

Water Resources Research Center

Annual Technical Report

FY 1999

Introduction

The Maryland Water Resources Research Center carries out a research and teaching program from 104 funds granted by the United States Geological Survey (USGS). Proposals for research are solicited by contacting scientists from institutions of higher learning in the State. Our current mailing list contains about 185 names. Most of the proposals focus on the Chesapeake Bay, Maryland largest economic enterprise. Recent funded projects deal with atmospheric transport of pesticides into a large watershed associated with the Bay, nitrate removal from storm waters entering the Bay, development of biological indicator systems that can monitor health of tributaries feeding the Bay and reducing arsenic sources associated with geochemical processes. In the educational area, the Center offers an annual class (Chem 729) dealing with current environmental water issues. In the past, courses have been given on Pesticides in Soils and Water; Regional Climate Change, Endocrine Disruptors in Water, Reclamation of Soils at Superfund Sites, and Heavy Metals in the Environment. The Center hopes to teach a course on Pharmaceuticals in Water during the fall semester of 2000. In addition to the course work offered, the Center administers an NSF Training Grant in Water Chemistry and Hydrology to selected graduate fellows at the University. The Center is also involved in the Gemstone program, which is a campus wide effort to educate some of our brightest undergraduate students on scientific issues associated with the Chesapeake Bay. We also serve on the Chesapeake Bay Scientific Advisory Committee, and a National Academy of Sciences panel dealing with funding water projects in the Middle East. The Center has a number of cooperative activities with the USGS Baltimore Office, including an annual job opportunities day at the University, submitted articles to our newsletter from USGS scientists on current topics and serving on NAWQA committees.

Research Program

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

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 contamination in the environment has resulted from arsenical pesticides, mine tailings, as well as wood-preserving and other industries. However, a large portion of arsenic in drinking water supplies originates from geothermal sources, rocks and soils naturally containing high levels of arsenic, which can contaminate the groundwater. Reevaluation of the current U.S. drinking water MCL (0.05 mg/L) for arsenic is in progress due to recent risk assessments that suggest a link between exposure to low concentrations of arsenic and certain types of cancers (Smith et al., 1992). Because of its high toxicity and persistence, the USEPA is considering lowering the MCL for arsenic to the 0.005 mg/L range. Bioremediation, the technology in which microorganisms are used to degrade toxic chemical compounds, is currently raising interest for the efficient cleanup of polluted systems. One purpose of this project is to investigate As(III) reduction using the enrichment of As(III)-reducing bacteria provided by a mixed culture and furthermore to increase our understanding of the reduction processes in controlling arsenic cycling in natural environments. A second goal is to evaluate chemical and microbial processes controlling the weathering of As₂S₃(s) and the concurrent release of soluble arsenic.

Methodology

Measurements of total soluble arsenic were performed with an atomic absorption spectrophotometer (Perkin Elmer 5100 ZL) using the hydride generator flame. Prior to analyses for total arsenic concentrations, all samples were centrifuged for 25 min. at 2500 rpm and then filtered (0.2 μ m). Probes directly inserted into batch test reactors measured solution pH and ORP (oxidation/reduction potential). Enrichments of As(III)-reducing cultures were performed in 4-L anaerobic reactors fed with a medium containing As(III) and Na-lactate to acclimate the microbial population to toxic As(III). 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/L NaHCO₃, and 20 mg As(III)/L. Later, an identical reactor was established with 10 mg As(III)/L. The biomass grown inside the reactors was characterized by measuring the MLVSS (mixed liquid volatile suspended solids) and the MLSS (mixed liquid suspended solids) following the procedures presented in Standard Methods (APHA, 1995). Average temperature during growth in the reactors was 24°C \pm 3 °C. In selected cases, cells were washed with deionized water to examine effects of attached biological layers. Batch tests were performed to observe the effects of several factors on the arsenic reduction. These tests were conducted in 125 mL plastic bottles using biomass from both reactors, supplemented with additional Na-lactate and As(III). The bottles were constantly shaken horizontally at 25°C. Samples were taken periodically, centrifuged, and the supernatant filtered and analyzed for total arsenic concentration. To evaluate effects on total arsenic reduction with different As

(III) input concentrations, 50 mL of mixed culture (pH = 7.2) were complemented with 500 mg/L Na-lactate and As(III) concentrations of 10, 16 and 20 mg/L. The effects of electron acceptors, sulfate (50 mg/L as S) and nitrate (50 mg/L as N) on As reduction were tested in batch reactors with 10 mg/L As (III) input concentration. Acetate (500 mg/L) and glucose (500 mg/L), together with Na-lactate (500 mg/L) were examined to observe the effect of different electron donors. Na₂-fumarate, found to help selenium reduction when introduced as a supplement in the synthetic medium used for the growth of biomass (Tomei et al., 1992), was tested to observe its influence on the arsenic reduction. Also, effects of MnO₄⁻ (20 mg/L as Mn), SeO₃⁻ (20 mg/L as Se) and Cr₂O₇⁻² (20 mg/L as Cr) were studied. The latest experiments have been focused on understanding the fate of As(III) in the system. Experiments were performed to determine the processes responsible for the removal of As(III) observed in the presence of bacterial cells. Possible mechanisms include (1) biological reduction of As(III) to As(0) via enzymatic dissimilatory metal reduction, (2) As(III) binding to or inside the cell (adsorption processes), (3) abiotic precipitation of As(III) with sulfide, and (4) abiotic As(III) reduction in conjunction with precipitation of As(0) species. Batch tests were performed with biomass samples taken from the reactor acclimated with 10 mg/L As(III). To distinguish between a biological or an abiotic process, 40 mg/L HgCl₂ was added to the biomass and decreases in total arsenic concentrations were compared with results obtained from control batches. The same test was evaluated with washed cells in the presence of phosphate buffer solution and synthetic medium. For testing abiotic precipitation, 40 mg/L Na₂S·9H₂O was added to biomass and arsenic concentrations were compared with those obtained from the control experiments. The above experiments were repeated using AAS (aerobic activated sludge) in order to test the capability of mixed biomass adapted to the arsenic to reduce it to less toxic concentrations. ESEM (environmental scanning electron microscope) and TEM (transmission electron microscope) analyses were performed on the biomass in order to observe if any precipitate is formed inside the cells during growth on As(III). Experiments were conducted also to extract arsenic from the biomass in order to confirm a mass balance in the system. A digestion method with HNO₃ (APHA, 1995) was used to determine the total mass of arsenic held by the biomass. Several studies were completed to isolate the arsenic-reducing bacteria using procedures from Standard Methods for the "Enumeration, Enrichment and Isolation of Iron and Sulfur Bacteria" (APHA, 1995) and from Shelton and Tiedje (1984). One sample (30 mL, pH = 7.2, ORP = - 212 mV) of As(III) enrichment from the batch reactor (10 mg/L As (III)) was withdrawn in an anaerobic centrifuge tube and centrifuged for 25 minutes at 2500 rpm. The supernatant (pH = 6.78, ORP = -128 mV) was removed, filtered and preserved for total As analysis. The washed cells were mixed up to 30 mL with a synthetic medium (Tomei et al., 1992), 500 mg/L Na-lactate as carbon source and 10 mg/L As(III). Serial dilutions (10⁻¹, 10⁻², and 10⁻³) of this sample were inoculated in 10 mL volumetric flasks containing the synthetic medium. A small drop of each of the above 4 samples was transferred by the use of a sterile Pasteur pipette to small Petri dishes containing an agar medium (4 % Noble Agar and synthetic medium, Na-lactate, 10 mg/L As(III)). The sample was spread on the surface of the dish at 24°C and in ambient light. For observing light sensitivity, some dishes were kept in the dark (24°C) and some were kept in the light (24°C). Also, some dishes were stored in an oven (28°C) to test the growth of colonies at higher temperature.

Principal Findings and Significance

Batch microbial results performed over a period of 10 days showed a reduction from a total arsenic concentration of 19 mg/L to 12, from a total arsenic of 16 mg/L to 9, and from 10 mg/L to 4. Results from several batch tests that were performed using washed cells did not show significant difference in arsenic reduction compared to mixed cells. In comparison with the control batch (50 mL washed cells, 10 mg/L As (III), 500 mg/L Na-lactate, pH = 7.3, ORP = -115 mV, T = 28 °C, MLVSS = 2340 mg/L) in which total arsenic decreased from 9.8 mg/L to 4.3 mg/L in 9 hours, the presence of nitrate did not greatly affect the arsenic reduction, whereas the presence of sulfate slightly inhibited it. From

preliminary studies it was concluded that Na-lactate is the best electron donor for arsenic reducing microorganisms and therefore Na-lactate was used as the primary carbon source in all standard experiments. The use of glucose in the batch tests did not have any influence on arsenic reduction in comparison with the lactate control. However, acetate slightly inhibited the arsenic reduction (Figure 1). Se(IV) and Cr(VI) slightly inhibited the arsenic reduction while Mn(VII) did not show significant difference in comparison with the control. The presence of 800 mg/L Na₂-fumarate did produce a more rapid reduction in total arsenic in comparison with the Na-lactate control. Enrichment culture experiments showed that colonies grew in less than two days in both cases studied, in the presence and absence of light. Faster colonies' growth was observed under higher temperature (28°C). No difference among cells grown in the presence of light and those grown in the absence of light was noticed. Further microscopic evaluation is needed in order to identify those cells responsible only for the As(III) disappearance. Almost total reduction of arsenic was achieved after 4 hours in batch tests performed using 10 mg/L As(III)-grown biomass in the presence of 40 mg/L HgCl₂-Hg. The HgCl₂ concentration added to these tests should kill the cells responsible for As reduction. However, the results with HgCl₂ showed decreases in As concentrations similar with those obtained in the control batch, indicating that the reduction may be a chemical process rather than a biological one. The effect of 40 mg/L HgCl₂-Hg was tested again using the same conditions as above but with AAS samples instead of the arsenic-reducing biomass. A much slower decrease in total arsenic concentration was found with AAS (MLSS = 3120 mg/L, 10 mg/L As(III), pH = 7.1, ORP = -60 mV) proving that the arsenic-acclimated biomass was more effective than the AAS. Similar with the arsenic-biomass samples, no effect of HgCl₂ on As reduction was noted in the AAS tests indicating that the decrease in As concentration is not a biological process (Figure 2). The presence of 40 mg/L Na₂S·9H₂O in 10 mg/L arsenic-biomass did not affect the As reduction in comparison with the control test. In both tests, less than 1 mg/L total arsenic is obtained from an initial concentration of 12 mg/L after 4 hours, suggesting that arsenic sulfide precipitation is not occurring in the presence of the arsenic-biomass. The decrease in As concentration in these batch tests may therefore be due to an adsorption process. However, the ESEM and TEM analyses revealed the presence of a solid containing arsenic and sulfide inside the biomass. Further experiments are needed in order to identify this chemical (e.g., As₂S₃). Preliminary work was done in order to study the chemical dissolution of As₂S₃. After 27 hours oxygen exposure at pH 4, a slow increase in dissolved arsenic was found with a concurrent increase in SO₄²⁻. Current work has shown that a mixed culture provided by an anaerobic sludge acclimated to As(III) can be used to reduce dissolved arsenic to less toxic levels. The capability of arsenite reduction is dependent on the availability of organic carbon and on factors such as electron acceptors and electron donors. The latest results revealed that this arsenic reduction could be due to a chemical mechanism. Arsenic-grown cultures may be used in engineered treatment systems, or may exist in nature, affecting arsenic mobility. References: 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). Shelton, D. R. and Tiedje, J., M. (1984) "Isolation and Partial Characterization of Bacteria in an Anaerobic Consortium that Mineralizes 3-Chlorobenzoic Acid," Appl. Environ. Microbiol., 48(4), 840-848. Smith, A., Hopenhayan-Rich, C., Bates, M., Goeden, H., Hertz-Picciotto, I., Duggan, H. M., Wood, R., Kosnett, M., Smith, M. (1992) Environ. Health Perspect., 97, 259-267. 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.

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, in particular nitrate, is a substance of critical concern with respect to water quality. Control of nitrate from urban stormwater runoff can have a significant impact on nitrate levels in local waters. Therefore, a low impact treatment facility to remove nitrate from stormwater runoff before it enters receiving waters would be extremely beneficial. One such approach is bioretention, a simple plant- and soil-based low impact treatment/infiltration facility for use in developed areas to provide treatment to stormwater runoff.

Within the concept of bioretention for stormwater runoff treatment, two issues emerge with respect to nitrogen management. The first is the uptake of nitrogen compounds during the time scale of storm

events. Based on previous research (Davis et al., 1998), ammonia is moderately removed from infiltrating stormwater due to sorptive interactions with the soil media. However, nitrate has near negligible affinity for soil components due to its anionic form, and consequently nearly no nitrate is removed. The second nitrogen issue in bioretention is on the long-term time scale. As organic and ammonia nitrogen are accumulated in the bioretention system, processes for their benign removal from the bioretention facility must be developed and optimized. The most desirable process is to promote the conversion of accumulated nitrogen species to nitrogen gas, with the off-gas release of nitrogen to the atmosphere. Work by Davis et al. (1998) indicates that this accumulated organic and ammonia nitrogen can be converted to nitrate during the days between storm events, presumably via the biologically-mediated processes of ammonification and nitrification, and that this nitrate is washed from the facility by succeeding rain events.

The goal of this study is to systematically examine the removal of nitrate from urban runoff by re-engineering the concept of bioretention. Specifically, a modification to incorporate a continuously submerged anoxic zone with an overdrain is being evaluated for its capacity for nitrate removal via denitrification ([Figure 1](#)). In this evaluation, conditions that optimize the denitrification reaction will be determined so that design parameters can be established for use in bioretention systems. 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.

The work to date, which is described in this progress report, has focused on selecting an electron donor and carbon source that will promote significant denitrification and be stable for a long period of time in the subsurface. The electron donor and carbon source to be used in bioretention must be readily metabolizable, as well as low cost and readily available.

Methodology

Based on the selection criteria and past related research, one inorganic substrate--sulfur--and six organic substrates--alfalfa, leaf mulch compost, newspaper, sawdust, wheat straw and wood chips--were chosen as potential electron donors (e.g., Vogan, 1993; Blowes et al., 1994; Robertson and Cherry, 1995; Volokita et al., 1996; Schipper and Vojvodic-Vukovic, 1998; Shikora and Keeney, 1976; Zhang and Shan, 1999). The organic substrates were evaluated in two experimental sets: Set #1, alfalfa, newspaper, and leaf mulch compost; and Set #2, sawdust, wood chips, and wheat straw. The alfalfa, newspaper, and wheat straw were prepared by cutting the materials, and passing them through a 4-mm sieve; the sawdust and the leaf mulch compost were prepared by passing them through a 2-mm sieve. The wood chips were prepared by cutting them using a blender, and then passing the material through a 2-mm sieve. The inorganic substrate, sulfur, was evaluated in experimental Set #3. The sulfur

(International Sulfur, Inc., Mt. Pleasant, TX) was sieved into two size fractions: "large" particles, ranging from 2 to 2.36 mm, and "small" particles, ranging from 0.6 to 1.18 mm. Three variations were compared in this set: large sulfur particles alone, large sulfur particles with limestone, and small sulfur particles with limestone. The limestone (Southdown, Inc., Easton, PA) was sieved to obtain a size range from 0.6 to 1.18 mm and was added to buffer the acid production during denitrification with sulfur as the electron donor.

For each electron donor substrate, the total mass required for denitrification was calculated based on the nitrate loading for a 60-day experiment and using the appropriate reaction stoichiometry (McCarty, 1975). In the case of the organic electron donors, the total organic carbon (TOC) concentration used in the stoichiometric calculations was measured on a dry weight basis via a TOC analyzer (Shimadzu, Model 5000). In addition, the corresponding stoichiometric amount of limestone required for buffering in the sulfur experiments was also calculated (Zhang and Shan, 1999). The calculated material requirements were multiplied by a safety factor of 20 and the mass of material was uniformly mixed with silica sand that had been washed to minimize effects of residual organic carbon.

The electron donor/sand mixtures were then transferred into 40 cm long by 6.4 cm inner diameter Plexiglas columns, with sampling ports that penetrated to the center installed every 10 cm along the column. A total of 4 columns were set up for each experiment 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. All four columns were operated at room temperature ($22\pm 2^\circ\text{C}$).

The columns were seeded with the supernatant (settled at room temperature for 24 hours) of a secondary effluent sample from an activated sludge plant where denitrification was being performed. To inoculate the columns, the seed material was pumped into the column in an upflow mode and recycled through the column for 2 days.

After the 2-day inoculation procedure, synthetic stormwater runoff was introduced into each column in an upflow mode at a flow rate of 4 cm/hr (2.2 mL/min). The synthetic stormwater runoff was made using tap water with addition of 2.0 mg/L nitrate as N, 120 mg/L CaCl_2 , 0.6 mg/L Na_2HPO_4 as P, and the pH adjusted to 7 (Davis et al., 1998). The tapwater was dechlorinated with NaHSO_3 and continuously purged with N_2 to remove O_2 , resulting in influent dissolved oxygen concentrations < 2 ppm. In all experiments, samples for analysis were taken daily for nitrate, and periodically for Total Kjeldahl Nitrogen (TKN), and turbidity. In addition, during the sulfur/limestone experiments, samples were also taken for sulfate, total alkalinity, and nitrite analysis. Nitrate and sulfate concentrations were quantified via ion chromatography (Dionex DX-100) using a AS4 column with a 1.3 mM Na_2CO_3 /1.5 mM NaHCO_3 eluent. Nitrite and TKN analysis were performed using Standard Methods 4500- NO_2^- B. Colorimetric Method and 4500- N_{org} B. Macro-Kjeldahl Method, respectively (APHA et al., 1995). Turbidity levels were quantified using a HACH 2100N turbidimeter. Alkalinity was measured following Standard Method 2320 B. Titration Method (APHA et al., 1995).

Principal Findings and Significance

The experimental columns in each set were run for 35 to 40 days. This was sufficient time for the systems to reach a quasi-steady-state condition with respect to nitrate removal and the average percent nitrate removal during this period was calculated for each experimental set (Figure 2). In Set#1, the nitrate removals observed in the alfalfa and newspaper columns were essentially 100%, while that for the leaf mulch compost column was about 60% (Figure 2). The removal in the control column was only about 7%. However, treated water from the alfalfa column showed some odor, increased turbidity (À 27 NTU) and residual TKN (2-3 mg/L N), while that from the newspaper and mulch did not demonstrate any of these problems.

The Set#2 organic electron donors, sawdust, wheat straw, and wood chips, all performed well, with >95% nitrate removal, compared to <10% for the control column (Figure 2). However, the effluent quality based on other parameters was variable. In particular, the wheat straw column had somewhat high residual TKN (0.5-1.4 mg/L N), and high turbidity (up to about 16 NTU). The sawdust and wood chips had similar TKN levels in the effluent (roughly 0.3 mg/L N) during the quasi-steady-state period. The turbidity was somewhat higher in the wood chip effluent compared to the sawdust column (average 2.4 NTU compared to 0.8 NTU); however, the wood chip system provided consistently better nitrate removal than the sawdust system throughout the course of the experiment, and showed more rapid removal of nitrate along the length of the column.

In Set#3, only the small sulfur particle/limestone combination performed well over the course of the experiment, with about 90% nitrate removal during the quasi-steady-state period (Figure 2). The large sulfur only, and large sulfur/limestone columns produced only about 30% nitrate removal during the quasi-steady-state period, while the control had about 10% removal. Effluent sulfate concentrations in all three columns were approximately equal to the stoichiometric amount expected based on the nitrate removal. No clear trends were found in the alkalinity data; the buffering capacity seemed to be sufficient whether limestone was added to the columns or not, although the alkalinity levels in the sulfur-only column were generally somewhat lower. These results were expected based on the alkalinity levels in the simulated stormwater (roughly 30 mg/L as CaCO₃), which should be sufficient to buffer the acid production at the tested nitrate concentration in the absence of added limestone. Interestingly, the small sulfur/limestone column effluent had relatively high nitrite levels during the quasi-steady-state period (about 0.5-0.6 mg/L N). Turbidity levels were low (<0.4 NTU) in all of the sulfur columns.

Based on the Set#1 and Set#2 experiments for the organic substrates, alfalfa, newspaper, sawdust, wheat straw, and wood chips all appeared to be efficient electron donors and carbon sources for the removal of nitrate from stormwater runoff. However, it is also critical that the effluent water quality leaving the bioretention basin not be diminished compared to the influent and that the nitrate nitrogen removal from the system occurs via denitrification. Based on these criteria, the newspaper and wood chips are the best candidates, as they provide better effluent quality and total nitrogen removal than the other organic substrates. In the alfalfa and wheat straw systems, both of which had relatively substantial TKN in the column effluent, the nitrate was essentially completely removed from the pore water by the 20 cm height and there was qualitative evidence that sulfate reduction was occurring. One possible explanation for the high effluent TKN is that alfalfa and wheat straw have a lower C:N ratio than sawdust, wood chips, and newsprint (Rynk, 1992). Therefore, it is possible that more ammonification occurred in the alfalfa and wheat straw systems, resulting in increased TKN. It is also known that some microorganisms, including sulfate-reducing bacteria (Hansen, 1994), can reduce nitrate to ammonia in a dissimilative process, and it is possible that this is the source of the TKN in the effluent. This microbial process has been observed to be favored in anaerobic environments when carbon availability is high relative to nitrate availability (Tiedje et al., 1982), as was the case in these relatively short-term column

systems. Dissimilatory reduction of nitrate to ammonia is an undesirable process in bioretention because nitrogen is conserved. This is a challenge in engineering bioretention basins for denitrification because of the relatively low nitrate levels, coupled with the need to provide suitable quantities of electron donor/carbon source to sustain the system for extended periods; however, this problem should decrease with time.

The results in Set#3 with the sulfur systems are interesting. Although the same mass of sulfur was added to all three columns, and sufficient buffering capacity was present in all three cases, significantly better nitrate removal occurred in the column with the small sulfur particles/limestone. This is probably a result of the increased number of sulfur particles and the increased surface area of the sulfur available per unit volume of reactor with the smaller sulfur particles. Thus, with the smaller particles, more surface area was available for contact with the nitrate-laden water, and for growth of the denitrifying microorganisms (Liu, 1992, referenced in Zhang and Shan, 1999). It is possible that with longer hydraulic retention times, the large sulfur particle systems would demonstrate improved nitrate removal efficiency (e.g., Koenig and Liu, 1996). Based on this evaluation, the small sulfur/limestone combination appears to be a good candidate system, although there is some concern at this point that relatively high levels of nitrogen may be leaving the system in the form of nitrite. This is being further investigated. Accumulation of nitrite is a characteristic of the chemolithotrophic denitrifying bacterium *Thiobacillus denitrificans* (Baalsrud and Baalsrud, 1954). It may be that nitrite concentration levels can be decreased with longer residence times (e.g., Sikora and Keeney, 1976).

One interesting finding from these experiments is that a suitable inoculum was provided in all cases by the settled supernatant of a secondary effluent sample. For example, in the case of the organic substrates, which are all complex, cellulose-rich, carbon sources, no steps were taken to select for a cellulose-degrading inoculum. In addition, in the case of sulfur, a sufficient inoculum of chemolithotrophic denitrifying bacteria was provided in the secondary effluent. This is consistent with other research suggesting that these organisms are present in a variety of environments, including domestic wastewater (Zhang and Lampe, 1999; Zhang and Shan, 1999)

Based on the experiments performed, excellent nitrate removal from synthetic stormwater runoff was observed in anoxic sand-packed columns containing alfalfa, newspaper, wheat straw, wood chips, and sawdust. However, based on total nitrogen removal and other water quality characteristics, newspaper and wood chips are the best candidates out of these sets for providing the electron donor/carbon source in bioretention basins engineered for nitrate removal. These substrates are also attractive for other reasons as well. For example, they are both waste products that are readily available in many areas. Furthermore, these are both cellulose-rich substrates, and cellulose is an abundant renewable resource.

The results with the sulfur and sulfur/limestone systems indicate that sulfur also holds promise as a electron donor for denitrification in engineered bioretention, in particular, with small sulfur particle sizes. Importantly, as discussed by others (Zhang and Shan, 1999), sulfur is also a relatively inexpensive resource (\$0.018/kg; \$16/ton).

The next stage in this work includes the optimization of the anoxic zone (e.g., sizing, porous medium). This will be performed using the electron donors that gave the best nitrate removal efficiency and effluent quality in the experiments reported here: newspaper, wood chips, and small sulfur particles/limestone. In addition, the performance of the optimized system will be evaluated under conditions of intermittent loadings, such as are expected in the field. This is a unique challenge of bioretention that distinguishes it from many other engineered systems for biological denitrification.

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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 cropland and receives the highest pesticide application of any coastal area in the nation. Over 2.1 million kilograms per year are being applied. At the same time, the Chesapeake Bay estuary contains important aquatic habitat areas. 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. The extent of local or regional atmospheric transport and deposition of pesticides to this area is poorly understood and may be an important contributor to the overall pesticide budget for the region. Currently, little information with respect to atmospheric loading of pesticides is available. Baseline measurements are needed to determine rain fluxes of pesticides at different locations.

Traditionally, the methods used to collect and measure pesticides in rain were passive inducing errors in collection and analysis. Specific objectives of this project are: 1. Develop methods to allow for active air and rain sampling and calibrate these methods for the analysis of currently used pesticides. 2. 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. 3. 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. 4. Determine site-specific degradation rate constants and assess the influence of different water constituents on the overall fate of selected pesticides. **Principal Findings and Significance** In our objective of determining the contribution of atmospheric inputs of pesticides and site-specific degradation rates, progress has been made in two major areas: 1. In the development of a new, more efficient, in-line extraction method for precipitation sampling to determine wet deposition loads of pesticides. Optimization of high-volume air sampling and extraction methods for the analysis of currently used pesticides. 2. Significant progress has been made in understanding the fate of chlorpyrifos under the variable water quality conditions present in the Chesapeake Bay, particularly on the effect of Cu as a catalyst for hydrolysis of OP's.

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

Establishment of Automated Precipitation Sample Collection Method and High Volume Air Sample Collections for Currently used Pesticides in the Choptank River Watershed. Current methodologies for determining currently used pesticides in rain include capturing bulk rain samples in the field, followed by a time consuming filtering and extraction process in the laboratory. Significant concerns with this type of methodology exist due to the time interval between sample collection and extraction, partitioning between particle and the dissolved phase during sample holding times, and degradation of analytes. Kuang Zhihua, the University of Maryland PhD graduate student assigned to 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. This method has several advantages. First, the rainwater is extracted immediately, saving time in the laboratory. Cartridges and filters can be quickly changed between rain events and mailed from a field site to the laboratory. The performance of the cartridges used in this method do not require the adsorbent to remain wet or to be conditioned, so control of the water level in the sampling train is not necessary, thus simplifying the system. Cartridges and filters used in the method are commercially available and are relatively inexpensive, allowing event-based sampling at a reasonable cost. The following is a summary of the results and a manuscript is currently in preparation. A MIC-B automated rain collector (Meteorological Instrument Center, Ontario, Canada) was used in this study. It contains a 0.2 m² stainless steel funnel that is covered with a lid that remains closed during non-rain events. The sampling train attached to the bottom of the funnel is Teflon and includes an in-line filter holder containing a Whatman GF/F glass fiber filter (0.7 µm nominal pore size) to capture particles. A solid phase extraction cartridge containing 200 mg ENV+ (Isolute) resin was used to capture dissolved-phase material. A peristaltic pump was used to pull rainwater through the filter cartridge assembly into a 20-L glass bottle to determine sample volume. The peristaltic pump is activated when the lid of the sampler is open. The major factors investigated in the method development were: 1. Recovery of target analytes at different flow rates through the system. 2. Recovery of target analytes at different sample volumes. The performance of the SPE cartridges used in the method has already been tested for our target analytes in previous studies (Lehotay et al., 1999). However, the previous studies were carried out with a 4-L sample size and only at one flow rate. These experiments were carried out by spiking different volumes of distilled water and passing the water through the entire funnel sampling train. After collection, the SPE cartridge was wrapped with aluminum foil and stored at 4 °C for no more than 7 days until elution. Just before elution, the cartridge was dried using high purity N₂ combined with vacuum. Analytes were eluted from the cartridge with 6mL dichloromethane (DCM) followed by 9 ml 3:1 acetone: acetonitrile (MeCN) solvent mixture. The resulting extract was concentrated to a volume of about 0.5 ml under a gentle stream of high purity (99.9%) nitrogen gas. And then another 2 ml MeCN was added and the solution was blown down to 1.0 ml, which was quantitatively transferred to an amber autosampler vial. Internal standards of 50ul d10- Anthracene (30.18 ppm) and d10- Chrysene (25.68 ppm) were added to the vial for subsequent gas chromatography (GC)/mass spectrometry (MS) analysis. Flow rate was an important factor in recovery efficiency. At low flow rates (= 48.8 mL/min), recoveries were generally > 80% for sample volumes of 4-6 L. Recoveries dropped significantly at the higher flow rates, especially for chlorothalonil, endosulfan sulfate, α-HCH, γ-HCH and malathion whose recoveries were at least 20% lower compared with those at the lower flow rates. Recoveries remained high even at a volume of 10-L, which would equate to a rain event of up to 5 cm (200 ml/mm rain). Breakthrough to a second cartridge at a volume of 10-L at 30 mL/min revealed only traces of some analytes on the back cartridge. Air sample collection and extraction methods have been optimized for the polar currently used pesticides targeted in this study. A Grasby-Anderson modified high volume air sampler was used equipped with an aluminum sampling train containing a Gelman A/E glass fiber filter followed by two 3"x3" polyurethane foam plugs to capture particles and gas-phase pesticide residues, respectively. Extraction of the foam plugs and filters using chromatographic grade ethyl acetate provided recoveries

of our target analytes of > 80%. A sample collection site has been established at University of Maryland Horn Point Environmental Laboratory in Cambridge Maryland near the Choptank River. Through a cooperative agreement with UM faculty, event-based sample collection began in April 2000, along with weekly high volume air sample collection and monthly surface water sample collection from sites along the lower Choptank River. Funds are currently being sought to expand this study to include more sites on the Delmarva peninsula in order to gain a better understanding of the atmospheric deposition loadings of pesticides to this intensely agricultural region of the Chesapeake Bay watershed. Site Specific Degradation Rates for Chlorpyrifos In a study of chlorpyrifos hydrolysis rates in water from the mouth of different Chesapeake Bay tributaries, results 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 distilled 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 oC. In summary, observed chlorpyrifos hydrolysis 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 cannot 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. A 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, we believe that a model of chlorpyrifos hydrolysis can be constructed to predict the persistence of this chemical under specific site conditions. Over this summer additional controlled and site spiked experiments are being conducted to test this hypothesis and develop a kinetic model for the degradation of Chlorpyrifos.

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 Chemosphere

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

Basic Project Information

Basic Project Information	
Category	Data
Title	Structural and Funtional Assessment of Stream
Project Number	03-00
Start Date	03/01/2000
End Date	02/28/2001
Research Category	Biological Sciences
Focus Category #1	Nutrients
Focus Category #2	Ecology
Focus Category #3	Water Quality
Lead Institution	University of Maryland

Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
William O Lamp	Associate Professor	University of Maryland	01

Problem and Research Objectives

Agriculture in Maryland's Coastal Plain results in elevated levels of phosphorus and nitrogen in running waters that eventually impact the Chesapeake Bay. Procedures for measuring the impact of nutrients on stream ecosystems have emphasized structural assessment tools, such as species diversity, taxa richness, or the Ephemeroptera, Plecoptera, Trichoptera (EPT) index. Here, we propose one-year study to determine the utility of functional assessment tools (e.g., metrics representing leaf decomposition rates) as measures of ecosystem integrity. The objectives of this project are: 1. To measure leaf decomposition in coastal plain streams in agricultural and non-agricultural regions in Maryland; 2. To compare leaf decomposition rates to structural indices of water quality; and 3. To measure the functional response of stream biota to the addition of phosphorus and nitrogen. There are several structural tools already in use that classify a water system based on chemical analyses, the abundance and diversity of biological organisms, and physical characteristics of the river or stream. In the past, water quality tests depended primarily on chemical assessments to characterize lotic systems. There are two distinct advantages to this method: 1) chemical analyses reflect point source contamination problems, and 2) they provide highly quantitative regulatory levels for agencies to monitor. However, in recent years there has been a growing trend to use biological monitoring techniques due to their greater sensitivity to a wide range of

pollutants and their early warning capabilities. Rosenberg and Resh (1993) provide a detailed description and evaluation of the utility of biological monitoring methods, with particular attention given to methods based on sampling benthic macroinvertebrates. Unlike chemical data, which provides water quality information at a discrete point in time, biological organisms are long-term integrators of environmental stresses. Different species of organisms exhibit a range of responses to environmental impacts. Macroinvertebrates in particular provide a very good indicator tool of environmental degradation. They are widespread and are relatively sessile in their aquatic phase, and can be inexpensively sampled. These organisms can be used for laboratory studies, including toxicological, physiological, behavioral, or functional assessments, in order to better understand a particular contaminant's effect (Rosenberg and Resh 1993). The Maryland Department of Natural Resources has created a region specific index of biological integrity to assess water quality and potential impacts across the State of Maryland (Maryland Biological Stream Survey 1997). The strength of this technique is its combination of multiple metrics in order to develop a greater picture of the stream or river condition (Karr and Chu 1999). The MBSS has also included a benthic macroinvertebrate metric based on the Hilsenhoff's biotic index to assist in rapid biological assessments in aquatic systems (Hilsenhoff 1988). Both of these measurement tools provide a static view of the aquatic conditions focusing on the structural components of the system. The techniques utilize the presence or absence of specific organisms as well as their relative abundance to identify and classify the degradation in an aquatic environment. Other measurable characteristics of streams that can increase our understanding of environmental impacts may be found in the functions or streams, such as nutrient processing. Such functions may be expected to change in predictable ways when the stream is exposed to contaminants. Understanding how the biotic organisms process organic material, for example, can expand our ability to assess impairments by measuring how well the organisms are breaking down the materials in a given stream system. The dynamic view of assessing the system function under impacted conditions could conceivably become the most critical tool in managing the resource. At a minimum, the functional component will provide a greater understanding of how to assess environmental degradation of a stream or river. This approach provides information on the production of the aquatic system (phytoplankton and zooplankton), the processing of organic materials (the uptake of both allochthonous and autochthonous materials), and the transportation of materials. For these reasons, we intend to develop this functional approach to be used in concert with the structural methods currently used. The development of such assessment tools will provide the resource manager with more comprehensive information regarding detrimental nutrient levels, and will enhance the scientific information available for environmental policy-makers.

Methodology

We propose a one year effort to develop a better assessment tool for understanding of the fate and transport of agricultural nutrients within the surface water. The study intends to link the effects of elevated nutrients to changes in functional aspects of the stream system. It involves the following efforts: A. To measure leaf decomposition in streams representing agricultural and non- agricultural regions in Maryland Here, our objective is to test for variations in leaf pack processing between sites within the same watershed, as well as between watersheds. We plan to perform both baseline chemical and physical tests as well as field leaf decomposition studies for this investigation. Monitoring of selected streams on the agricultural impacted Eastern Shore and in the more pristine forested streams of southern Maryland will help to identify chemical, physical, and structural differences between the two environments. We have collected water chemistry, benthic macroinvertebrate samples, and hydrologic data over the past year on two different watersheds in Maryland: the Nassawango Creek south of Salisbury and the Nanjemoy Creek in Southern Maryland. These tests are performed on a monthly basis at 5 sample sites within each stream system. The study sites on the Eastern Shore of Maryland have

yielded elevated phosphorus levels, on the order of 170-2750 ug PO₄-P/L. These extremely high ambient conditions warrant studies focused on the biotic community and their functional capacity under an environmentally degraded scenario. The study sites in Southern Maryland have not shown such high phosphorus levels, 20-940 ug PO₄-P/L, and therefore can be used as a comparison. This baseline data will provide the foundation for our further investigation into the effects of phosphorus on the stream system and the development of potential monitoring tools. Leaf decomposition studies will be performed in the field to examine relationships between the stream phosphorus levels and the biotic processing of the leaf matter. These studies will be performed six times during the year. We plan to use tube traps containing 2.5 grams of desiccated red maple leaves. The tube traps will be constructed of PVC tubing with a coarse holes on the upstream side to allow macroinvertebrate entry and fine mesh on the downstream end to prevent leaf matter loss. The tube traps will be secured to bricks and placed on the stream bottom. There will be 8 replicates at each site. The traps will be collected after 21 days to process. The leaves will then be rinsed. After sample dry weights will be measured, followed by the samples being ashed using a muffle furnace. We will calculate the proportion of organic matter decomposed using these weights and compare these values to pre-determined organic matter proportions for maple leaves. This comparison will provide the percentage organic matter loss due to decomposition within the stream environment. These field trials coupled with the monitoring data may illustrate other potential factors influencing the stream function.

B. To compare leaf decomposition rates to structural indices of water quality The objective is to compare structural and functional indices in order to assess the effectiveness of a new environmental stress indicator. The first step is to gather structural information on the two watersheds. We use artificial leaf packs to collect the macroinvertebrates six time within the year. Five grams of desiccated red maple leaves are bound to a brick and left in the stream for 30 days. We use 8 replicate leaf samples at each site. These leaves are then collected from the field and preserved at 40 Celsius until processed. The leaves are rinsed in a pan and the macroinvertebrates are trapped by filtering the water through a 425 micrometer mesh size sieve. Each sample is then labeled and preserved in Kahle's solution. The macroinvertebrates are then identified to genus level. Number of taxa, number of individuals, and various other community indices [e.g., the Ephemeroptera, Plecoptera, Trichoptera (EPT) index] will be calculated. This data will assist in defining the community structure present as well as provide information as to which organism could best be used in laboratory bioassays. Regression analysis will then be performed to assess the differences between the structural and functional measurements. The monthly sampling will continue to provide a longitudinal database that will then be analyzed to compare the decomposition results with the expected structural classification of the stream. This comparison will be based on established models, such as the Maryland Biological Stream Survey (MBSS). The State of Maryland has established regional specific metrics to assess the stream conditions in the different ecoregions within the State (Maryland Department of Natural Resources 1998). The MBSS will provide a good comparison tool to use with these decomposition trials (Maryland Department of Natural Resources 1997). The two different methods of classification will then be compared using multivariate statistics.

C. To measure the functional response of stream biota to the addition of phosphorus and nitrogen The objective is to identify the effects of varied nutrient concentrations, both phosphorus and nitrogen, on the different biological trophic levels, as well as the effects on the decomposition of the allochthonous leaf matter. This will be accomplished by constructing artificial stream environments and subjecting known organisms to different nutrient enrichment levels. The artificial stream environment consists of 200 ml of natural stream water, collected immediately before each test, in a 250 ml Erlenmeyer flask equipped with a glass tube to supply air under pressure. The air maintains a water current and high oxygen levels comparable to a riffle area of a natural stream. Effects of elevated nutrients will be tested using bacteria and macroinvertebrates. Both of these organisms use the leaf material as a food source. We plan to use *Pycnopsyche* sp. (Trichoptera: Limnephilidae) for the macroinvertebrate toxicology tests to assess nutrient effects on primary production. *Pycnopsyche* sp. was selected as an appropriate test species due to its presence in the Nanjemoy Creek as well as its functional feeding. It is a shredding

macroinvertebrate which breaks down the coarse particulate organic matter (CPOM) to fine particulate organic matter (FPOM). This processing of organic matter leads to further decomposition by microbial consumers (Hauer and Lamberti 1996). Three experiments will be conducted with *Pycnopsyche* sp. and bacteria present and then it will be repeated with only the bacteria present. For each, at least four treatments with six replicates will be established with a control, a high, a medium, and a low concentration of nutrients. The water will be spiked with either phosphorus or nitrogen and then with both. Before and after each test red maple leaf discs will be weighed and leaf area determined by a CI-400 CIAS system (CID, Inc.). Leaf discs will also be ashed to determine leaf decomposition rates. Bacterial respiration will be measured using a respirometer to assess their activity level and any potential toxicological effects. Laboratory trials will assist in honing in on individual parameters and their corresponding toxicological effects. Understanding how these organisms are affected by different nutrient concentrations will provide insight into the functional capacity of the stream system. These experiments will be analyzed using ANOVA and regression analysis. Lastly, continued monthly monitoring of the stream water chemistry and hydrologic parameters coupled with laboratory bioassays will help to delineate how elevated nutrients effect the stream system. Multivariate analyses (e.g., principle components, factor analysis) will be conducted to relate decomposition rates to physical, and chemical conditions.

Principal Findings and Significance

The expected results of this project will be a better understanding of the cause-effect relationships between elevated nutrient levels and the organic material breakdown capability of a stream system. It will study the interactions between the biotic community structure and its capacity to function under different aquatic chemical conditions. Elevated nutrients, with specific emphasis on phosphorus, will be the focal point of the studies. The project will develop a preliminary stream assessment tool based on functional responses with an analysis of its effectiveness in two watersheds. In addition, comparison of this new approach to established tools already in use will be completed. The work done in this study can be used to construct a better assessment tool for biological monitoring and classifying the impacts on stream systems. Knowledge of how the biotic community processes organic materials under elevated nutrient conditions will provide another dimension of understanding, and will increase the variety and number of tools available for State and local agencies making resource management decisions. Another potential benefit is that this study may provide additional information on the coastal plain region of Maryland. This new data will contribute to both the Maryland Department of Natural Resources database for these streams, as well as the United States Environmental Protection Agencies (US EPA) National Nutrient Strategy. The US EPA is in the process of establishing region specific nutrient criteria for rivers and streams (US EPA 1998). Augmenting the available databases will improve the understanding about the specific stream conditions for each of the different regions. References: Hauer, F.R. and G.A. Lamberti. 1996. *Methods in stream ecology*. Academic Press. New York. Hilsenhoff, W.L. 1988. Rapid field assessment of organic pollution with a family-level biotic index. *Journal of North American Benthological Society*. 7(1):65-68. Karr, J.R., and E.W. Chu. 1999. *Restoring life in running waters: better biological monitoring*. Island Press. Washington, DC. Maryland Department of Natural Resources. 1997. *Maryland biological stream survey: ecological status of non-tidal streams in six basins sampled in 1995*. Rosenberg, D.M. and V.H. Resh. 1993. *Freshwater biomonitoring and benthic macroinvertebrates*. Chapman and Hall. New York. pp. 1-27. US EPA. 1998. *National strategy for the development of regional nutrient criteria*. EPA 822-R-98-002.

Descriptors

Bioindicators, Benthos, Functional Measurements, Leaf Processing, Nitrogen, Phosphorus, Water

Quality

Articles in Refereed Scientific Journals

Book Chapters

Dissertations

Water Resources Research Institute Reports

Conference Proceedings

Other Publications

Information Transfer Program

The Center sponsored its second career opportunities day on Monday, March 6, 2000. USGS employees from the Baltimore Office provided information on employment and research opportunities in the agency to students at the University of Maryland. Denett Jablicki, Personnel Specialist, distributed pamphlets and bulletins on how to apply for a job and listed some of the currently available summer jobs. Dr. Cherie Miller, Chemist, covered the highlights on the kinds of research activities conducted in USGS. The session was well attended by students from across the College Park campus and there was follow-up by e-mail on several jobs. A new web site has been created on the Center's home page entitled "Water on the Web". The new site covers Maryland's water resource activities under nine categories: dredging, drought, education, recreation, water quality, water supply, water use, watersheds and wetlands. Under each category are web addresses linked to various Federal and State agencies with in-depth information on the various areas of concern. The site is intended for any one who has an interest in Maryland water; homeowners, students, farmers, watermen, State and local administrators, or residents concerned about one of our most important natural resources. To see the new site, go to our home page:

http://www.life.umd.edu/water_resources and look in the bottom left hand corner for Water on the Web. We hope to continue building this site over the next several years.

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	1	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	4	N/A	N/A	N/A	N/A

Awards & Achievements

Publications from Prior Projects

Articles in Refereed Scientific Journals

Book Chapters

Dissertations

Water Resources Research Institute Reports

Conference Proceedings

Other Publications