Water Resources Research Center

Annual Technical Report

FY 2000

Introduction

INTRODUCTION The Maryland Water Resources Research Center is in a period of transition at this time. In Oct. 2000, Dr. George R. Helz announced his intention to step down as Director after ten years in that position. The University is in the process of finalizing its selection for a new Director and we anticipate an announcement will be made by late July 2001.

The Center funded two research proposals: Sustainable Oil and Grease Removal from Stormwater Runoff Hotspots using Bioretention and Atmospheric Deposition of Currently Used Pesticides to Chesapeake Bay Watersheds. In addition, the Center funded 3 graduate assistantships of $3500 each for the summer of 2001. Priority was given to proposals in under-represented areas such as scio-economic studies, policy studies, geology, ecology, agronomy and related fields.

The Center also sponsored a seminar course, Chem 729, Pharmaceuticals in the Environment. A travel grant from the Joint Institute for Food and Applied Nutrition (JIFSAN) for $5000 allowed us an opportunity to invite some outstanding speakers for this course. One of our featured speakers was Dr. Thomas Ternes, Institute fuer Wasserforschung and Wassertechnologie, Wesbaden, Germany. Other speakers came from the USGS, FDA, CDC, USEPA, Science News, Johns Hopkins University and Vice Presidents from Bristol-Myers Squibb and Glaxo-SmithKine. The course was well attended by University and Federal scientists in the Washington area.

Research Program

Basic Information

Title:	Structural and Functional Assessments for Evaluating Elevated Nutrient Levels in Maryland Streams
Project Number:	03
Start Date:	3/1/2000
End Date:	2/28/2001
Research Category:	Biological Sciences
Focus Category:	Non Point Pollution, Water Quality, Ecology
Descriptors:	Bioindicators, Benthos, Functional Measurements, Leaf Processing, Nitrogen, Phosphorus
Lead Institute:	University of Maryland
Principal Investigators:	William O Lamp

Publication

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. We conducted a 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 were:

1. To measure leaf decomposition in 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

Other measurable characteristics of streams that can increase our understanding of environmental impacts may be found in stream functions such as leaf decomposition. Such functions may be expected to change in predictable ways when the stream 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. This 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

1. <u>To measure leaf decomposition in streams representing agricultural and non-agricultural regions in Maryland</u>

Here, our objective was to test for variations in leaf pack processing between sites within the same watershed, as well as between watersheds. We performed both baseline chemical and physical tests as well as field leaf decomposition studies for this investigation. We have collected water chemistry, benthic macroinvertebrate samples, and hydrologic data over the past two years on two different watersheds in Maryland: the Nassawango Creek south of Salisbury and the Nanjemoy Creek in Southern Maryland. A

suite of physical and chemical parameters was regularly monitored at our field sites. These tests were performed on a monthly basis at 5 sample sites within each stream system.

Leaf decomposition studies were performed in the field to look for relationships between the stream phosphorus levels and the biotic processing of the leaf matter. We used tube traps containing 2.5 grams of desiccated red maple leaves. The tube traps were 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 were secured to bricks and placed on the stream bottom with 8 replicates at each site. The traps were collected after 28 days to process. The leaves were rinsed, weighed, and ashed to determine the amount of leaf decomposition.

2. To compare leaf decomposition rates to structural indices of water quality

The objective was to compare structural and functional indices in order to assess the effectiveness of a new environmental stress indicator. The first step was to gather structural information on the two watersheds. We used artificial leaf packs to collect the macroinvertebrates. Five grams of desiccated red maple leaves were bound to a brick and left in the stream for 30 days. We used 8 replicate leaf samples at each site. These leaves were then collected from the field and preserved at 4^{o} Celsius until processed. The leaves were rinsed in a pan and the macroinvertebrates trapped by filtering the water through a 425 micrometer mesh size sieve. Each sample was then labeled and preserved in Kahle's solution. The macroinvertebrates were identified to genus level. Number of taxa, number of individuals, and various other community indices [e.g., the Ephemeroptera, Plecoptera, Trichoptera (EPT) index] was calculated.

3. To measure the functional response of stream biota to the addition of phosphorus and nitrogen

The objective was 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 was accomplished by constructing artificial stream environments and subjecting known organisms to different nutrient enrichment levels. The artificial stream environment consisted of 200 ml of natural stream water, collected immediately before each test, in a 250 ml Erlymeyer 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.

Principal Findings and Significance

The study sites on the Eastern Shore of Maryland have yielded elevated phosphorus levels, on the order of 170-2750 ug PO_4-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 PO_4-P/L, and therefore can be used as a comparison. Nitrate-N, reactive P, total P, conductivity, and pH were all significantly greater at the Nassawango sites compared to the Nanjemoy sites. This baseline data will provide the foundation for our further investigation into the effects of nonpoint source pollutants on the stream system and the development of potential monitoring tools.

Community structure, based on leafpack inhabitants, was similar in the two watersheds in spite of the differences in physical and chemical parameters. The number of taxa per leafpack averaged 5.2 at the Nanjemoy sites, compared to 4.1 at the Nassawango sites, with no significant differences between them. The number of individuals per leafpack averaged 12.4 and 12.5 at the two watersheds, respectively.

The coarse mesh decomposition tubes did have significantly greater rates of decomposition than the fine mesh tubes. As expected, the number of macroinvertebrates colonizing the tubes was much greater in the coarse mesh tubes, and this likely explains the difference in decomposition rates. Although decomposition rates between watersheds were not significant, the data suggest that the macroinvertebrate contribution to decomposition was greater in the Nanjemoy watershed as compared to the Nassawango watershed. Further analysis and studies are being conducted to follow up on these results.

The project presents a preliminary stream assessment tool based on functional responses with an analysis of its effectiveness in two watersheds. We also have a comparison of this new approach to established tools already in use. The work done in this study will used to construct a better assessment tool for biomonitoring 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.

Basic Information

Title:	Engineered Bioretention for Nitrogen from Urban Stormwater Runoff
Project Number:	B-02
Start Date:	3/1/1999
End Date:	2/28/2001
Research Category:	Engineering
Focus Category:	Non Point Pollution, Nutrients, Water Quality
Descriptors:	Storm Water Management, Nitrate, Runoff, Water Quality
Lead Institute:	University of Maryland
Principal Investigators:	Allen P. Davis, Eric Alan Seagren

Publication

1. Kim, H., Seagren, E.A., and Davis, A.P. (2000) "Engineered Bioretention for Removal of Nitrate from Stormwater Runoff," in WEFTEC 2000 Conference Proceedings on CDROM Research Symposium, Nitrogen Removal, Session 19, Anaheim CA, October 2000.

Final Report: Engineered Bioretention for Removal of Nitrate from Stormwater Runoff

Problems and Research Objective

Nitrogen-containing compounds are considered to be important pollutants and are responsible for rapidly growing environmental and human health problems. For example, high nitrate and ammonia concentrations that are discharged to surface-water systems promote eutrophication and have been linked to outbreaks of *Pfiesteria piscicid*, a toxic microorganism. A maximum contaminant level (MCL) of 10 mg/L as nitrogen for nitrate in drinking water has been established by the U. S. Environmental Protection Agency (EPA) and a similar limit of 50 mg/L $-NO_3^-$/L (11.3 mg/L NO_3^--N) also has been set by the World Health Organization (WHO, 1984). It is therefore important to limit the input of nitrogen to the water supplies. Recent investigations of urban stormwater runoff have shown high levels of several nitrogen species, indicating the significance of this source. Because a major portion of Maryland's 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.

Despite its importance, little research has focused on N removal from stormwater runoff. One potential approach is bioretention, a simple plant- and soil-based low impact treatment/infiltration facility for use in developed areas to treat stormwater runoff. Previous research by Davis et al. (2001) using pilot bioretention boxes demonstrated that high reductions in metals (copper, lead, and zinc, >92%) and moderate reduction for phosphorus (~ 80%), TKN (65 to 75%), and ammonia (60 to 80%) could result. However, little nitrate was removed. In additions, nitrate production was noted due to

nitrates contained near negligible affinity for soil components because the accumulated organic and ammonia nitrogen captured during stormwater events can be converted to nitrate during the days between storm events, presumably via the biologically-mediated processes of ammonification and nitrification. This nitrate is washed from the facility by succeeding rain events. Therefore, modifications are required to engineer bioretention systems to remove nitrogen pollutants (Figure 1). In particular, nitrate is of concern because it is the most difficult of the nitrogen species to address and it is not attenuated in a typical, conventional bioretention facility.

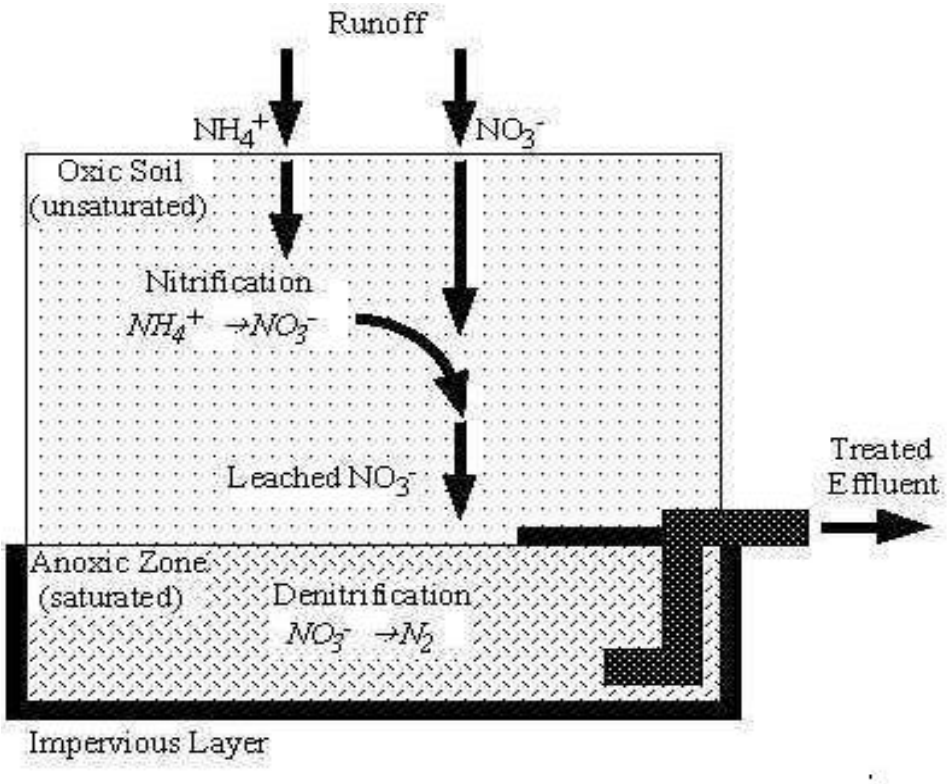

Figure 1. Diagram of Modified Bioretention for Denitrification

This research examines the fate of nitrate in model bioretention systems with a focus on the biological transformation and removal of nitrate. The overall 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 was evaluated for its capacity for nitrate removal via denitrification (Figure 1). In this evaluation, conditions to optimize the denitrification reaction were determined so that design parameters could be established for use in bioretention systems. Thus, the specific objectives of this research were to :

1. Determine (an) electron donor(s) and carbon source(s) that are (is) stable for a long period of time in the subsurface, but do (does) 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. Optimize the system with the electron donor(s) that gave the best nitrate removal efficiency and effluent quality by varying nitrate loading and hydraulic retention time for use in sizing the anoxic zone in a bioretention system.
3. Evaluate the performance of the optimized system under conditions of intermittent loadings, such as are expected in the field.
4. Scale up the optimized condition to a pilot scale bioretention system.

Methodology

The four objectives stated above lead to four experimental phases: (1) electron donor selection and evaluation study, (2) nitrate loading and flow rate study, (3) Study of viability after long dormant periods, and (4) pilot scale bioretention study.

The first task was to screen a variety of potential electron donors using sand columns simulating the anoxic zone and synthetic stormwater runoff. 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; Sikora and Keeney, 1976; Zhang and Shan, 1999).

The substrates were evaluated in three experimental sets: Set #1, alfalfa, newspaper, and leaf mulch compost; Set #2, sawdust, wood chips, and wheat straw, and Set #3, small sulfur/lime, large sulfur/lime, and large sulfur only. The properly cut organic substrates were prepared by cutting and sieving (alfafa, newspaper and wheat straw <4 mm; sawdust, leaf mulch compost and woodchips <2mm) and the inorganic substrate was prepared by sieving ("small" sulfur particles: 0.6 to 1.18 mm, "large sulfur particles: 2 to 2.36 mm, limestone: 0.6 to 1.18 mm). The electron donor substrates were mixed with silica sand and 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 (Figure 2). The total mass of each electron donor substrate required for denitrification was calculated based on the nitrate loading for a 60-day experiment and using the appropriate reaction stoichiometry (McCarty, 1975). 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.

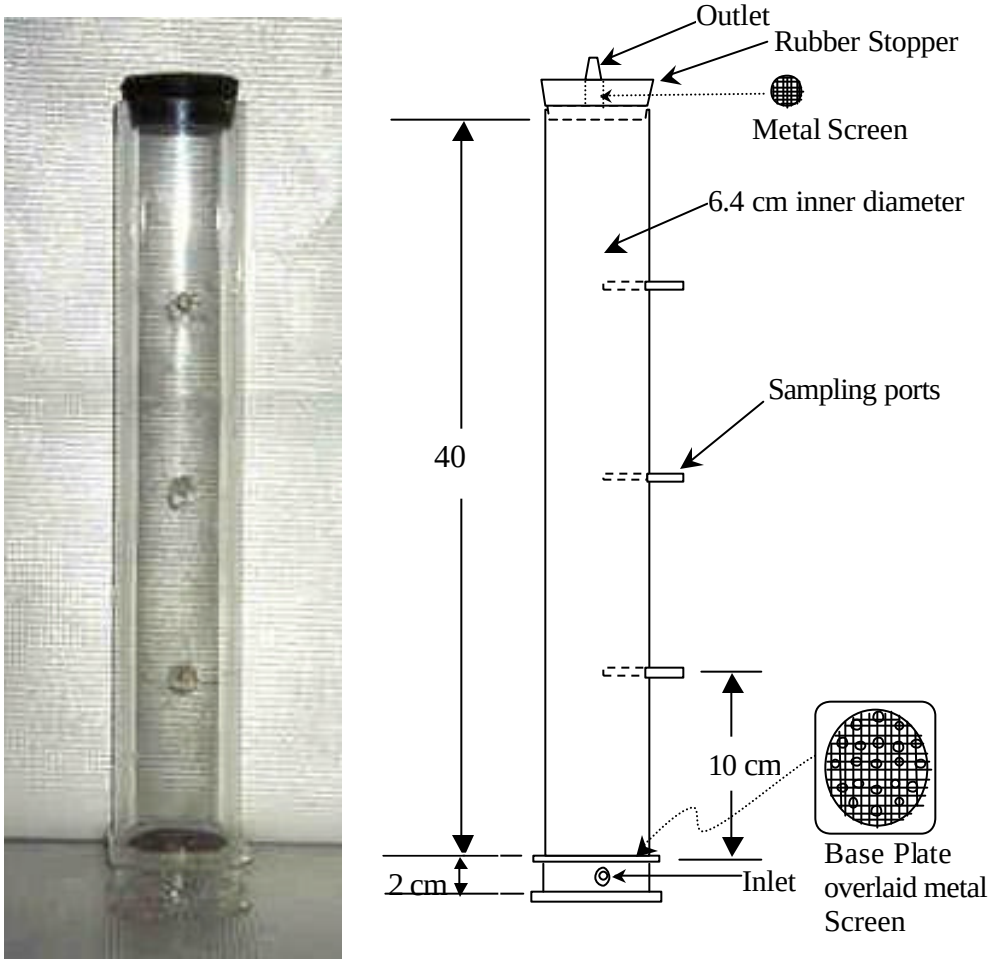

Figure 2. Basic Column Design

A total of 4 columns were set up for each experiment including a control column, which was packed with washed silica sand only. All four columns were operated at room temperature (22 ± 2 °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. After pumping and recycling seed materials through the column for 2 days, 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 using an activated carbon column cartridge and $NaHSO_3$ and continuously purged with N_2 to remove O_2, resulting in influent dissolved oxygen concentrations < 2 ppm.

The second task was to optimize the system with the electron donors that gave the best nitrate removal efficiency and effluent quality by varying nitrate loading and hydraulic retention time. Newspaper, woodchips and "small sulfur" were selected from each of the first phase experimental sets. The basic reactor design (Figure 2) and electron donor material preparation were the same as described above. Four columns (newspaper, woodchips, sulfur and limestone, and sand-only control columns) were set up and run under continuous flow with identical conditions for all four columns. Initially, the columns were run for 37 days at 4.1 cm/hr with approximately 2 mg/L nitrate-N in the influent until those columns showed steady state nitrate removal efficiency. Afterward, variable nitrate loadings and flowrates were studied (Table 1). For each nitrate loading and flow rate, the columns were run until they showed steady state nitrate removal.

Table 1. Influent Nitrate Concentrations and Flow Rates used in Nitrate Loading and Flow Rate Study

Items	*Nitrate Concentraton (mg/L as N)**	*Flow Rate (cm/hr)*	*Column Running Period (day)*
Initial condition	2	4	Day 1-38
Nitrate loading 1	4	4	38-80
Nitrate loading 2	8	4	81-104
Initial condition	2	4	104-108
Flow rate 1	2	6	108-129
Flow rate 2	2	8	129-175
Flow rate 3	2	12	177-196
Flow rate 4	2	20	196-216
Initial condition	2	4	216-225

* The approximate input concentration of NO_3^- -N

The third task was to evaluate the performance of the optimized system under conditions of intermittent loadings. Six columns were set up with newspaper as the electron donor. Under the same environmental and input conditions, all six columns were initially run for 47 days to provide microorganism growth and steady state nitrate removal for sufficient period of time. Two columns (columns # 1 and # 2) were used as control columns that ran continuously throughout the experiment. After confirming steady state nitrate removal for 47 days, the influent feeding to the other columns (columns #3 - #6) were stopped. The water in the reactors was drained out to field capacity. Column #3 - #6 sat for 7 days with opened inlet and outlet ports. Afterwards, these ports were sealed. Columns #3 and # 4 sat for another 23 days for a total dormant period of 30 days. After the dormant period, synthetic runoff was introduced again to

columns #3 and #4. Initial effluent nitrate concentration from the two columns were measured on an hourly basis. Column #5 sat for a total 84-day dormant period. Synthetic runoff was then applied and nitrate in the effluent was measured.

A pilot scale bioretention study was completed in the final task, which was to scale up the column operating conditions. The reactor consisted of a 76 cm long by 40 cm wide plastic box with sufficient depth for up to 36 cm of material and a 10 cm free board (Figure 3). Newspaper was cut to <5cm and added to a sand layer based on the volumetric ratio of the pilot scale bioretention volume to the volume of the columns used in the previous studies. Thus, 75 kg of dried sand was well mixed with 1284 g newspaper and the media was packed to 18 cm high (Figure 3). Next, a plastic liner was emplaced to cover 80% of the sand media surface and prevent the synthetic stormwater runoff from infiltrating in this area. The plastic was subsequently overlaid by an 18 cm high soil layer (Figure 3). A photograph of the complete experimental setup of the pilot-scale bioretention is shown in Figure 4.

After packing the media, a volume of synthetic stormwater runoff equivalent to pore volume of the the bottom sand layer media was introduced to the reactor until water just came out from the effluent tubes. Then, the feeding of synthetic runoff was stopped and the reactor was allowed to sit for 1 day to inoculate the reactor. Denitrifying bacteria in soil were expected to inoculate the sand layer; thus, activated sludge seeding material was not used in this phase. After one day, the first experiment was performed. Synthetic runoff was applied to the pilot-scale bioretention at a flow rate of 4 cm/hr over a 6-hour duration. Two additional experiments were also completed using this box.

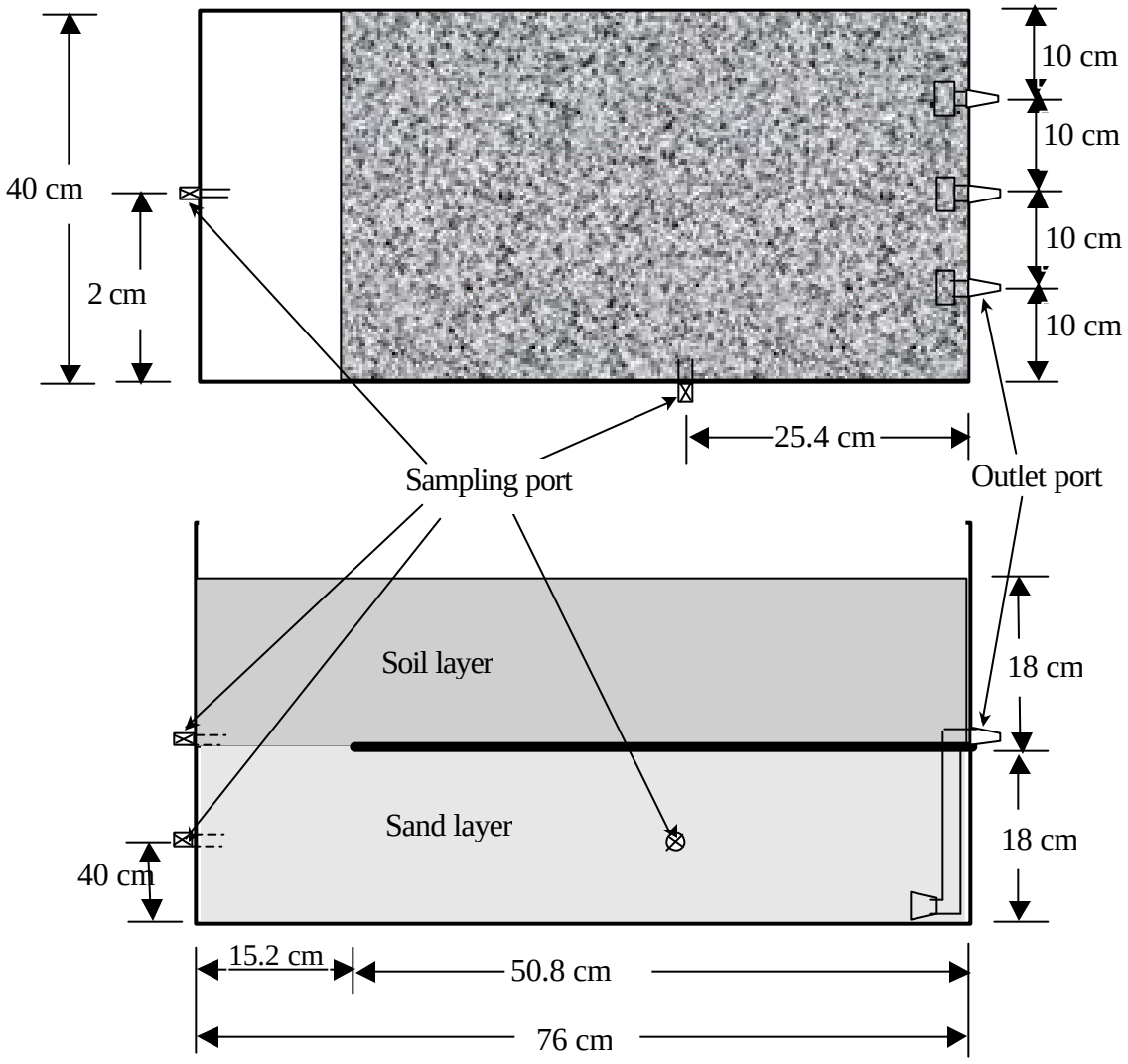

Figure 3. Basic Pilot-Scale Bioretention Design

Nitrate and sulfate concentrations in all samples were quantified via ion chromatography (Dionex DX-100) using a Dionex AS4 anion column. 1.3 mM Na_2CO_3/1.mM $NaHCO_3$ solution was used for the eluent. TKN was measured via Standard Method 4500-N_{org}, Macro-Kjeldahl Method (APHA et al., 1995). Standard Method, 4500-NO_2^- B, colorimetric method (APHA et al., 1995) was used for nitrite

analysis. Absorbance at 543 nm was used to measure nitrite via spectrophotometry (Bausch and Lomb, Spectronic 21). Turbidity was measured using Standard Method, 2130 B, Nephelometric Method via a HACH 200N turbidity meter (APHA et al., 1995). Alkalinity was measured following Standard Method 2320 B, Titration Method (APHA et al., 1995). Dissolved oxygen was measured using Standard Method 4500-06, Membrane Electrode Method (APHA et al., 1995) with an Orion oxygen meter model 860 and Orion DO electrode (Part # 086010) (Orion research, Inc. Beverly, MA). The probe/meter were calibrated before every DO measurement.

Figure 4. Pilot-Scale Bioretention Setup

Principal Findings and Significance

Electron donor selection and evaluation study

Providing an appropriate electron donor is a key environmental factor affecting denitrification. The electron donor for use in promoting denitrification in bioretention should be stable for a long period of time in the subsurface, but still should not limit the denitrification process, which means that it should be a readily metabolizable solid. Furthermore, low cost and ready availability are required from the economic perspective. The column study using various electron donors for denitrification was performed in order to select promising electron donor candidate(s) in bioretention. Ideally, the decomposition rate of the added carbonaceous materials in columns isjust fast enough to accomplish complete reduction of any introduced nitrate to N_2 via the denitrifying process. Excessive decomposition rate of organic material is undesirable because it may be in the extra addition of organic materials in the water, which can cause undesirable effluent water quality such as high TOC, turbidity, color, odor and TKN. Based on the nitrate removal efficiency (Figure 5) as well as the effluent water quality (TKN and turbidity) (Table 2) in these studies, the newspaper from Experimental set #1 and the woodchips from Experimental set #2 were considered to be the best electron donor candidates.

One possible explanation for the high effluent TKN from the alfafa and wheat straw columns is that alfafa 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 alfafa system. 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 highly relative to nitrate availability (Tiedje et al., 1982) as was the case in these relatively short-term columns with relatively well decomposed carbon material such as alfafa and wheat straw. Dissimilatory reduction of nitrate to ammonia is undesirable in bioretemntion because nitrogen is conserved.

In Experimental set #3, only the "small" sulfur particle/limestone combination performed well over the course of the experiment, with 91% nitrate removal during the quasi-steady state period (Figure 5). 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). The results with the "small" sulfur and limestone indicate that sulfur also holds promise as a electron donor for denitrification in engineered bioretention, in particular, with small sulfur particle sizes. Relatively low TKN and turbidity values were found from sulfur/limestone systems compared to those from the previous organic columns, which can hold significant advantages for a bioretention system using denitirfication. Importantly, as discussed by others (Zhnag and Shan, 1999), sulfur is also a relatively inexpensive resource ($0.018/kg, $16/ton). One interesting finding from theses 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 sufficientinoculum 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)

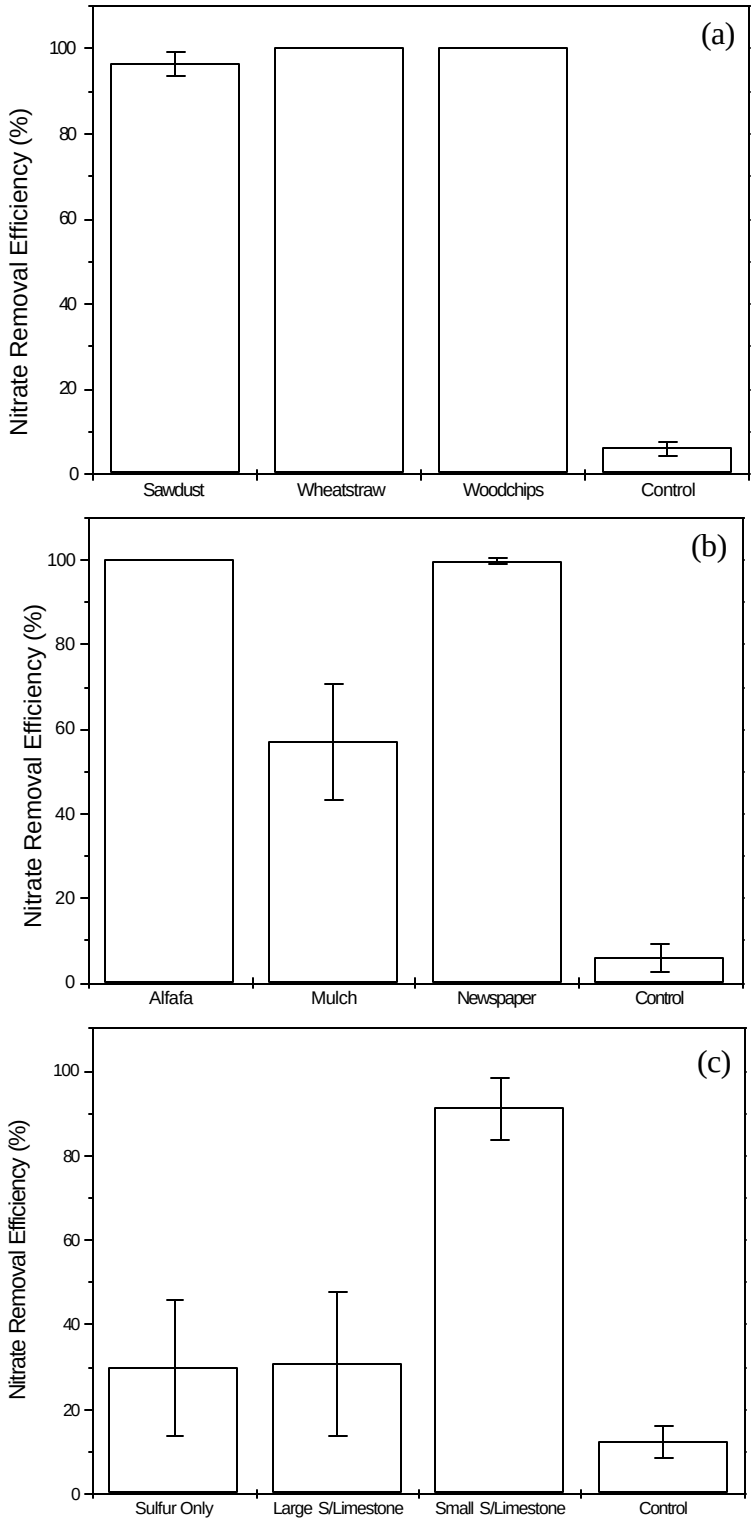

Figure 5. Average Quasi-steady-state Nitrate Removal (%) for the columns (Error bars represents ± standard deviation) (a) Experiemental Set #1 (b) Experiemtal Set #2 (c) Experimental Set #3

Table 2. Effluent Water Characteristics From Electron Donor Selection Study

Set	Column	TKN (mg/L as N)*	Turbidity (NTU)**
#1	Alfafa	2 – 3	27 ± 21
	Leaf Mulch Compost	0.3 – 0.4	0.7 ± 0.19
	Newspaper	0.1 – 0.5	1.8 ± 0.27
	Control	0.1	0.21 ± 0.06
	Influent	0.1	0.24 ± 0.03
#2	Sawdust	0.2 – 0.7	0.75 ± 0.56
	Wheat Straw	0.5 – 1.4	7.3 ± 5.8
	Wood chips	0.3 - 0.5	2.4 ± 1.7
	Control	0.1 – 0.2	0.14 ± 0.03
	Influent	0.1	0.15 ± 0.03

Set	Column	Turbidity (NTU)**	SO_4^{2-} (mg/L)**	Alkalinity (mg/L as $CaCO_3$)**
#3	Sulfur only	0.25 ± 0.02	11 ± 2.0	24.4 ± 1.8
	Sulfur & limestone (Large particles)	0.26 ± 0.26	9.9 ± 1.9	27.6 ± 2.1
	Sulfur & limestone (Small Particles)	0.34 ± 0.34	21 ± 1.93	31.3 ± 2.5
	Control	0.20 ± 0.2	7.6 ± 0.1	27.9 ± 1.3
	Influent	0.20 ± 0.2	7.5 ± 0.12	27.1 ± 0.9

* Range ** Mean ± Standard Deviation

Nitrate loading and flow rate study

Three different ranges of nitrate loadings were studied by changing influent concentrations. Complete removal of nitrate and nitrite was observed at about 2 mg/L as N for all three columns used in this study (newspaper, wood chips and sulfur/limestone). However, nitrogen percent removals for all three columns decreased linearly as the nitrate loading increased. The newspaper column showed the best N removal efficiency at all three ranges of nitrate loadings (Figure 6).

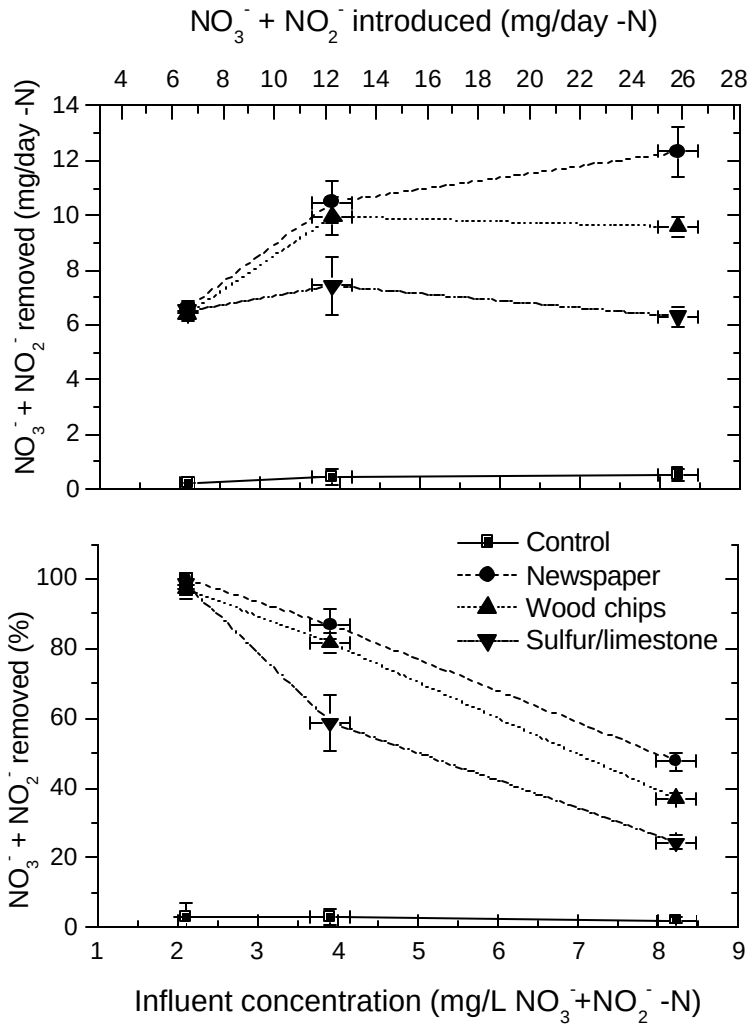

Figure 6. Effect of N loadings on N removal

Interestingly, the trends with respect to the mass of N removed per day for each column as function of the N Loading were was variable. The Nitrate and nitrite mass removed per day increased consistently for the newspaper column as the nitrate influent loading increased, while for the wood chips and sulfur/limestone columns mass removed did not increase when N loading increased from 12 to 26 mg/day as N. This difference is caused by more nitrite accumulation that occurred during denitrification using wood chips and sulfur/limestone. Relatively high nitrite concentrations in the wood chip and

sulfur/limestone columns were observed at influent N loadings of 12 and 26 mg/day as N. This can be explained by a limiting rate of supply of the electron (energy) source and competition between electron transport reductase enzymes for electrons (i.e., competition between nitrate and nitrite reductases) when the electron donor is scarce (Oh et al., 1999).

Five different flow rates were also studied (4, 6, 8, 12 and 20 cm/hr), which correspond to influent nitrate loadings of 6.5, 11.2, 14.0, 22.2, 39.0 mg/day with average influent concentration 2.07, 2.38, 2.24, 2.35, 2.48 mg/L, respectively. The newspaper column showed the best N removal efficiency at all five flow rates (Figure 7). However, significant decreases of nitrate percent removal were observed at the highest flow rate for all three columns (Figure 7). The percent N removals in the wood chips and sulfur/limestone columns decreased more significantly than that of newspaper during the influent loading change from 11.2 to 14.0 (flow rate change from 4 to 6 cm/hr).

Based on the amount of nitrate and nitrite removed per day, there is the optimum flow rate for each electron donor studied at which maximum nitrogen mass removal can be achieved in each column. The significant decrease in the mass removal rate at the higher flow rates can be explained by the washout of bacteria, enzymes or substrates (Volokita et al., 1996).

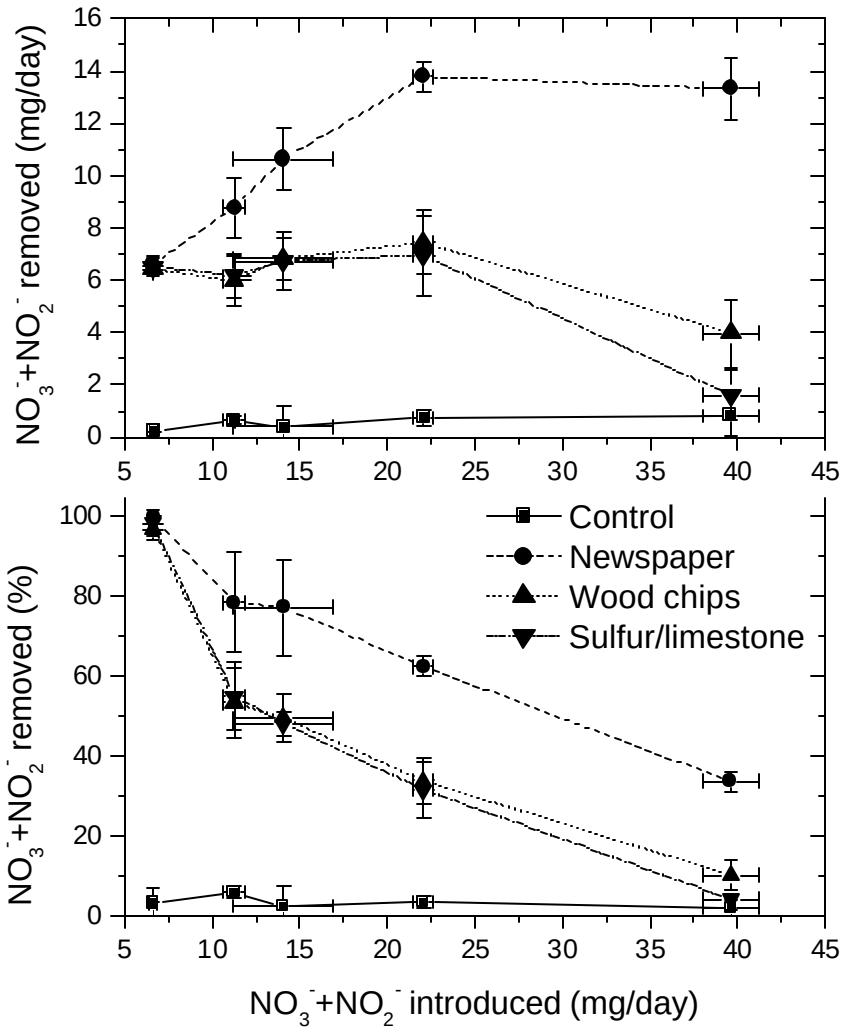

Figure 7. Effect of flow rate on N removal

Study of viability after long dormant period

The initial recovery of columns after two dormant periods, 30 days and 84 days, were studied by measuring initial effluent nitrate concentration. Columns #3 and #4 (30 day dormant period) showed >90% nitrate removal efficiency within 14.5 hours since first effluent came out, while it took 30 hours for Column #5 (84 day dormant period) to reach 90% nitrate removal (Figure 8). These studies demonstrate that bioretention

systems engineered for biological denitrification should work under condition of intermittent loadings by showing fast initial recovery under the extreme dormant periods. Furthermore, after recovery of the dormant columns, steady nitrate removal (>90%) was observed for all the columns. However, it appears that the initial system recovery may increase with increasing lengths of time without nitrate addition.

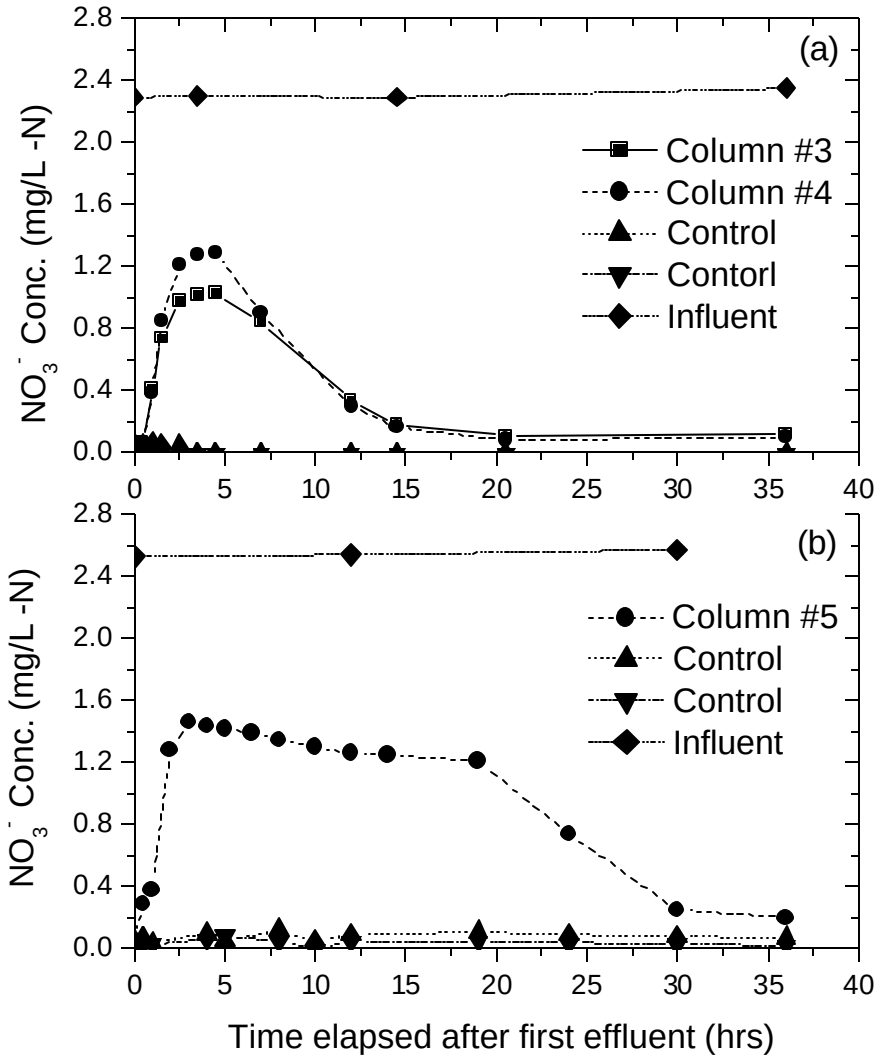

Figure 8. Nitrate concentration during startup after dormant periods: (a) 30 days dormant, and (b) 84 days dormant

Pilot scale bioretention study.

The first experiment using a pilot scale bioretention did not showed any nitrate removal, which may be due to insufficient inoculation time for microorganisms. The second experiment, a week after first experiment, demonstrated approximately 80% nitrate and nitrite removal. No nitrate (<0.02 mg/L as N) or nitrite (<0.01 mg/L as N) were observed in treated effluent until 2.5 hrs after beginning the experiment because the water which had been introduced from the first experiment and sat for a week in the reactor was flowing up to that time (Figure 9). The third experiment, 37 days after the second, showed around 65% nitrate and nitrite removal. The decrease of nitrogen removal in the second experiment may be because of dormant period effects. One interesting finding in these experiments is that a suitable inoculum for denitrification was achieved via the soil and sand in the reactor, without addition of specific inoculum materials.

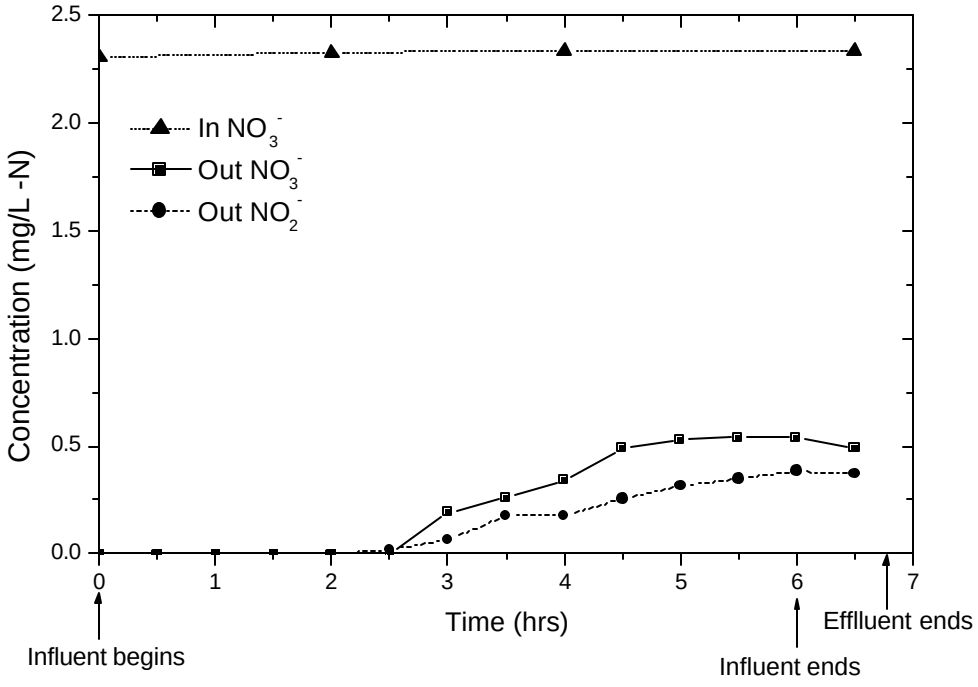

Figure 9. NO_3^- and NO_2^- Concentrations for the Second Pilot Scale Experiment

Summary

Column and pilot scale studies have been completed examining the removal of nitrate from synthetic stormwater runoff and evaluating the re-engineered concept of bioretention, which incorporates a continuously submerged anoxic zone with an overdrain, for its capacity for nitrate removal via denitrification. Based on the four phase of these investigations, engineered bioretention for removal of nitrogen from stormwater runoff can be applied to urban stormwater treatment practice and should be effective for nitrate removal from the stormwater runoff.

The results of first phase of experiments (electron donor selection and evaluation study) indicate that on the basis of nitrate removal efficiency as well as the effluent water quality (TKN and turbidity), the newspaper from Experimental set #1 and the woodchips from Experimental set #2 are the best electron donor candidates for supporting denitrification. In addition, throughout the second phase of experiments (nitrate loading and flow rate study), the newspaper showed better N removal efficiency than wood chips and sulfur/limestone at all three ranges of nitrate and at all five flow rates. This suggests that newspaper is overall the best electron donor substrate out of the set studied.

Studies of viability after long dormant periods (30 and 84 days) demonstrate that a bioretention system engineered using newspaper as an electron donor for biological denitrification should work under conditions of intermittent loadings. Specifically, fast initial recoveries were observed after extreme dormant periods, with a return to >90% nitrate removal efficiency within 14.5 hours after a 30 day dormant period and within 30 hours after a 84 day dormant period. Finally, pilot-scale bioretention studies confirmed

the effectiveness of the proposed design to reengineer bioretention, showing nitrate and nitrite removals of up to 80%.

Overall, this study demonstrates the effectiveness of the re-engineered concept of bioretention, which incorporates a continuously submerged anoxic zone with an overdrain, for nitrate removal via denitrification. The nitrate removal capacity shown in this study coupled with the metal removal shown in previous study by Davis et al(2001) illustrates the great potential for pollutant removal in engineered bioretention systems. Further study is needed to refine the design for better nitrate removal (i.e., amount of electron donor addition effect on denitrification).

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Basic Information

Title:	Multi-faceted Investigation of Arsenic Biogeochemistry
Project Number:	02-98
Start Date:	9/1/1998
End Date:	8/31/2000
Research Category:	Water Quality
Focus Category:	Geochemical Processes, Toxic Substances, Water Quality
Descriptors:	Arsenic, geochemistry, orpiment
Lead Institute:	University of Maryland
Principal Investigators:	Allen P. Davis, Alba --- Torrents, Oliver Hao

Publication

1. Floroiu, R. M., O. J. Hao, A. P. Davis, and A. Torrents. "Removal of arsenic As(III) from aqueous solutions in the presence of arsenic reducing bacteria," 220th ACS National Meeting, Washington, D.C., August 20-24, 2000. (Extended Abstract only)

Multi-Faceted Investigation of Arsenic Biogeochemistry:
Chemical Transformation of Arsenic

1) Research Objectives

Many sulfide minerals, including orpiment (As_2S_3), arsenopyrite (FeAsS), and realgar (As_2S_2), are disposed under reducing conditions with mill tailings, either as waste products or as unrecovered ore minerals (McCreadie *et al.*, 2000). However, if these sulfides are exposed to oxidizing environments, they undergo redox reactions during the weathering process and therefore become unstable. The products of metal sulfide oxidation are of environmental concern because the acids of S that are formed may lead to acidic drainage at mine sites. The leaching of arsenic from these minerals is hazardous to biota, which are sensitive to high levels of As, especially aqueous arsenite, considered as being the most biologically toxic and soluble form of arsenic found in the environment (Nesbitt *et al.*, 1995). There are therefore, practical reasons to understand how the redox products of these sulfide minerals are formed since their transformations can have major implication in the management of large volumes of reducing environments high in arsenic and sulfides.

This part of the project concentrates on elucidating chemical pathways in the transformation of As_2S_3 to oxidized arsenic and sulfur species under different environmental conditions. These species exist as final or intermediate products resulting from possible orpiment reactions under varying factors such as pH and O_2 and Fe(III) levels. As(III) and As(V) represent the major arsenic species of interest, whereas sulfate, sulfide, thiosulfate and elemental sulfur are the potential sulfur species in the system. The overall goal is to extend our knowledge on the effects of mineral surface weathering and redox transformations of orpiment, to obtain insight into processes effective during oxidative dissolution, and to understand ways to possibly halt the dissolution and release of potentially toxic constituents to solution. Therefore, two specific objectives were pursued in order to reach this goal: 1) investigate the likely factors (e.g., pH, dissolved oxygen, Fe(III)) and mechanisms (dissolution and/or oxidation) involved in dissolving arsenic from orpiment; and 2) identify the products resulting from orpiment dissolution and determine the speciation of the arsenic and sulfur released from the mineral in aqueous solution under different conditions in order to describe the reactions that govern the orpiment chemistry.

From the literature it is known that: 1) orpiment dissolution shows a pH dependency where greater arsenic is dissolved at higher pH; 2) orpiment undergoes leaching in the presence of air and therefore dissolved oxygen is a primary oxidant for orpiment; and 3) Fe(III) was found to improve the rate of arsenopyrite dissolution when added to the mineral (Breed *et al.*, 1997). Therefore, a series of systematic experiments are conducted at pH values ranging from 2 to 8 for a specific As_2S_3 concentration under anaerobic conditions, aerobic conditions, and/or in the presence of Fe(III) to evaluate the dissolution and oxidation rates of orpiment.

2) **Methodology**

All dissolution experiments were conducted in a 250 mL glass beaker representing the reaction vessel. Openings were cut through the vessel lid to permit sample extractions, pH and temperature measurements, and oxygen or nitrogen gas bubbling. A magnetic stirrer apparatus provided the mixing. An Accumet Model 25 Fisher Scientific pH meter was used to continuously record the solution pH throughout the experiments, performed at 25°C.

The effect of pH on the dissolution of orpiment (As_2S_3) was explored for a period of 8 hours. At the beginning of each experiment, the 200 mL experimental solution contained 0.02 g As_2S_3 (from Acros Organics-Fisher Scientific) (~ 60 mg As/L, ~ 40 mg S/L) and an ionic strength of 5×10^{-3} M NaCl or $NaClO_4$. Aeration with nitrogen gas (anaerobic conditions) or oxygen (aerobic conditions) was begun at least ½ hour prior to the addition of the solid orpiment in order to achieve gas transfer equilibrium. During this time, pH adjustments were made with 0.1 M HCl or 0.1 M NaOH for each kinetic experiment to fix the solution pH, ranging from 2 to 8. The pH was held constant over the kinetic run by addition of acid/base. Once the desired experimental conditions were achieved and the solid was added to the solution, samples were taken immediately (time = 0 hrs.), then every half an hour for the first two hours (time = 0.5, 1.0, 1.5, and 2.0 hrs.) and then every 2 hours for the remainder of the run (time = 4, 6, and 8 hrs). Samples were immediately filtered using a 0.2 μm Gelman membrane filter with a 25 mm easy pressure syringe filter holder (Gelman Sciences) into sealed polystyrene tubes. Approximately 5-mL of the filtered sample were used for the analyses of arsenic and sulfur species.

To obtain greater detail on the oxidative dissolution of orpiment, the reaction was also studied in the presence of Fe(III). Two initial $FeCl_3$ concentrations (5×10^{-3} and 5×10^{-4} M) were tested at pH 2, 3, and 8. A range of several Fe(III) concentrations will be tested in future experiments.

Total soluble arsenic and arsenic species (As(III), As(V)) concentrations were determined by using flow injection hydride generation atomic absorption spectrophotometry (FIA-HGAAS). An atomic absorption spectrophotometer (Perkin Elmer, Model 5100 ZL) was used in conjunction with hydride generation based on a modified method for As measurements (APHA *et al.*, 1995). The T-shaped quartz absorption tube heated at 925°C was used as the atomization cell. The sample, collected by the arm of an autosampler, 6 N HCl, and sodium borohydride (0.05 M $NaBH_4$/0.12 M NaOH) were combined and followed by a gas-liquid separator from which arsine gas (AsH_3) was swept into the AAS cell by argon carrier gas. The optimum reagent concentrations for the generation of arsenic hydride are 6 M HCl and 0.2 % $NaBH_4$. The detection level for total arsenic was < 0.1 μM and linear through 0.3 μM.

Speciation of arsenic (arsenite and arsenate) was analyzed by a method based on selective retention of arsenic species on specific solid-phase cartridges (Le *et al.*, 2000). A silica-based anion-exchange cartridge (500 mg sorbent of 40 μm particle size and 60 A

pore size, Supelco) retained As(V) from the sample. Before use, the cartridges were preconditioned with 50% methanol and deionized water. The unretained arsenic in the effluent solution was collected in a polyethylene tube for FIA-HGAAS analyses as a measure of As(III) in the original sample. As(V) was eluted from the cartridge using 2 mL of 1.0 M HCl and 2 mL of eluting buffer. As(V) concentrations were determined by FIA-HGAAS and the values were verified by the difference between the total arsenic concentrations and the As(III) concentrations for the same sample passed through the cartridge.

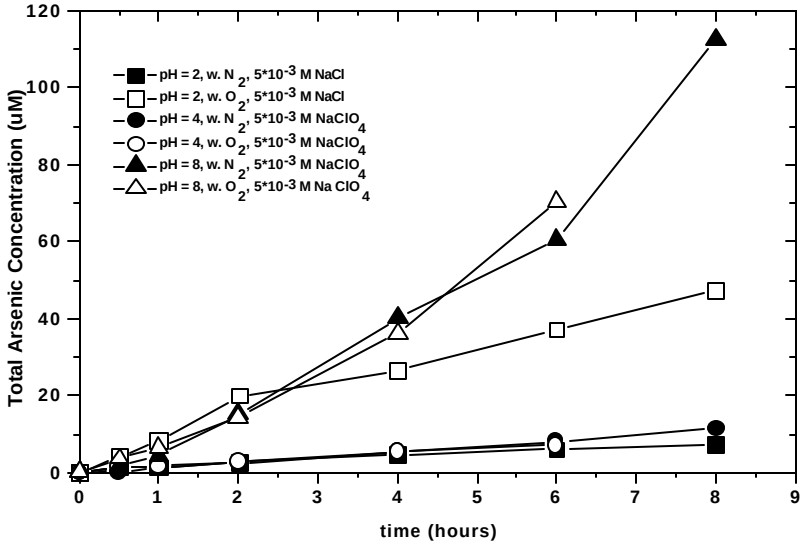
Samples were analyzed for dissolved sulfide S(-II) through photometric color measurement (UV-vis, Shimadzu) using the methylene blue method (APHA *et al.*, 1995). In the presence of *N*, *N*-dimethyl-*p*-phenylenediamine oxalate and ferric chloride, sulfide forms methylene blue. The absorbance is measured at a wavelength of 670 nm with a 1-cm cell. The detection limit was < 3 μM S and linear through 60 μM S.

Samples were analyzed for sulfate (SO_4^{2-}), sulfite (SO_3^{2-}) and thiosulfate ($S_2O_3^{2-}$) by ion chromatography with a Dionex DX-100 integrated ion chromatograpy (IC) system coupled to a suppressed conductivity detector and equipped with a Wescan Anion/R column (100×4.6 mm). The mobile phase was 1.7 mM sodium carbonate/1.8 mM sodium bicarbonate in 0.3 mM p-cyanophenol solution, employed at a rate of 2.5 mL/min. The detection limit was < 1.0 μM sulfur species.

3) Principal Findings and Significance

i) *Anaerobic conditions*. The total arsenic concentration is analyzed after 8 hours at 100 mg As_2S_3/L (~ 60 mg As/L or ~ 800 μM) in the presence of nitrogen. For each of the pH values analyzed, the dissolved total arsenic concentration slowly increases with time. After 8 hours of anaerobic reaction, less than 1% of the total arsenic input is dissolved in solution at pH 2, about 1% at pH 4, and approximately 7% at pH 8 (Figure 1). The faster rate at higher pH is expected since As_2S_3 is more soluble at higher pH.

Figure 1. Anaerobic/Aerobic release of As into Solution from As_2S_3.

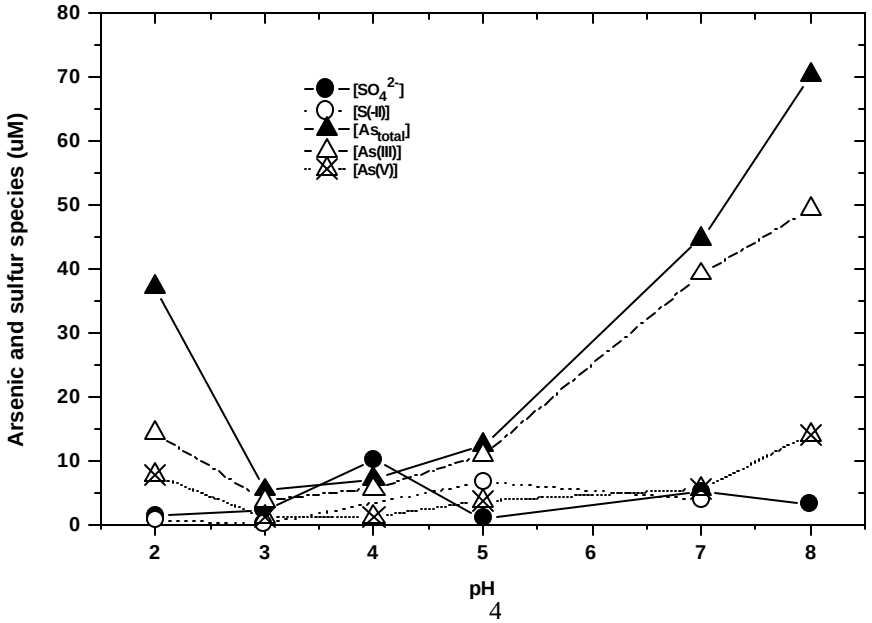


The sulfur molar ratio, [Total $S_{dissolved}$/Total $As_{dissolved}$] decreases as pH increases. The theoretical stoichiometric value for this fraction is 1.5. The sulfur species included in Total $S_{dissolved}$ are SO_4^{2-} and S(-II); greater [S(-II)] than [SO_4^{2-}] values are detected over the pH range studied. In the case of arsenic species, both molar ratios [$As(III)_{dissolved}$]/[Total $As_{dissolved}$] and [$As(V)_{dissolved}$]/[Total $As_{dissolved}$] have constant value at pH 2 through 8. Most of the dissolved arsenic was As(III), but some As(V) was detected.

ii) *Aerobic conditions.* Under aerobic conditions, similar [Total $As_{dissolved}$] results with those performed under N_2 conditions are observed at pH 4 and 8. However, at pH 2 there is a significant increase in arsenic release in the presence of O_2 as compared with results with no O_2. At pH 2, less than 1% of total arsenic is dissolved in solution after 6 hours of anaerobic reaction, whereas about 5% [Total $As_{dissolved}$] is detected in the presence of O_2. Since more arsenic is released in the presence of O_2 than in the presence of N_2 at pH 2 and no O_2 contribution is observed at higher pH values, it is suggested that oxygen can have an influence on the release of arsenic from As_2S_3 only under very acidic conditions (Figure 1).

The predominant dissolved arsenic species over the entire pH range studied is the arsenite, As(III). The trend of [$As(III)_{dissolved}$] follows closely the one of [Total $As_{disolved}$] with the exception of the extreme pH values, where lower values are observed. At pH 2, 3% of initial As_2S_3 concentration is in the As(III) form as compared to 5% for [Total $As_{dissolved}$] and at pH 8, 6.2% of the initial orpiment input is in the arsenite form as compared to 9% found as [Total $As_{dissolved}$].

Figure 2. The effect of pH on As_2S_3 dissolution at time = 6 hours.



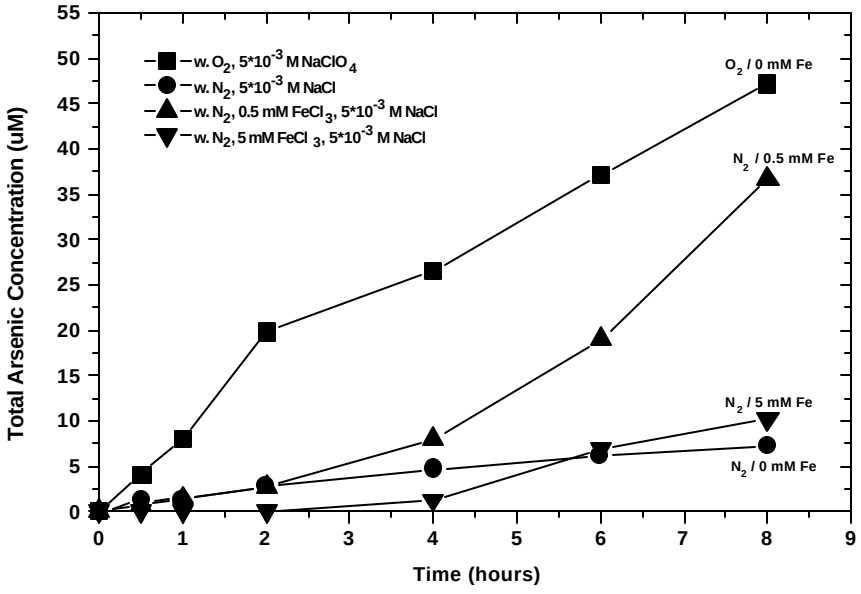
Arsenate was found in much lower concentrations than As(III) but following similar dependency with pH. For the pH range 2-8, [As(V)] released from the orpiment dissolution is 1%. Arsenate is found because part of the arsenite that is initially dissolved from the orpiment undergoes an oxidation from the dissolved oxygen (Figure 2).

The arsenic molar ratio $[As(III)_{dissolved}]/[Total\ As_{dissolved}]$ increases slowly until pH 5 and then decreases when pH is 8. However, the arsenic molar ratio $[As(V)_{dissolved}]/[Total\ As_{dissolved}]$ shows a roughly constant trend.

Under the pH range studied in the presence of O_2, sulfate and sulfide are the detected sulfur species. Thiosulfate ($S_2O_3^{2-}$) and sulfite (SO_3^{2-}) were tested as possible sulfur species but their concentrations have been found to be insignificant (at least two order of magnitude lower then $[SO_4^{2-}]$ and [S(-II)]) and therefore are not considered as contributing to the sulfur mass balance in the systems studied. Under aerobic conditions the molar ratio, $[Total\ S_{dissolved}/Total\ As_{dissolved}]$ increases when pH increases, which is the opposite trend observed under the anaerobic conditions.

iii) *Fe(III) Addition.* An initial concentration of 5×10^{-3} M $FeCl_3$ seems to inhibit the release of arsenic in solution in the first 2 hours of reaction and only 1.3% of the orpiment concentration is found in solution after 8 hours at pH 2. The same Fe^{3+} concentration tested in an experiment at pH 4 leads to no detection of any arsenic or sulfur species because of low iron solubility at this pH. Therefore, a lower iron concentration of 5×10^{-4} M Fe^{3+} (as $FeCl_3$) was tested, which enhanced the dissolution of orpiment at pH 2. However, oxygen remains a better oxidant than Fe^{3+} under the tested conditions for As_2S_3 dissolution (Figure 3). The importance of the pathway involving oxidation of orpiment by Fe^{3+} is clearly dependent upon the concentration of Fe^{3+}.

Figure 3. Effect of O_2 and Fe(III) oxidants on As_2S_3 dissolution at pH = 2.



Arsenite and arsenate are both detected in solution when 5×10^{-4} M Fe^{3+} is reacted with As_2S_3 at low pH. Approximately 40% of the total arsenic dissolved at pH 2 is present as As(III), but 27% of As(V) is also observed after 8 hours of reaction under anaerobic conditions. The difference in the arsenic mass balance could be accounted for by possible arsenic-sulfide species such as $HAs_3S_6^{x-3}$ that are formed in solution (Helz *et al*., 1995) but not detected by the speciation method used. Under both pH values studied in the acidic region there is appearance of As(V) in solution over the entire reaction time. An examination of the redox potentials shows that Fe(III) should oxidize As(III) and perhaps this is the cause of dissolved arsenate (Barett *et al*., 1993). Overall, arsenic species are more readily oxidized than sulfur species during the reaction of orpiment with ferric iron. The arsenic species molar ratios, $[As(III)_{dissolved}]/[Total\ As_{dissolved}]$ and $[As(V)_{dissolved}]/[Total\ As_{dissolved}]$ have constant values and do not demonstrate changes with pH over time studied.

With iron addition it is found that sulfate is the dominant sulfur product present in solution. S(-II) and SO_3^{2-} were detected at concentrations less than an order of magnitude than the $[SO_4^{2-}]$ values, and therefore these species are considered as being negligible. In comparison with O_2, the presence of iron improves the sulfur molar ratio, $[Total\ S_{dissolved}/Total\ As_{dissolved}]$ at acidic pH.

Current work has shown that three types of reaction mechanisms can be proposed for the As_2S_3 dissolution: the pH-dependent solubility-controlled dissolution of orpiment, an oxidation via O_2 that enhances the dissolution under acidic conditions, and an increase in orpiment dissolution at pH < 4 in the presence of iron. The stoichiometric ratios of the end products in the orpiment transformation depend on pH and the type of oxidizing agent (oxygen or Fe^{3+}).

Overall, it is possible that under environmental conditions predominant in mine tailings (very low pH values), the transformation of orpiment is an oxidation process, whereas under higher pH values arsenic release is a pure dissolution process. Moreover, it can be concluded that O_2 is an important orpiment oxidant under very acidic conditions.

From preliminary tests it is observed that the rate of total arsenic concentration in solution depends on several factors:

$$d[Total\ As_{disolved}]/dt = f([H^+], [O_2], [As_2S_3], [Fe^{3+}])$$

Future work will concentrate on examining the kinetics of dissolution of orpiment that will help in proposing a reaction mechanism for $As_2S_3(s)$ transformation in solution.

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Le, X. C., Yalcin, S., and Ma, M. (2000) "Speciation of Submicrogram per Liter Levels of Arsenic in Water: On-Site Species Separation Integrated with Sample Collection," *Environ. Sci. Technol.*, **34(11)**, 2342-2347.

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Information Transfer Program

Basic Information

Title:	Pharmaceuticals Course and Graduate Assistantships
Start Date:	3/1/2000
End Date:	2/28/2001
Descriptors:	Pharmaceuticals, Riparian Zones, Total Maximum Daily Load, Intensive Grazing
Lead Institute:	University of Maryland
Principal Investigators:	George R. Helz, Philip Kearney

Publication

1. Adelson, Jordan, George Helz and Cherie Miller (2001) Using sedimentary molybdenum to chronicle modern coastal anoxia. Geochim. Cosmochim. Acta 65, 237-252.
2. Rock, Melanie, George Helz and Bruce James. (2001) Hydrogen peroxide effect on chromium oxidation state and solubility in four diverse, chromium-enriched soils. In press, Environ Sci. Tech,

INFORMATION TRANSFER PROGRAM

Lectures from the course entitled: Pharmaceuticals in the Environment were televised to 2 other sites in the University of Maryland System. Audiotapes were prepared of the 13 invited speakers for the course . These tapes may be an effective educational tool, and provide good overviews of the speakers areas of expertise. Editors for the American Chemical Society, Journal Environmental Science and Technology, have reviewed some of the tapes for preparation of a feature article some time this fall.

The Center funded three summer assistantships for 2001. These projects, students and advisors participating in this program were: Evaluating the Influence of Diverse Riparian Leaf Litter of Stream Food Webs, Christopher M. Swan, Advisor - Dr. Margaret Palmer, Department of Biology; A Status Report on the Ability of Maryland's Total Maximum Daily Load (TMDL) Program to Reduce Nonpoint Source Pollution to Meet the States Water Quality Standards, Michelle Perez, Advisor - Advisor - Matthias Ruth, School of Public Affairs; and The Impact of Management Intensive Grazing on Nutrient Losses to Ground and Surface Waters, Rachel E. Gilker, Advisor - Ray R. Weil, Department of Natural Resources and Landscape Architecture. The students are required to provide a two page progress report on their projects in September 2001. These reports will be distributed to interested State personnel.

USGS Summer Intern Program

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	2	0	0	0	0
Masters	1	0	0	0	0
Ph.D.	2	0	0	0	0
Post-Doc.	0	0	0	0	0
Total	5	0	0	0	0

Notable Awards and Achievements

The Maryland Water Resources Research Center was awarded a grant from the Joint Institude for Food Safety and Applied Nutrition (JIFSAN) of $5,000 for travel of speakers to present lectures in a course entitled Pharmaceuticals in the Environment. This course, like others in the past, were funded in part from 104 funds.

Publications from Prior Projects