

**Auburn University Environmental Institute
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Introduction

Within any state, the range and complexity of water-related issues, problems, and opportunities are daunting. Alabama is no exception and, consequently, an organization striving to enhance water must identify key goals and design approaches that include as many layers of disciplinary expertise as each particular issue requires. The Alabama Water Resources Research Institute reflects a broad array of expertise; however, the power of that expertise is restricted unless it is framed within the context of a flexible, yet guided, approach.

As human activities have increased in Alabama and the southeast, levels of contaminants in surface and ground water have risen accordingly. Similarly, the hydrology of streams and rivers has been modified (both intentionally and unintentionally) by extraction of water for cities and agriculture, as well as impoundments for recreation and other purposes. As a result, both water quality and quantity issues have increased. Beyond these cumulative impacts, water and other resources along our coastline are also under direct, localized pressures from increased urbanization and other land uses that apply additional burdens on water resources quality.

The project synopses provided in this report describe research conducted in the areas of water quality, stormwater nutrient removal, and destruction of emerging contaminants.

Research Program

Investigating the Role of Surface-Groundwater Interactions on Surface Water Quality

Basic Information

Title:	Investigating the Role of Surface-Groundwater Interactions on Surface Water Quality
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Principal Investigators:	Cevza Melek Kazezyilmaz-Alhan, Prabhakar T. Clement

Publication

1. Hogan, M. B., Understanding the flow and mixing dynamics of saline water discharge to coastal aquifers, MS Civil Engineering Thesis, Auburn University 2007
2. Hogan, M. B., R. R. Goswami, K. G. Villholth, T. H. Illangasekare, and T. P. Clement, Understanding the Flow and Mixing Dynamics of Saline Water Discharge into Coastal Freshwater Aquifers, Proceedings of the SWIM/SWICA joint meeting, Sardinia, Italy, September 25-29, 2006.
3. Clement, T. P., R. R. Goswami, M. Hogan, Understanding the Dynamics of Freshwater and Saltwater Mixing Processes in Unconfined Aquifers - Laboratory Scale Model Results, Proceedings of the International Conference on MODFLOW and More 2006 Managing Ground Water Systems, Golden, Colorado, May 2006, P. 16-17.
4. Goswami, R. R. and T. P. Clement, Laboratory-scale Investigation of Saltwater Intrusion Dynamics, Water Resources Research, Vol. 43, W04418, doi:10.1029/2006WR005151, 2007.

INVESTIGATING THE ROLE OF SURFACE-GROUNDWATER INTERACTIONS ON WATER QUALITY

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A. PROBLEM STATEMENT AND OBJECTIVES

In the state of Alabama, most of the population obtain their water supply from a combination of surface water and groundwater sources. Therefore, it is important to understand and solve the problems related to groundwater-surfacewater interactions. In recent years, there has been a growing interest in understanding the mechanisms involved in surfacewater/groundwater interactions since researchers have established that these interactions play a crucial role in controlling the behavior of contaminant transport in both systems. Surface/groundwater interactions can influence the downstream water quality significantly since the concentration distribution in both systems (stream or groundwater) can change due to the biogeochemical reactions that occur between the minerals/nutrients in the subsurface and the stream. In this project, we completed both theoretical and experimental investigations to quantify the contaminant exchange patterns between surfacewater and groundwater. The theoretical analysis was designed to measure the lateral path of a contaminant plume as it interacts between the surfacewater and groundwater along the flow path. Laboratory-scale experiments were completed to demonstrate the existence of a vertical transport pathway for a contaminant plume in the stream as it interacts with the subsurface water beneath it.

Recent natural disasters such as Katrina and the Asian-tsunami have created a need for understanding saline surfacewater transport into unconfined groundwater systems after a large inundation event. Therefore, in addition to studying the traditional stream-groundwater interaction pathways, we also explored the interactions between coastal surfacewater and groundwater during a hurricane-induced flooding event. Hurricane surge waves and tsunamis have the potential to inundate large areas of coastal aquifer region with saline water. Estimating the impacts of these flood waters on groundwater quality is a part of any disaster management program. Our second objective was to conduct multiple experiments to quantify the contaminant transport processes and associated times scales within a coastal unconfined aquifer after an inundation event. Controlled experiments were completed by discharging a surge wave over an unconfined aquifer. Observations were made to study the fate of the dense surfacewater as it migrated across the water table boundary.

B. RESEARCH METHODOLOGY AND RESULTS

B.1. Experimental setup to study groundwater stream interactions

To observe the vertical flow between surface water and hyporheic zone which lies under the streambed, we built a straight stream by using the small-scale plexi-glass model. We filled the plexi-glass model with uniform silica sand to represent the porous media and developed a straight channel cross-section within the material with a constant depth and cross-sectional area to simulate a stream segment shown in the schematic (see Figure 1). In this setup, we first maintained a constant flow rate at upstream and then injected a dye beneath the channel. We observed the vertical path of the dye within the streambed. We observed the path of the tracer as it was transported vertically within the stream bed. All of these conceptual experiments were completed to demonstrate the vertical exchange processes which were hypothesized in our theoretical model.

B.2. Experimental setup to study groundwater and coastal water interactions

Saline surfacewater flooding experiments were conducted in a rectangular flow tank. The tank was constructed using 6 mm thick Plexiglass™. The internal dimensions of the porous media region are: 53 cm (length) × 2.7 cm (width) × 30.5 cm (height). A conceptual diagram of the experimental setup is

shown in Figure 2. The flow tank was divided into three distinct chambers: a central flow chamber containing the porous medium, and two constant head chambers containing salt and fresh waters. The constant head chambers are 5 cm long and are separated from the porous media chamber by two fine screens of mesh size US # 16. Uniform silica beads of average diameter 1.1 mm, obtained from Potter Industries Inc., were used as the porous medium. Self-adhesive measurement tapes were pasted on the sides and at the bottom of the tank to allow direct measurements. The experiments were recorded using Nikon Coolpix digital camera in a high resolution mode. The digital data allowed us to zoom and observe small-scale variations occurring at the millimeter scale.

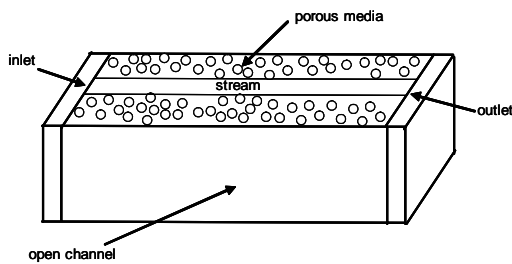


Fig 1. Experimental setup to study stream/GW interactions

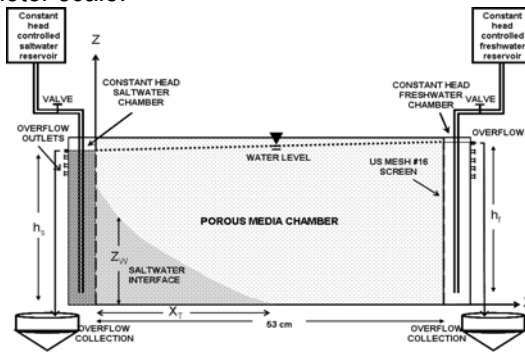


Fig 2. Experimental setup to study coastal-water/GW interactions

B.3. Results of the theoretical investigation

For steady state open channel flow over a permeable bed, there is an open channel – groundwater interaction mechanism for interface flow. This analysis should be considered as an order of magnitude analysis until more complete modeling and experimental verification is completed. For small vertical flow velocities it can be assumed that the variation of $y(x)$ in the surface water defines the head variation in the ground water. Thus, Darcy's law for the groundwater flow and the gradually varied flow equation for open channel flow can be expressed in terms of $y(x)$

$$q = -K \frac{dh}{dx} = -K \frac{dy}{dx}, \text{ Darcy's law.}$$

$$\frac{dy}{dx} = \frac{S_0 - S_f}{1 - F^2}, \text{ the gradually varied flow equation for open channel flow.}$$

$$F = \frac{v}{\sqrt{gy}} = \text{the Froude number.}$$

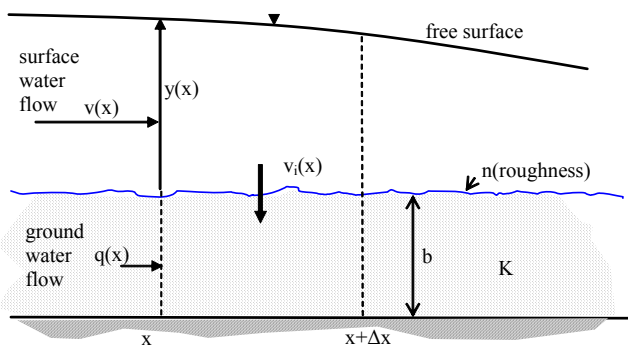


Figure 3. Surface and Ground Water Interaction: $y(x)$ = surface water depth, b = subsurface aquifer thickness, $v(x)$ = surface water velocity, $q(x)$ = subsurface Darcy velocity, $v_i(x)$ = surface transfer velocity, K = aquifer hydraulic conductivity, n = Mannings roughness coefficient for the open channel.

The preliminary laboratory data collected in this study have indicated the type of interface flow hypothesized in our theoretical analysis. This data is shown in Figure 4 below.

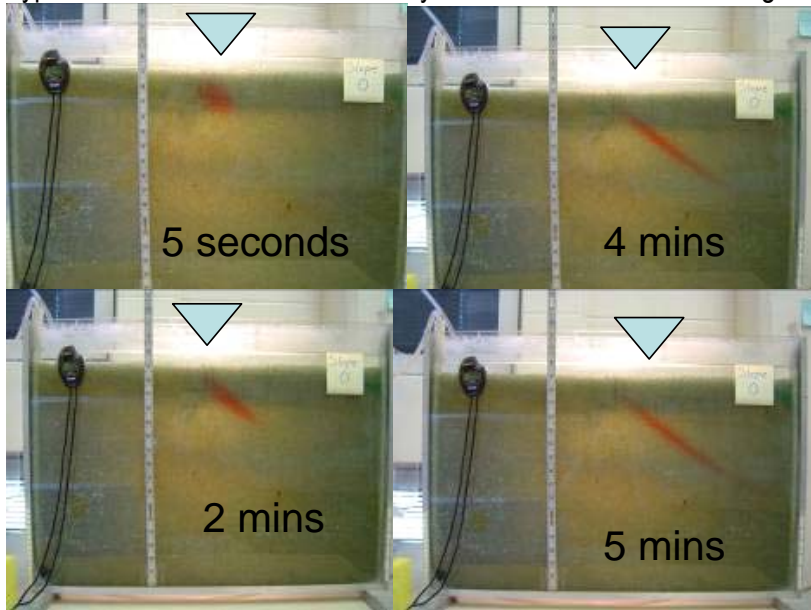


Figure 4. Laboratory data indicating vertical velocities induced by surfacewater flow

For open channel, steady state flow, the depth variation, $y = y(x)$ is nonlinear. Darcy's law for the subsurface flow indicates that $q = \text{constant}$ if the $y(x)$ is linear. Thus, q is not constant which implies there must be some interface velocity between the surface water and the groundwater. Preliminary analysis indicates that this interface velocity is small and it can be either positive or negative describing flow from or into the ground water formation. Preliminary laboratory experiments have shown vertical flow velocity in porous media below the free surface flows. Enhanced physical-chemical modeling of contaminant transport between the surface and ground water depends on further quantification of laboratory and analytical descriptions of the scale of this interface transport velocity. For subcritical flow $F < 1$, and the further constraint that $v \ll (gy)^{0.5}$, then $1-F^2 \rightarrow 1$. This limiting case then can be analyzed to obtain an approximate method to explain a mechanism of surface water (open channel flow) and ground water flow under the channel bed. For these constraints two approximate expressions for interface flow can be derived.

Case 1: For horizontal channel: ($S_0 = 0$)

$$v_i = \frac{\left(bK\alpha^2 \frac{10}{3} \right)}{y^{23/3}}$$

Case 2: For a channel with constant bed slope, $S_0 \neq 0$,

$$v_i = -bK\alpha \frac{10}{3} y^{-13/3} (S_0 - \alpha y^{-10/3}).$$

The results show that interface velocity may be positive or negative, that is into the aquifer or from the aquifer. It is true that for typical values of the physical parameters these calculated interface velocities are very small. Acting over large areas and over long time periods, the interface velocity could contribute to surface and ground water quality. Transient effects on the interface velocity can, however, be more significant. Water depths in the channels can change due to changes in hydrologic conditions in the watersheds and can change due to variable downstream depth controls. Downstream control depths change rapidly due to hurricane surge waves and tsunamis. These types of depth changes are also accompanied with the influence of density differences between the fresh water and dense coastal waters, which can augment the interface flow.

B.4. Results of dense coastal water and groundwater exchange experiments

The aim of the first set of experiments was to study the fate and transport of saline plume evolving from a surfacewater pond. The flow tank and the porous medium used in this study were similar to the one described in Figure 2. The saline water was supplied as a source to the surface of the porous media through a continuous volume displacement peristaltic pump at a constant rate. A small amount of red food coloring was added to the saltwater to differentiate the salty surfacewater from the fresh ground water. It is assumed that the contaminant source (i.e., flooded lagoon or the inundated region) is located at a distance inland such that the effects of the ocean water boundary can be ignored. Several experiments under various flow conditions were completed in this study. An example dataset for an unstable plume migrating from a dense surfacewater pond is shown in Figure 5.

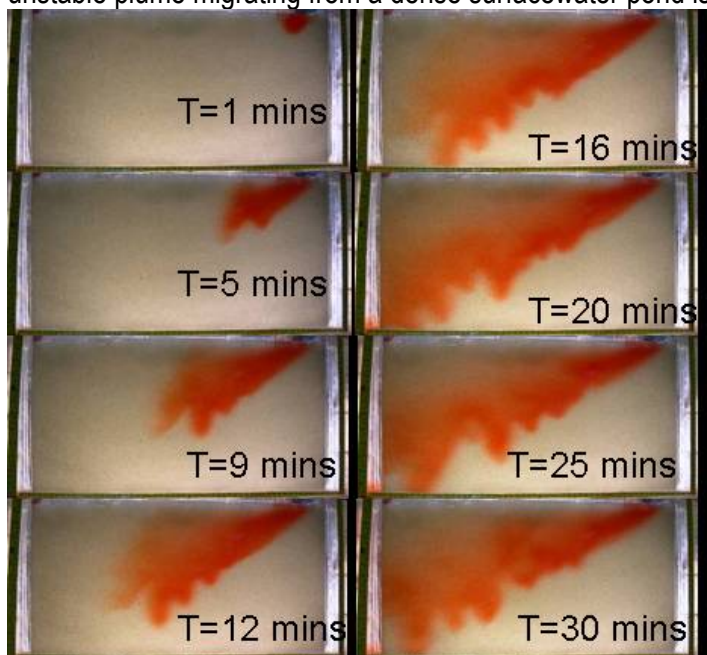


Figure 5: Dataset for an unstable plume

The aim of the second set of coastal water/ groundwater exchange experiments was to study the fate and transport of saline water dumped over a freshwater aquifer after a large-scale inundation event such as a hurricane or a tsunami wave. The flow container described above was also used in this inundation experiment. The surfacewater water flood was simulated by instantaneously distributing a fixed volume of saline water directly over the top boundary of the model. Experiments were performed under high- and low-flow groundwater flow conditions. The data shown in Figure 6 show the transport of this dense saline water over a time period of 11 minutes. Note that under high groundwater flow conditions the contaminant slug was transported quickly through the systems and formed a rather shallow contamination zone. On the other hand, when the ambient flow was low, the saline water migrated downward and contaminated larger volume of aquifer. There was also more intense fingering in the low flow case.

D. RESEARCH FINDINGS AND SIGNIFICANCE

The behavior of contaminant transport in streams is greatly influenced by the processes that exchange fluid between surface and ground waters. We derived an analytical approach to model the vertical exchange between a surfacewater body and the stream bed. The exchange process was also demonstrated through a conceptual experimental study. In the second phase of this work, we studied the interactions between groundwater and coastal waters. The recent natural disasters such as Katrina and the Asian-tsunami have created the need for understanding the saline water transport processes within an unconfined groundwater system, after a large-scale, surfacewater inundation event. We

provide several detailed data sets to illustrate the interactions between a dense surfacewater body (e.g., ocean) with a local unconfined aquifer. The first type of experiment involves the study of saline water migration from surfacewater storage ponds located along coastal dunes. The second type of experiment involves simulation of saline water migration patterns into a local unconfined aquifer after a large-scale flooding event.

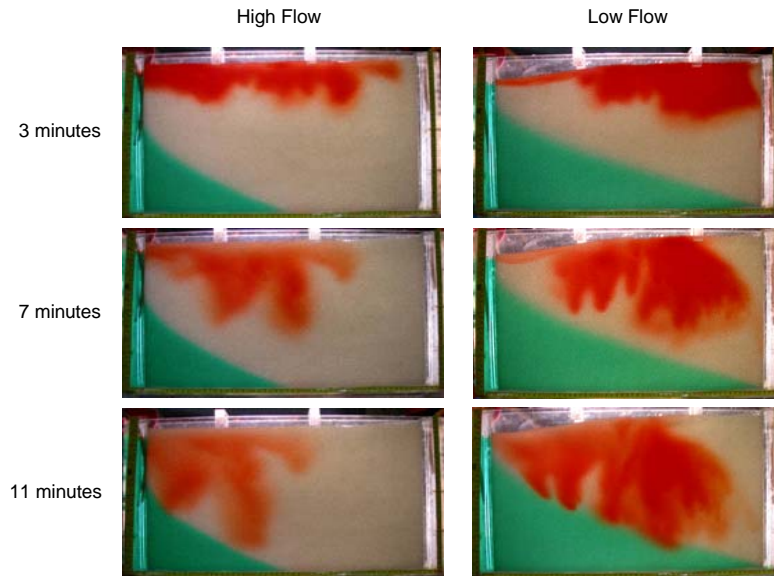


Figure 6: Beach face infiltration in a high GW flow (left photographs) and low GW flow conditions (right photographs)

Pilot Testing an Innovative Remediation Technology for In-situ Destruction of Chlorinated Organic Contaminants in Alabama Soils and Groundwater Using a New Class of Zero Valent Iron Nanoparticles

Basic Information

Title:	Pilot Testing an Innovative Remediation Technology for In-situ Destruction of Chlorinated Organic Contaminants in Alabama Soils and Groundwater Using a New Class of Zero Valent Iron Nanoparticles
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Principal Investigators:	Dongye Zhao

Publication

1. He, F. and D. Zhao, In-situ Destruction of Chlorinated Solvents in Soils and Groundwater Using a New Class of Stabilized Fe-Pd Nanoparticles, Proceedings of The 20th Annual Alabama Water Resources Conference, Perdido Beach, AL., Sept. 6-8, 2006.
2. Zhao, D. and F. He, 2007, Field Assessment of Carboxymethyl Cellulose Stabilized Fe/Pd Bimetallic Nanoparticles for Groundwater Remediation, Environmental Science and Technology. (Manuscript Submitted).

PILOT-TESTING AN INNOVATIVE REMEDIATION TECHNOLOGY FOR IN-SITU DESTRUCTION OF CHLORINATED ORGANIC CONTAMINANTS IN ALABAMA SOILS AND GROUNDWATER USING A NEW CLASS OF ZERO VALENT IRON NANOPARTICLES

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A. PROBLEM STATEMENT AND OBJECTIVES

Chlorinated hydrocarbons, such as polychlorinated biphenyls (PCBs), tetrachloroethylene (PCE) and trichloroethylene (TCE), are well-known potent toxins to human health and the environment. Although the uses of chlorinated hydrocarbons have now been either banned or highly restricted, the past massive production and applications have left an environmental legacy that large areas of soils and groundwater in Alabama are contaminated with dangerously high concentrations of chlorinated hydrocarbons.

Unfortunately, there have been no cost-effective and environmentally benign remediation technologies available for remediation of chlorinated soils and groundwater despite tremendous research efforts in the past three decades. To a great extent, current remediation practices rely on excavation and landfill of contaminated soils, which are extremely costly and environmentally disruptive (the associated cost is between 100-700 dollars/yard³). For cases like the capital plume site, since the site is located in the heavily populated downtown area, engineered processes (e.g., excavation) are highly restricted. Currently, Alabama owns 12 EPA-designated NPL (National Priorities List) sites and 2 proposed NPL sites. Of all toxins detected at these sites, chlorinated hydrocarbons are among the most wide-spread and most harmful contaminants to our groundwater, which serves as over 60% of the State's drinking water source. Using current technologies, clean up of each of these sites would claim for multi-millions of dollars over the next several decades, which constitutes a serious threat to the sustainable development of Alabama economy. Consequently, there is an urgent need for developing new cost-effective in-situ technologies for the clean-up of Alabama soils/groundwater contaminated by chlorinated hydrocarbons.

Our prior highly successful AWRRI project resulted in a new class of zero-valent iron (ZVI) nanoparticles and a patented remediation technology based on the nanoparticles. The nanoparticles have been considered suitable for in situ dechlorination uses, and the technology has attracted national interest. To ultimately apply this promising technology in the field, pilot-test is a critical and logical step, and will yield critical information on the technical and cost effectiveness and necessary design and operating parameters.

Therefore, this research aims to pilot-test this cutting edge in-situ remediation technology for rapid and complete destruction of chlorinated hydrocarbons such as PCE, TCE and PCBs in Alabama soils and groundwater. The specific research objectives are to:

- 1). Test the feasibility (dispersibility, reactivity, and reactive longevity) of the iron nanoparticles when applied under field conditions at a chlorinated solvent site in Northern Alabama; and
- 2). Probe the effects of field environmental conditions (pH, dissolved oxygen (DO), oxidation and reduction potential (ORP), ionic strength, and dissolved organic matter (DOM)) on the effectiveness.

B. RESEARCH APPROACH

B1. Bench-Scale Feasibility Studies.

Prior to the field-scale tests, laboratory feasibility studies were conducted using the groundwater from the site. During the tests, 20 mL stabilized Fe suspension (1 g/L, 0.5% sodium carboxymethyl cellulose or CMC, Pd/Fe = 0.1% w/w) was mixed with 23 mL groundwater obtained from a monitoring well (MW-3). The batch vials (43 mL) were then cap-sealed with Teflon-lined septa and placed on a rotary shaker at 50 rpm for degradation tests. Parallel experiments were also performed to degrade PCE and TCE in deionized water solution. To test the change in particle reactivity with the particle aging (i.e. storage time in water), replicate samples of 0.1 g/L lab-synthesized Fe-Pd nanoparticle suspension were stored in sealed glass vials (with zero headspace) and kept in a refrigerator at 4 °C for up to 9 days before being tested. The particle reactivity was then tested through the degradation experiments of TCE following the procedure described in our prior work (He and Zhao, 2005, *Environmental Science and Technology*, 39, 3314-3320).

The soil mobility of the CMC-stabilized Fe-Pd nanoparticles was tested by measuring the breakthrough behaviors of the nanoparticles through a 2.7 mL of a loamy sand soil bed (obtained from Auburn, AL) packed in a glass column (1 cm I.D.). For comparison, parallel tests were also carried out with a tracer (0.6 g/L KBr) and non-stabilized Fe-Pd particles. The salient soil properties are as follows: porosity = 0.35; hydraulic conductivity = 0.25 cm/min; sand content = 84%; silt = 10%; clay = 6% clay. In the breakthrough tests, a solution containing the tracer, 1.0 g/L (as Fe) of non-stabilized or CMC-stabilized (1% w/w CMC) iron nanoparticles was passed through the soil bed under a constant static hydraulic head of 7.1 cm. The particle breakthrough history was then followed by analyzing the total iron in the effluent until the full breakthrough was achieved. Then, DI water was pumped into the column by an HPLC pump at a constant superficial liquid velocity of 0.23 cm/min. Iron elution history was then followed for ~10 pore volumes.

B2. On-site preparation of CMC-stabilized iron nanoparticles

The field preparation of the stabilized Fe suspension is briefed as follows. Approximately 28 gallons of tap water were placed in a 65 gallon polyethylene reactor and rapidly stirred with a 1/3 horsepower motorized impeller. Then, 564 g of sodium carboxymethyl cellulose (CMC) was then added near the impeller while mixing, and the solution was mixed until no visible clumps (i.e. CMC was fully dissolved) were observed (~ 3 hours). During mixing, nitrogen gas was also supplied to purge the oxygen out of the reactor and facilitate mixing. Then, approximately 564 g of FeSO₄·7H₂O (Fisher, Fair Lawn, NJ) was first dissolved in 1 gallon nitrogen-purged tap water and added into the reactor. While the stirring and N₂ purging continued, 146 g of NaBH₄ (98%, Acros Organics, Morris Plains, NJ) was first dissolved in 1 gallon nitrogen-purged tap water, and then, pumped into the reactor at a flow rate of 0.5

L/min to reduce Fe^{2+} to Fe^0 . The solution in the tank turned from a milky white to inky black as the nanoparticles were produced. Finally, about 0.5 g of $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ (Strem, Newburyport, MA) was dissolved in 100 mL tap water and slowly added into the reactor. In this way, Pd was coated on the surface of iron nanoparticles to form CMC-stabilized Fe-Pd bimetallic nanoparticles. The resultant nanoparticle suspension contained 0.5% by weight CMC, 1 g/L of Fe, 1 mg/L Pd (or Pd/Fe = 0.1% (w/w)). Before injections, the 1 g/L Fe suspension was then diluted by pumping it into a 200-gallon tank containing 120 gallons of nitrogen-purged tap water. The final diluted Fe suspension (150 gallons) contained 0.2 g/L Fe, 0.1% CMC and 0.2 mg/L Pd. Before the injection, 34 g of KBr as a tracer (dissolved in 100 mL water) was added into nanoparticle suspension. Figure 1 shows the reactor used for the nanoparticle preparation and the black nanoparticle suspension.



Figure 1. A picture of the CMC-stabilized Fe-Pd particles (Fe = 1 g/L) taken from the reactor 5 min after preparation. The dark color indicates the presence of ZVI nanoparticles which are fully dispersed in the water solution.

B3. Suspension injection and groundwater monitoring

The field test was carried out at a northern Alabama site in collaboration with the Golder Associates. This abandoned site was contaminated with high concentrations of PCBs, TCE, PCE and other chlorinated hydrocarbons. The subsurface is characterized as heterogeneous with a relatively shallow semi-confined aquifer. The head gradient at the site before the test 0.012. The hydraulic conductivity ranged from 20 feet/day. The effective porosity is about 0.15. Based on all the pump tests that were done at the site, the epikarst always acts confined although technically it should be semi-confined. The 0.2 g/L nanoparticle suspension was injected into the ground through a 5-ft screened interval at 44.5-49.5 ft below ground of injection well IW-1. A peristaltic pump was set at a rate of ~0.67 gallon/min to deliver the nanoparticle suspension to the injection well, however, the pump did not exert additional pressure, i.e. the suspension was driven into the aquifer only by the static hydraulic gradient (or gravity flow) between injection well and the aquifer. Groundwater samples were collected from two monitoring wells MW-1 (5 ft down gradient) and MW-2 (10 ft down gradient) before and after injection. Samples were collected without purging using 12V submersible pumps installed at each of the monitoring wells. Also, a multi-parameter probe with a flow-through cell was used to measure pH, specific conductance, oxidation-reduction potential (ORP), dissolved oxygen (DO), and temperature readings during sampling activities.

C. PRINCIPAL FINDINGS AND SIGNIFICANCE

The key findings from this research are briefed as follows:

- It is practically feasible to synthesize the CMC-stabilized ZVI nanoparticles on site and on a relatively large scale. The resultant nanoparticles can be easily introduced into the contaminated aquifer under gravity.
- In accord with our prior experimental data, the CMC-stabilized nanoparticles exhibited unprecedented soil mobility and reactivity for destroying the primary contaminants such as PCE, TCE and PCBs under field conditions. The concentrations of PCE, TCE and PCB1242 in MW1 were lowered by up to 77%, 85%, and 83%, respectively, after deducting dilution effect in the first 10 days and continuously reduced by 59%, 96%, and 10% at the end of 29 days. In MW2, the concentrations of PCE, TCE and PCB1242 were lowered by up to 98%, 82%, and 95% respectively in the first 10 days and continuously reduced by 99%, 100%, and 93% at the end of 29 days.
- Application of the nanoparticles greatly boosted sustained biodegradation of the primary contaminants. As the degradation data are still being monitored, steady degradation of all the three chlorinated compounds was continuously observed four months after the treatment.

The results indicate that the in situ technology is technically highly feasible and can potentially save millions of remediation costs. Given the current and future impacts of chlorinated organic contaminants on our economy and human health, the successful implementation of this low-cost cutting-edge technology will save millions of dollars for both Alabama and the nation at large.

The Fate, Transport, and Effects of Veterinary Antimicrobial Mixtures in the Environment

Basic Information

Title:	The Fate, Transport, and Effects of Veterinary Antimicrobial Mixtures in the Environment
Project Number:	2006AL49B
Start Date:	3/1/2006
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Funding Source:	104B
Congressional District:	Third
Research Category:	Water Quality
Focus Category:	Non Point Pollution, Management and Planning, Agriculture
Descriptors:	Animal waste, contaminant transport, leaching, risk management, solute transport
Principal Investigators:	Puneet Srivastava, Jacob H Dane, Yucheng Feng

Publication

1. Sanders, S. 2007. The Fate and Transport of the Antimicrobials Sulfadimethoxine and Ormetoprim in the Environment. M. S. Thesis. Auburn University, Auburn, AL.
2. Sanders, S., P. Srivastava, Y. Feng, J. Dane, J. Basile, and M. Barnett. 2007. Sorption of the Veterinary Antimicrobials, Sulfadimethoxine and Ormetoprim, in Soil. *J. Environ Qual.* (in review)
3. Sanders, S., P. Srivastava, J. Basile, J. Dane, and Y. Feng. 2007. The Fate and Transport of Veterinary Antimicrobials in the Environment. ASABE Paper No. 072278. ASABE Annual International Conference, Minneapolis, MN. June 17-21, 2007.
4. Sanders, S., P. Srivastava, J. Basile, Y. Feng, J. Dane, and M. Barnett. 2007. The Fate and Transport of Veterinary Antimicrobials, Sulfadimethoxine and Ormetoprim, in the Environment. AWRA 2007 Summer Specialty Conference, Emerging Contaminants in the Environment: Issues, Investigations, and Solutions. Vail, CO., June 25-27, 2007.
5. Sanders, S., P. Srivastava, J. Basile, J. Dane, and Y. Feng. 2006. The Fate and Transport of Veterinary Antimicrobials in the Environment. ASABE Paper #062135. ASABE Annual International Conference, Portland, OR., July 9-12, 2006.

Statement of Problem and Research Objectives

Pharmaceuticals and personal care products (PPCPs) have recently been classified as “emerging” environmental contaminants. Among the emerging PPCPs, occurrences of antibiotics in the environment have raised particular concerns because their bioactivity often remains after excretion in human and animal wastes and because they have been linked to the development of antibiotic resistant genes in nature. Antibiotics belong to a class of bacterial static and bactericidal compounds collectively referred to as antimicrobials. Antimicrobials are used for therapeutic purposes in human and veterinary medicine, and also for nontherapeutic purposes such as growth promotion in farm animals.

Sulfadimethoxine (SDM) and Ormetoprim (OMP) are two veterinary antimicrobials belonging to the antimicrobial classes of sulfonamides and diaminopyrimidines, respectively. The drug combination of SDM and OMP is approved for use in dogs, chickens, partridges, ducks, catfish, salmonids, and turkeys. Of particular interests are its usages in catfish and chickens because of the potentially high risks of environmental contamination. The combination administered to poultry (Rofenaid® 40) and catfish (Romet® 30) primarily enters the environment through land-applied poultry waste and via fish feed and fish excrements.

The poultry and aquaculture industries are important food supplier and generate a great percentage of economic gains in many southern states. These important industries must rely on the use of antimicrobials to maintain healthy animals; however the environmental risks of using these antimicrobials should be fully understood. In order to quantify the ecological risks posed by antimicrobials and to develop management practices to reduce these risks, sound estimates are needed of predicted environmental concentrations (PECs). Calculating accurate PECs requires a thorough understanding of fate and transport processes. The fate of SDM and OMP is often the soil or sediment. Therefore, understanding the SDM and OMP fate and transport in soil is important for the determination of their potential mobility to surface and ground water.

The goal of this research was therefore to study the fate and transport of SDM and OMP in soils and sand representative of poultry and aquaculture in the southeastern United States. Specific objectives were to:

1. Determine the sorption of OMP and SDM and calculate their respective sorption coefficients using batch sorption equilibrium experiments; and
2. Compare the sorption of OMP and SDM when administered in combination as co-solutes as well as when administered individually as single solutes.

Methodology

Two soils representative of agriculture and aquaculture in the southeastern United States were chosen for this experiment. A Coastal Plain soil (Soil 1) was collected from Geneva County, AL and a Tennessee Valley soil (Soil 2) was collected from Sevier County, TN. Because southeastern U.S. soils are generally sandy, pure sand, Ottawa 4.0 was also used to understand the sorption by sand alone (i.e., no clay minerals or organic matter). Antimicrobial sorption will at a minimum be affected by clay and organic matter content, cation exchange capacity and pH; therefore, the selected soils represent several of the physical and chemical characteristics commonly found in the southeastern U.S. Major soil physical and chemical properties (Table 1) were determined at the Soil Testing Laboratory at Auburn University. Both soils were air-dried, ground, and sieved (≤ 2 mm diameter). The sand was muffled at 550°C for four hours to eliminate any possible organic matter. Following this, the sand and soils were irradiated using a ^{60}Co source at 5MRads to eliminate microorganisms that could potentially biodegrade the antimicrobials. The antimicrobials, Ormetoprim (OMP; 2,4-diamino-5-(4,5-dimethoxy-2-methylbenzyl) pyrimidine) and Sulfadimethoxine (SDM; N'-(2,6 Dimethoxy-4-pyrimidinyl) sulfanilamide), were obtained from Chem Service, Inc., West Chester, PA and Sigma Aldrich, St. Louis, MO, respectively. For the development of the stock solutions, both antimicrobials were initially dissolved in methanol such that the final working solutions contained less than 0.2% methanol.

Table 1. Physical and chemical properties of the selected soils and sand.

Soil Acronym	Description	Order	pH	%Organic Matter	%Sand	%Silt	%Clay	eCEC* (cmol _c /kg)
Soil 1	Plintic Kandiodults	Ultisol	5.03	1.5	81.5	13.5	5	3.19
Soil 2	Typic Eutorchrepts	Inceptisol	4.66	2.07	52	38	10	6.64
Sand	Ottawa 4.0	---	4.92	0	100	0	0	0.33

* eCEC: effective cation exchange capacity

In order to determine the time for SDM and OMP to reach sorption equilibrium ($dC/dt = 0$) in Sand, Soil 1, and Soil 2, batch kinetic experiments were conducted at the natural, unaltered pH of the media. Preliminary soil/solution ratio experiments were performed and the optimum ratio for all combinations was determined to be 1:20 (soil:solution). Antimicrobials were administered to a working solution of 0.01 M CaCl₂ in deionized water. A 100 µg·L⁻¹ concentration was chosen for these experiments because it is approximately the midpoint concentration for batch equilibrium experiments. One gram of each soil or sand was weighed and placed into a 50 mL polypropylene centrifuge tube, the sorbate (OMP or SDM, 20 mL) was added, and the suspension was placed on a reciprocating shaker for a specified time at 25°C. Duplicate samples were removed from the shaker after 1, 2, 5, 8, 16, 24, 39, 48, and 68 hours, respectively. Additionally, duplicate controls were run for each time slot (no sand or soil; solution only). After the specified times, samples were centrifuged at 1200 g for 45 minutes. The supernatant was determined to be clear, immediately removed from the soil (sorbent), filtered with a 0.45 µm PTFE membrane filter, placed in 750 µL polypropylene autosampler vials, and acidified with formic acid for sample preservation so that the final amount of acid was less than 1%. The results for the kinetic experiments suggested that apparent equilibrium was reached for both SDM and OMP in all three media after 24 hours. However, 48 hours was chosen as the equilibrium time for both antimicrobials.

Batch sorption equilibrium experiments were used to determine the sorption of SDM and OMP individually as single solutes and in combination as co-solutes in the selected soils and sand. In other words, three separate experiments were performed in each soil and sand, one with OMP only, one with SDM only, and one with OMP and SDM administered in combination. Concentrations of 5, 10, 50, 100, 250, and 500 µg·L⁻¹ were employed for sorption isotherms because they equated to the range of antimicrobial concentrations found in the environment. Each soil or sand (1 g) was placed into a 50 mL polypropylene centrifuge tube, solution was added (20 mL), and the suspension was equilibrated on a reciprocating shaker in the dark at 25°C. The above procedure was performed in triplicate for each of the six concentration levels. Additionally, duplicate controls for each concentration (no sand or soil; solution only) were run to verify the initial concentration, while a blank (sand or soil, CaCl₂ solution only) was analyzed to verify the lack of laboratory contamination. After equilibration, the samples were centrifuged and prepared for analysis using the procedure described above.

Results

OMP and SDM sorbed differently in Sand, Soil 1, and Soil 2 (Table 2). All distribution coefficients and Freundlich sorption coefficients were similar to those found for other mobile antimicrobials. OMP linear sorption coefficients, K_d , for the single solute and co-solute experiments ranged from 1.3 to 89.7 L·kg⁻¹. The SDM K_d value in Soil 1 was 25.8 L·kg⁻¹. Research performed on other sulfonamides have determined low sorption coefficients, K_d , in the range of 0.62-10 L·kg⁻¹, indicating a relatively high mobility of these compounds.

The carbon normalized sorption coefficient, K_{oc} , was determined for each antimicrobial in the single solute and co-solute systems for Soil 1 and Soil 2 (Table 2). The Tennessee soil sorbed more antimicrobial than the Alabama soil, even when normalized to the organic carbon fraction. The K_{oc} were nearly twice as much in Soil 2 than in Soil 1 for OMP single solute, OMP

co-solute, and SDM single solute. The SDM co-solute K_{oc} , however, only exhibited a 28% increase in Soil 2 compared to Soil 1. The large increase in K_{oc} values between soils either indicates that factors other than soil organic carbon are contributing to the antimicrobial sorption or that the carbon of one soil was more reactive than that of the other soil. Soil 2 has a higher cation exchange capacity, higher clay content, and lower pH than Soil 1. At the lower pH, more of SDM and OMP would be in the cationic species and would likely have a stronger attraction to the negatively charged soil surface.

Table 2. Sorption model coefficients for ormetoprim (OMP) and sulfadimethoxine (SDM) administered as single solutes and co-solutes in two soils and sand. OMP and SDM administered concentration range, 5-500 $\mu\text{g}\cdot\text{L}^{-1}$. Performed at the natural, unaltered soil pH.

Sorbent	Solute	Linear parameters			Freundlich parameters		
		K_d^a	R^2	K_{oc}^a	K_{Fr}^b	n	R^2
Sand	OMP single solute	1.3 (1.0-1.6) ^c	0.60	--	16.0 (11.3-22.8)	0.58 (0.50-0.67)	0.94
	OMP co-solute	4.96 (4.2-5.7)	0.85	--	12.2 (9.5-15.7)	0.86 (0.79-0.92)	0.98
	SDM single solute	0.4 (0.4-0.5)	0.95	--	3.1 (2.1-4.6)	0.64 (0.52-0.75)	0.98
	SDM co-solute	2.5 (1.2-3.8)	0.72	--	79.8 (31.7-201.0)	0.44 (0.24-0.64)	0.65
Soil 1	OMP single solute	21.9 (19.7-24.1)	0.93	2517.24	47.1 (34.0-65.4)	0.90 (0.80-0.99)	0.96
	OMP co-solute	30.9 (28.4-33.4)	0.95	3551.72	50 (38.4-65.1)	0.93 (0.85-1.01)	0.98
	SDM single solute	10.4 (9.2-11.6)	0.94	1195.40	2.1 (0.9-5.1)	1.32 (1.09-1.55)	0.92
	SDM co-solute	12.5 (10.0-15.0)	0.80	1436.78	134.9 (82.9-219.8)	0.54 (0.41-0.67)	0.89
Soil 2	OMP single solute	58.3 (53.9-62.8)	0.96	4855.91	84.9 (57.8-124.6)	0.97 (0.84-1.10)	0.94
	OMP co-solute	89.7 (84.6-94.9)	0.98	7471.26	115.1 (93.8-141.2)	0.98 (0.90-1.05)	0.98
	SDM single solute	25.8 (23.1-28.5)	0.94	2148.93	14.5 (10.3-20.4)	1.10 (1.01-1.20)	0.98
	SDM co-solute	22.1 (19.7-24.6)	0.94	1840.75	106.8 (80.1-142.5)	0.71 (0.63-0.79)	0.97

^a K_d , K_{oc} in units $\text{L}\cdot\text{kg}^{-1}$; ^b K_{Fr} in units $\text{L}\cdot\text{kg}^{-1}$ if $n=1$, else in units $\mu\text{g}^{1-n}\cdot\text{L}^n\cdot\text{kg}^{-1}$; ^cConfidence Intervals (95%)

Each, an increased cation exchange capacity and clay content, and a reduced pH could enhance sorption and appear to be significant based on the dramatic differences in the K_{oc} values of the two soils. Additionally, Sand had a relatively low sorption capacity for either antimicrobial, which indicates that the sand in the soils likely does not play a large role in sorption. The predicted carbon normalized sorption coefficients, K'_{oc} , were calculated based on antimicrobial octanol/water partition coefficients, K_{ow} . The K'_{oc} based on K_{ow} underestimated K_{oc} for both OMP and SDM. The K'_{oc} for OMP was calculated to be $7.42 \text{ L}\cdot\text{kg}^{-1}$, which is much less than the resulting K_{oc} values for OMP (Table 2). The SDM K'_{oc} of $18.45 \text{ L}\cdot\text{kg}^{-1}$ also underestimated the actual K_{oc} .

OMP overall was best fit by the Freundlich equation with all correlation coefficients (R^2) ≥ 0.94 (Table 2); however, the linear isotherm also yielded $R^2 \geq 0.93$ for both Soil 1 and Soil 2 but not for Sand, which did not yield a good linear fit for OMP. This was contributed to the low sorption potential of sand with OMP, in which the sand approached a limited number of sorption sites; however, it was not fit well with the Langmuir isotherm (data not shown). SDM also fit

reasonably well with the Freundlich equation ($R^2 > 0.92$) (Table 2), but was perhaps best fit with a linear isotherm for Soil 1 and Soil 2. The Freundlich models for Soil 1 and Soil 2 with SDM yielded slightly unfavorable sorption ($n > 1$) indicating that these two soils have very little sorption capacity for SDM at low concentrations, but have an increased capacity as the SDM concentration increases. Both SDM and OMP were found to fit better with the Freundlich or linear relationship than by the Langmuir equation. This is likely because the concentrations used in these experiments were limited to the relatively low concentrations found in the environment. Perhaps at higher concentrations, the soils or sand would reach a maximum number of sorption sites for the OMP and SDM.

The co-solute batch sorption equilibrium experiments involved the same approach as the single solute systems except in co-solute batch experiments both antimicrobials were administered together. Model results from these experiments are also presented in Table 2. SDM and OMP followed the same sequence of sorption for co-solute as for single solute systems, viz., Sand < Soil 1 < Soil 2. This was necessarily expected because it follows the sequence of increasing soil organic matter (SOM), cation exchange capacity, clay content (more surface area for sorption), and decreasing pH (Table 1). As stated earlier, the decreasing pH would cause cationic speciation of SDM and OMP, where there would be more affinity for the negatively charged soil surface.

The co-solute sorption of OMP was fit well by both the linear and Freundlich equation (Table 2). However, in the co-solute sorption, the Freundlich nonlinearity coefficient, n , is closer to 1 than in the single solute sorption, indicating that sorption for OMP is more linear in the co-solute system. Additionally, more OMP sorption occurs when in combination with SDM than when administered as a single solute. SDM co-solute sorption is fit best by the Freundlich isotherm and is more nonlinear than the single solute isotherm. The SDM co-solute sorption in the two soils exhibited favorable sorption ($n < 1$) whereas the SDM single solute experiment exhibited unfavorable sorption ($n > 1$).

Sorption of OMP and SDM in this study followed the sorption trend of Sand < Soil 1 < Soil 2. This was expected due to the increasing SOM. The relatively low sorption coefficients for SDM and OMP found in this study suggests that both of these antimicrobials will be relatively mobile in soils and have potential to reach surface and groundwaters. The presence of both SDM and OMP in combination illustrated an enhanced sorption of OMP and a more favorable sorption of SDM ($n < 1$). However, in the low environmentally relevant concentrations, there does not appear to be much difference in the single solute and co-solute experiments. The results of this study further suggest that more attention be given to predicting antimicrobial sorption than simply relying on the organic carbon sorption predictions alone. For OMP these predictions were shown to underestimate the carbon normalized sorption coefficient. This study reveals that OMP sorbed more strongly in the soils and sand than SDM, but both antimicrobials are likely to be relatively mobile and may be found in nearby water sources.

Evaluating Bioretention Nutrient Removal in a Rain Garden With and Internal Water Storage (IWS) Layer

Basic Information

Title:	Evaluating Bioretention Nutrient Removal in a Rain Garden With and Internal Water Storage (IWS) Layer
Project Number:	2006AL50B
Start Date:	3/1/2006
End Date:	2/28/2007
Funding Source:	104B
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Research Category:	Engineering
Focus Category:	Non Point Pollution, Water Quality, Nutrients
Descriptors:	Bioretention, Stormwater Management, Nonpoint Source Pollution
Principal Investigators:	Mark P. Dougherty, Charlene M LeBleu

Publication

1. Dougherty, Mark, Charlene LeBleu, Eve Brantley, Christy Hartsfield, April 9-12, 2007, Evaluating Bioretention Nutrient Removal in an Urban Rain Garden, in Emerging Issues Along Urban/Rural Interfaces: Linking Land-Use Science and Society, Auburn University Center for Forest Sustainability, Atlanta, GA.
2. Dougherty, Mark, Charlene LeBleu, Eve Brantley, Christy Hartsfield, June 17-20, 2007, Evaluation of Bioretention Nutrient Removal in a Rain Garden with an Internal Water Storage (IWS) Layer, in ASABE Annual International Meeting, ASABE, Minneapolis, MN (Paper #077085)
3. LeBleu, Charlene, Mark Dougherty, Eve Brantley, Christy Hartsfield, August 15-19, 2007, Assessing Nutrient Reduction in a Rain Garden With an Internal Water Storage (IWS) Layer, in The Council of Educators in Landscape Architecture (CELA) Annual Meeting, Council of Educators in Landscape Architecture, State College, PA.

Project Synopsis

Title: Evaluating Bioretention Nutrient Removal in a Rain Garden with an Internal Water Storage (IWS) Layer.

Funding period: March 1, 2006 - February 28, 2007

Investigators:

- Dr. Mark Dougherty, Assistant Professor, Auburn University Department of Biosystems Engineering, Auburn, AL
- Ms. Charlene LeBleu, Assistant Professor, Auburn University Landscape Architecture & Community Planning, Auburn, AL
- Ms. Eve Brantley, Alabama Cooperative Extension System, Water Quality Program, Auburn, AL
- Ms. Christy Francis, Former Curator, Arboretum/Biological Sciences, Auburn, AL

Statement of the problem and research objectives;

Stormwater runoff has been identified as a major source of pollution in urban and suburban streams. There are several innovative stormwater practices that integrate stormwater infiltration and storage to improve the quality of runoff, including bioretention areas such as rain gardens. This paper reports first year results comparing two different bioretention (rain garden) designs constructed at the Donald E. Davis Arboretum on the Auburn University campus, one using conventional, aerobic treatment and the other incorporating an internal water storage (IWS) layer.

An explanation of the research methodology used;

The rain garden demonstration-research project described in this paper is located at the Auburn University Arboretum in Auburn, Alabama. Construction of two rain gardens was completed in the summer of 2006. During the research monitoring portion of the study, predetermined volumes of stormwater runoff from campus are designed to be pumped into two rain gardens for collection, treatment, and analysis. At the conclusion of all controlled research, diversion berms installed above each rain garden will be removed to provide functional stormwater management and bioremediation for the Arboretum grounds. Although the two rain gardens were constructed at the same time, rain garden #1 had to be re-excavated in September 2006 to due improper drainage installation. Consequently, only raingarden #2 (RG #2) is used for the current study. Monitoring of RG #1 is scheduled to begin in summer 2007.

Principal findings and significance;

Initial evaluation of outflow from the newly installed rain garden #2 revealed several trends directly related to the chemical and physical properties of the fill media. Results support what is known in the literature about the linkage between outflow rain garden

water quality and the inherent soil properties of the fill media. In addition, it was observed that settlement and consolidation of in-place rain garden media immediately following construction resulted in gradually reduced outflow peaks during the 6-month study period from July through December 2006. Significant removal of particulate phosphorus and total phosphorus constituents was found under both conventional and IWS operation of the rain garden and some beneficial nitrogen removal was also detected from the IWS layer towards the end of the study. Beneficial hydrologic effects of the rain garden included significantly reduced outflow hydrograph peaks and reduced total outflow volumes, both effects which would act to reduce total contaminant load to receiving waterways. In addition, within six months after construction, the peak outflow from the rain garden was seen to decrease until a near steady-state outflow was achieved.

Information Transfer Program

Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	5	0	0	0	5
Masters	5	0	0	0	5
Ph.D.	3	0	0	0	3
Post-Doc.	0	0	0	0	0
Total	13	0	0	0	13

Notable Awards and Achievements

Researchers derived an analytical approach to model the vertical exchange between a surface water body and the stream bed. This exchange process was demonstrated through a conceptual experimental study.

As a result of research conducted through a project funded by this grant, a number of rain gardens have been constructed in surrounding cities to assist those cities with stormwater runoff. There are at least two additional rain garden projects scheduled for construction this fall.

Field testing of a low-cost cutting edge technology using a new class of zero-valent iron (ZVI) nanoparticles and a patented remediation technology based on the nanoparticles has shown that the CMC-stabilized ZVI nanoparticles exhibited unprecedented soil mobility and reactivity for destroying the primary contaminants such as PCE, TCE, and PCBs under field conditions. The concentrations of PCE, TCE, and PCB1242 in monitoring well 1 were lowered by up to 77%, 85%, and 83% respectively, after deducting dilution effects in the first 10 days and continuously reduced by 59%, 96%, and 10% at the end of 29 days. In monitoring well 2, the concentrations of PCE, TCE, and PCB1242 were lowered by up to 98%, 82%, and 95% respectively in the first 10 days and continuously reduced by 99%, 100%, and 93% at the end of 29 days. The results indicate that this in-situ technology is technically highly feasible and can potentially save millions of dollars in remediation costs.

Publications from Prior Projects

None