is very closed to that reported in the literature of 49 days, in distilled water at pH = 6.0 and at a temperature of 25 °C. Thus, to summarize our results, chlorpyrifos hydrolysis observed half-life in Susquehanna River water is 126 days, in Choptank River water is 56.3 days, in Patuxent River water is 24.4 days, and in Pocomoke River water is 26.5 days. Such deviations can not be explained by the difference in pH alone. For example, while Susquehanna River water and Pocomoke River water have practically the same pH, the hydrolysis rate of chlorpyrifos in these two waters varies by a 5-fold. Possible explanation might be that while the hydrolysis is pH dependent, other factors such as sorption and the presence of dissolved metals, dominated the hydrolysis rate. Copper concentration emerged as an independent predictor from a multiple variable correlation analysis of the water constituent data. Results from this study are consistent with other studies' findings that illustrate that Cu exerts a strong catalysis towards the hydrolysis of OPs. An important observation from this study is that even though total copper concentration in natural waters is very low, the catalytic effect can be strong and Cu can induce a significant decrease on hydrolysis half-life. However more experiment data is needed for validation of the model in the future study. Using pH, temperature and copper concentration data from different regions of the Chesapeake Bay, a model of chlorpyrifos hydrolysis can be constructed to predict the persistence of this chemical.

Descriptors

non-point source pollution; Atmospheric Processes; Agriculture; Contaminant Transport; Estuaries; Pesticides; Rainfall; Trace Organics

Articles in Refereed Scientific Journals

Liu, B.; McConnell, L. Torrents, A. "Hydrolysis of Chlorpyrifos under environmental conditions at the Chesapeake Bay" To be submitted to Journal of Agriculture and Food Chemistry, November 1999.

Book Chapters

Dissertations

Water Resources Research Institute Reports

Conference Proceedings

B. Liu, L.L. McConnell, A. Torrents "Herbicide and Insecticide mass loadings from the Susquehanna River to the Northern Chesapeake Bay". Presented at the Seventh Symposium on the Chemistry and Fate of Modern Pesticides in Lawrence, KS, Sept. 1999.

Other Publications

Information Transfer Program

USGS Internship Program

Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 RCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	N/A	N/A	N/A	N/A	N/A
Masters	2	N/A	N/A	N/A	N/A
Ph.D.	3	N/A	N/A	N/A	N/A
Post-Doc.	N/A	N/A	N/A	N/A	N/A
Total	5	N/A	N/A	N/A	N/A

Awards & Achievements

Publications from Prior Projects

Articles in Refereed Scientific Journals

MacCrehan, W.A., Jensen, J.S. and Helz, G.R. (1998) Detection of Sewage Organic Chlorination Products That are Resistant to Dechlorination with Sulfite. *Environ. Sci. Technol.* 32, 3640-3645.

Jameel, R.H. and Helz, G.R. (1999) Organic Chloramines in Disinfected Wastewaters: Rates of Reduction and Toxicity. *Environ. Toxicol. Chem.* 18,1899-1904.

Jensen, J.S., Lam, Y.-F. and Helz, G.R. (1999) Role of Amide Nitrogen in Water Chlorination; Proton NMR Evidence. *Environ. Sci. Technol.* 33, 3568-3573.

Walch M, Weiner RM, Colwell RR, et al. (1999) Use of L-DOPA and soluble bacterial products to improve set of *Crassostrea virginica* (Gmelin, 1791) and *C. gigas* (Thunberg, 1793). *J SHELLFISH RES* 18(1) 133-138.

Labare, M.L, Coon SL, Matthias C et al. (1997) Magnification of tributyl tin toxicity to oyster larvae by bioconcentration in biofilms of *Shewanella colwelliana* *APPL ENVIRON MICROB* 63(10) 4107-4110.

Weiner, R. E. Chang,S., Coon and M. Walch.(1999) Microorganisms and the Impact of Heavy Metals in Marine Ecosystems. in *Recent Research Developments in Microbiology*. S. Pandalai, ed. Research Signpost. Travandrum, India.3391-414.

James BR, Petura JC, Vitale RJ, et al. Oxidation reduction chemistry of chromium Relevance to the regulation and remediation of chromate contaminated soils *J SOIL CONTAM* 6(6) 569580 1997

Vitale RJ, Mussoline GR, Petura JC, et al. Cr(VI) soil analytical method A reliable analytical method for extracting and quantifying Cr(VI) in soils *J SOIL CONTAM* 6(6) 581593 1997

Vitale RJ, Mussoline GR, Rinehimer KA, et al. Extraction of sparingly soluble chromate from soils Evaluation of methods and E(h)pH effects *ENVIRON SCI TECHNOL* 31(2) 390394 FEB 1997

Hug SJ, Laubscher HU, James BR Iron(III) catalyzed photochemical reduction of chromium(VI) by oxalate and citrate in aqueous solutions *ENVIRON SCI TECHNOL* 31(1) 160170 JAN 1997

Book Chapters

Dissertations

Water Resources Research Institute Reports

Conference Proceedings

USGS Recruiting Conference - On April 23, 1999 personnel from the USGS Water Resources Division, MD-DE-DC District, 8987 Yellow Brick Road, Baltimore, MD presented a recruiting conference at the University of Maryland, College Park, MD. The conference was jointly sponsored by the USGS and the Maryland Water Resources Research Center. A speaker from the Administrative Management Program explained how to learn about jobs in USGS and the forms needed for application. A District scientist gave an excellent overview of the goals, mission and accomplishments of USGS. There was a good question and answer period following the presentations. We intend to hold this same activity again next year. Ninth Annual V. M. Goldschmidt Conference, August 22-27, 1999 Harvard University, Cambridge, Mass. Symposium on Geochemistry of Hydrothermal Ore Deposits and Aqueous Geochemistry, Organized by George R. Helz. Conference consisted of four half day sessions with 42 papers presented by an outstanding series of invited speakers in the field of geochemistry. Dr. Helz presented a paper on Molybdenum (VI) speciation and kinetics in sulfidic waters. The Maryland Water Resources Research Center offered a course (Chem 729) on Heavy Metals (HM) in the Environment in the Department of Chemistry, University of Maryland, College Park. The course was given during the Fall semester of 1999. The enrollment is primarily aimed at students interested in water science, and includes people from Agronomy, Civil Engineering, Agricultural Engineering, Chemistry, Geology and the MEES program (Chesapeake Bay Studies). Some of the lectures included Control of Methyl Mercury in Aquatic Environments; Speciation of Arsenic in Bangladesh Groundwater; Health Effects and EPA Policy on Mercury; Release of HM from Dredged Materials and Biosolids; Impact of Dredging on Release of HM; Ecological Risk Assessment of Tributyl Tin in the Chesapeake Bay Watershed; and Trends in Lead Residues in Sediments. Attendance is required of all Fellows in our NSF Trainee Program on Groundwater Chemistry and Hydrology. Rock ML, Helz GR, James BR Peroxide oxidation in soils containing chromium minerals or chromium waste. ABSTR PAP AM CHEM S 217U846U846 Part 1 MAR 21 1999

Other Publications