

**Missouri Water Resources Research Center
Annual Technical Report
FY 2006**

Introduction

WATER RESOURCES RESEARCH CENTER ANNUAL TECHNICAL REPORT FY 2006-2007

WATER PROBLEMS AND ISSUES OF MISSOURI

The water problems and issues in the State of Missouri can be separated into three general areas: 1) water quality, 2) water quantity, and 3) water policy. Each of Missouri's specific problems usually requires knowledge in these three areas.

Water Quality: New media attention to the occurrence of pesticides in drinking water in the Midwest has raised a serious public concern over the quality of Missouri's drinking water and how it can be protected. With the large agricultural activity in the state, non-point source pollution is of major interest. Because of several hazardous waste super-fund sites, hazardous waste is still of a concern to the public. The Centers' research has been to evaluate the quality of current waste sources and improve the methods to protect them. Areas of research for the past ten years have included (but are not limited to): erosion, non-point pollution reclamation of strip mine areas, hazardous waste disposal acid precipitation, anthropogenic effects on aquatic ecosystems and wetlands.

Water Quantity: Missouri has a history of either inadequate amounts of rainfall, or spring floods. Because of the 1987-89 drought years and the floods of 1993 and 1995, water quantity has become a major topic of concern. Research is needed to better understand droughts and flood conditions.

Water Policy: Policies and program need to be formulated that will ensure continued availability of water, as new demands are placed on Missouri's water. The social and economic costs may no longer be held at acceptable levels if water becomes a major issue in cities and rural areas. Past droughts and possible lowering of the Missouri River have raised serious questions over states rights to water and priority uses. Research areas in this program have included drought planning, legal aspects, perception and values, economic analysis, recreation, land/water use policy and legislation, and long-term effects of policy decisions.

SUMMARY OF ADVISORY COMMITTEE ACTIVITIES

The following individuals have participated in the selection and development of our 2006 research program.

UNIVERSITY OF MISSOURI FACULTY ADVISORY COMMITTEE

1. Steven Anderson, University of Missouri-Columbia, 302 Abnr Bldg.-Soil Science, Columbia. MO.
2. Patrick Osbourne, University of Missouri-St. Louis, 224 Research Building, St. Louis, MO 63121.

STATE OF MISSOURI ADVISORY COMMITTEE MEMBERS

1. John Schumacher, U.S. Geological Survey, 1400 Independence Road, Rolla, MO 65401.
2. Dr. Steve McIntosh, Water Resources Program, Department of Natural Resources, PO Box 176, Jefferson City, MO.
3. Cindy Wolken, Acting Section Chief, Watershed Protection Section, PO Box 176, Jefferson City, MO 65102
4. Dr. Jack Steiert, Biology, Southwest Missouri State University, Springfield, MO.
5. Mike McKee, Resource Scientist, Department of Conservation, Columbia, MO.
6. Robert Gale, Research

Chemist/Section Leader Organic Chemistry, Columbia environmental Research Center, Biological Resources Division of USGS, Columbia, MO. 7. John Ford, Environmental Special, Department of Natural Resources, Jefferson City, MO.

Research Program

RESEARCH PROGRAM

PROGRAM GOAL AND PRIORITIES

The Missouri Water Resources Research Centers goals are 1) establish active research programs to aid in understanding and solving Missouri's and the nation's water problems; 2) provide educational opportunities in research for students with an interest in water resources and related fields, and 3) be actively dedicated to the dissemination of water related information, using all aspects of the media.

With these goals, the Center is able to mobilize the best faculty expertise in the state to examine specific water resources problems. The Center is familiar with research needs and activities, and its goals are to help researchers avoid duplicate efforts and to serve as a link between the research community and potential users of research results such as industries, planning commissions, and state agencies.

Because Missouri's economy revolves around its water resources, the director and principal investigators have worked closely with the state in addressing their problems by providing research data which are necessary in order to solve present and future water problems. Each of the research projects forwarded for regional competition has undergone a thorough evaluation process by the water Centers Advisory Committee to determine its importance in solving Missouri's and the nation's water problems.

EEM Fluorescence Spectroscopy Fingerprints and Monitoring of NDMA and TTHM Formation Potentials

Basic Information

| | |
|---------------------------------|---|
| Title: | EEM Fluorescence Spectroscopy Fingerprints and Monitoring of NDMA and TTHM Formation Potentials |
| Project Number: | 2006MO61B |
| Start Date: | 3/1/2006 |
| End Date: | 2/28/2007 |
| Funding Source: | 104B |
| Congressional District: | 9th |
| Research Category: | Water Quality |
| Focus Category: | Wastewater, Treatment, Methods |
| Descriptors: | None |
| Principal Investigators: | Baolin Deng, Baolin Deng |

Publication

1. Hua B, A. Koirala, K. Veum, J. Jones, T. Clevenger, B. Deng, 2007, Fluorescence fingerprints and total trihalomethanes and N-nitrosodimethylamine formation potentials, *Environmental Chemistry Letters*, 5(2), 73-77.

EEM Fluorescence Spectroscopy Fingerprints and Monitoring of NDMA and TTHM Formation Potentials

Principal Investigator:

Baolin Deng, Ph.D.

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1. Summary

Excitation-emission matrix (EEM) fluorescence spectroscopy is becoming a valuable tool in water quality monitoring, based on identifying fluorescence emitting organic substances (fluorophores) present in water systems. This study continued our effort to apply the sensitive fluorescence EEM monitoring technique for water quality management. Specifically, the EEM approach was applied to the identification of the precursors of total trihalomethane (TTHM) and *N*-nitrosodimethylamine (NDMA) formation of the waters from 55 lakes in Missouri. Water samples were analyzed for their EEMs and the formation potentials of TTHM and NDMA. Comparing the EEM fingerprints with TTHM formation revealed that water with higher fluorescence intensity generally exhibited higher TTHM formation potential. Moreover, waters with fluorescence center at excitation: 290-310 nm/emission: 330-350 nm were related to high NDMA and TTHM formation potentials. The results suggest that EEM fingerprints could be used as surrogate parameters for monitoring TTHM and NDMA formation potentials. The study also monitored the fluorescence fingerprints and major fluorescent components in waters from a landfill, a wastewater treatment plant effluent, and Missouri River. Humic-like, protein-like and xenobiotic-like fluorophores identified from EEMs were consistent with recent published studies. The three sample sources were clearly differentiated based on their fluorescing composition.

2. Graduate and undergraduate students training

This project has provided partially supports to two master level graduate students, Mr. Amod Koirala who defended his thesis July 2006, and Mr. Benjamin Teymouri who defended his thesis in May 2007.

3. Information Access

Journal papers:

Hua B, Koirala A, Veum K, Jones J, Clevenger T, Deng B (2007) Fluorescence fingerprints and total trihalomethanes and *N*-nitrosodimethylamine formation potentials. *Environmental Chemistry Letters*, 5(2), 73-77.

Adsorption of the Isoxaflutole Degradate Diketonitrile to Aluminum and Iron Hydrous Oxides

Basic Information

| | |
|---------------------------------|--|
| Title: | Adsorption of the Isoxaflutole Degradate Diketonitrile to Aluminum and Iron Hydrous Oxides |
| Project Number: | 2006MO63B |
| Start Date: | 3/1/2006 |
| End Date: | 2/28/2007 |
| Funding Source: | 104B |
| Congressional District: | 9th |
| Research Category: | Water Quality |
| Focus Category: | Toxic Substances, Groundwater, Solute Transport |
| Descriptors: | None |
| Principal Investigators: | Keith W Goyne, Stephen H Anderson, Robert N Lerch, Chung-Ho Lin |

Publication

1. Wu, Si-Hyun, K.W. Goyne, R. N. Lerch, C.-H Lin, and S. H. Anderson. 2006. Adsorption of isoxaflutole degradates to aluminum and iron hydrous oxides. CD-ROM. Indianapolis, IN. 12-16 Nov. 2006. ASA, CSSA, SSSA International Meetings.

Progress Report for the United States Geological Survey, Department of Interior

Adsorption of the Isoxaflutole Degradate Diketonitrile to Aluminum and Iron Hydrated Oxides

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Summary

Herbicides used for weed control in agroecosystems are common contaminants in water resources of the United States, and concerns surrounding the presence of herbicides in surface and ground waters are attributable to the toxic and potential carcinogenic effects of these agrichemicals. One agrichemical of concern is the relatively new pre-emergence herbicide isoxaflutole (IXF) used on ~10% of all corn planted in Midwestern states. IXF is rapidly transformed to a diketonitrile degradate (DKN), the active herbicide principle, shortly after field application. Subsequently, DKN is more slowly degraded to a benzoic acid (BA) derivative. Both degradates are very highly mobile compounds that have been detected in soil leachate, surface waters, and aquifers of the Midwest. A principle factor governing pollutant fate and transport in the environment is compound interactions with soil components (i.e., sorption processes). We are investigating IXF degradate adsorption and retention by hydrated aluminum and iron oxides (HAO and HFO, respectively). These variable-charge minerals have high specific surface areas and reactive surface function groups, thus, they function as major “sinks” for an array of environmental pollutants.

The original objectives of this research were to (1) quantify DKN adsorption and retention by HAO and HFO, (2) assess changes in DKN uptake by mineral surfaces as a function of aqueous chemical composition (i.e., pH and initial DKN concentration), and (3) employ infrared spectroscopy to investigate the mechanism(s) through which DKN binds to HAO and HFO surfaces. However, we have modified the objectives to investigate BA in all of our studies as well. Research conducted to date includes (1) development of techniques to synthesize DKN and BA from the parent compound IXF, (2) development of HPLC techniques to analyze concentrations of the compound in solution, (3) synthesis and characterization of HAO and HFO, (4) sorption isotherm experiments investigating DKN sorption to both metal oxides and BA sorption of HAO. Throughout the remainder of the year we will complete sorption edge experiments to investigate IXF degradate sorption of HAO and HFO as a function of pH and spectroscopic studies to elucidate mechanisms of DKN and BA sorption to the metal oxides.

This research will enhance our understanding of how HAO and HFO in soils and sediments impact the environmental fate and transport of IXF degradates. A thorough understanding of DKN and BA sorption processes will enhance predictive capabilities of pollutant transport models and aid in identifying soil characteristics that reduce DKN migration to water resources.

Title: Adsorption of the Isoxaflutole Degradate Diketonitrile to Aluminum and Iron Hydrated Oxides

Names: Keith W. Goyne, Robert N. Lerch, Chung-Ho Lin, and Stephen H. Anderson

Nature, Scope, and Objectives of Research

The development and use of herbicides for controlling weeds and grasses in agroecosystems has resulted in enhanced food production to meet the needs of Earth's growing population¹. However, solute transport processes in soil can result in migration of these compounds from areas of application to surface and ground waters. Due to potential carcinogenic and endocrinological effects and toxicity of these compounds to non-target organisms, herbicides and herbicide degradates pose a significant contamination threat to water resources of Missouri² and the United States³⁻⁴.

Within soils, sorption (i.e., adsorption and absorption) to organic and mineral components is of primary importance for determining organic pollutant fate and transport in the environment⁵. Organic matter (OM) strongly retains nonpolar herbicides and it is the dominant soil component retaining these compounds in horizons containing > 3% OM (e.g., surface soil horizons). Clay minerals and metal oxides are also important herbicide sorbents when compounds are polar and/or OM content is low⁶. Owing to the fact that much geomedia in the vadose zone contains little OM, studies investigating herbicide and herbicide degradate retention by soil minerals is particularly relevant.

Isoxaflutole, sold under the trade names Balance™, Balance Pro™ and Epic™, is a relatively new herbicide that rapidly hydrolyzes to the degradate DKN after application to soil. Subsequently, DKN is more slowly degraded to form a benzoic acid (BA) derivative. However, information regarding interactions of DKN and BA with specific soil components is lacking. The overarching goal of this research proposal is to investigate DKN sorption and retention by important soil minerals and elucidate how differing chemical reactivities of these components may influence DKN mobility in the pedosphere. However, we have modified our goal to investigate BA sorption as well. We are working to achieve our goals by investigating DKN and BA interactions with highly reactive and variable-charge hydrated aluminum and iron oxides (HAO and HFO, respectively) which are common accessory minerals found in soil. Specific objectives include: (1) assessing the influence of soil mineral chemical composition (HAO and HFO) on DKN and BA sorption and retention; (2) determining the influence of aqueous chemical composition (pH and organic compound concentration) on DKN uptake and sequestration; and (3) elucidating the mechanism(s) of DKN binding to metal hydrated oxide surfaces.

This research will enhance our understanding of how reactive mineral surfaces in soils, sediments, and aquifers may diminish (or enhance) environmental mobility of DKN. Data collected will have utility for modeling DKN transport in geomedia by providing quantitative parameters for use as retardation coefficients in convective-dispersion equations. In addition, this study will provide land managers and regulatory agencies information that can be incorporated into comprehensive plans aimed at minimizing IXF degradate loss from source areas. The proposed research will contribute significantly to the research focus area *Quality of Surface and Groundwater in Missouri*.

Methodology and Principal Findings

Mineral Synthesis and Characterization. HAO was synthesized by gradually neutralizing 0.5 M AlCl_3 solution with 0.5 M NaOH to pH 7.0. The suspension was held at room temperature for 48 h to allow time for mineral neosynthesis⁷. HFO was prepared by dissolving ferric nitrate in 0.01 M HCl to create a 0.2 M $\text{Fe}(\text{NO}_3)_3$ solution. Solution pH was then rapidly increased to pH 7 by titration with 0.1 M NaOH and the suspension was kept at room temperature for 48 h⁷. Synthesized minerals were centrifuged at 5000 rpm for 20 min to concentrate the mineral as a pellet. After centrifugation, the supernatant solution was aspirated and electrical conductivity (E.C.) of the solution was measured and recorded. HFO and HAO were resuspended in Barnstead ultra-pure water, the pellet was resuspended, and suspension was centrifuged again. This process was repeated until no change in E.C. was observed. Minerals were then frozen at -20°C , freeze-dried, and stored in a dessicator.

Powder X-ray diffraction (XRD) analysis was used to confirm the amorphous nature of the synthesized minerals. HAO analysis was conducted on random-oriented, back-filled sample and diffraction patterns were collected on a MiniFlex Desktop XRD using Ni-filtered CuK_α radiation at 40 kV and 40 mA. A continuous scan mode was used to collect 2θ data from 20 - 80° with a step size of approximately 0.04° . Scan speed was 0.1 degrees per minute and the divergent slit was 0.125° . Following similar procedures, HFO was analyzed using Nicolet I2 diffractometer using Ni-filtered CuK_α radiation equipped with single monochromator. Diffraction patterns shown in Fig. 1 confirm that HAO and HFO are amorphous in nature.

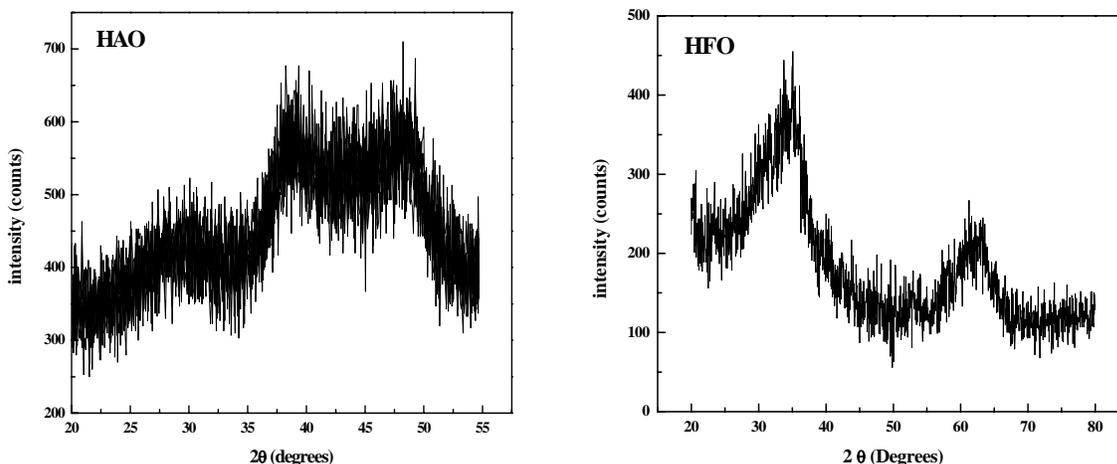


Figure 1. X-ray diffraction (XRD) patterns of HAO and HFO.

Specific surface area (SSA) of the adsorbents was examined using N_2 sorptometry by the Micrometrics Analytical Services (Micrometrics TriStar 3000; Norcross, GA). Samples (1.000 g) were out-gassed prior to analysis, and adsorption-desorption isotherms were measured at 77.3 K. SSA was estimated using multi-point adsorption data from the linear segment of the N_2 adsorption isotherms in the relative pressure range 0.05 – 0.30 using Brunauer-Emmett-Teller (BET) theory. The SSA of HAO and HFO were $201.2 \pm 0.38 \text{ m}^2 \text{ g}^{-1}$ and $152.9 \pm 5.05 \text{ m}^2 \text{ g}^{-1}$, respectively.

Purification and Analysis of DKN and BA. In order to obtain DKN and BA from IXF, 200 mg of IXF (99.99% purity; Sigma-Aldrich, St. Louis, MO) was dissolved in 1000 ml of ultra pure water. Solution pH was increased to pH 9 via addition of 0.1 M Ca(OH)₂ and the solution was heated at 40°C for 7 d to accelerate transformation of IXF to DKN. The BA degradate of IXF was prepared by dissolving 100 mg of Ca(OCl)₂ in 250 ml of DKN solution and allowing the sample to react until transformation was complete (~24 h).

Aliquots of the DKN and BA stock solutions were analyzed using high performance liquid chromatography (HPLC) on a temperature controlled (40°C), reverse-phase column (Phenomenex Columbus C₈, 4.6 x 100mm, 5µm particle size; Torrance, CA) attached to a Beckman HPLC system (San Ramon, CA) equipped with UV detector⁸⁻⁹. DKN and BA are detected and quantified by UV absorbance at 280 nm (Table 2). The mobile phase consists of 0.1% phosphoric acid (H₃PO₄) buffer (pH 2.2) and 100% acetonitrile (MeCN) solution mixed to give an isocratic mixture of 40% MeCN:60% H₃PO₄ buffer at a flow rate of 1 mL min⁻¹. The retention times for BA and DKN are 3.3 min. and 7.6 min., respectively (Table 1, Fig. 2). Analyte concentrations were determined from standard curves. HPLC calibration standards were prepared from analytical standards obtained from Bayer CropScience (Pittsburgh, PA). Calibration standards (10-100 µg L⁻¹) containing DKN and BA showed good linearity (r²> 0.99).

Table 1. Summary of UV response and stock concentrations of DKN and BA measured using HPLC.

| Wavelength (λ, nm) | Compound | Retention time (min) | Stock Conc. (mg L ⁻¹) |
|--------------------|----------|----------------------|-----------------------------------|
| 280 | DKN | 7.60 | 81.26 |
| 280 | BA | 3.30 | 46.80 |

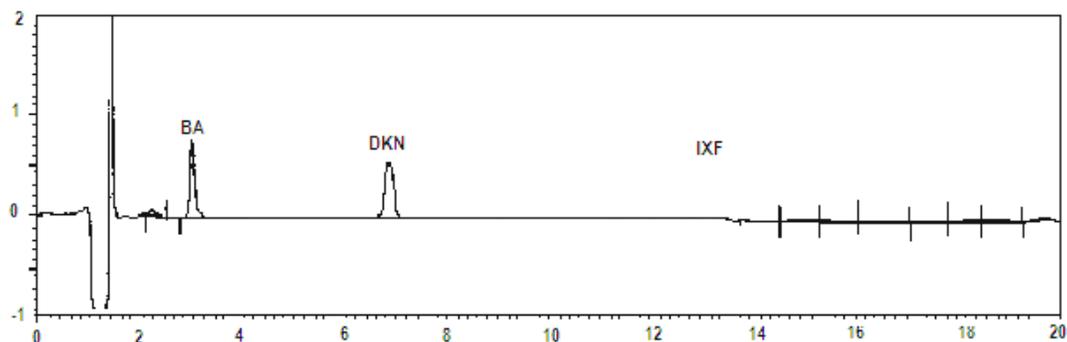


Figure 2. HPLC-UV chromatogram of DKN and BA.

Adsorption and Desorption Experiments. To generate adsorption isotherms, mineral adsorbents (0.500 g) are suspended in 20.00 mL of 0.01 M CaCl₂ solution in polypropylene co-polymer (PPCO) centrifuge tubes. Solutions of 0.03 M HCl or 0.01 M Ca(OH)₂ are added to yield a final pH of 5.5 after 24 h of reaction. Samples are then spiked with DKN or BA stock solutions to achieve varying concentrations (0, 0.25, 0.5, 1.0, 2.5, 5.0 µmol L⁻¹), and reacted in the dark on end-over-end shakers (7 rpm) at 25°C for 24 hrs. Samples and controls (no mineral) are conducted in triplicate and duplicate, respectively. After reaction, samples and controls are

centrifuged at 14,000 g for 30 min at room temperature, supernatant solutions are removed by pipette, and solutions are saved in PPCO bottles for analysis of degradate concentrations and pH. The adsorbed amount of DKN and BA was calculated as:

$$\Gamma_{ads} = \frac{(C_{ads,B})(V_B) - (C_{ads,S})(V_S)}{m_s} \quad (1)$$

Where Γ_{ads} is the surface excess after the reaction period ($\mu\text{mol kg}^{-1}$), $C_{ads,B}$ and $C_{ads,S}$ are the equilibrium DKN (or BA) concentrations ($\mu\text{mol L}^{-1}$) in blank (B) and samples (S) after reaction, V_B and V_S are the volume of solution (L) added to samples and blanks, respectively, and m_s is mass of mineral (kg).

Desorption experiments are initiated immediately after the adsorption step by adding a mass of 0.01 M CaCl_2 solution, adjusted pH 5.5, equivalent to the mass of supernatant removed. Adsorbate retention was calculated from Eq.(2):

$$\Gamma_{des} = \Gamma_{ads} - \left\{ \frac{(C_{des,S})(V_{des}) - (C_{ads,S})(V_{ent})}{m_s} \right\} \quad (2)$$

Where Γ_{des} is the surface excess remaining on the surface after the desorption period ($\mu\text{mol kg}^{-1}$), $C_{des,S}$ is the equilibrium DKN (or BA) concentrations in solution after desorption reaction period, V_{des} is the volume of solution in the reaction vessel during desorption phase, and V_{ent} is the volume of entrained solution remaining in the adsorption pellet after aspiration of adsorption phase supernatant.

Adsorption of IXF degradate to metal oxide adsorbents was fit to the Freundlich equation (Eq. 3) to provide a concise set of parameters for comparison of adsorbent affinity.

$$\Gamma_{ads} = AC_{ads}^N \quad (3)$$

Where parameters A and N are the intercept and slope, respectively, in a log-log plot of adsorption isotherm data.

Results from the adsorption/desorption experiments are in Figs. 3-6 and Table 2. The data indicate that DKN and BA are adsorbed to the variable-charged minerals HAO and HFO at pH 5.5 (Fig. 3). Thus, validating that these minerals may be important sorbents for IXF degradates. Additionally, DKN was adsorbed more readily to surface functional groups present on HFO than HAO over a wide range of initial concentrations, and BA is sorbed to HAO to a greater extent than DKN at higher initial concentrations but not at low initial concentrations. Hysteresis was not observed between DKN adsorption/desorption isotherms for HFO (Fig. 5), but was observed between the isotherms for HAO (Fig. 4). These data suggest that DKN may interact with surface functional groups on HFO via weak electrostatic interaction and interact with HAO through a stronger mechanism of adsorption (e.g., a ligand exchange mechanism). However, spectroscopic experiments must be conducted to verify hypotheses of adsorption mechanisms. Although these

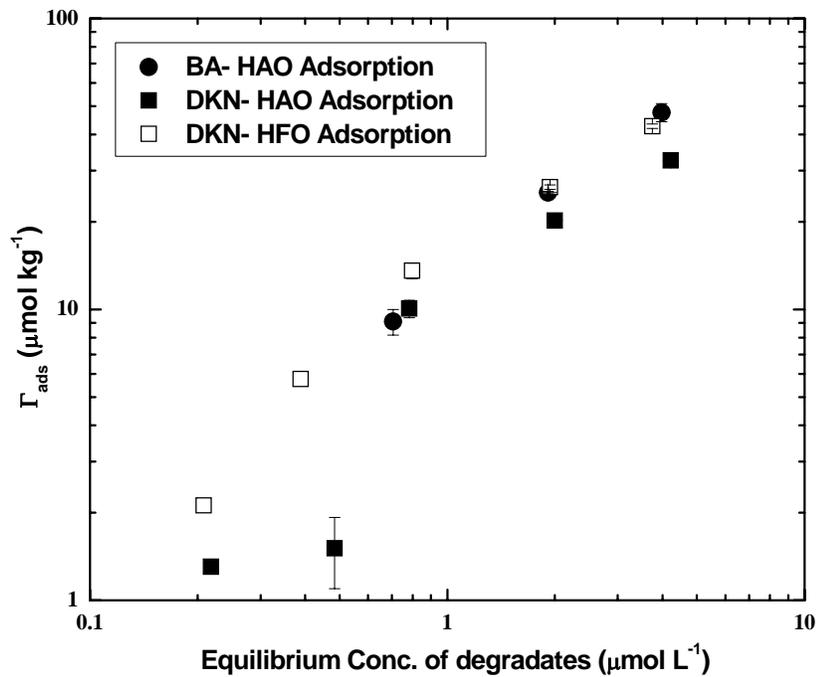


Figure 3. Adsorption of DKN and BA to HAO and HFO at pH 5.5 as a function of initial degradate concentration. Error bars, where observed, represent 95% CI.

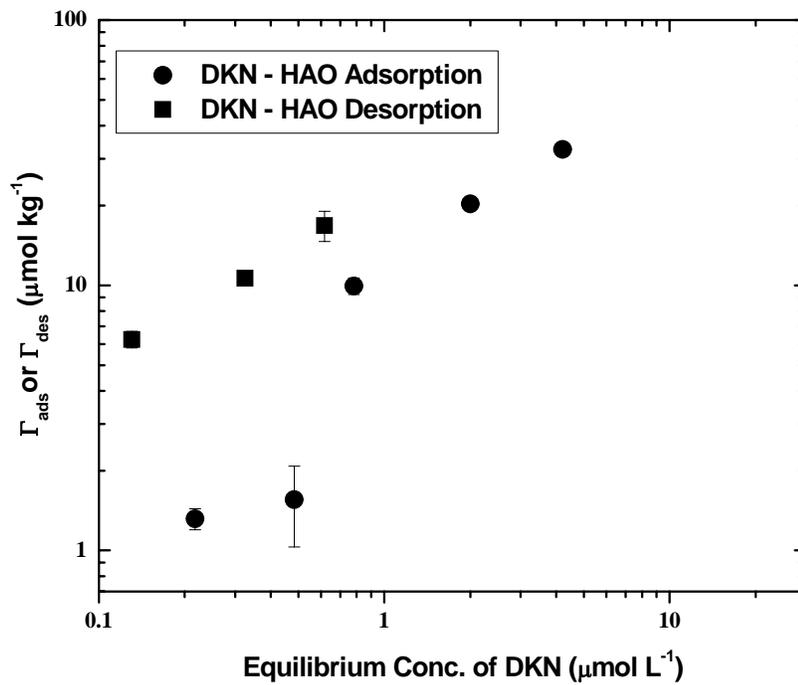


Figure 4. . DKN adsorbed on HAO after adsorption and desorption reactions at pH 5.5. Error bars, where observed, represent 95% CI.

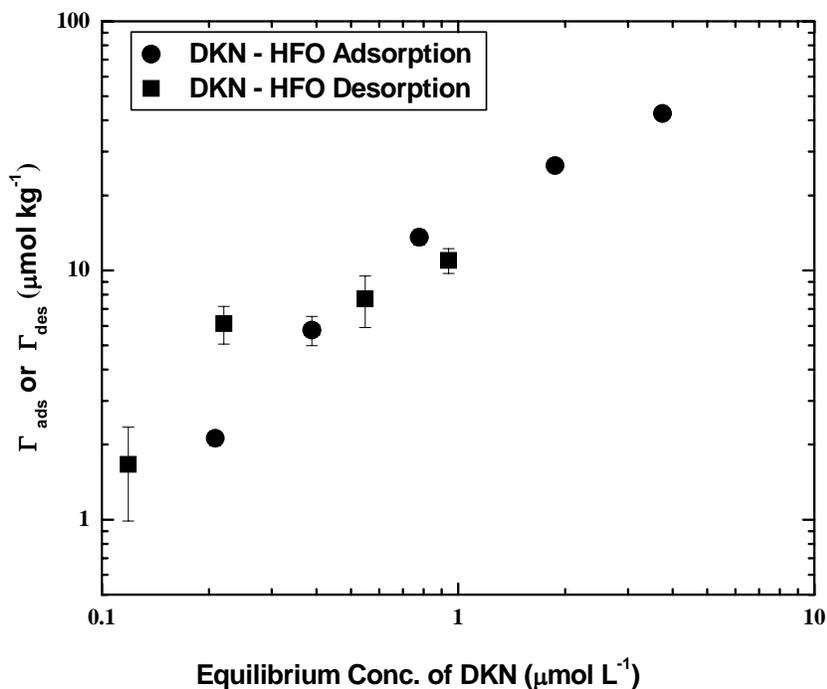


Figure 5. DKN adsorbed on HFO after adsorption and desorption reactions at pH 5.5. Error bars, where observed, represent 95% CI.

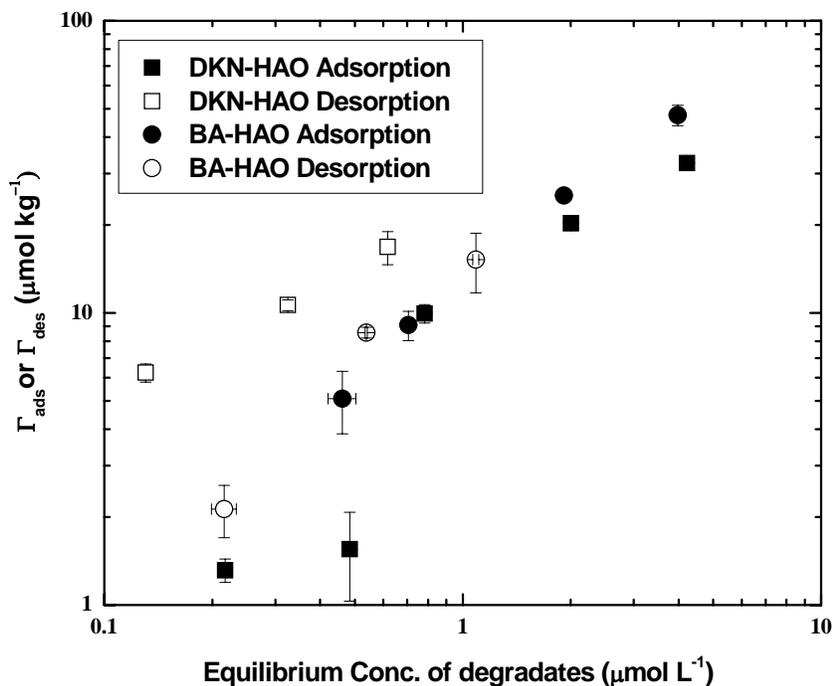


Figure 6. DKN and BA adsorbed on HAO after adsorption and desorption reactions at pH 5.5. Error bars, where observed, represent 95% CI.

Table 2. Freundlich parameters for BA and DKN sorption to HAO and HFO.

| Degradate | Adsorbent | $\log K_f \pm 95\% \text{ CI}$ | $N \pm 95\% \text{ CI}$ | $r^2 (n)^\dagger$ |
|-----------|-----------|------------------------------------|---------------------------|-------------------|
| DKN | HAO | $0.86 \pm 0.12 \text{ a}^\ddagger$ | $1.20 \pm 0.27 \text{ a}$ | 0.88 (15) |
| | HFO | $1.13 \pm 0.05 \text{ b}$ | $1.01 \pm 0.12 \text{ a}$ | 0.96 (15) |
| BA | HAO | $1.09 \pm 0.03 \text{ b}$ | $1.01 \pm 0.07 \text{ a}$ | 0.97 (12) |

[†] Where (n) represents the number of data points used in the linear regression analysis.

[‡] Mean values within a column followed by the same letter (a, b) are not significantly different ($\alpha = 0.05$).

results may seem contradictory, for example greater sorption to HFO through weaker mechanisms of adsorption, one possible explanation is that the HFO surface may be populated with a greater number of reactive surface functional groups. Measurements of surface charge will need to be conducted to verify this assumption.

Figure 6 demonstrates that BA sorption to HAO is greater at higher initial concentrations than sorption of DKN. Additionally, hysteresis between adsorption and desorption isotherms of BA is not observed, but hysteresis is observed between the DKN isotherms. This suggests that BA is more weakly retained on the mineral surface, relative to DKN. We hypothesize that this may be related to DKN chelating the metal centers on the mineral surface to form a stable 6-member ring structure that is more stable than a monodentate complex that can be formed by BA. Similar results have been observed by Furrer and Stumm¹⁰ with respect to mineral dissolution in the presence of vary types of organic acids.

Significance of Project

Significance of research to Missouri needs, as well as regional and national significance and potential users: Contamination of surface and ground waters by organic agrichemicals used as pesticides continues to degrade water quality in Missouri and surrounding states²⁻⁴. The DKN degradate of IXF may contribute to this problem via herbicide drift during application or offsite migration after field application. Based on our lack of knowledge regarding interactions of DKN with specific soil components, the proposed research is particularly relevant and timely.

IXF is registered for use in Missouri, however, it may not be applied to soils with loamy sand or sand surface/subsurface horizons having an average OM content in the upper 30 cm of less than 2% by weight¹¹. Additional restrictions, imposed by the Missouri Department of Agriculture, prohibit use of this herbicide in the Southeast Missouri Delta because of ground water contamination threats¹². Statistical data on the usage of this IXF in Missouri are unavailable. However, IXF is used on ~ 10% of total acreage planted to corn in surrounding states with watersheds draining into the Missouri and Mississippi Rivers (Table 3). Thus, IXF and IXF degradation products may pose a significant contamination threat to water resources of Missouri. Detection of these compounds in waters of Nebraska suggests that this is a likely scenario¹³.

Table 3. Use of isoxaflutole (IXF) in states surrounding Missouri †.

| State | Acres receiving IXF | Mass applied (kg) |
|--------------|---------------------|-------------------|
| Illinois | 672,000 | 19,955 |
| Indiana | 560,000 | 15,420 |
| Iowa | 2,108,000 | 61,225 |
| Kansas | 174,000 | 2,721 |
| Nebraska | 1,134,000 | 25,397 |
| Ohio | 165,000 | 3,628 |
| South Dakota | 440,000 | 13,605 |
| Total | 5,253,000 | 141,950 |

† Data obtained from USDA-NASS ¹⁴.

The research being conducted will provide quantitative information regarding the interaction of DKN with highly reactive minerals prevalent in soils, particularly subsoils. This will enhance our understanding of DKN sorption and retention within the vadose zone and aqueous chemical conditions that enhance or diminish DKN migration to surface and ground waters. We anticipate that land managers and regulatory agencies will be able to use obtained results as part of an overall evaluation regarding use of IXF on Missouri soils. Results will also have utility in predictive chemical transport models by providing data that can be inserted into convective-dispersion equations as a retardation coefficient.

Student involvement: USGS funds have been used to support one Ph.D. student (Ms. Si Hyun Wu), who has been actively working to complete this project. This research will be used to partially fulfill the requirements of Ms. Wu's graduate degree program.

Additional Funds Garnered and Grants Submitted Based on this Research: The USDA, Agricultural Research Service (ARS) has agreed to provide 1.5 years of additional student support (tuition and stipend) toward completing the proposed research and additional research on DKN and BA interactions in soil. The grant listed below is pending:

Interactions of Isoxaflutole and Its degradates in the Rhizosphere of Vegetative Buffers: Sorption, Degradation, and Impacts on Microbial Communities. USDA, CSREES, Soil Processes Program. \$399,615, 9/01/07 – 8/31/11. K.W. Goyne, R.J. Kremer, R.N. Lerch, C.-H. Lin, and T. Wong.

Abstract and Presentation from International Meeting:

Wu, Si-Hyun, K.W. Goyne, R. N. Lerch, C.-H Lin, and S. H. Anderson. 2006. Adsorption of isoxaflutole degradates to aluminum and iron hydrous oxides. CD-ROM. Indianapolis, IN. 12-16 Nov. 2006. ASA, CSSA, SSSA International Meetings.

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Low Rate Mixing & Struvite Precipitation: Paired Treatment for Swine Waste

Basic Information

| | |
|---------------------------------|--|
| Title: | Low Rate Mixing & Struvite Precipitation: Paired Treatment for Swine Waste |
| Project Number: | 2006MO67B |
| Start Date: | 3/1/2006 |
| End Date: | 2/28/2007 |
| Funding Source: | 104B |
| Congressional District: | 9th |
| Research Category: | Water Quality |
| Focus Category: | Agriculture, Water Quality, Education |
| Descriptors: | None |
| Principal Investigators: | Joel Burken |

Publication

Low Rate Mixing & Struvite Precipitation: Paired Treatment for Swine Waste

Joel G. Burken (University of Missouri Rolla)

Summary: The project was off to a slow start due to the difficulty of finding a promising graduate student at the timing when the grant was established. After a slow start, the project took a slight re-direction as it was determined that adding the a mixer to a new lagoon as proposed was cost-prohibitive under the limited funds available. Alternatively, the collaborating company, Absolute Aeration, offered to share data from a similar project with municipal wastewater in California. This data has served as a solid source of data, and takes the place of the second mixed lagoon. Struvite precipitation has been evaluated in the laboratory, revealing the base addition that is needed is reduced by aeration, and that solids in the wastewater does not inhibit struvite precipitation as was previously hypothesized. Overall, the project did get off to a delayed start, but now is generating solid data and will lead to one masters degree, and likely two publications. A No cost extension was request for the end of 2007.

Progress: Struvite precipitation was evaluated with swine waste solids at controlled levels. The tested levels of solids ranged up to 250 mg/l, Figure 1, and removal was not significantly different from earlier tests without solids. Struvite precipitation conditions were carried out at a pH of 8.5 to 9.0. Research also revealed that anaerobic lagoon wastewater can reach a pH of up to 8.0 to 8.2 through aeration alone. Aeration strips the CO₂ from the solution and increases the pH nearly to the pH values necessary for efficient struvite precipitation, shown to be near 8.7 in previous research.

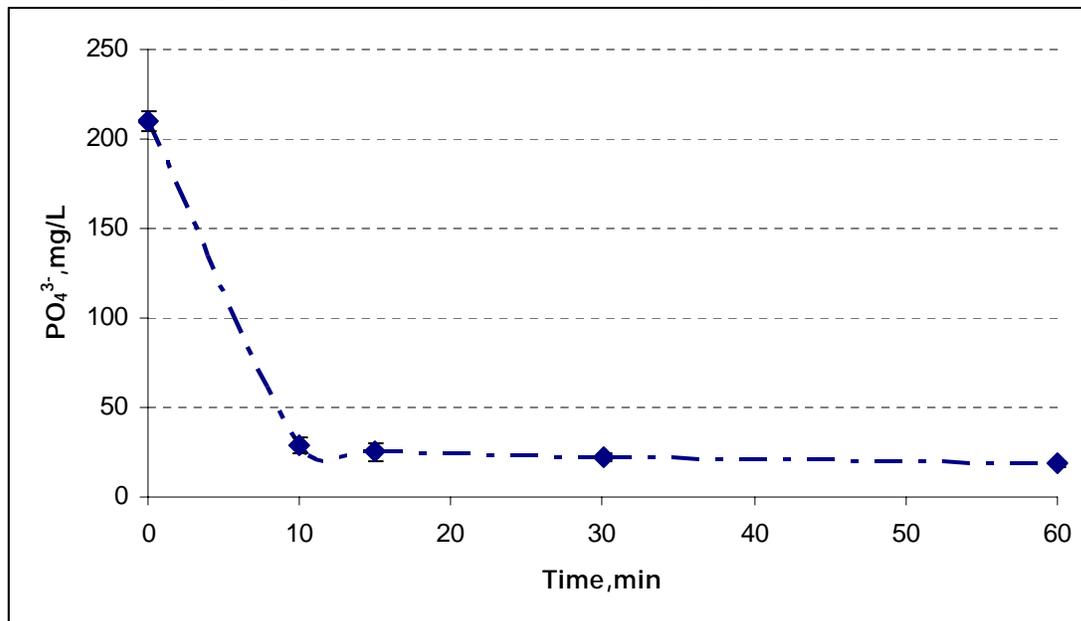


Figure 1 Phosphate removal over time with 250 mg/l swine waste solids in the wastewater.

Research was also conducted to evaluate the mixing dynamics of the constructed struvite precipitation reactor. A reactor model will soon be completed and will be used in process

optimization and application. A possible test site in Idaho has been identified. The animal production facility has been cited for P problems in their lagoon effluent and may be closed without attention. Owners are considering a pilot struvite precipitation process.

Lagoon Monitoring: The existing mixed lagoon has continued to be mixed, although a mechanical problem had the mixer down for 2 months this fall. Data from the sampling is shown in Table 1. COD and Ammonia levels have reached all time lows since the mixing was initiated over 4 years ago. Mixing was halted for much of 2005. Consistent P levels have not been maintained. Struvite precipitation that had been observed is no longer occurring spontaneously. Monitoring is ongoing.

Table 1 Mixed lagoon properties.

| Sampling date | COD (mg/L) | Ammonia (mg/L) | PO ₄ (mg/L) |
|---------------|------------|----------------|------------------------|
| 5/9/2002 | 801 ± 208 | 231 ± 26 | 54 ± 3 |
| 9/5/2003 | 574 ± 77 | 150 ± 11 | 47 ± 7 |
| 10/3/2003 | 428 ± 219 | 170 ± 11 | 45 ± 33 |
| 10/24/2003 | 434 ± 231 | 170 ± 11 | 9 ± 3 |
| 11/20/2003 | 530 ± 240 | 173 ± 19 | 29 ± 8 |
| 12/17/2003 | 378 ± 87 | 168 ± 18 | 13 ± 3 |
| 3/22/2004 | 655 ± 92 | 200 ± 13 | 122 ± 21 |
| 4/20/2004 | 774 ± 559 | 217 ± 22 | 106 ± 30 |
| 5/20/2004 | 759 ± 323 | 233 ± 28 | 34 ± 2 |
| 6/23/2004 | 458 ± 104 | 237 ± 13 | 56 ± 7 |
| 7/24/2004 | 355 ± 168 | 213 ± 22 | 84 ± 29 |
| 6/27/2006 | 205 ± 10 | 139 ± 37 | 52 ± 4 |
| 7/20/2006 | 213 ± 11 | 88 ± 17 | 46 ± 7 |
| 8/31/2006 | 167 ± 30 | 77 ± 6 | 26 ± 3 |
| 9/11/2006 | | | 28 ± 3 |
| 9/12/2006 | | | |

* Values are mean ± standard deviation

Tulare Data: Data from municipal, aerated lagoons in Tulare California was offered from Absolute Aeration. Of the 5 ‘trains’ of lagoons, one was converted to similar low rate mixers analyzed in this study. The mixers were fitted aerators that injected micro-bubble aerators. An aerial figure of the site is shown in figure 2. In the figure, train B was down for maintenance. Train D was converted to use the mixer/aerators. Through the use, started in fall 2006, the BOD and SS levels appeared to fall or at least stabilize in the first 6 months. The level of sludge also is dropping, revealing that the lagoon aerator can lead to lower maintenance for the lagoons, as well as better effluent quality. The biggest benefit is an estimated energy savings of over 60% that could be nearly \$500,000 annually. UMR is serving to evaluate treatment quality in collaboration with Absolute Aerations. We are hoping to publish this work, and perhaps pursue a SBIR development grant.

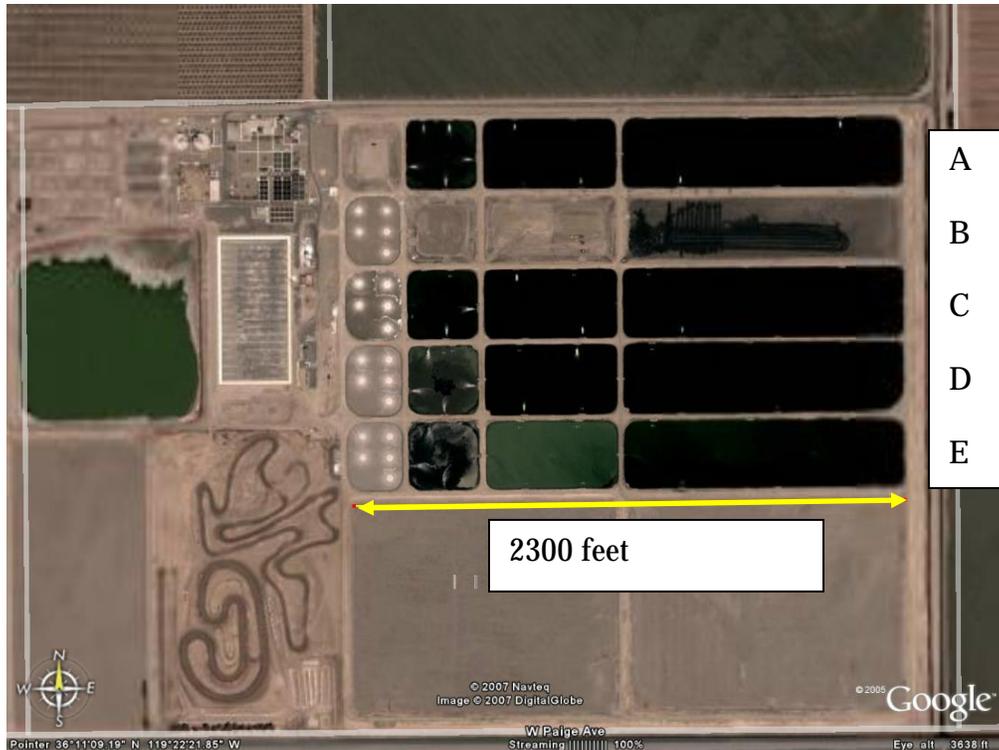


Figure 2 Aerial view of Tulare lagoons

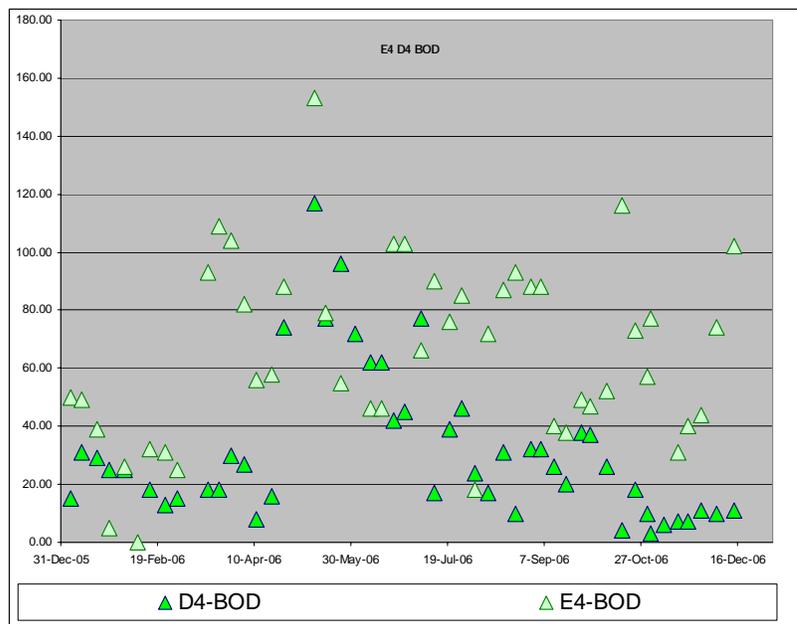


Figure 3 showing the BOD levels in lagoon E4 and D4 following the start-up of the aeration-mixers in lagoons D2,3,4. Lagoon trains E and D are closest in the characteristics of waste received.

Plans: The Tulare data for Jan – June 2007 is expected very soon and the treatment of actual waste from swine facilities is currently continuing. Full evaluation is planned for July – September 2007. Publications are in preparation and will be forwarded once finished.

Students trained:

- ◆ Sushmita Dhakal. Ms Dhakal is on target to receive her MS degree in Environmental Engineering in December 2007.
- ◆ Michael Pyles. Mr Pyles assisted with the project as an undergraduate and is currently on coop.
- ◆ Phillip McGee. Mr. McGee is currently assisting with this project, and will continue to assist through the summer.

Information Transfer Program

Student Support

| Student Support | | | | | |
|------------------------|-----------------------------------|-----------------------------------|---------------------------------|--------------------------------|--------------|
| Category | Section 104 Base Grant | Section 104 NCGP Award | NIWR-USGS Internship | Supplemental Awards | Total |
| Undergraduate | 3 | 0 | 0 | 0 | 3 |
| Masters | 2 | 0 | 0 | 0 | 2 |
| Ph.D. | 1 | 0 | 0 | 0 | 1 |
| Post-Doc. | 0 | 0 | 0 | 0 | 0 |
| Total | 6 | 0 | 0 | 0 | 6 |

Notable Awards and Achievements

Publications from Prior Projects

None