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Introduction

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Fate of Veterinary Antibiotics in Manure Lagoons

Basic Information

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Principal Investigators:	Say Kee Ong, Thomas B. Moorman

Publication

1. Kolz, A.C., S.K. Ong, and T.B. Moorman. 2005. Sorption of Tylosin onto Swine Manure, Chemosphere, 60(2):284-289.
2. Kolz, A.C., T.B. Moorman, S.K. Ong, K.D. Scoggin, and E.A. Douglas. 2005. Degradation and metabolite production of tylosin in anaerobic and aerobic swine manure slurries, Water Environment Research, 77(1):49-56.

Fate of Veterinary Antibiotics in Manure Lagoons

Say Kee Ong, Ph.D. and Tom Moorman, Ph.D.

Problem and Research Objectives

Antibiotic residues and increased numbers of antibiotic-resistant bacteria have been reported near confined animal feeding operations (CAFOs) and in agricultural watersheds. A major route for entry of veterinary pharmaceuticals into watersheds is through land application of animal biosolids and spills of animal waste at facilities using these drugs. Swine CAFOs often use antibiotics for therapeutic or growth-promoting purposes. Manure generated at CAFOs, and containing excreted residues, is commonly stored in earthen lagoons for several months before land application. Incomplete degradation of pharmaceuticals in vivo and during manure storage, before biosolids are land-applied, could be a contributing form to the presence of these drugs in waterways.

The fate of these chemicals is of environmental importance as it has been shown that highly resistant pathogens may develop within the manure management facilities and that these chemicals may interfere with the endocrine system of various aquatic species. Currently, research on the fate of these compounds in the manure management system and in the environment is very limited. The objectives of this study are to investigate the fate of two common antibiotics, tylosin and sulfamethazine, used in the swine industry. The focus will be on the sorption and degradation of these antibiotics in manure lagoons under anaerobic and aerobic conditions.

Methodology

The proposed research consists of analytical methods development, batch sorption studies, and batch degradation studies. The antibiotics to be tested are tylosin and sulfamethazine, two major antibiotics used in the swine industry. Manure will be obtained from various manure lagoons and characterized for pH, total organic carbon, total dissolved solids, and ammonia.

A key aspect of studying antibiotics in the environment is the ability to analyze the antibiotics in various media and in low concentrations. Different solvents for extraction of antibiotics from both liquid and sludge from waste manure were tested. The antibiotics were analyzed using liquid chromatograph and liquid chromatograph-mass spectroscopy (LC-MS).

Batch sorption experiments were conducted according to the American Society of Testing and Materials E1195-01 (ASTM, 2002). Sodium azide was added to each vial to inhibit microbial degradation. Anaerobic degradation studies were conducted using a series of 120 mL serum bottles containing sludge from manure lagoons. The serum bottles were spiked with a given amount of antibiotic and the vials were purged with nitrogen to ensure dissolved oxygen was removed. At different times, vials were sacrificed and the concentrations of the antibiotics in both liquid and solid phases analyzed. The parent compound remaining and metabolites, if any, were determined using LC-MS. Aerobic degradation experiments will be similarly conducted.

Work for tylosin has been completed, while research on sulfamethazine is ongoing.

Principal Findings and Significance

Tylosin disappearance followed a biphasic pattern where rapid initial loss was followed by a slow removal phase. The 90% disappearance times for tylosin, relomycin (tylosin D), and desmycosin (tylosin B) in anaerobically incubated slurries were 30 to 130 hours. Aerating the slurries reduced the 90% disappearance times to between 12 and 26 hours. Biodegradation and abiotic degradation occurred, but strong sorption to slurry solids was probably the primary mechanism of tylosin disappearance. Dihydrodesmycosin and an unknown degradate with molecular mass of m/z 934.5 were detected. Residual tylosin remained in slurry after eight months of incubation, indicating that degradation in lagoons is incomplete and that residues will enter agricultural fields.

Sorption of tylosin was conducted on manure solids (<2 mm) and colloidal materials (<1.2 lm) collected from open (OL) and covered (CL) anaerobic swine manure lagoons. The aqueous concentration of tylosin in the sorption studies bracket the levels expected in lagoons, between 1 mgL^{-1} and 30 mgL^{-1}. Sorption isotherms were found to be slightly non-linear for 2 mm solids, with Freundlich distribution coefficients (K_f) of 39.4 with $n = 1.32$ for CL slurry and 99.5 with $n = 1.02$ for OL. These values are comparable to those reported for loam soils, but higher than those reported for sandy or clay soils and lower than those reported for fresh manure. Normalization of K_d to the organic carbon content of the solids gave K_{oc} values of 570 L/kg^{-1} and 818 L/kg^{-1} for CL and OL solids, respectively. The K_d and K_f values were not significantly different between colloids and 2 mm solids in OL slurry but were significantly different in CL due to the non-linearity of the colloid isotherm. Based on the K_d values obtained and comparing the K_d values of other antibiotics, tylosin is strongly sorbed to manure and would be more mobile than tetracyclines but less mobile than sulfonamides, olaquindox, and chloramphenicol. However, tylosin mobility may be facilitated through transport with colloidal manure materials.

We are currently conducting sorption and degradation studies on sulfamethazine in manure and in soils.

Sequestration of phosphorus with iron mine tailings

Basic Information

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Publication

1. Schwemm, A., R. Pasker, M. Clayton and E. Brown. 2005. Fate and transport of phosphate through the Beaver Valley Wetlands in the Cedar River watershed. J. Undergraduate Research (in press).
2. Pasco, Elodie. 2005. Phosphorus sequestration in sediments with iron mine tailings. MS Thesis, University of Northern Iowa, Cedar Falls, IA. 68pp.
3. Clayton, M.E., S. Liegeois and E.J. Brown. 2004. Phosphorus sequestration in lake sediment with iron mine tailings. Soil and Sediment Contamination. 13:421-431.

Sequestration of Phosphorus with Iron Mine Tailings

Edward J. Brown

Problem and Research Objectives

Orthophosphate (PO_4^{3-}) is found in surface and ground waters as a result of the natural weathering and solution of minerals; soil erosion and transport; use of soluble phosphate compounds in detergent manufacture, water treatment and industry; and soil fertilization. Controlling the total load of phosphorus in a lake is critical to controlling eutrophication since phosphorus is usually the biomass limiting nutrient in natural aquatic ecosystems. The phosphorus cycle does not allow atmospheric venting (as the nitrogen cycle does), so phosphorus tends to accumulate in the sediments of lakes. In a healthy, well aerated lake, this does not cause a problem because the phosphates precipitate or are tightly adsorbed to common minerals in the sediments and are thus unavailable for biological uptake. In oxygen-depleted waters, however, the internal loading of phosphorus results from a problem known as the "phosphorus trap." Phosphorus accumulated in the sediments is mobilized through dissolution or desorption to the aqueous phase under low-oxygen conditions in the sediments, resulting in a stimulation of biomass production and ultimately a further decrease in the levels of oxygen in the water column and sediments. If phosphorus in lake sediments can be sequestered in a form which is not released under anaerobic conditions, internal phosphorus loading would be reduced.

Iron, in both the ferric (Fe^{3+}) and ferrous (Fe^{2+}) oxidation states, is known to react with phosphate (PO_4^{3-}), leading to precipitates and hydrous ferric oxides that tie up the phosphorus so that it becomes unavailable for the growth of plants in general and algae in particular. Fe^{3+} is the most common metal in soils and rocks and is the form of iron that is primarily found in both aerobic water and many naturally occurring minerals, including hematite. Most forms of this ion are insoluble but, if solubilized (usually under acidic conditions), Fe^{3+} will react with phosphate. The simplest reaction which immobilizes phosphate is the direct precipitation of solids such as strengite ($FePO_4 \cdot 2H_2O$), which is essentially insoluble (Hutchinson, 1957).

Because ferric iron is insoluble, many current methods for the treatment of wastewater phosphate consist of reducing ferric to ferrous iron under anaerobic conditions and then precipitating the phosphate either before or during re-oxidation of the iron to Fe^{3+}. One of those methods treats phosphate by the reductive iron dissolution (RID) process in which ferrous iron is made available by the reductive dissolution of ferric iron solids that are contained in a reactive porous media. The media is placed in direct contact with the unoxidized sewage so that reducing conditions are maintained. As a result, Fe^{3+} is reduced to Fe^{2+} and subsequently solubilized (Freeze and Cherry, 1979). Ferrous iron in solution can then attenuate phosphate in two ways (Robertson, 2000). The ferrous iron can react with phosphate, resulting in the precipitation of Fe^{2+} - P solids, for example vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$). If the effluent is also subsequently oxidized, Fe^{3+} - P solids can precipitate in the same way as described above under aerobic conditions.

Another wastewater treatment method is based on the same principle, but the reduction of ferric iron is enhanced by microorganisms. In this case, a flow-through chamber providing Fe^{2+} for treatment of wastewater contains a quantity of Fe^{3+} material such as taconite or magnetite and a consortium of microbes that utilize Fe^{3+} as a terminal electron acceptor to degrade organic compounds in wastewater. The chamber is constructed to maintain anaerobic conditions, and nutrients (e.g. from wastewater and sewage) are added to initiate the generation of soluble Fe^{2+}. When the aqueous output containing Fe^{2+} is introduced to oxygenated water, it is oxidized to Fe^{3+} which binds and precipitates phosphorus in the sewage (Hogen and Robin, 1996).

In this paper, we investigate whether this wastewater treatment principle can be applied to runoff catchment basins and constructed wetlands for treatment of phosphate pollution in lakes and other surface waters. In this case, large amounts of ferric iron as contained in low cost mine tailings would serve as the biological oxidant for sediment organic material as well as serving as a phosphate sink. We hypothesized that the iron would be reduced by anaerobic bacterial respiration because Fe^{3+} is an electron acceptor in a wide variety of film-forming bacteria and the biological reduction of Fe^{3+} is a major mechanism leading to the production of ferrous iron in natural systems. The potential of the Fe^{3+}/Fe^{2+} couple is very electropositive, and because of this, Fe^{3+} reduction can be coupled with oxidation of several organic and inorganic electron donors (Frossard *et al.,* 1995) during anaerobic respiration. We hypothesized that the soluble ferrous iron that would be produced could then react with phosphate present in the sediment/water interface or be re-oxidized by other soluble electron acceptors (i.e. nitrate), leading to precipitates that immobilize phosphorus in the sediment by the reactions described above.

Ore from the Cuyuna iron range in east-central Minnesota contains multiple carbonate micronodules comprised of a rhodonite core surrounded by calcite, rhodochrosite and hematite (Fe_2O_3) (McSwiggen and Cleland, 2003). Therefore, iron mine tailings from the Cuyuna range contain various amounts of hematite. Hematite has a simple, repeating crystalline structure: iron and oxygen atoms coordinate to form two-dimensional layers, leaving small open spaces between them (Blake *et al.,* 1966; Smith, 1998). Hematite can fix atoms or molecules when they are introduced into those spaces by absorption, or molecules can adsorb to the surface of the mineral. In either case, the attraction can be physical or chemical, involving ionic or covalent bonds. Furthermore, it has been shown that reactions of water with hematite can involve dissociation of water, resulting in the formation of surface hydroxyl groups (Kendelewicz *et al.,* 1997) which may increase its ability to sorb compounds such as phosphates. Additionally, depending on its chemical environment, hematite can also make available iron and oxygen ions for chemical reactions such as oxidation/reduction. In particular, hematite releases iron ions in aqueous solutions.

In this study, we designed experiments to investigate whether the oxidized iron in mine tailings will serve as electron acceptor (oxidant) for anaerobic respiration of organic matter, become soluble, and then immobilize sediment phosphate. The experiments were designed to measure sediment phosphorus available for algal uptake and growth in Silver

Lake, Iowa. This phosphorus includes soluble reactive phosphorus (SRP) in sediment slurries as well as phosphorus released from sediments after extraction with dilute acid.

Methodology

Sediment Source. Approximately 1L of wet sediment was collected by grab sample from the middle of Silver Lake in Delhi, IA in May 2002. Silver Lake is highly eutrophic, with total phosphorus concentrations ranging from 504 – 926 µg P/L in surface water and varying from 12 – 1279 µg P/g dry weight in the top 5 cm of the sediment (unpublished data). The Silver Lake sediment used for these experiments contained 206 µg P/g dry weight sediment. Aliquots of the same sediment sample were stored in a sealed plastic bag at 4° C and were used in all of the experiments. The water content of the sediment was determined after drying a sediment aliquot to a constant weight at 105 ºC.

Phosphorus Concentrations in Sediment and Hematite. All glassware used in the experiments was acid washed in 1 N HCl and rinsed with deionized (DI) water. Total phosphorus was measured in the Silver Lake sediment sample and in a sample of the hematite obtained from mine tailings from the Cuyuna iron range in east-central Minnesota (courtesy of Emily Sand and Gravel, Emily, MN) according to the method of Clesceri *et al.* (1998). Briefly, a known volume of deionized (DI) water was added to 2 g sediment (wet weight) and the samples were subjected to persulfate digestion (Clesceri *et al.,* 1998). Following digestion, the samples were centrifuged for 10 min at 5000 x g, after which phosphate concentrations in the supernatant were measured by the ascorbic acid method (Clesceri *et al.*, 1998).

To quantify the amount of phosphorus in sediment that was potentially available for algal growth, the sediment was extracted with various strengths of acid (H_2SO_4) and the amount of phosphorus released into solution was compared with the total phosphorus in the sediment as determined above. Total P as determined by the persulfate digestion procedure is generally assumed to include sediment organic P and most forms of inorganic P, although some highly insoluble minerals may not hydrolyze with persulfate digestion. However, the operational definition of total P (Clesceri *et. al.*, 1998) relates quite well to the amount of phosphorus which may be ultimately available for algal growth and is often used to describe the trophic status of surface waters. Phosphorus released with mild acid extraction (about 0.02 N) is an operational definition which generally represents sediment phosphorus immediately available for algal and plant growth (e.g. Bray's P; Tiessen and Moir, 1993).

Deionized water amended with various volumes (V) of 3.571 M H_2SO_4 was added to each sediment or hematite sample (volume V_0) to reach the desired acid concentration (0, 0.02, 0.05, or 0.1 N). After the addition of DI water or acid, the sample was shaken vigorously by hand for 1 minute, allowed to settle for 5 minutes, shaken again for 1 minute, and allowed to settle for an additional 5 minutes. Following this procedure, 2–5 mL of the solution were removed with a syringe and filtered through a 0.45 µm membrane filter. The filtrate (1 mL for acidic solutions or 5 mL for solutions containing only DI water) was diluted to 50 mL with DI water and analyzed for soluble reactive phosphate (SRP) by the ascorbic acid method (Clesceri *et al.,* 1998).

Phosphorus Release from Sediment. The various treatments for each experiment were conducted in duplicate or triplicate. For each experiment, 2 g of wet sediment were placed in a known volume (V) of DI water. For some experiments, mine tailings were mixed with wet sediment in a 1:1 ratio by weight. Sediment, with or without mine tailings, is referred to as the "solid phase" with respect to phosphorus chemistry. Treatments to the sediment slurries (solid phase + DI) included variations in the oxygen level, biological activity, and incubation time. Phosphorus concentrations in the aqueous and solid phase were measured in triplicate at various times for each treatment as described above. All phosphorus concentrations were standardized to sediment dry weight.

Oxygen levels influence the redox state of iron which, in turn, affects phosphorus sequestration. We employed two methods to make the sediment environment anaerobic in order to study the effects of oxygen on phosphorus chemistry. One method was to purge sediment slurries with N_2 (physical removal of oxygen), and the other was to incubate slurries under conditions favorable for microbial growth (biological removal of oxygen). To physically remove oxygen from the sample, the solid phase was placed in a 60 mL glass vessel designed for anaerobic work which was then filled with 30 mL of deionized water. The vessel was sealed with an airtight septum through which a needle was inserted to purge the vial with N_2 gas for approximately 30 minutes. The dissolved oxygen concentration in the sample was measured with a CHEMets kit (Fisher, Chicago, IL). Purging continued until the dissolved oxygen concentration was less than 2 mg/L. After the purge, the samples were allowed to equilibrate for 2 days. The required time for reaching anaerobic equilibrium was determined in a separate experiment (data not shown).

In order to remove oxygen from the sample by biological processes, approximately 0.4 g of the solid phase was placed in a 15 mL glass vessel designed for anaerobic work. The vessel was then filled with 13 mL of DI water containing 1% (w/w) glucose, leaving just enough headspace for phosphorus extraction (about 1 cm^3), and sealed with an airtight septum. The samples were left to incubate at room temperature for approximately 1 week, at which point dissolved oxygen was measured as above. Phosphorus concentrations were measured by the method outlined above after the 1 week incubation.

Data Analysis. The percent of available phosphorus released from the sediment was determined by dividing the phosphorus released under each treatment condition by the total phosphorus available in the sediment sample (206 μg P/g dry weight sediment). In order to compare sediments treated with hematite to the controls (untreated sediment), paired Student *t*-tests were performed. Significance was determined at the 0.05 level.

Principal Findings

Total phosphorus in the Silver Lake sediment sample used for these experiments was 206 µg P /g dry weight sediment. The mine tailings also contained some phosphorus (82 µg total P/g dry weight), although only a small portion of this phosphorus could be considered to be biologically available, as only 11 µg P/ g dry weight was extracted with 0.02 N H_2SO_4.

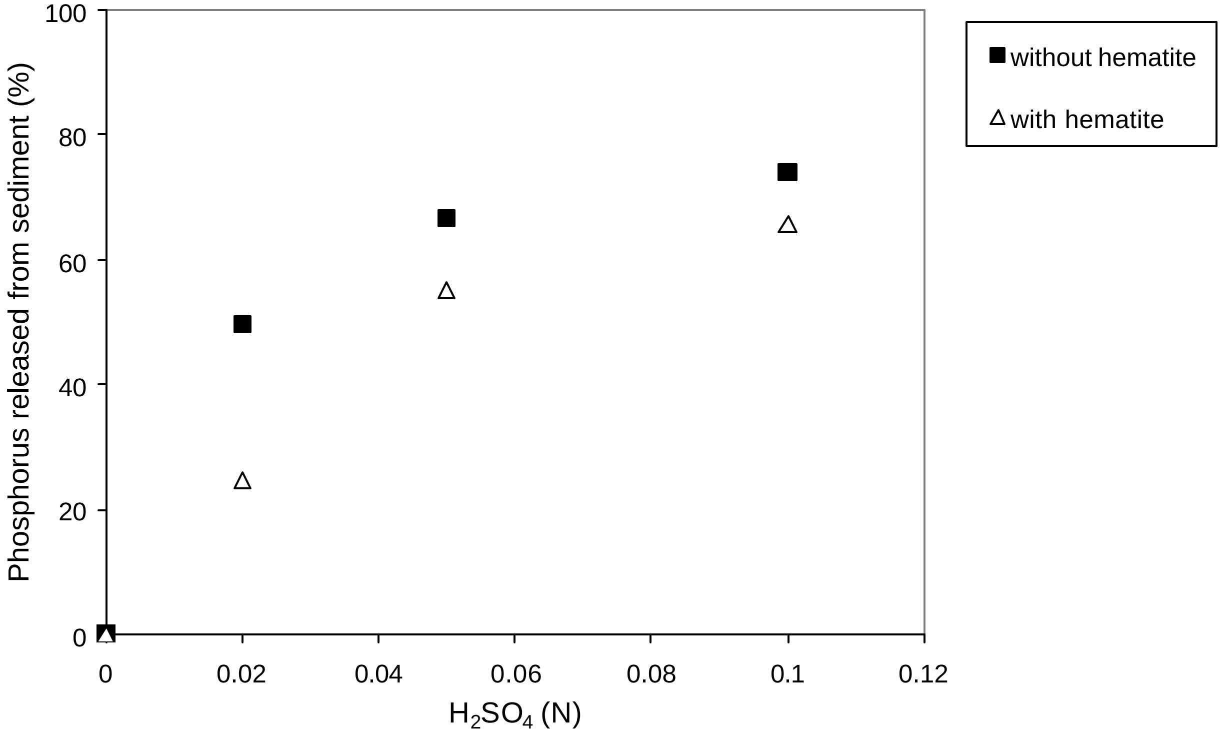

Figure 1. Release of phosphorus from Silver Lake sediment under aerobic conditions. Sediment samples (filled squares) and sediment mixed in a ratio of 1:1 (w/w) with hematite (open triangles) were extracted with deionized water and increasing concentrations of sulfuric acid. The total phosphorus content of the sediment was 206 ?g P/g dry weight.

Under aerobic conditions (dissolved oxygen concentration approximately 5.6 mg/L), little phosphorus was released into the aqueous phase, but significant amounts of phosphorus could be extracted from both the untreated lake sediment and from sediment mixed 1:1 with mine tailings as extraction conditions contained increasing concentrations of acid (Figure 1).

As expected, the degree of phosphorus release was related to the extraction conditions. Under conditions which represent phosphorus availability for algal growth (extraction with 0.02 N H_2SO_4), the untreated sediment released approximately twice as much phosphorus as the sediment mixed with mine tailings containing hematite (102.2 and 50.9 µg P/g dry weight sediment, respectively). However, phosphorus release from sediments and iron-containing compounds would be expected to be low under oxidizing conditions.

Therefore, further experiments were done to measure the release of phosphorus from sediments under anaerobic conditions.

Under anaerobic conditions (dissolved oxygen concentrations ~ 1 mg/L) generated by purging the system with N_2, mine tailings added to sediment did not increase phosphorus sequestration (Figure 2).

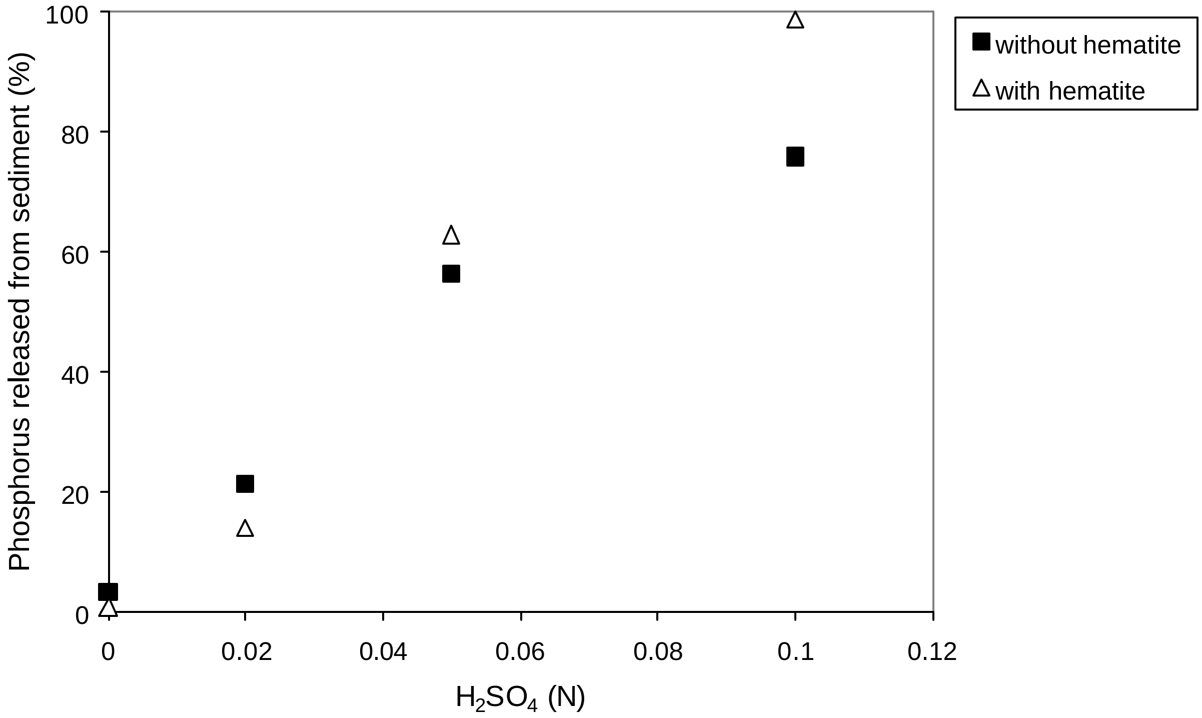

Figure 2. Release of phosphorus from Silver Lake sediment under anaerobic conditions after the sediment was purged with N_2 for 2 days. Sediment samples (filled squares) and sediment mixed in a ratio of 1:1 (w/w) with hematite (open triangles) were extracted with deionized water and increasing concentrations of sulfuric acid. The total phosphorus content of the sediment was 206 ?g P/g dry weight.

After extraction with 0.02 N H_2SO_4, phosphorus release from the sediment (whether untreated or treated with hematite) was similar to that from aerobic sediment treated with hematite (44.2 and 41.3 µg P/g dry weight sediment for untreated and treated sediment, respectively).

When the Silver Lake sediment was incubated for 1 week with an added carbon source (glucose) to stimulate microbial growth, approximately half of the phosphorus in the sediment was released into the aqueous phase, even without the addition of acid (Figure 3).

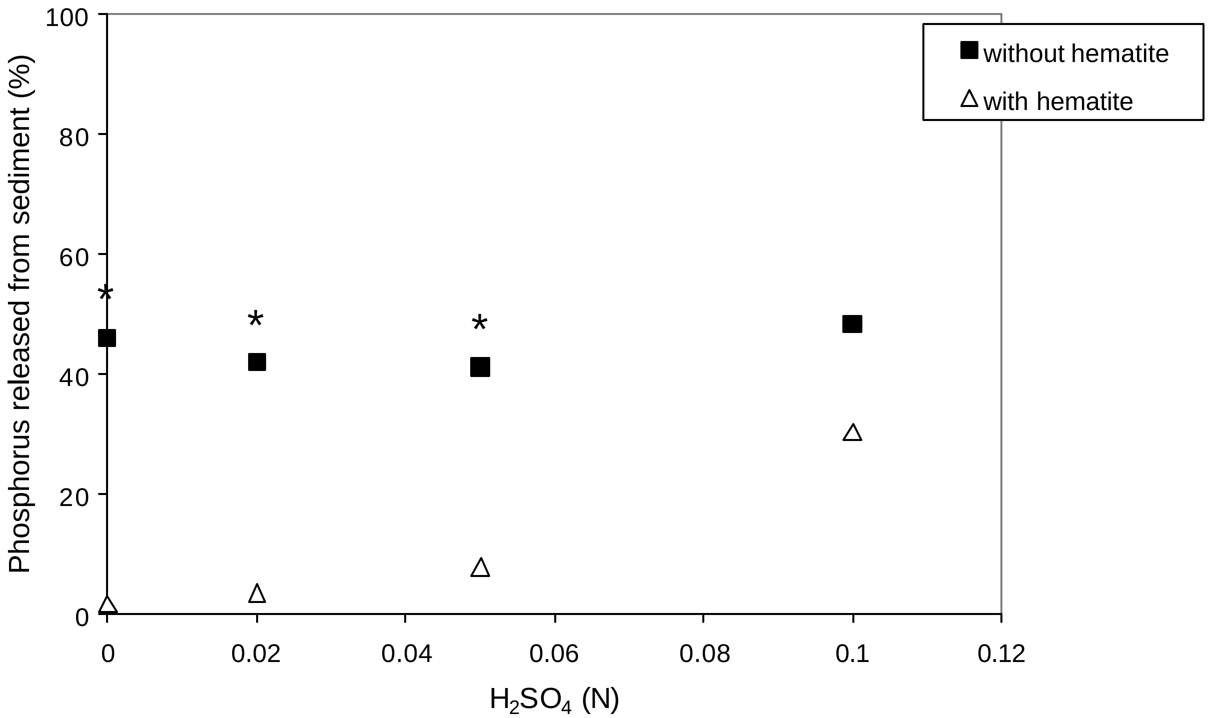

Figure 3. Release of phosphorus from Silver Lake sediment under anaerobic conditions after the sediment was incubated with glucose (1% w/w) for one week.

However, when these sediments were mixed with mine tailings and subjected to similar conditions, the phosphorus remained sequestered until the sediment was extracted with acid at concentrations in excess of 0.05 N. Oxygen concentrations in these samples were similar to those in the samples purged with nitrogen (~ 1 mg O_2/L).

When the glucose addition was combined with the nitrogen purge, approximately 40% of the total phosphorus in the Silver Lake sediment was released into the aqueous phase (Figure 4), and nearly 60% was released with mild acid extraction (0.02 N). With hematite present in the system, most of the phosphorus remained sequestered in the sediment until the sediment was extracted with 0.1 N sulfuric acid.

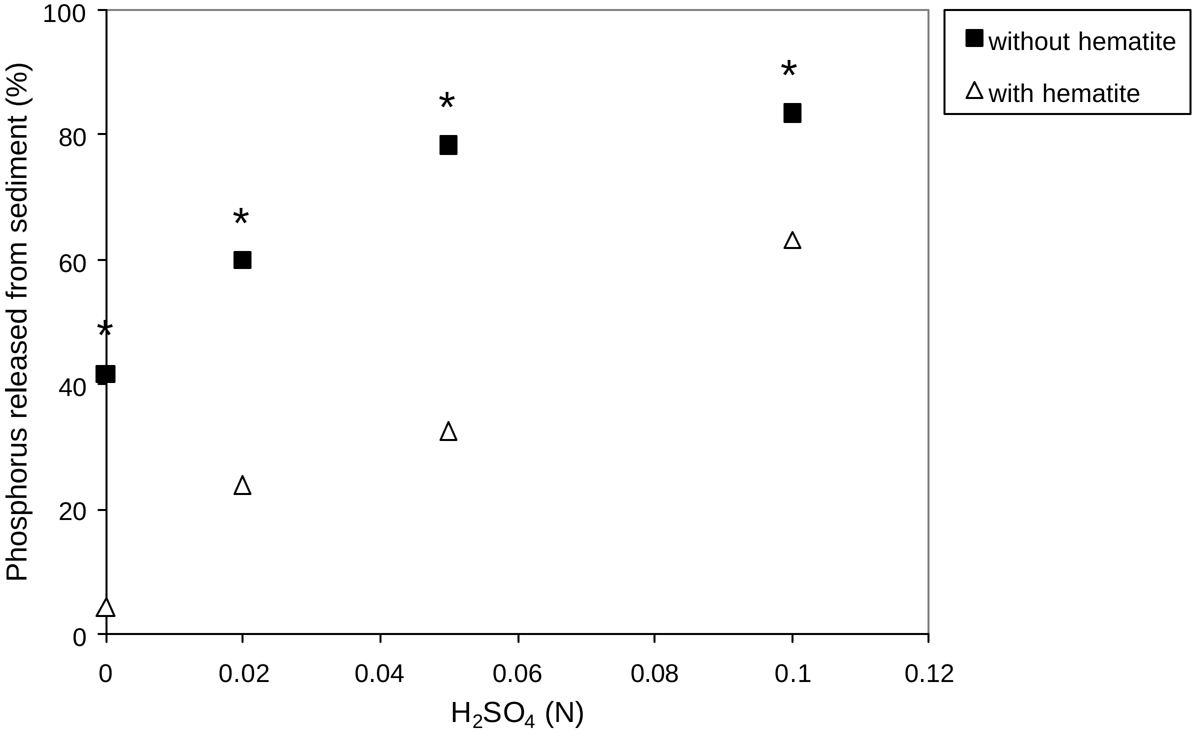

Figure 4. Release of phosphorus from Silver Lake sediment under anaerobic conditions after the sediment was purged with N_2 and incubated with glucose (1% w/w) for one week to stimulate microbial growth. Sediment samples (filled squares) and sediment mixed in a ratio of 1:1 (w/w) with hematite (open triangles) were extracted with deionized water and increasing concentrations of sulfuric acid. The total phosphorus content of the sediment was 206 ? g P/g dry weight. Statistically significant differences ($p < 0.05$) between the treated and untreated sediment samples are indicated by an asterisk.

This sequestration is comparable to the situation in which the system is aerobic (Figure 1), although the final oxygen concentrations were $\leq$ 1 mg O_2/L in all of the anaerobic treatments.

Significance

Iron mine tailings from the Cuyuna Range in Minnesota containing hematite proved to be effective for preventing the release of phosphate into aqueous solution from phosphorus-laden Silver Lake sediments, even under anaerobic conditions. In both of the treatments in which anaerobic conditions were initiated biologically, the release of bioavailable phosphorus was significantly reduced in the sediments mixed with hematite as compared to sediment solutions alone, even though the dissolved oxygen concentrations were similar to those of the nitrogen purged system. The fact that the best results were seen in samples in which glucose was added to stimulate the growth of microorganisms suggests that the process of phosphorus sequestration was microbially mediated. We suggest that the hematite in the mine tailings served as an electron sink for microbial respiration, but that the reduced iron released into solution continued to sequester phosphorus, either as it re-oxidized, forming hydrous ferric oxide complexes containing phosphorus (HFO-P), or through precipitation as vivianite. The nature of the iron-phosphorus compound(s) formed in these reactions should be investigated further.

Conventionally, the presence or absence of O_2 is considered to be the main determinant of both iron and phosphorus chemistry in surface water. Indeed, anoxia does initiate the release of both Fe and P from the sediment into the water column. For this reason, aerators are commonly used in the restoration and management of shallow basins to oxygenate the water for aquatic organisms and to help prevent the release of phosphorus from surface sediments. However, it is known that Fe^{3+}, as well as oxygen, can serve as the sole electron acceptor in some microbes through dissimilatory Fe^{3+} reduction (Fe^{3+} respiration) which leads to the oxidation of organic matter and the reduction of Fe^{3+} (see reviews by Lovley, 2000; Lovley, 2001). This process is likely to be particularly important in shallow basins with high concentrations of organic matter (Lovley, 2001), a common situation in eutrophic surface waters. We suggest that this process is responsible for the sequestration of phosphorus observed in our glucose-treated sediment amended with mine tailings. Further studies are planned to study the microorganism(s) involved and the effect of adding other carbon sources (e.g. acetate) to optimize their growth.

Other treatments for phosphorus sequestration in lake sediment have been described previously. These remediation techniques include the addition of aluminum (Rydin and Welch, 1998; Kopácek *et al.*, 2001; Van Hullebusch *et al.*, 2002; Lewandowski *et al.*, 2003), ferric sulfate (Perkins and Underwood, 2001), ferric aluminum sulfate (Foy, 1985), ferrous iron (Deppe *et al.*, 1999; Deppe and Benndorf, 2002), gypsum (Bastin *et al.*, 1999; Varjo *et al.*, 2003), CaO (Dittrich *et al.*, 1997), iron-based layered double hydroxides (Seida and Nakano, 2002), or hydroxyapatite seed crystals (cow bone; Jang and Kang, 2002). We believe that phosphorus sequestration with hematite offers additional benefits in that this microbially mediated technique also has the potential to remediate other contaminants in the system.

Dissimilatory Fe^{3+} reduction has also been shown to influence the mobility of a variety of contaminants in aquatic systems. For example, some iron reducers can also transfer electrons to uranium, reducing mobile U^{6+} to insoluble U^{4+}; similar results have been seen with technetium, chromium, and cobalt (Lovley and Anderson, 2000). Dissimilatory Fe^{3+} - reducing microorganisms can also utilize organic contaminants (including toluene and phenol) as carbon sources, oxidizing them to carbon dioxide and providing an added environmental benefit (Lovley and Anderson, 2000).

Nitrate is also a powerful oxidant for anaerobic respiration (denitrification). Senn and Hemond (2002) found that, in the presence of nitrates (NO_3^-) under anaerobic conditions, ferrous iron can be oxidized biologically to produce hydrous ferric oxides (HFO). The reduction of nitrate is coupled with the oxidation of As^{3+}, resulting in the formation of As^{5+} which, like phosphate, is more reactive with particles (including HFOs) and is thus sequestered. Harvey and colleagues observed a similar process when they added nitrate to arsenic-contaminated groundwater and observed a decrease in dissolved arsenic concentrations (Harvey *et al.*, 2002). If surface waters or runoff are enriched in nitrate as well as phosphate, these reactions could sequester PO_4^{3-} by a mechanism similar to that of arsenate sequestration and remove nitrate by denitrification in the process (Foy, 1986).

In theory, other oxidized iron compounds could be used in place of mine tailings. Since mine tailings are very inexpensive, however, they may prove useful for preventing phosphorus from entering surface waters. For example, large amounts of mine tailings could be used in runoff catchment basins, mixed with dredge spoil or used to filter outflow from wetlands drainage systems before such drainages enter streams or lakes.

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Identification of Relationships Between Soil Phosphorus and Phosphorus Loss Through Tile Drainage to Improve the Subsurface Drainage Component of the Iowa Phosphorus Index

Basic Information

Title:	Identification of Relationships Between Soil Phosphorus and Phosphorus Loss Through Tile Drainage to Improve the Subsurface Drainage Component of the Iowa Phosphorus Index
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Focus Category:	Water Quality, Non Point Pollution, Nutrients
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Principal Investigators:	Antonio P. P. Mallarino, Matthew J. Helmers, Ramesh S. Kanwar

Publication

Identification of Relationships Between Soil Phosphorus and Phosphorus Loss through Tile Drainage to Improve the Subsurface Drainage Component of the Iowa Phosphorus Index

Antonio P. Mallarino, Rameshwar S. Kanwar, and Matt J. Helmers

Problem and Research Objectives

The problem addressed by this project and the objectives were explained in the original proposal and have not changed. Therefore, only a brief summary is included.

Many questions related to the impact of current P management practices on P-related water quality are being asked by the public, government agencies in charge of nutrient regulations, producers, and researchers. Because of inappropriate fertilizer or manure management or the need to dispose of manure, excess P often is delivered from agricultural fields to water resources. Management guidelines and regulations are being established based on a P risk assessment tool often referred to as the P index. Although a P index has been developed for Iowa and many other states, gaps and insufficient information about some processes have created a great deal of uncertainty for some P index components. This project focuses on excess dissolved P loss through subsurface drainage that can occur when soil P concentration increases. Although many studies have monitored P concentration in tile drainage, few (and none in Iowa) have studied relationships between soil-test P and P loss through tiles. Soil-test P is affected by P fertilization, manure application, crop production, and several management practices. Although results of agronomic soil P tests are currently used in P indices, environmental P tests have been proposed as an alternative to these to measure P in soil and runoff water. There is little information concerning correlations of P extracted by either agronomic or routine tests and P loss through subsurface drainage. Limited information led the team that developed the Iowa P index to include approximate estimates of relationships between soil-test P and P loss in its subsurface drainage component.

The overall goal of the project is to establish relationships between soil P measured by various tests, fertilizer and manure P management, and P loss through subsurface drainage. The work is an interdisciplinary effort that uses existing facilities and inter-departmental cooperation to achieve objectives at a low cost. Specific objectives include:

1. Study the impact of fertilizer and manure applications on soil P measured with routine agronomic soil tests and environmental soil test methods that emphasize an assessment of potential P losses to water supplies;
2. Establish relationships between soil-test values and P concentrations in subsurface tile drainage for selected manure/fertilizer management systems; and
3. Develop equations that can be included in future revisions of the soil P factor of the subsurface drainage component of the Iowa P index.

Methodology

The methods used during the first year of the project followed those explained in the original proposal and only a brief summary is included here. Soil and tile drainage samples were collected during 2004 from three long-term field experiments. The experiments included replicated manure treatments or a combination of nutrient and cropping systems treatments. All plots have a tile collection system with automatic water sampling devices. One experiment at the Northeast Research Center evaluates cropping (tilled or no-till) and manure/fertilizer management systems for corn-soybean rotations. The systems include only N and P fertilizer according to crop needs, only manure according to the N needs of the corn, manure according to the P needs of the corn (and N fertilizer supplementation), and manure according to the estimated N removal by both the corn and soybean crops. Two other experiments are established at the Agronomy and Agricultural Engineering Research center near Ames. One experiment includes various rates of poultry manure compared with equivalent N fertilizer rates for the corn-soybean rotation. The other experiment evaluates swine manure placement (broadcast, injected) and time of application (fall, spring) for the corn-soybean rotation. Soils were sampled to a depth of 3 feet.

Principal Findings and Significance

No detailed results for the first year can be reported at this time because many samples are still being analyzed in the laboratory or results are being summarized into computer files. For example, all water samples collected along the season at the three sites were analyzed for orthophosphate P, but data are still being studied for possible outliers before calculating average concentrations for the year and P loads. Approximately 400 soil samples (considering all plots and various sampling depths) were processed; many analyses were completed, but others are still in progress and a database generation needs all results completed. Soil is analyzed for P by routine soil P tests (Bray-P1, Mehlich-3 P, and Olsen), pH, two environmental P tests (Fe-oxide impregnated paper strips and water extraction), and total P.

The preliminary results indicate that the treatments applied to these experiments resulted in large differences in soil-test P values for the 6-inch top layer of soil. This is a good result because it guarantees meaningful relationships between soil-test P levels and P in tile drainage. For example, the results of agronomic soil tests indicate that soil-test P ranged from values near optimum for corn and soybean production (for which maintenance P fertilization is recommended) to values as high as six times the optimum values (higher than 120 ppm by the Bray-1 or Mehlich-3 tests and higher than 70 ppm by the Olsen test). The largest soil P values were observed for plots in which manure was applied every year at estimated N-removal rates or when manure was applied only for corn but at rates higher than needed according to current recommendations for N fertilizer application.

Observation of P concentrations in tile water also showed large variation, although raw data have not been summarized at this time for all sites or treatments. For example, data available for the Northeast Research Center indicate that average orthophosphate P in tile water ranged from values less than 20 ppb (parts per billion) to almost 210 ppb. The highest value corresponded to a treatment in which swine manure is applied to both corn and soybean crops in the rotation at rates based on N needs of corn and expected N removal with soybean harvest. The lowest values corresponded to treatments in which either fertilizer or manure P was applied according to current Iowa recommendations for both crops. Interestingly, however, P in tile water was also low for plots of a treatment involving application of swine manure at N-based rates only for corn. This result, together with results of soil P tests, suggests that manure application only for corn at amounts that supply the N needs of corn and at the same time approximately the P needs for the two crops of the rotation does not result in elevated P concentrations in tile drainage. The tile water flow data are also available for these sites, but calculations of P loads have not been completed at this time.

Vegetative Filter Education and Assessment in the State of Iowa

Basic Information

Title:	Vegetative Filter Education and Assessment in the State of Iowa
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Principal Investigators:	Steven K. Mickelson, Kapil Arora, Matthew J. Helmers

Publication

Vegetative Filter Education and Assessment in the State of Iowa

Steven K. Mickelson, Matt Helmers, Kapil Arora

Problem and Research Objectives

Reduction of sediment and nutrients in surface runoff to rivers and lakes is important to Iowa's initiative to reduce the number of impaired water bodies. Vegetative filters help to reduce the deterioration of the surface waters through retention of the sediments and nutrients from surface runoff from agricultural fields. Vegetative filter strips (VFS) have been shown to be most effective for shallow, uniform surface runoff conditions, but it has also been shown that, in the case of heavy overland flows, the flow concentrates and only a portion of the vegetative filters proves to be effective in sediment and nutrient retention in the filter. Determining the most important design considerations for VFS is important for maximizing the water quality benefits for the VFS. Therefore, the on-site assessment of existing vegetative filter strips to examine and document critical design criteria is highly significant. It is also important to extend the findings and knowledge found in the field assessment to the stakeholders and upcoming generation so that they implement these designs and protect the environment. Therefore, the following objectives are considered important to be achieved in relevance to the existing scenario. The objectives include:

1. Development of an assessment tool for evaluating the effectiveness of VFS using past and current research literature findings;
2. Identification of VFS sites for in-field data collection and assessment;
3. Education of grade school, junior high, and high school students on VFS performance and surface water runoff issues related to water quality and biodiversity;
4. Assessment of the performance of VFS in a local watershed within Iowa using site assessment tools developed by this study and students educated through the project; and
5. Calibration and validation of a computer model (VFSMOD) for use in education related to the effectiveness of VFS in Iowa.

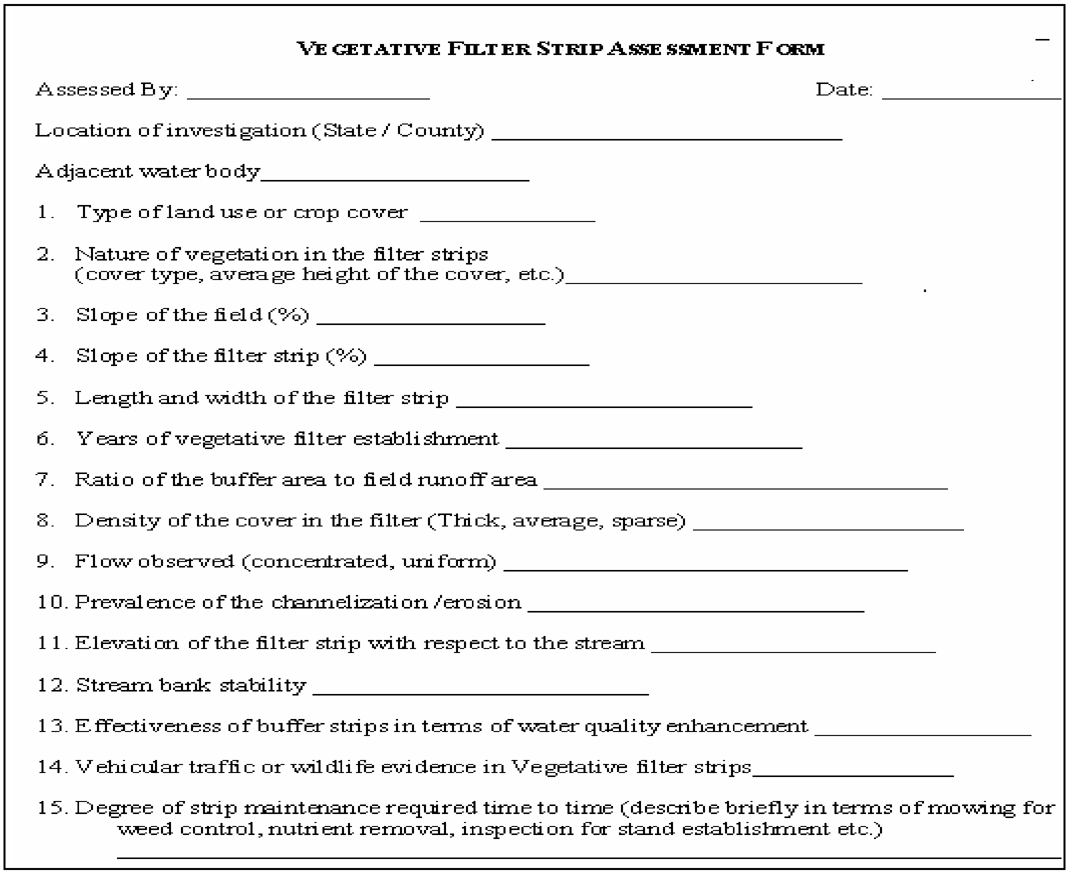
Methodology

Using data from past and current research projects on VFS, an on-site assessment tool will be developed to evaluate the performance of Iowa's VFS in key impaired water bodies. The major component of this study constitutes assisting grade school, junior high, and high school students in evaluating current VFS in an impaired watershed(s) close to their location. These training sessions will help the students to better understand the processes and impacts of nutrients from agriculture on water quality and the impact of sediment accumulation on aquatic life in lakes and streams. The Rock Creek Watershed next to Newton, Iowa has been selected by the research team. This site was selected since it was in the extension Agricultural Engineer's (Kapil Arora) region and due to the ease of collaboration with the local NRCS county office and the local educators. The students will make an efficient site evaluation with the guidance of the field staff and research team. The site evaluation will include the following parameters related to the filter strips:

- Vegetative filter length and width
- Slope and shape of the filter
- Type of vegetation
- Uniformity/space distribution of vegetation
- Tiller count
- Area ratio (contributing area to filter area)
- Rill and gully erosion evidence/measurements
- Residue cover of upland field
- Presence of drainage tile
- Evidence of wildlife
- Evidence of stream bank stability and/or instability
- Visual evidence of flow patterns (residue strips)
- Biomass/area

Validation checks will be made for the assessment at each subwatershed site within the Rock Creek watershed by the research team. The data from the site evaluations will be used to develop an assessment tool in Geographic information Systems (GIS). This software will combine the site evaluation data of each point on the filter strip into layers of information at that point on the map of the watershed to give a better understanding of the runoff hydrology at that point. The technique of Digital Elevation Model (DEM) will be employed for the digital representation of the topographic surfaces as a regular grid of spot heights. It will also help us to estimate the elevation at different points in the watershed, hence helping in the estimation of the slope at various places. DEM will also help to identify the sinks in the drainage area, generate flow accumulation and flow direction in the watershed from which the drainage/stream network of the watershed can be established. This assessment tool will help to analyze and quantify the performance of the filter strips towards the prevention of surface water pollution.

We will also integrate the use of a simulation model known as VFSMOD (developed at North Carolina State University) to model VFS benefits under various hydrologic conditions with the help of data on rainfall, topography, land use, land cover, etc. The simulation model's graphical representation of study results will also prove to be an efficient educational tool for the high school students. High schools in the vicinity of Rock Creek Lake Watershed have been contacted, including the Grinnell High School FFA and Newton Senior High School FFA. Both FFA chapters have shown keen interest in participating in this project, and Structure of Intellect (SOI) at Thomas Jefferson Elementary in Newton has also agreed to participate. The students will fill out an Assessment Form (Figure 1)at a given VFS site. This will help students in their assessment of the filter strips. Qualitative measurements on the form will have supportive rubrics attached that more adequately describe various levels of quality related to a specific measurement. This learning activity is planned for September 2005. The team also met NRCS staff in September 2004 in regard to acquisition of the data related to the site. Information obtained through the surveys will be analyzed for flow patterns. As a result of this meeting, several potential sites were identified based on their vegetation growth, time (years since establishment), filter width, and drainage area served. Out of these sites, land owners of ten sites have agreed to partner in this project. The land owners have agreed to provide access to the sites for the team to carry out their evaluations. The team visited the Rock Creek Lake Watershed in November 2004. During this visit, a few sites were evaluated for vegetation stand and visual observations of flow paths.



VEGETATIVE FILTER STRIP ASSESSMENT FORM

Assessed By: ____________________ Date: ____________

Location of investigation (State / County) ______________________________

Adjacent water body____________________

1. Type of land use or crop cover ____________
2. Nature of vegetation in the filter strips
   (cover type, average height of the cover, etc.)______________________
3. Slope of the field (%) ________________
4. Slope of the filter strip (%) ________________
5. Length and width of the filter strip ______________________
6. Years of vegetative filter establishment ______________________
7. Ratio of the buffer area to field runoff area ______________________________
8. Density of the cover in the filter (Thick, average, sparse) ____________________
9. Flow observed (concentrated, uniform) ______________________________
10. Prevalence of the channelization /erosion _________________________
11. Elevation of the filter strip with respect to the stream _____________________
12. Stream bank stability _________________________
13. Effectiveness of buffer strips in terms of water quality enhancement ________________
14. Vehicular traffic or wildlife evidence in Vegetative filter strips______________
15. Degree of strip maintenance required time to time (describe briefly in terms of mowing for weed control, nutrient removal, inspection for stand establishment etc.)
   ____

Figure 1. Rough Draft of VFS Assessment Tool

Principal Findings and Significance

The majority of the first year of this study has been spent on reviewing the key literature related to VFS for the purpose of designing the best on-site VFS assessment tool. Significant time was also given to developing the assessment tool, choosing the correct watershed, collecting in-field survey data, and setting up collaborations with the Newton educators. Therefore, objectives 1 and 2 have been completed and work is continuing this year on objectives 3–5. The following section is a summary of the findings from key literature sources that have been used in creating the VFS assessment tool.

The transport of sediments and the range of applied agrochemicals from agricultural fields into surface water bodies is one of the major environmental threats. This transport is a result of heavy rainfalls or huge amounts of overland flow. Controlling the amount of agrochemicals and sediments by planting close growing vegetation or tall, stiff grasses is a significant management practice that helps reduce the transport of these substances to receiving waters. These VFS offer important advantages where runoff concentrates and are considered effective in filtering sediment and slowing down runoff velocity. These VFS, also called vegetative buffer strips, prove to be an impediment to the movement of suspended material in the runoff, hence promoting the settling of the suspended solids (i.e., sediments and applied agrochemicals). Therefore, it is important to assess the effectiveness of the VFS in removal of the sediments and nutrients from the runoff. The effectiveness of the strip is dependent on its width, types of vegetation, age, level of development, and many more factors. The quantification of the effectiveness of a VFS also helps to quantify the amounts of the sediments and the chemical runoff averted from the waterways.

Use of vegetative filter strips stands as an effective measure to filter pollutants from runoff leaving the agricultural lands. VFS displace land from crop production, hence, minimizing the filter area. Therefore, it's important to determine its effectiveness. One of the research studies of VFS involved experimentation in which UAN (source of N) and broiler litter were used as the nutrient sources (Magette et al., 1989). The study was conducted under the assumption that P movement is dependent on total soluble solids (TSS) transport; whereas N can move in soluble form more freely. Also, the soil taken was rich in P although no supplemental P was applied. The results showed higher losses of P during UAN tests and that those losses diminished as the number of tests progressed, while losses of TSS did not decrease. P losses generally decrease with an increased number of filter strips; as do TSS losses. The conclusions of the study indicated that the performance of the VFS generally diminishes as the ratio of vegetated to non-vegetated area decreases. Also, it was observed that the nutrient removals are affected as the number of runoff events increase.

In another study, strips of tall, stiff grasses were planted perpendicular to the slope to form a runoff and erosion control practice (Meyer et al., 1995). This offered an important advantage where runoff concentrates. If flow concentrates, the retarding and filtering effectiveness of the VFS is reduced. Stiff grass hedges are more resistant to erosion than VFS, as these have more robust stems, whereas narrow hedges promote sediment deposition primarily by slowing the runoff in ponded backwater. It was concluded from the experimentation that hedges retarded the flow and caused a hydraulic jump several meters upslope of the hedges, leading to the deposition of the coarser sediments just past the hydraulic jump. The formation of the hydraulic jump and sediment deposition enhanced the flow retardance and deepened the ponded flow. Sediment trapping resulted mostly from the upslope ponding by the hedges rather than the filtering action, so the physical characteristics of the different grasses such as stem density, diameter, stiffness, etc., were considered important primarily to the extent that they retarded flow. The sediment was observed to be trapped because it had sufficient settling time in the ponded flow and not because of its inability to pass through the voids in the grass. These results emphasized the effectiveness of the stiff grass hedges. Trapping effectiveness depended upon the size distribution of the sediment load rather than on the flow rate of the runoff.

Patty et al. (1997) studied the use of grassed buffer strips to remove pesticides, nitrate, and soluble phosphorus compounds from runoff water on three research farms. Grassed buffer strips were seen to be effective in restricting the pollutant transfer in runoff by large margins. The literature data and conclusions drawn showed that sowing perpendicular to the slope proved to be beneficial in reducing pesticide content in runoff and also indicated that all the conservation tillage systems reduced the herbicide runoff by an average of 60% when compared to moldboard plowing. Sorption of herbicides onto organic matter and vegetation in the grassed buffer strip was considered to be the active mechanism which contributed towards the effectiveness of the filter strips. It was also inferred from the experiment that a shorter time lapse between the application of fertilizer and rainfall leads to greater residues in runoff. Therefore, the ability of the grass buffer strips is best evaluated in the first events, when transfer probability is maximal.

Majed Abu Zrieg (2001) studied the factors affecting sediment trapping in VFS using a simulation study called VFSMOD. A wide range of parameters was selected for studying the VFS performance such as filter length, filter slope, manning roughness coefficient, soil type, and characteristics of incoming sediments from adjacent fields. Computer simulations revealed that the length of the filter was the most significant factor influencing the VFS sediment removal efficiency, followed by the grain size of the incoming sediment. Higher amounts of silt particles in comparison to the clay particles were observed to be trapped in a particular length of the filter, which implies that the clay particles are trapped over greater lengths of filters. Manning’s roughness coefficient, which increases with increase in land cover, land slope, and soil type, was seen to have a moderate effect on VFS performance in short filters.

Dosskey et al. (2002) studied that a concentrated flow of surface runoff from agricultural fields may limit the capability of the riparian buffers to remove pollutants. In other words, the concentrated flow may greatly limit the filtering effectiveness of the riparian buffers. Four study farms were considered and a method was developed for assessing the flow and evaluating the impact of the flow on sediment trapping efficiency. Sediment trapping efficiency was evaluated using the mathematical model that was largely based on the ratio of the buffer area to field runoff area. Results in the case of the gross buffer area were highly impressive in relation to sediment retention, as compared to that of the effective buffer area. This was because the field runoff contacted only a minor fraction of the gross area of the riparian buffer. It was noted that sediment trapping could only be improved by avoiding the concentrated flow, which is generally caused due to the deposition of soils from channelization activities within the buffer zone.

Lee et al. (2003) conducted a study to determine the effectiveness of an established multi-species riparian buffer in removing non-point source (NPS) pollutants from agricultural areas. Riparian buffers are being used as a best management practice to reduce the transport of NPS pollutants in agricultural runoff before they enter surface waters. The friction of soil surfaces can reduce the velocity of the runoff that consequently results in the sedimentation of particles, but riparian buffer vegetation and the layer of organic litter on the soil surface are much more effective in slowing the velocity of surface runoff (Correll, 1997). Triplicate plots were installed for this study where each of the cropland source areas was paired with no buffer, a switchgrass buffer, and a switchgrass/ woody plant buffer located at the lower end of each plot. A significant negative correlation was observed between the trapping effectiveness of the buffers and the intensity and total rainfall of individual storms. Actually, buffers helped to reduce the mass transport of total N and total P in surface runoff from cropland due to the mechanism of infiltration. Infiltration provided the pathway for water and soluble chemicals to enter the profile, but suspended fine soil particles with adsorbed chemicals also entered the profile, thus decreasing the surface runoff and sediment transport capacity. Water samples that were collected from the field showed a significant decrease in surface discharge of runoff, sediment, and nutrients. Particle size distribution in the surface runoff changed through the buffers, indicating that there was a selective process in which large particles deposited prior to the small particles. It was observed that more than 90% of the sediment in the surface runoff from the buffered plots was in the <0.05 mm size. The differences in the amount of sediment and nutrients trapped by the various buffers were also attributed to the differences in cropping. The results therefore indicated that the selection of one buffer over the other should be based on the problems and conditions of each site.

Wu et al. (2003) conducted a study in order to compare the effectiveness of switchgrass and tall fescue filter strips in removing the dissolved copper pesticide from runoff flowing at 2.7L and 6.0L over 0.9m soil surface area. About 60% of the applied copper was removed by both the grasses from runoff at 6.0 L flow rate, whereas with the slow flow rate, grasses helped remove all the applied copper. Adsorption to soil appeared to be the primary mechanism of the removal of copper from overland flow. The copper adsorbed by the soil was calculated as the difference between the initial concentration and the equilibrium concentration. It was observed that major amounts were retained in the upslope one third of the filter strips, hence, reducing the dissolved copper in runoff by increasing its infiltration and its retention by soil. Results also emphasized that performance of the two grass species in promoting the infiltration mechanism varied with the flow rate.

Carpena R. Munoz and J.E. Parsons (2003) devised a design procedure for vegetative filter strips using VFSMOD-W. The objective of this procedure is to obtain the minimum filter length to achieve a desired runoff sediment reduction from a disturbed source area during a design storm of a given return period. VFSMOD, which is a main component of the VFSMOD-W, is a field-scale, mechanistic, storm based model developed to route the incoming hydrograph and sedigraph from an adjacent field through a VFS and to calculate the resulting flow, infiltration, and sediment trapping efficiency. A front end model, Unit Hydrograph, was developed and added to VFSMOD-W to generate the necessary source area design inputs for VFSMOD. The application of the design procedure for a particular area involved determining the size and duration of rainfall events, the range of source area conditions, and the lengths, slopes, and types of vegetative composition of the VFS. From the experimentation, the optimal filter lengths of 1–4 m for sandy soils and 8–44 m for clay soils were determined, but certain limitations were found as to the use of VFSMOD-W. VFSMOD handling of overland flow as sheet flow could pose problems when a filter is not properly maintained and concentrated flow occurs within the filter. Filter trapping algorithms assume the formation of a regular sediment wedge deposition in the front of the filter. Also, the sediment trapping component considers no erosion and transport in the filter, which is not a problem with the well maintained filter. Therefore, the design procedure is only applicable to well constructed and maintained filters where uniform, shallow overland flow is present, which is a major limitation. The potential strength of the model is that the conservation practices in the disturbed area and filter characteristics can be studied together.

Majed Abu Zrieg et al. (2004) conducted an experimental investigation of runoff reduction and sediment removal by VFS. It was observed that the length of the filter up to 10 m had the greatest effect on sediment trapping, followed by vegetation density and inflow rate. The sediment trapping efficiency was observed to be decreased exponentially beyond 10 m. The sediment trapping efficiency was observed to increase with a decrease in inflow rates but in a non-linear fashion. Greater vegetation densities resulted in greater contact time between the soil and vegetation, resulting in less erosive power and less transport capacity of the runoff and, therefore, greater settling of the sediments and nutrients.

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Hydrologic Modeling of Subsurface Drainage for Predicting Drainage Outflow

Basic Information

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Principal Investigators:	Matthew J. Helmers

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Hydrologic Modeling of Subsurface Drainage for Predicting Drainage Outflow

Matthew J. Helmers

Problem and Research Objectives

Movement of water and nutrients through subsurface drainage systems is a concern in many midwestern agricultural watersheds, including the Des Moines Lobe of Iowa. Although subsurface drainage has its benefits—it improves the productivity of croplands and generally reduces surface water runoff—these systems result in a greater volume of subsurface drainage flow to downstream water bodies, thereby increasing nitrate-nitrogen movement to the same. In order to reduce excess water movement and nitrate-nitrogen movement in these watersheds, hydraulic modifications of drainage systems are being considered as water quality management practices. At the Iowa Water Summit held at Iowa State University on November 24, 2003, three of the five work groups (Nonpoint Sources, Nutrients, and Impaired Water Restoration) identified the need for assessment and demonstration of hydrologic modifications as a new way of addressing water quality concerns, particularly nitrate-nitrogen leaching. Two hydrologic modifications commonly proposed are shallow drain tube installation and controlled drainage. Shallow drainage consists of placing conventional tile drains at shallow depths (e.g., at 24-30” rather than at 48-60”). Controlled drainage raises the outlet of the drainage system at certain times to raise the water table. These modifications to the drainage system are expected to have a direct effect on the volume of subsurface flow and nitrate-nitrogen concentrations and loading from subsurface flow.

However, to evaluate effectively the performance of tile-drained landscapes and potential impacts of modifications, water and nutrient outflow in the system must be accurately estimated or predicted under different scenarios. Use of hydrologic models affords one the opportunity to evaluate the impact of different management strategies on water quantity and quality in subsurface drainage systems; but in order to have confidence in the modeling results, the models should be calibrated and validated. Through calibration and validation the impact of parameters that affect drainage volume—specifically, soil hydraulic properties and climate conditions—can be better understood. With this information in hand, researchers gain confidence in the models’ ability to predict subsurface flows and ultimately make use of them in management decisions.

DRAINMOD (Skaggs, 1978) and MIKE SHE (Refsgaard and Storm, 1995) are two hydrologic models that have the ability to model subsurface drained systems. DRAINMOD is a field-scale water management simulation model that uses climate data to predict water table depth, subsurface and surface drainage, evapotranspiration, and seepage on a day-to-day and hour-to-hour basis. In addition, a freezing and thawing component has been developed for DRAINMOD to enhance its use in colder climates (Luo et al., 2000). DRAINMOD has been used successfully under a variety of soil, crop, and weather conditions. MIKE SHE is a deterministic, distributed and physically based model that allows for simulation of all major processes occurring in the land phase of the hydrologic cycle. The model allows for spatially varying precipitation, vegetation, soil hydraulic properties, and land uses. Water movement modeling in MIKE SHE includes overland and channel flow, unsaturated and saturated water flow, interception, and evapotranspiration. Since MIKE SHE is a distributed model, it has the potential to simulate areas with and without tile-drainage; subsurface drainage can be specified for each cell within the model area. MIKE SHE could have the potential to model areas where tile drainage is random, and the pattern drainage, as simulated in DRAINMOD, may not be as applicable. The MIKE SHE model was developed by the Danish Hydraulic Institute, and its use has been limited in the Midwest. However, a recent study at the University of Nebraska found that MIKE SHE performed well in simulating two-dimensional overland flow in a vegetative filter (Helmers et al., 2003).

The modeling associated with this project would allow for evaluation of drainage systems using a long-term data set (1988–present) in a geographic area of importance in subsurface drainage and nitrate-nitrogen leaching (the Des Moines Lobe). In addition to modeling the drainage system, this long-term drainage record allows comparison of annual drainage volume and the temporal subsurface flow patterns from a fifteen-year precipitation and drainage record.

The objectives of this investigation are:

1. to evaluate the ability of DRAINMOD to simulate water flow through subsurface drainage systems;
2. to evaluate the ability of MIKE SHE to simulate water flow through subsurface drainage systems;
3. to evaluate differences in soil hydraulic properties for the different drainage area plots used and the impact of varying levels of site-specific soil-hydraulic-property information on simulated subsurface drainage; and
4. to review a fifteen-year drainage record to investigate the timing and quantity of subsurface drainage.

The hypotheses associated with this work are that DRAINMOD and MIKE SHE can be used to adequately predict drainage outflow, that significant variability in soil hydraulic properties from one plot to the next affect subsurface drainage, and that the accuracy of modeled and measured subsurface drainage is improved with site-specific soil hydraulic properties. This research has applicability in addressing the suitability of models for predicting subsurface drainage and the level of input data required to make accurate predictions. This research is focusing on the drainage outflow, with possible future research in this area to focus on the ability to predict nitrate-nitrogen leaching.

Methodology

In 1988, a research site in Gilmore City, Iowa, was established for studying subsurface drainage from agricultural land. A total of 78 research plots were constructed. Individual plots are 38.1 m long and 15.2 m wide. A 76 mm diameter perforated drain line was buried 1.4 m deep in the center of each plot. Another 76 mm drain line was installed on each side of the plots to prevent subsurface movement of water from one plot to another. The center line tile has been monitored in the plots for flow volume and water quality.

Hourly rainfall and daily maximum and minimum temperature are requirements for the DRAINMOD weather input. Daily rainfall and maximum and minimum temperature were obtained from an on-site weather station. This daily rainfall was distributed over 12 hours within the 24-hour period for the initial modeling with DRAINMOD. Future work will estimate hourly precipitation from the daily amount using the CLIGEN weather generator. There were short periods during the fifteen years when data was not collected with the on-site station so information from nearby stations (Pocahontas and Humboldt, IA) was used.

The Rosetta Model (Schaap, 1999) can produce all the parameters that DRAINMOD requires for soil properties by inputting soil particle distribution. Bulk density, water contents at -0.33 bar and -15 bar are optional input for Rosetta. For the Soil Survey estimation method, as referred to herein, the soil name for each plot was found in the soil map of Soil Survey of Pocahontas (United States Department of Agriculture, Soil Conservation Service, 1985), and the soil texture and bulk density of corresponding soil was determined from the Iowa Soil Properties and Interpretations Database (Version 7.0, 1/03/2004). The water content at -0.33 bar and -15 bar were estimated by graphs developed by Rawls and Brakensiek (1983) when the soil texture is known. For the Soil Texture estimation method, soil samples were extracted from 4 locations in each plot, and for each location, 3 samples were extracted from 3 different depths of 15, 38 and 61 cm. Both data of soil survey and soil test were input into the Rosetta Model; then, the results were input into the DRAINMOD to perform the drainage simulations from 1990–2004. Hydraulic conductivity and the soil-water retention curve are major factors of the soil that affect drainage volume. These data are also being gathered from laboratory testing to estimate plot specific soil hydraulic property information. This data will then also be used for the drainage modeling. This would be termed the Soil Test estimation method. Within the course of this project we will be comparing results from the Soil Survey, Soil Texture, and Soil Test estimation methods.

Rooting depth of the crop is an input parameter within DRAINMOD. Rooting depth of corn in Minnesota, which is included as a default file in DRAINMOD, was selected as the crop data in this case. The maximum Effective Rooting Depth for corn in this case was 30 cm, which is supported by Mengel and Barber (1974).

Principal Findings and Significance

From nearby weather records, the 30-year (1975–2004) average annual precipitation is 820 mm (Table 1) and the 30-year average for the primary drainage season months of April through November is 700 mm. During the fifteen years of this study, both the average annual and average drainage season precipitation were below the 30-year normal. The wettest year at the site was 1991 (918 mm) and the driest year was 1997 (471 mm). The amount of drainage varied significantly from a low of 11 mm in 1997 to a high of 587 mm in 1993. Overall, from the fifteen years, the ratio of drainage to precipitation for the April to November time period was 41% (Table 1). From the fifteen-year project site precipitation record, the greatest precipitation months are April through August (Figure 1). June had the greatest monthly mean precipitation during this period with a mean precipitation of approximately 125 mm. From Table 1, there were large differences in the amount of drainage season precipitation and drainage, and drainage volume also varied with similar precipitation amounts. Years 1999 and 2000 had nearly equal precipitation amounts (560 and 555 mm), but the drainage amounts were dissimilar with 133 mm in 1999 and 15 mm in 2000. The climatic conditions that affect drainage volume include not only amount but also when the precipitation occurred, timing since last precipitation event, and intensity and duration of the event. Despite this, we found a strong correlation in precipitation and drainage for the months of April through November for the study period (Figure 2).

Table 1. Summary of yearly precipitation, drainage, and ratio of drainage to precipitation

	Precipitation (mm)		Drainage (mm)	Drainage Ratio	
Year	Annual	Drainage Season (April–November)	Drainage Season (April–November)	Drainage to Annual Precipitation	Drainage to Drainage Season Precipitation
1990	839	715	353	0.42	0.49
1991	944	776	362	0.38	0.47
1992	815	656	386	0.47	0.59
1993	942	787	587	0.62	0.75
1994	656	528	21	0.03	0.04
1995	721	600	268	0.37	0.45
1996	763	651	465	0.61	0.71
1997	525	421	11	0.02	0.03
1998	708	592	243	0.34	0.41
1999	675	560	133	0.20	0.24
2000	687	555	15	0.02	0.03
2001	702	600	278	0.40	0.46
2002	680	651	237	0.35	0.36
2003	684	599	439	0.64	0.73
2004	767	610	235	0.31	0.39
Avg.	741	620	269	0.35	0.41
30-yr Normal	820	700			

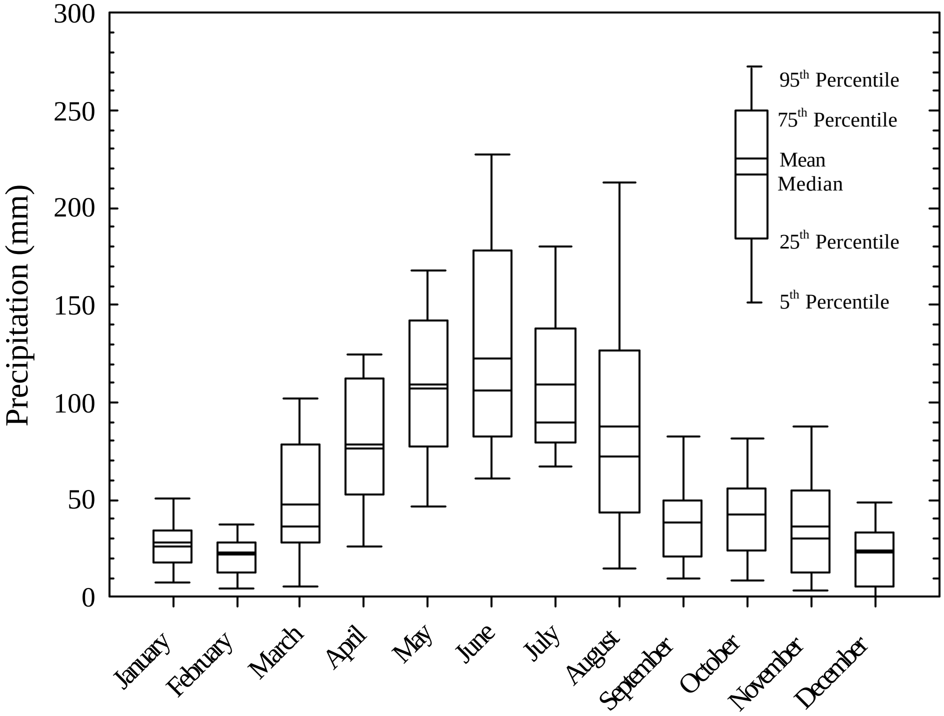

Figure 1. Distribution of monthly precipitation at the project site

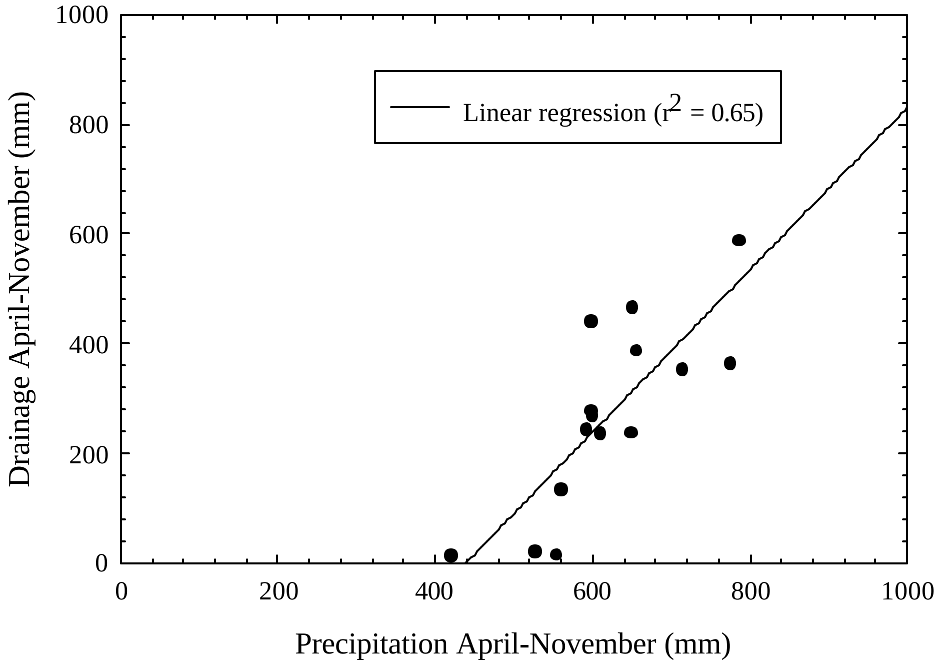

Figure 2. Correlation of precipitation and drainage (April–November)

From the monthly precipitation, it is evident that the rainfall is not uniformly distributed throughout the year; spring and summer months have greater precipitation than late fall and winter. A review of the precipitation and drainage data during the predominant drainage season (April–November) indicated that October was the driest drainage month with 6% of the drainage season rainfall and only 1% of the total season drainage (Figures 3a and 3b). Approximately 50% of the drainage season precipitation occurs in April, May, and June, resulting in 70% of the total drainage observed. The wettest of these three was June with 20% of the rainfall and 31% of the drainage. On average, there is rainfall in September, October, and November but little drainage. This is likely a result of the rainfall recharging the soil profile after the soil moisture was depleted by the growing season. As discussed above, on average, there is little drainage in the months of August, September, October, and November. While the significant drainage periods from April through June correspond with periods of significant rain, most of this time also coincides with periods without much vegetative growth. The ratio of drainage to precipitation is greater in April, May, and June than any of the other months (Figure 4).

The time periods of greatest drainage also correspond to a time of the year when drainage is essential to maintain trafficability, crop germination, and early crop development. So, including drainage management practices that may manage outflow during certain times of year would need to be considered carefully so they are effective in reducing drainage volume while also ensuring adequate drainage capacity to reduce any potential negative effects of drainage management on crop production. Likewise, a wetland downstream from a drainage system would need to be sized and designed to accommodate most of the drainage water entering the system in a three-month time span on average. Since there is little water use during the time period of April through mid-June, any excess rainfall and soluble pollutants within the soil profile are susceptible to leaching. Methods to promote more water use during this time may have positive impacts on reducing drainage volume and subsequent loss of pollutants. For instance, a crop system that includes vegetation which could remove excess precipitation via transpiration in April and May could significantly reduce drainage volumes while not adversely affecting soil moisture since much of the precipitation is lost to drainage in these months.

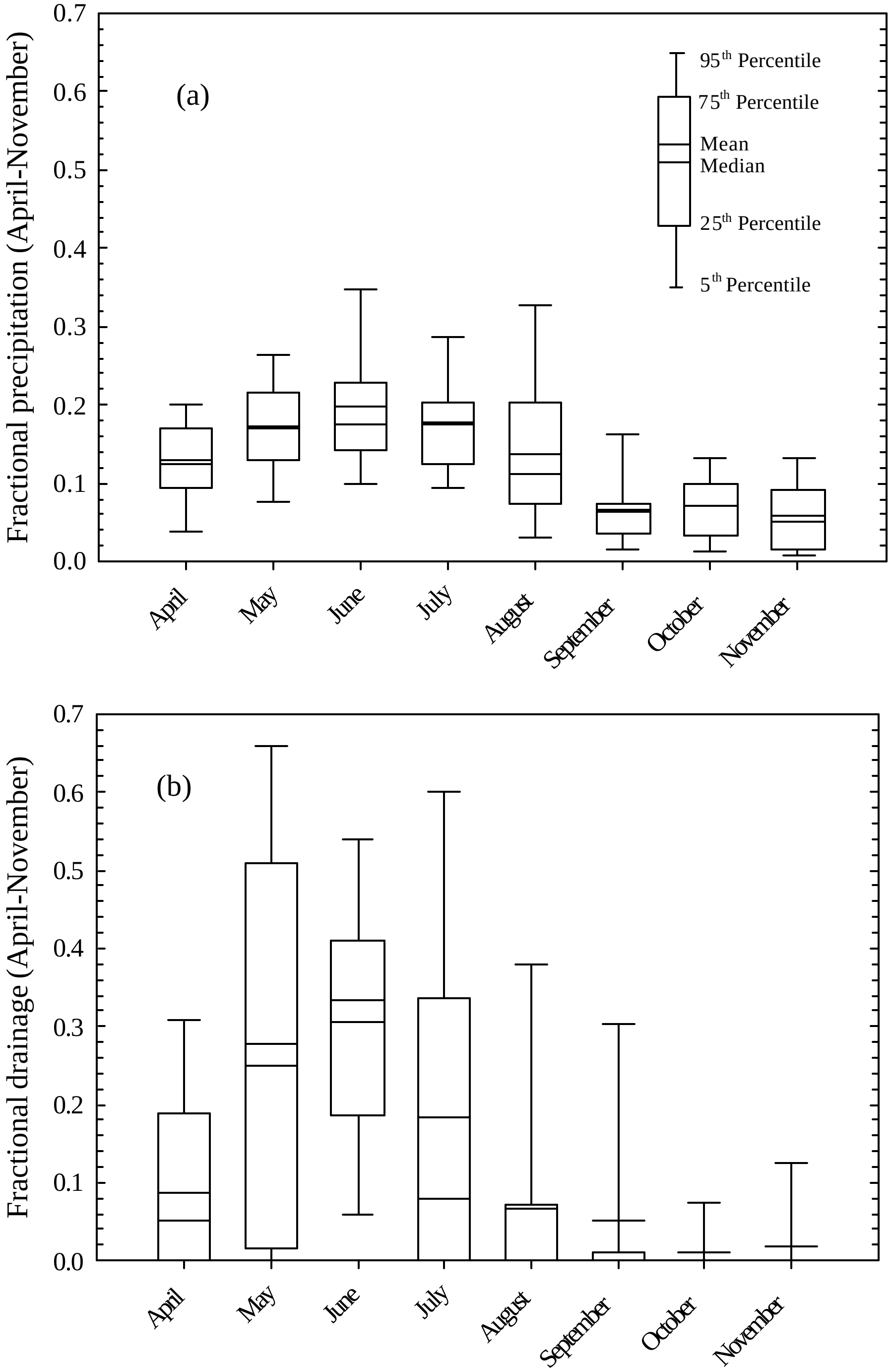

Figure 3. Box plot diagrams of monthly fraction of drainage season (a) precipitation and (b) drainage

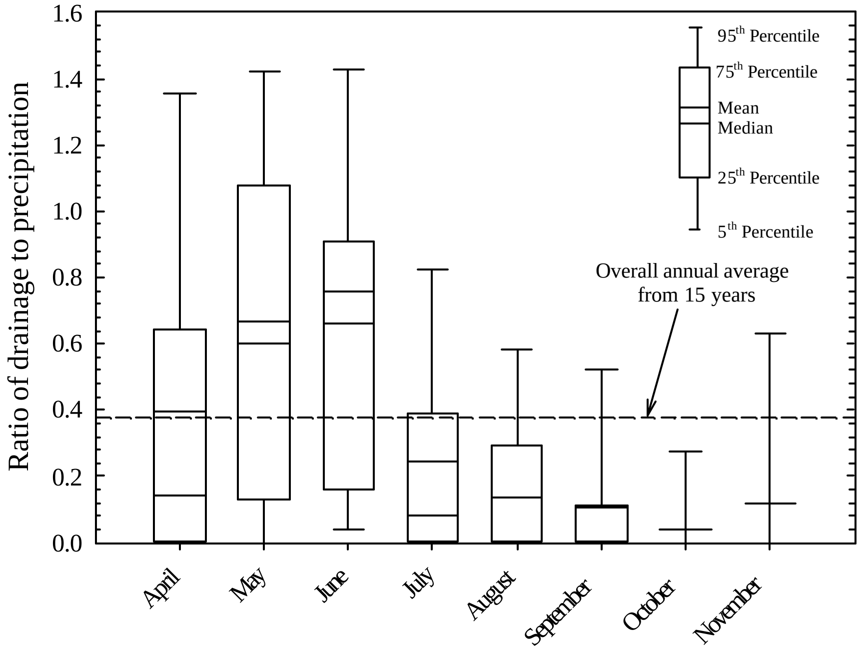

Figure 4. Ratio of monthly drainage to monthly precipitation

DRAINMOD simulations have been performed for the study plots using Soil Survey input data for soil properties as well as Soil Texture input from soil samples gathered at the project site. Cumulative drainage flow, both measured and simulated, for three of the representative plots is shown in Figures 5, 6, and 7. Again, these simulations were performed using two levels of soil input information—Soil Survey and Soil Texture—and were performed without calibration of the model. Of note from these initial simulations is that the estimated evapotranspiration and crop rooting depth were found to have a relatively significant impact on simulated drain flow. From these initial results, the model seems to perform relatively well in simulating drain flow from some of the plots, but additional work is required to explain some of the discrepancies evident when comparing measured and simulated outflow. For plots 19-3 and 6-1, the measured and simulated cumulative drainage for the fifteen-year period differed by 7 and 10%, respectively. The simulated cumulative drainage for plot 17-2 was 65% greater than the measured drainage. There was little difference between the simulated results using either the Soil Survey or Soil Texture input parameters for soil hydraulic properties (Figures 6, 7, and 8).

While DRAINMOD performed relatively well in predicting drainage outflow for some of the plots simulated as part of this study, future work on this project will focus on developing site-specific soil hydraulic property input data. In addition, the estimates of rooting depth and potential evapotranspiration will be reviewed relative to values reported in the literature to ensure the most appropriate estimates are used in the modeling. Once this information is finalized, the model will be calibrated to assess calibrated values of evapotranspiration and rooting depth along with the variability of calibrated values for soil parameters. Future work will also involve using MIKE SHE to assess its ability to simulate subsurface drainage. Since this is a spatially explicit model, this component of the project could prove important for future projects because, if the model proves accurate and useful in the tile-drained landscape, it could be used to investigate watershed scale impacts of subsurface drainage where areas with and without subsurface drainage can be simulated. Reliable models and parameterization of these models for subsurface drainage have great significance for understanding agricultural water quality because, while subsurface drainage is essential for agricultural production in many areas and in many cases can reduce surface water runoff and pollutant loss via surface water runoff, subsurface drainage contributes to nitrate loss and movement of nitrate to downstream surface water bodies.

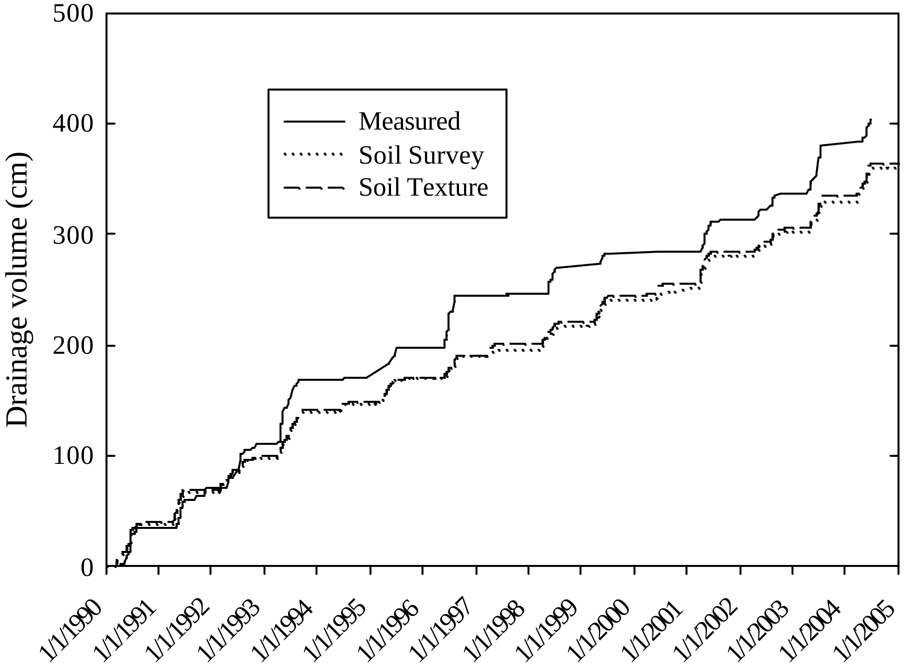

Figure 5. Comparison of measured and simulated drainage from plot 6-1 (simulations used soil properties from Soil Survey data or Soil Texture data)

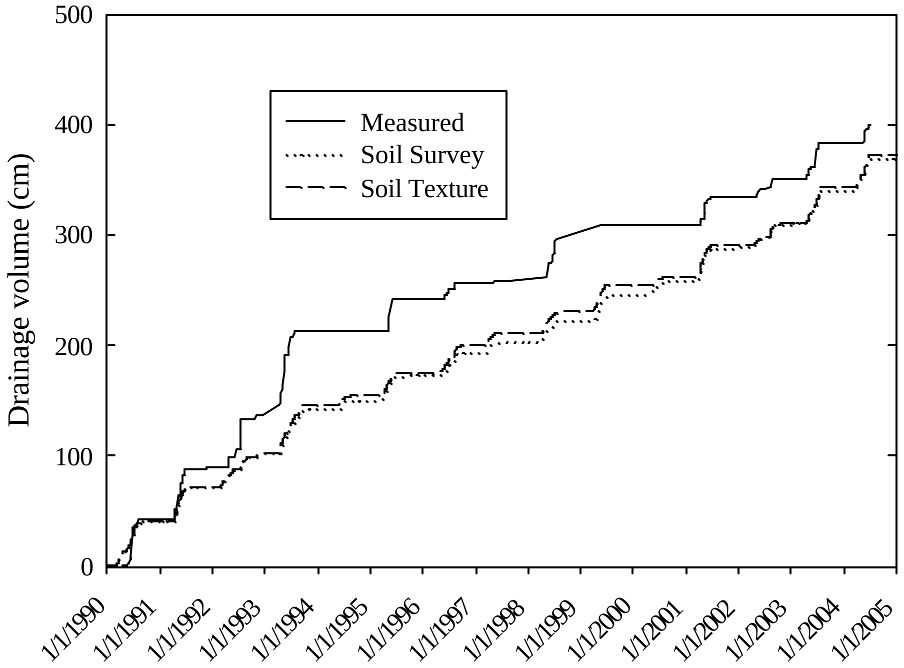

Figure 6. Comparison of measured and simulated drainage from plot 19-3 (simulations used soil properties from Soil Survey data or Soil Texture data)

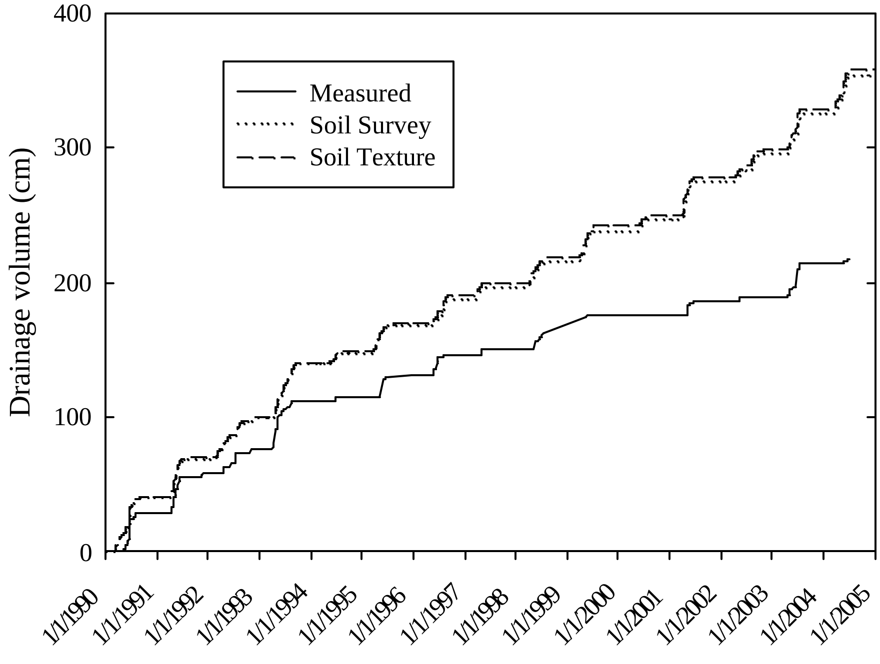

Figure 7. Comparison of measured and simulated drainage from plot 17-2 (simulations used soil properties from Soil Survey data or Soil Texture data)

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Complementary Investigations for Implementation of Remote, Non-Contact Measurements of Streamflow in Riverine Environment

Basic Information

Title:	Complementary Investigations for Implementation of Remote, Non-Contact Measurements of Streamflow in Riverine Environment
Project Number:	2001IA1021G
Start Date:	9/1/2001
End Date:	3/31/2005
Funding Source:	104G
Congressional District:	Iowa 1st
Research Category:	Engineering
Focus Category:	Methods, Surface Water, Water Quantity
Descriptors:	free-surface velocity index, streamgaging stations, in-situ measurements, non-contact measurements, discharge measurements
Principal Investigators:	Marian V.I. Muste, Allen Bradley, Ralph Cheng, Anton Kruger

Publication

1. Polatel, C. 2003. Signature of Bed Characteristics on Free Surface Velocity in Open Channel Flows, International Association of Hydraulic Research Congress XXX.
2. Polatel, C., M. Muste, V.C. Patel, T. Stoesser, W. Rodi. 2005. Double-averaged velocity profile over large-scale roughness. Submitted to XXXI International Association of Hydraulic Engineering and Research Congress, Seoul, Korea.
3. Polatel, C. 2005. Indexing by free surface velocity: A prospect for remote discharge estimation. Submitted to XXXI International Association of Hydraulic Engineering and Research Congress, Seoul, Korea.
4. Stoesser, T., W. Rodi, C. Polatel, V.C. Patel, M. Muste. 2005. Large eddy simulations of the flow over two-dimensional dunes. Submitted to XXXI International Association of Hydraulic Engineering and Research Congress, Seoul, Korea.
5. Polatel, C., T. Stoesser, M. Muste. 2005. Velocity Profile Characteristics in Open Channel Flow over Two-Dimensional Dunes with Small Relative Submergence. Submitted to World Water and Environmental Resources Congress 2005, Alaska, USA.

6. Balachandar, R., C. Polatel, B. Hyun, K. Yu, C. Lin, W. Yue, V.C. Patel. 2002. LDV, PIV and LES Investigation of Flow Over a Fixed Dune, in ETH Sedimentation and Sediment Transport Symposium.

Complementary Investigations for Implementation of Remote, Non-contact Measurements of Streamflow in Riverine Environment

M. Muste, A. Bradley, A. Kruger, R. Cheng

Problem and Research Objectives

This research has originally involved laboratory measurements aimed at establishing relationships between mean free-surface velocity and depth-averaged velocity for a range of flow conditions in open-channel flows. In a follow-up development, Large-Eddy Simulation numerical modeling was conducted to complement the experimental work. The research project is conducted to support the work of national importance pioneered by the Hydro-21 committee related to remote, non-contact, real-time assessment of stream discharges for improved data collection, research, and management.

Methodology

To investigate the relationship between free surface velocity and depth-averaged velocity, a set of experiments was conducted in a 10m long, 0.61m wide and 0.5m deep, recirculating tilting open channel flume. Two non-intrusive methods were employed; Laser Doppler Velocimetry (LDV) was used to measure velocities in the water column, while Large Scale Particle Image Velocimetry (LSPIV) was used for free surface measurements. Two-dimensional dunes and square ribs were used as the bed roughness. A train of two-dimensional fixed dunes was attached to the bottom along the length of the channel. The dune height (k) was 20 mm, and the dune wavelength (?) was 400 mm, so that ?/k = 20, which is typical of many previous studies. For flow over rib roughness, 1cm × 1cm square ribs were placed at the channel bottom. Measurements were performed at six locations over dunes and at two locations over the ribs.

Numerical simulations performed with LES were conducted to parallel the experimental results and to extend the flow cases beyond those experimentally tested. Double averaging (spatial and temporal) over the individual roughness elements was used to allow characterization of the dunes and ribs as lump roughness types. The double-averaged profiles were further used to define the virtual origin, the extent of the area directly disturbed by roughness near the wall, and shift in the velocity profiles produced by the roughness elements.

Principal Findings and Significance

The comparison of the experiments with simulation has shown very good agreement. The good agreement both validated the robustness and accuracy of the simulation and allowed us to use the much denser information provided by the numerical simulations for conducting the analysis of the main study objectives, i.e., the appropriate mean velocity profile and its relationship to the roughness characteristics and flow regime. The results of the experimental and numerical experiments demonstrate that ratio of free surface velocity to depth-averaged velocity depends on the channel bed roughness. For the given flow conditions, even though aspect ratios are smaller than the values seen in natural rivers, the surface velocity reacts to spatial changes in channel bottom. Thus, it is recommended to consider the channel bed roughness while estimating discharge by indexing. The consistency in the obtained trends of velocity indices with the flow depth supports the concept of using free surface velocity as the indexing velocity.

The findings of the study up to this point have been published and citations are provided in the Publications section.

Relationship of Nitroso Compound Formation Potential to Drinking Source Water Quality and Organic Nitrogen Precursor Source Characteristics

Basic Information

Title:	Relationship of Nitroso Compound Formation Potential to Drinking Source Water Quality and Organic Nitrogen Precursor Source Characteristics
Project Number:	2002IA16G
Start Date:	9/1/2002
End Date:	5/10/2006
Funding Source:	104G
Congressional District:	IA 1st
Research Category:	Water Quality
Focus Category:	Water Quality, Non Point Pollution, Toxic Substances
Descriptors:	drinking water, water quality, contaminants, non-point pollution, disinfection
Principal Investigators:	Richard Louis Valentine

Publication

1. Assuoline, Jason, 2004, An Exploratory Study of the Formation of N-Nitrosodimethylamine (NDMA) in Chloraminated Natural Waters, MS Thesis, Dept. of Civil & Environmental Engineering, University of Iowa, Iowa City, Iowa.

Relationship of Nitroso Compound Formation Potential (NCFP) to Drinking Source Water Quality and Organic Nitrogen Precursor Source Characteristics

Richard L. Valentine

Problem and Research Objectives

Recent research indicates that certain disinfection practices may result in the formation of significant amounts of N-nitrosodimethylamine (NDMA) and, quite likely, other nitroso compounds in drinking water. These compounds are believed formed when chlorine is added to water containing ammonia and certain organic nitrogen compounds ("precursors"). Measurements in several drinking water distribution systems suggest that unprotected sources receiving point and non-point waste discharges are particularly susceptible to their formation, especially when chloramination is practiced.

The formation of NDMA and possibly other nitroso compounds in drinking water is an emerging concern because they are generally carcinogenic, mutagenic, and teratogenic (Loeppky et al., 1994; O'Neill et al., 1984). For example, the nitrosamine, N-nitrosodimethylamine, NDMA $(CH_3)_2NNO$) is a particularly potent carcinogen. Risk assessments from California's Office of Environmental Health Hazard Assessment (OEHHA) and US EPA identify lifetime de minimis (i.e., 10^{-6}) risk levels of cancer from NDMA exposures as 0.002 ppb (2 ng/L) and 0.0007 ppb, respectively. In February of 2002 the California Department of Health Services established an interim action level of 0.01 ppb (10 ng/L) in drinking water.

Many drinking water sources in the Midwest and other parts of the country are unprotected receiving point and non-point waste discharges. Municipal and industrial waste discharges, and those associated with agricultural practices, are potentially important sources of the organic nitrogen precursors required for the formation of nitroso compounds. These waters are correspondingly expected to be susceptible to nitroso compound formation from chloramination. This may limit the use of some water sources for drinking water or restrict treatment options that otherwise have desirable characteristics. Initial observations indicate that some consumers are being exposed to undesirable levels of NDMA. Organic nitrogen is therefore not a simple, benign pollutant typically associated with nutrients as generally thought.

A need exists for an improved understanding of the nature and extent of this potential problem. Work is especially needed that relates nitroso compound formation potential to source water quality and origin of organic nitrogen precursors, watershed uses, and to biogeochemical processes that could influence the quantity and types of nitroso compounds potentially produced.

Based upon the ascertained research needs, the following specific objectives of this research study have been formulated with respect to the relationship of source water quality and nitroso compound formation potential (NCFP) as a newly recognized disinfectant by-product:

1. Characterize the NCFP in a variety of "susceptible" surface and groundwater drinking source waters.
2. Examine the relationship of NCFP to source water quality and land usage.
3. Conduct mechanistic studies to characterize precursors and the influence of potentially important physical, chemical, and biological processes of the NCFP.

Methodology

Overview. The primary focus of the work performed to date has been the measurement of NDMA “Formation Potential” (NDMAFP) in natural water samples obtained from a variety of agriculturally impacted sources in Iowa. The sample locations along various rivers were selected because they were identified as points within watersheds categorized by the USGS as bodies of water impacted by agricultural waste discharges. The NDMAFP was determined through a series of laboratory assays which focused on the amendment of the surface water samples with the disinfectant monochloramine (NH_2Cl). The NDMAFP in river water samples was examined by season and in relation to other water quality variables such as nitrite, nitrate, and organic nitrogen concentrations. Additional studies were conducted to delineate the potential importance of DMA as an identifiable NDMA precursor versus other unidentified nitrogenous substances.

An additional activity was an investigation of the influence of riverbank filtration (RBF) on the formation of NDMA after chloramination. RBF is a practice in which drinking water is withdrawn from shallow wells near a river. As such, the water is subjected to a variety of biogeochemical processes that influence its water quality. While RBF is effective at reducing the formation of many halogenated DBPs such as THMs and HAAs, the relationship between riverbank filtration and NDMA precursor removal is not known.

Source Waters. Surface waters were sampled monthly from April 2003 to February 2004 at four locations categorized by the USGS as being substantially impacted by agricultural runoff and waste discharges (Table 1). The relative agricultural impact at each sampling site was estimated based on historical data representing average nitrite+nitrate (NO_2+NO_3) data found on the USGS website (NAWQA website) for years 1996 to 2002.

Table 1 Summary table of USGS-NAWQA sampling locations used throughout the course of this study. Four liters of water were collected from each site near the beginning of each month in 1 liter amber bottles which were stored at 4^{o}C until analyzed. The relative agricultural impact ranking has been assessed by average NO_2+NO_3 for each site.

Station Number	Station Name	Historical[*] NO_2+NO_3 in mg/L as N	Relative Agricultural Impact[**]
05420680	S. Fork Iowa River NE of New Providence	9.19	1
05465500	Iowa River near Rowan	7.05	2
05449500	Wapsipinicon River near Tripoli	5.61	3
05451210	Iowa River at Wapello	4.72	4

* Historical data represents the average NO_2+NO_3 values based on monthly measurements taken from 1996 to 2002.

** 1=highest, 4= lowest

In this study, the influence of riverbank filtration on NDMA formation potential of two typical Midwestern river supplies was examined. Both facilities use similar treatment processes within the plant; however, minor differences in treatment process do exist. The IC treatment facility is located nearly 30 miles south of the CR plant in Southeastern Iowa. The IC plant is located on the Iowa River, where 2 well fields containing a total of 4 horizontal wells draw water through a previously pristine alluvial aquifer. The CR facility has three large well fields stretching along a meandering segment of the Cedar River where a combination of more than thirty vertical wells supplies water to the treatment facility. While this plant and its various wells have been operating for nearly 20 years, blending waters with a range of turbidity, organic carbon and other water quality characteristics, the IC facility came on line in 2003, during the course of this study.

Another difference between the two plants is that they use different chemical disinfectants. While both facilities originally planned to use chloramines, the IC plant, since it began using riverbank filtration, is able to rely solely on free chlorine to provide the required disinfectant dose while remaining within the guidelines of the Disinfectant/Disinfection By-Product Rule designated by the recent SDWA amendments. However, it should be noted that ammonia levels entering the plant are often substantial enough to lead to the incidental formation of monochloramine upon the addition of chlorine. This may have implications on NDMA occurrence at these facilities even in the absence of intentional chloramine usage.

Water samples were obtained from the raw river water and from monitoring wells located at several locations representing a span of hydraulic residence times. Water samples were also collected from several in the treatment plants. Table 2 summarizes the characteristics of two vertical wells which feed the 60 MGD CR treatment facility. Not all wells are operated continuously, yet in this study the same wells were sampled each time. The wells were selected because the water residence times differed greatly as estimated by the (USGS, 1995). The IC plant began full scale operation in October 2003 and therefore, sampling in November was one of the first times the wells were sampled after they had been in full service. The IC wells were situated about 50 feet from the banks of the Iowa River, and the horizontal sections of the collection wells extended from the wells, under the river. However, it was not feasible to estimate specific residence time within the aquifer since detailed hydraulic characterization for the new IC wells was not readily available for this study.

Table 2 Hydrogeologic characteristics for Seminole well field. Estimated travel time was calculated based on the distance from the well to the river and the approximate hydraulic conductivity initially measured at each specific well.

Sampling Well	Distance From River (ft)	Hydraulic Conductivity (ft/d)	Transmissivity (ft^2/d)	Specific Capacity (gpm/ft)	**Estimated Travel Time (d)**
Seminole 14	800	57.2	3,374	25.4	**14**
Seminole 17	63	192.7	11,177	73.1	**0.33**

Analytical Methods. The basis of the NDMA FP test has been described by Mitch and Sedlak, 2004. It is based upon addition of preformed monochloramine to water samples and a 7-day reaction time. The use of preformed monochloramine instead of the usual practice of in-situ formation by addition of free chlorine and followed by ammonia addition maximizes NDMA formation. Additional work (results not shown) indicated that NDMA formation was reduced significantly by pre-chlorination. While this suggests a strategy to reduce NDMA formation, it nonetheless creates an artifact difficult to control.

The first step in preparing the reactors was filtering the water samples through Millipore AP25 glass fiber filter designed to remove particles greater than 0.8-1.6 µm in size. Next, the filtered water was measured into the reactor jars so that the final volume of the solution containing sample water, buffer, and NH_2Cl would be 500 mL. Concentrated buffer solutions were used to create pH stability in the reactors throughout the incubation period. A 10 mM phosphate buffer was used for the lower pH 7 while 10 mM bicarbonate was added to maintain a pH near 8. These two pH levels were used in the agriculturally impacted surface water samples, however only the bicarbonate buffer was used for the riverbank filtration reactors. Blank samples for every site were amended with the appropriate buffer to form the same concentration as the reactors spiked with 1mM NH_2Cl. Duplicates were run when there was sufficient sample volume collected. Concentrated monochloramine stock solution with a 0.1 Cl/N molar ratio was prepared fresh prior to each experiment by addition of reagent grade ammonia and hypochlorous acid to a pH 10 solution containing 10 mM bicarbonate. Dosages added to the reactors ranged from 0.05 mM to 1 mM. The NH_2Cl was measured in control samples on a daily basis in order to ensure that high levels were present throughout the incubation period. NH_2Cl concentrations were determined by DPD-FAS titrimetric method (APHA, AWWA, and WEF; 1998).

Experiments were initiated by addition of the preformed monochloramine at a high dose of 1 mM, or 71 mg/L as Cl_2 was added to all agricultural watershed samples (approximately 20 times that of the typical residual allowed in drinking water distribution systems as dictated by the Stage 1 Disinfection/Disinfectant By-Product Rule). A much lower dosage of 0.05 mM was added to some of the riverbank filtration samples to mimic typical dosages used to maintain a substantial residual throughout a distribution system (approximately 4 mg/L as Cl_2).

All samples were incubated in the dark for 7 days (168 hours) at 20^{o}C. Reducing light exposure to the samples as much as possible ensured that the quantity of NDMA formed would not be significantly affected by photodegradation. After the 7-day incubation period, the final pH was measured to ensure buffer stability and minimal pH variation throughout the assays. A solid/liquid extraction process was used to concentrate the NDMA formed into a small volume of methylene chloride for analysis (Luo and Clevenger, 2003 and Taguchi et al., 1994). An internal standard of d6-NDMA was added to each reactor to form a baseline concentration of 100 ng/L. This internal standard, in conjunction with calibration curves developed for each assay, facilitated the subsequent quantification of these experiments.

NDMA was measured with a Varian GC CP3800 coupled with a Saturn 2200 MS/MS detector. The column used is Varian gas chromatograph had a length of 30 m, film thickness of 0.25 µm and insider diameter of 0.25 mm. The general temperature ramping protocol for the GC started with a temperature of 35^{o}C for 4 minutes. Next, the temperature was increased to 140^{o}C at a rate of 20^{o}C/min. A secondary ramp elevated the temperature to 200^{o}C at a rate of 50^{o}C/min. This temperature was held for 9.55 minutes. The total time each sample was 20 minutes. The Saturn 2200 MS/MS detector was used under the following settings: m/z 81 for quantification of d6-NDMA and m/z 75 for NDMA.

Glassware used in the experiments was washed thoroughly with warm tap water, soaked in a nitric acid bath and then rinsed again with copious quantities of deionized (DI) water. After washing, the glassware was baked in a muffle furnace at 500^{o}C for 1 hour. All solutions were prepared using DI water obtained from a Barnstead ROPure Infinity™/NANOPure Diamond™ system (Barnstead/Thermolyne Corp., Dubuque, IA). This treatment system produced water with a target resistivity of 18.2 mΩ-cm and [TOC] ≤ 3 ppb. All chemicals purchased and used in this study were ACS reagent grade and properly stored.

Principal Findings and Significance

NDMA Formation Potential in Watershed Samples. Figure 1 and Figure 2 are box and whisker plots showing the mean, quartile and extreme NDMA FP from July to February at each of the four locations sampled during this study. The extreme values at each site were fairly broad and ranged from 12.5 to 145.4 ng/L. Mean values for each site and at each pH value ranged from 45.6 to 92.9 ng/L. Despite significant fluctuations in the levels of NDMA formed in these samples, concentrations measured were consistently above the 10 ng/L California action level. This broad spectrum of measured NDMA in the reactors illustrates the role that fluctuations in water quality may play in the ultimate NDMA formation of a given water source. While avenues of this study are ongoing and some conclusions can be made from these results, seasonal trends were not apparent over this year. As aspects of this study continue based on these preliminary findings, seasonal trends may become more obvious.

Among the reactors tested in each sampling period, it should be noted that nearly all blank samples, those containing only sample water and buffer with no NH_2Cl, did not produce measurable levels of NDMA. This strongly suggests that background levels of NDMA in the source water for each sampling point was negligible throughout the course of the experiment and therefore NDMA formation was induced by the addition of NH_2Cl.

The relative agricultural impact of these watersheds was initially assessed based on total organic carbon (TOC), nitrite + nitrate (NO_2+NO_3) and organic nitrogen measurements performed by USGS scientists on historical samples. Relative agricultural impact for each sample location was based on the levels of these telltale water quality parameters as well as known agricultural operations in the area (see Table 1). The majority of historical data spans sample dates from 1996 until August, 2002. These parameters were not measured during this study; however, agricultural practices in the areas have not significantly changed since 2002. Statistical plots for the samples presented in Figures 1 and 2 suggest that there is no particular correlation between the relative agricultural impact on the watershed and NDMA formation because NDMA was consistently formed for all samples. A specific minimum threshold for these parameters influencing NDMA formation was not determined. Nonetheless, the fact that high levels of consistently quantifiable NDMA were formed suggests that these agricultural impact parameters play a role in the formation of NDMA when the samples are amended with NH_2Cl.

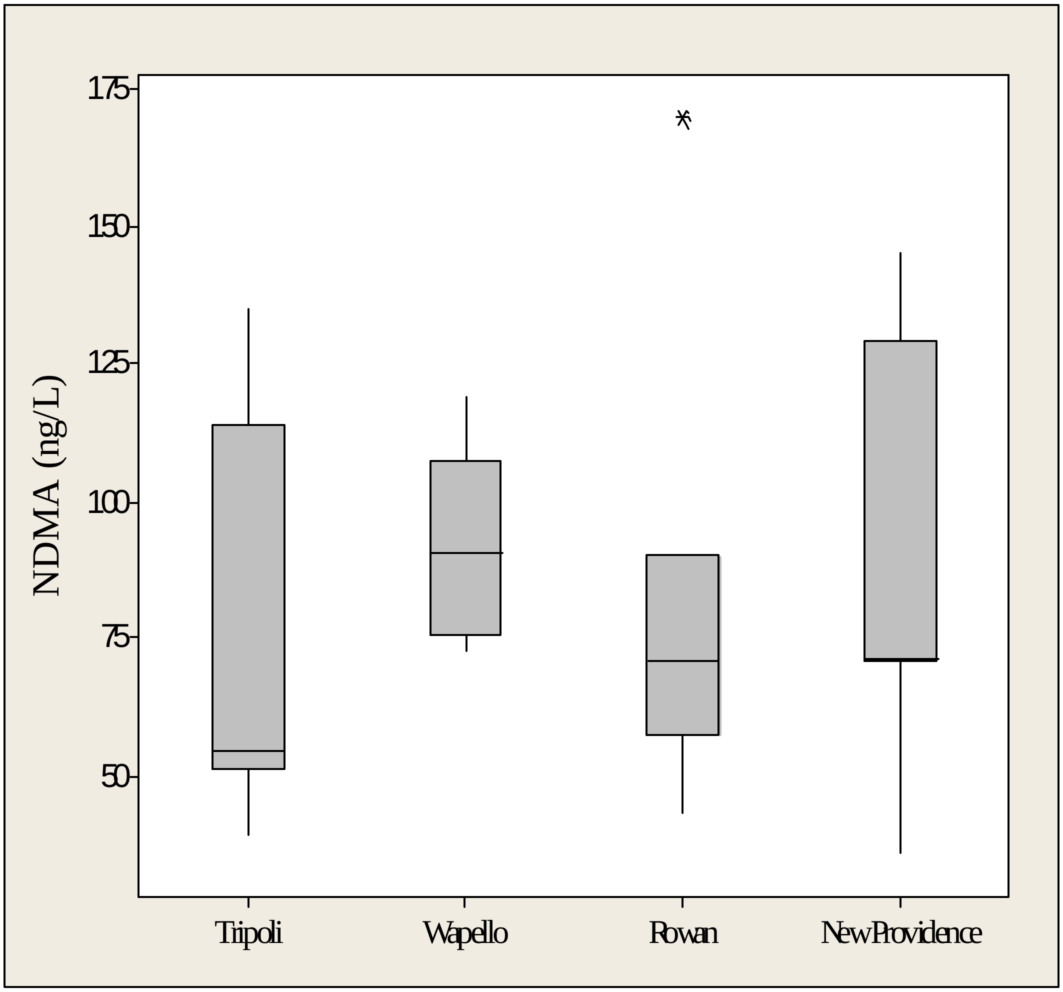

Figure 1. Box plot representing NDMA formation potential at pH~8 for each site pooled over the course of this study. The extremities of the whiskers show minimum and maximum NDMA formation potential at each site while the boxes define the quartile values and the median value. The “*” represents the outlier NDMA value measured in one of the Rowan sample months.

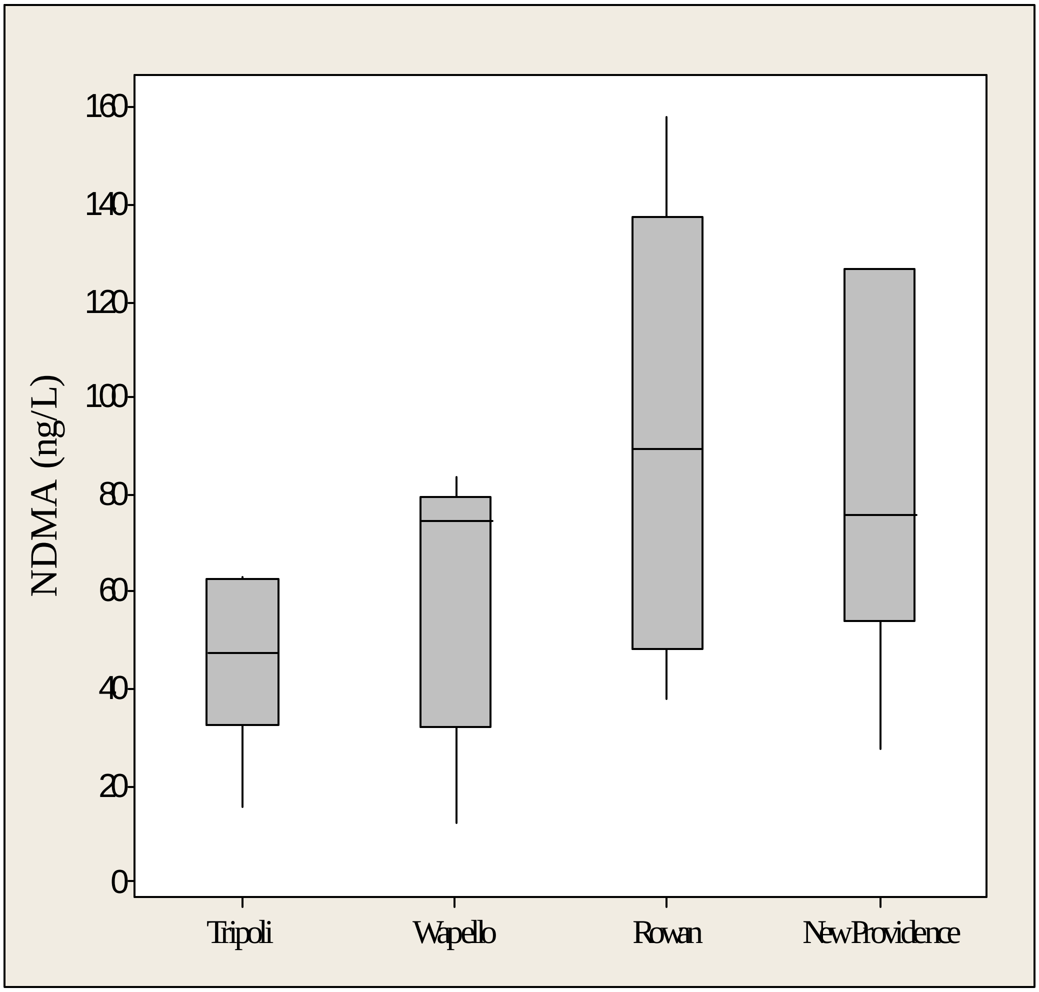

Figure 2. Box plot representing NDMA formation potential at pH~7 for each site pooled over the course of this study. The extremities of the whiskers show minimum and maximum NDMA formation potential at each site while the boxes define the quartile values and the median value.

Riverbank Filtration. The riverbank filtration samples shown in this section exhibit results from watersheds which are not directly influenced by agricultural practices, but can nonetheless have high levels of TOC, NO_2+NO_3 and NH_3 due to the migration of these parameters throughout surface waters in the state of Iowa. This can be seen in the levels of NDMA formed in the raw water (original surface water source for each facility) samples, which remained within the range previously observed in the samples defined as directly impacted by agricultural practices. Results from the samples collected from various locations at each of the two treatment facilities are shown in Figures 3 and 4.

Representative plots are presented (Figures 3 and 4) to show NDMA formation trends observed in several sampling events. In these graphs it can be seen that NDMA formation was significantly reduced by riverbank filtration at both the IC and CR locations when the high dose of 1 mM monochloramine was added. The NDMA levels dropped from 102 ng/L to 15 ng/L and 64 ng/L to 24 ng/L between the raw river water and the well samples. Interestingly, further conventional treatment did not appear to influence the NDMA FP at the higher NH_2Cl dose.

In contrast, neither riverbank filtration nor conventional treatment had a significant impact on NDMA formation when it was measured using the more practically significant monochloramine dose of 0.05 mM. Under these lower monochloramine dosage levels, NH_2Cl exhaustion may be occurring before the precursor reservoir in each sample is consumed.

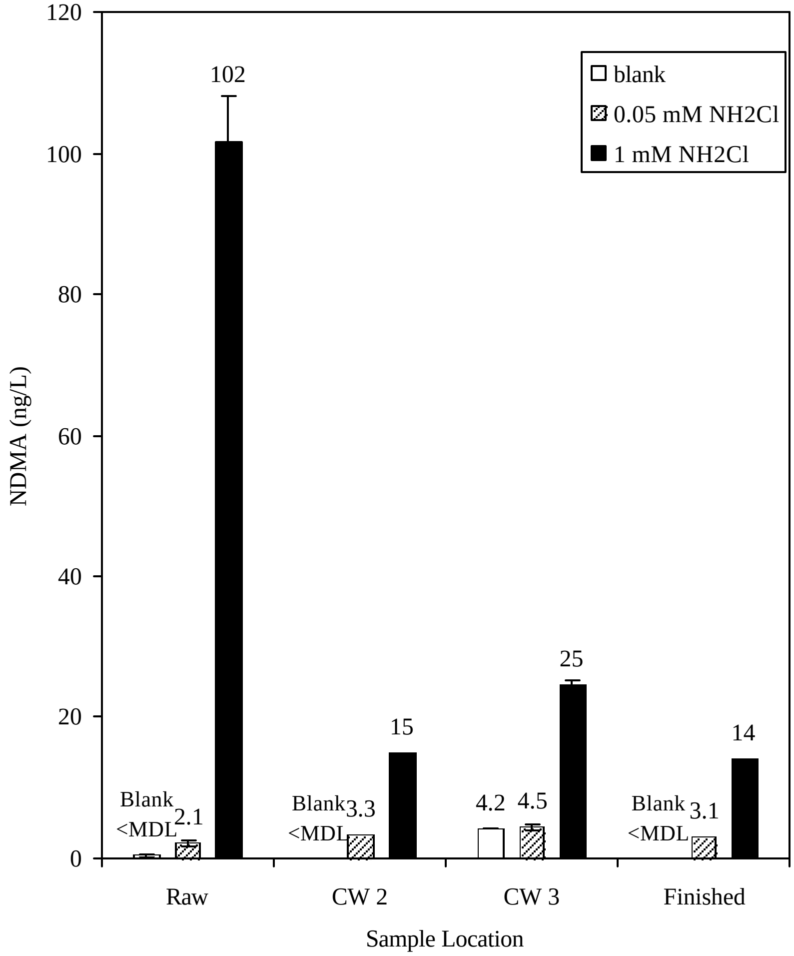

Figure 3. IC samples collected on 11-17-03. Monochloramine was added to the samples to produce a concentration in each reactor as indicated in the figure. Error bars are shown for reactors in which duplicates were run. All samples were incubated in the dark at 20°C for 7 days. The average pH of the bicarbonate buffered reactors was 8.27 ± 0.2.

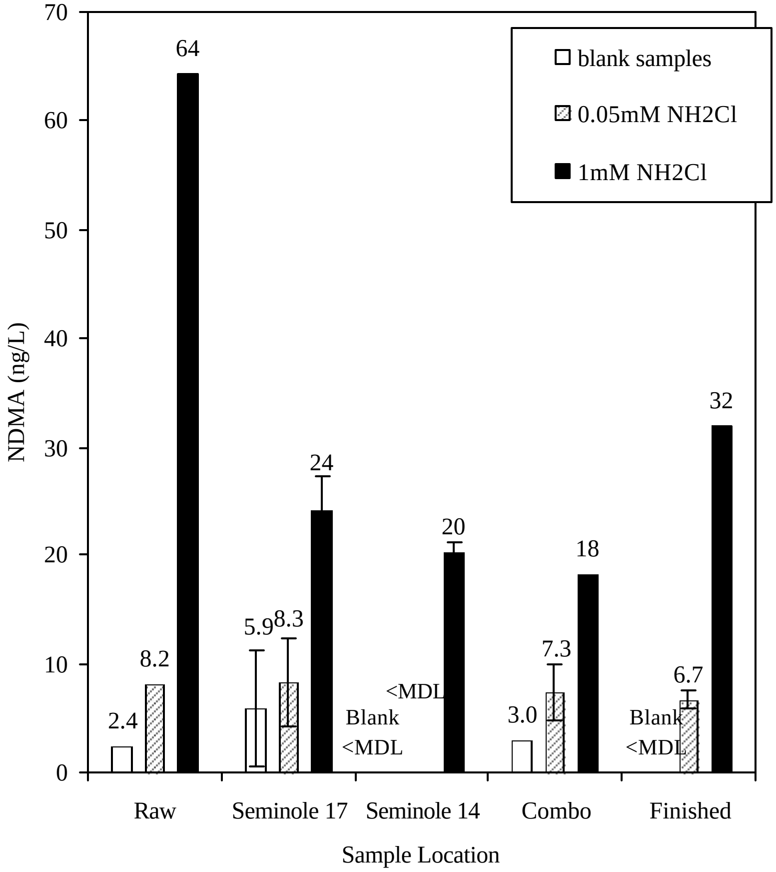

Figure 4. Cedar Rapids samples collected on 9-29-03. Monochloramine was added to the samples to produce a concentration in each reactor as indicated in the figure. Error bars are shown for reactors in which duplicates were run. All samples were incubated in the dark at 20°C for 7 days. The average pH of the bicarbonate buffered reactors was 8.20 ± 0.15.

Mechanistic Studies: Role of DMA. As little direct correlation was observed between NDMA FP and the agricultural indicator parameters, additional mechanistic studies were conducted to determine the role of DMA as a potential precursor of NDMA formation. DMA is a known NDMA precursor and a substance generally ubiquitous in water (Mitch and Sedlak, 2003). DMA was measured in samples obtained from four locations shown in Table 3, ranging from approximately 170 to 650 ng/L, supporting the notion that it could be an important precursor.

In order to determine the NDMA formed from observed levels of DMA, a controlled experiment was conducted to show how much NDMA could potentially be attributed to typical DMA levels measured in the water samples. DI water was spiked with 200 and 650 ng/L of DMA and preformed NH_2Cl was dosed as in other parts of this study. The levels of NDMA formed were then compared with what was measured in the natural samples.

The NDMA measured in relation to DMA addition is shown in Table 3. These results indicate that DMA could account for only approximately 3-6% of the NDMA FP in the collected water samples. These relative yields are slightly higher, yet relatively consistent with the findings of Mitch and Sedlak (2004) who observed that the DMA present in their water samples could only account for approximately 0.6% of the NDMA FP (Mitch and Sedlak, 2003). Our results indicate that DMA does contribute to NDMA formation but that it cannot account for most of the NDMA formed. Therefore, other more important precursors must be present in these surface waters.

Table 3 Results of NDMA formation and DMA analysis for samples collected July, 2003 in relation not specific DMA addition to DI water. The % NDMA attributed to DMA concentrations in the water is based on the NDMA formed in the DI samples, assuming no other NDMA precursors were present in the DI water.

Site	NDMA ng/L	DMA ng/L	% NDMA from DMA
DI water pH~8	4.5	200.0	100%
DI water pH~8	7.0	650.0	100%
New Providence	129.6	196.3	3%
Rowan	77.5	170.6	6%
Wapello	90.4	174.0	5%
Tripoli	114.0	651.2	6%

NDMA Precursor Exhaustion Study. Determining the class of likely precursors (e.g., agricultural indicators or DMA) was previously discussed as part of this study; however, regardless of what the NDMA forming precursors are, it was relevant to conduct additional studies to determine the extent of precursor exhaustion based on the experimental methods used. The kinetics of NH_2Cl autodecomposition as delineated by Valentine and Jafvert at various pH values was used to calculate the concentration-time (C*t) curve for each assay. C*t values were used to assess whether the observed disappearance of NH_2Cl over the course of each assay was due to reaction with precursor material in the samples or autodecomposition. Subsequent experiments measured NH_2Cl decay in DI water and Iowa River water under varying Cl/N ratios at the pH values relevant in this study. From these studies, monochloramine decay kinetics were measured and used to normalize NDMA formation potential to the calculated C*t for each reactor.

An experiment to fully exhaust all NDMA precursors in the water samples was conducted to measure the NDMA formation after 7 and 14 days. Iowa River water was collected from the University of Iowa water treatment plant and filtered through the same 1.6 µm glass fiber filters used in other experiments. Batch reactors were comprised of roughly 500 ml of water, 1 mM NH_2Cl and either 10 mM phosphate or bicarbonate buffers in order to maintain pH values around 7 and 8, respectively. Blank samples were not dosed with preformed NH_2ClAs in other experiments, measurements of NH_2Cl concentrations were measured on a daily basis for each reactor over the 7-day and 14-day reaction periods. Precursor exhaustion was therefore tested by comparing the amount of NDMA that could be formed by a second dosage of NH_2Cl, readjusting to the initial 1 mM NH_2Cl concentration, followed by 7 more days of incubation.

Based on the precursor exhaustion experiment performed, the majority of NDMA was formed within the first 7 days of the experiment. As shown in Figure 5, appreciable levels (between 5 and 21 ng/L) of NDMA are additionally formed after a subsequent respike of NH_2Cl which readjusted the concentration to 1 mM. Also, Table 4 shows the results of normalized NDMA formation (NDMA/C*t) based on the precursor exhaustion experiment. Due to the fact that the ratio of NDMA to C*t is significantly reduced between the 7-day and 14-day reactors, it can be surmised that the NDMA formation precursors initially present in the surface water samples were mostly consumed within the first 7 days. If this were not the case, the second chloramine dosage would form similar amounts of NDMA as the first dosage and the NDMA/C*t values would be closer.

This experiment was performed in order to provide a quantitative basis for past and future experiments involving the formation of NDMA in natural waters in conjunction with NH_2Cl decay. From the data measured, the Valentine Chloramine Stability coefficient for each reactor was measured and compared to theoretical calculations based on the average pH, initial and final NH_2Cl concentrations as well as the equilibrium coefficients associated with each buffer used. The normalization of NDMA formation with C*t demonstrate how precursor limitation was experienced in all reactors dosed with 1 mM NH_2Cl. From this, the potential for various NDMA formation precursors can be suggested based on NH_2Cl demand.

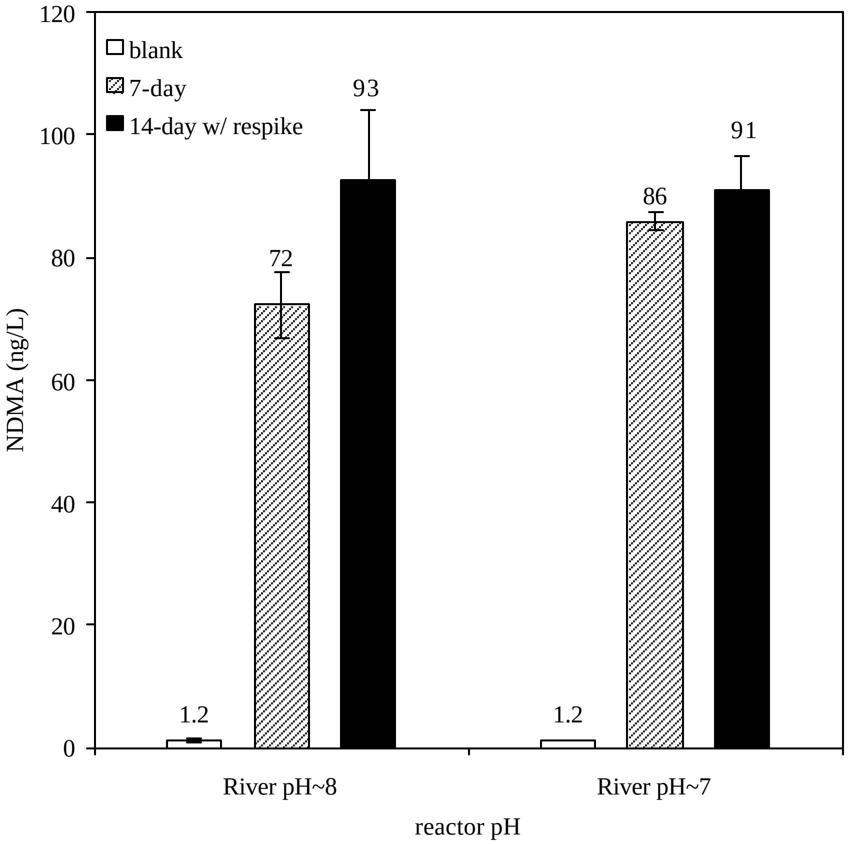

Figure 5. Precursor limitation experiment performed on 3-17-04 with filtered Iowa River water. All samples were buffered with either 10 mM bicarbonate or phosphate buffers in order to maintain pH values around 8 and 7, respectively. All reactors were incubated in the dark at 20^{o}C.

Table 4. Summary table of C*t normalized NDMA formation (NDMA/C*t) in Iowa River water at various pH values. The 7-day samples were dosed with 1 mM preformed NH2Cl and incubated in the dark at 20^{o}C. The 14 day samples were amended with sufficient NH2Cl in order to readjust the concentration to the original 1 mM.

Sample	NDMA (ng/L)	C*t (mg Cl_2-h/L)	NDMA/C*t	%NDMA formed in 7 days
7-day @ pH~8	72.3	8632	8.4	--
14-day @ pH~8	92.8	21874	4.2	78
7-day @ pH~7	85.8	6134	14.0	--
14-day @ pH~7	91.0	21431	4.2	94

Summary and Conclusions

Results from this exploratory study demonstrate that a significant NDMA formation potential exists in the agriculturally impacted surface waters sampled. Measurements of NDMA formation potential in two typical Iowa drinking water sources and treatment facilities further suggest that chloramination practices may need to be assessed based on potential NDMA formation in the distribution system. Maximum NDMA formation values were based upon monochloramine dosages approximately 20 times that typically used in drinking water disinfection. NDMA was also formed at quantifiable levels when samples were dosed with monochloramine at concentrations typically used in drinking water treatment. The maximum NDMA FP for samples amended with the higher concentrations of monochloramine is typically in a range that can exceed 100 ng/L which is 10 times higher than that generally considered acceptable by any regulatory or health risk standards.

No statistical evidence was obtained that showed a significant difference in NDMA FP between the four agriculturally impacted watersheds over the course of this study when data was pooled over all the sampling periods. Seasonal trends for predicting variations in formation potential were distinguishable over the course of this preliminary study. Additionally, NDMA FP did not conclusively correlate with nitrate, organic nitrogen, or total organic carbon at any location. The determination of these statistical correlations was limited by the sample size available for each parameter over the course of the study as well as the relatively short time period available for data collection and analysis.

Dimethylamine was measured in selected agriculturally impacted watershed samples as an established NDMA forming precursor. Experiments conducted in this study corroborated other research which suggests that DMA is not the sole NDMA precursor present in surface waters. Results from this study revealed that the DMA content measured could account for only a relatively insignificant amount (approximately 3-6%) of the NDMA FP, suggesting that the presence of other precursors also existed in the samples.

The influence of riverbank filtration (RBF) on NDMA formation was studied at both low (0.05 mM) and high (0.5 or 1.0 mM) monochloramine dosage. NDMA formation was generally greater at the higher monochloramine dosages but this trend was not always the case. The high monochloramine 7-day NDMA formation potential in the raw water was approximately 100 ng/L in IC and between 40 and 60 ng/L in CR. Riverbank filtration generally reduced the NDMAFP in IC water by 90 % and between 30% and 80% in CR water, for the higher monochloramine dosage.

Significant amounts of NDMA were also formed by the addition of 0.05 mM monochloramine when measured against the 0.7 ng/L EPA 10^{-6} cancer risk level. Raw water dosed with 0.05 mM NH_2Cl produced NDMA values of approximately 10 ng/L in IC water and 20 ng/L in CR water. Interestingly, neither RBF nor conventional surface water treatment techniques seemed to have a significant effect on reducing NDMA formation potential at the lower monochloramine dosage.

The study of NDMA formation from two sequential dosages of 1 mM NH_2Cl and two 7-day incubation periods support the hypothesis that most of the precursors present are exhausted after the first dosage and incubation period and the NDMA FP increased by only 5-10% after the second dosage. This may explain why NDMA FP did not correlate linearly with the concentration-time (C*t) values as it would if the precursor concentration were not reduced with monochloramine dosage. This may also explain why the NDMA FP was approximately the same at pH 7 and 8. While differences were observed in the NDMA FP between nominal pH values of 8 and 7, they were generally within approximately 10%. This may be attributable to near exhaustion of the NDMA precursors in both cases not necessarily reflective of identical formation kinetics.

From this research further work should be done to investigate precursors originally present in typical agriculturally impacted surface waters as well as additional compounds which may be introduced as a result of riverbank filtration and conventional drinking water treatment. Anthropogenic chemicals introduced in urban and agricultural watershed areas may both lead the augmentation of NDMA formation potential in source waters. The classification of NDMA formation potential should be recommended as part of future source water quality evaluations in newly designed treatment facilities located in potentially high risk areas. As a result of preliminary source assessments, alternative and or additional treatment strategies may be needed in order to reduce the risk of exposure to NDMA. Although this may increase the overall cost of treatment for a particular community, research presented here and in other studies demonstrates the importance of chronic NDMA exposure and the importance it plays in drinking water treatment.

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An Integrated Immunological-GIS Approach for Bio-monitoring of Ecological Impacts of Swine Manure Pollutants in Streams

Basic Information

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Research Category:	Water Quality
Focus Category:	Methods, Non Point Pollution, Agriculture
Descriptors:	water quality, fish, immunology, GIS, swine manure, non-point source pollution
Principal Investigators:	James A. Roth, Bruce Willard Menzel, Dusan Palic, Clay Lynn Pierce

Publication

1. Palic, D., C.B. Andreasen, D.E. Frank, B.W. Menzel, and J.A. Roth. (2005). A rapid, direct assay to measure degranulation of primary granules in neutrophils from kidney of fathead minnow (Pimephales promelas Rafinesque, 1820). Fish and Shellfish Immunology 19(3), 217-227.
2. Palic, D., C.B. Andreasen, D.E. Frank, B.W. Menzel, and J.A. Roth. (2005). Gradient separation and cytochemical characterization of neutrophils from kidney of fathead minnow (Pimephales promelas Rafinesque, 1820). Fish and Shellfish Immunology 18(3), 263-267.

An Integrated Immunological-GIS Approach for Bio-monitoring of Ecological Impacts of Swine Manure Pollutants in Streams

James A. Roth, Dusan Palic, Bruce W. Menzel, Clay L. Pierce

Problem and Research Objectives

Thirty years after enactment of the Clean Water Act, 40% of our nation's rivers, lakes, and coastal waters are still considered unfit for fishing, swimming, drinking or aquatic life. The U.S. EPA identified agricultural operations as the primary cause of non-point source pollution in the nation's impaired rivers and lakes. At least 10 % of the nation's impaired river miles are affected by pollution from livestock operations. In portions of the Midwest, confinement livestock operations are a particular problem in this regard. Spills and dumping of fecal material occurred over one thousand times at feedlots in the ten Midwest U.S. states between 1995 and 1998. Over the past two decades, swine production in the U.S. has increasingly shifted to a large-scale, corporate model. Today, two percent of the hog operations in the U.S. produce over 46% of the total hog population. In Iowa, the largest swine production state, about 21 million tons of manure are produced annually, chiefly at large-scale confinement operations. Commonly, the manure from such operations is held in earthen lagoons for anaerobic decomposition prior to application as a fertilizer to crop fields. As older-style lagoons age, their failure and leakage is a growing problem. Improper application of the fertilizer and its runoff from cropland also result in manure delivery to local waters. Because of its volume, composition, and handling methods, therefore, swine fecal contamination is a serious threat to environmental quality in regional waterways and especially in Iowa. Local citizens are becoming increasingly intolerant of the environmental cost of confinement livestock production.

Cases of massive deaths of aquatic organisms, often referred to as fish kills, are an extreme manifestation of the ecological impact of fecal contamination. Typically, they result from high concentrations of toxic ammonia contained in the manure or from depletion of dissolved oxygen in the water caused by decomposition of the pollutant. From 1995 to 1998, over 13 million fish were killed in more than two hundred documented manure spills in the Midwest. In the past 20 years, fecal pollution was the single most important cause of 495 documented fish kills in Iowa, accounting for over one-quarter of the diagnosed cases, and hog manure was the primary pollutant. Although cases of acute toxicity of manure pollution capture the headlines, there are other impacts that may be of equal, or perhaps greater, long-term ecological importance. For example, fecal pollutants contain nutrients, especially nitrogen and phosphorus compounds, microorganisms and other materials that upset ecological processes and impair water quality for human uses. Additionally, exposure to sublethal pollutant concentrations can interfere with normal life processes of wildlife such as feeding, reproduction, defense, and disease resistance. This can result in gradual declines and even extirpations of animal populations and communities. Such chronic effects of manure pollution are poorly known, because of the difficulty of measuring them and placing them in ecological context. Moreover, low-level delivery of fecal pollutants can portend larger catastrophic inputs, for example, when a gradually leaking storage lagoon eventually bursts or an erosive, manure-fertilized crop field receives heavy rainfall.

State and federal agencies engaged in reducing non-point source water pollution are interested in obtaining new technologies for identifying, measuring and anticipating pollution occurrence. Clearly, development of tools that could integrate biological and environmental information to produce site-specific predictive models for guiding pollution-prevention management practices is highly desirable. Benefits of such tools and management practices would accrue locally and more broadly throughout interstate drainage basins. The highly publicized Gulf of Mexico hypoxia situation is an example of the geographically widespread impacts of agricultural (and other) pollution in the Mississippi River basin. The proposed research would develop a novel tool that integrates molecular biological and ecological approaches to quantitatively evaluate environmental impacts of swine manure pollutants. Although the technique will be developed with specific reference to Midwestern waters, it will be more broadly applicable, both geographically and with reference to other forms of pollution that engender immune responses in animals. Thus, we believe that the technique has potential to be widely adopted by state and federal environmental management agencies.

The research conducted under this grant reflects the need for integrated, multidisciplinary approaches to deal with complex environmental issues. It combines physiological laboratory techniques, computer modeling of agricultural landscapes and non-point source pollution pathways, and field-based ecological analyses to create a new and integrated approach for evaluating impacts of livestock fecal contamination on Midwestern streams.

The research relates to two major priorities of the NIWR National Competitive Grants Program.

1. It will complement work by the USGS related to non-point source pollution, contributing to development of integrated watershed decision support tools for assessing organics' and microorganisms' transport and fate, along with their effects on aquatic systems.
2. It promises development of a new water quality sensor technology that will be based on integrated methodologies and will provide results that are readily accessible through the Internet.

This research is predicated on the hypothesis that low levels of swine liquid manure slurry and anaerobic lagoon liquid released to open water cause changes in immunological response in fish and increase fish susceptibility to infection.

The initial objectives, therefore, are 1) to evaluate this hypothesis through a series of laboratory immunological assays applied to the test organism, the fathead minnow (*Pimephales promelas*) and 2) to identify one or more assays for use as a bio-monitoring technique to detect ecological impact of manure pollution in nature. A subsequent task involves use of digital environmental databases that are maintained and managed by the USGS BRD Iowa Cooperative Fish and Wildlife Research Unit at Iowa State University. The objective is 3) to characterize a number of Iowa watersheds and stream systems according to their potential susceptibility to hog manure pollution and to use this information to design a water quality and fish sampling regime. Finally, water and fish collected at selected stream sites will be analyzed through a battery of chemical and immunological procedures with the objectives 4) to quantitatively measure ecological impact of manure pollution on the streams, and 5) to evaluate the utility of this approach as a biomonitoring tool for environmental protection agencies.

Methodology

The fathead minnow is a native Iowa species, abundant and ubiquitous in small streams. Thus, it is a good choice as a representative of fish communities exposed to low level concentrations of swine manure pollutants released into Iowa waters. Moreover, it is commonly used as a standard bioassay organism in toxicological analyses, so there is substantial knowledge on its tolerance to a wide array of environmental physical conditions and pollutants. Additionally, colonies can be easily established and maintained in the laboratory. Fathead minnows used for the experiment will be raised in a controlled environment, without previous exposure to swine manure.

The bacteriological composition and characteristics of swine manure slurry and lagoon liquid are generally known, a number of bacterial varieties being present. During manure storage and manipulation, some bacteria die and degrade. Consequently, it is expected that a number of chemical varieties of released bacterial lipopolysaccharides (LPS) are present in both manure forms, reflective of different bacterial sources. Since thorough bacteriological analyses of the manure and water are time consuming and expensive, the LPS component of the bacterial cell wall will be used as a measure of bacterial variety and concentration. Furthermore, since LPS is considered an activator and/or promoter of phagocytic cell activity, the amount of LPS in manure samples can serve as a measure of immunologically active substances present.

The immune response will be determined by activity of phagocytic cells through several forms of measurement. Evidence from limited research involving fish suggests that assays measuring respiratory burst and degranulation are useful for determining phagocytic function in fish, and the procedure also seems to hold promise as a bio-indicator for fish health. Additionally, histological examinations of melano-macrophage centers (MMC) in liver, spleen, kidneys, intestines, skin, and gills will be used to measure effects of long term exposure to manure.

Geographic Information Systems (GIS) technologies provide a tool to enter, store, manipulate, and integrate geo-referenced data on, for example, landscape features, water quality, and aquatic organisms. The project will apply GIS technology and landscape modeling to calculate possible swine pollutant flow path patterns in Iowa watersheds having large hog confinements and in those where liquid manure fertilizer is applied on crop fields. Using this approach, we will estimate temporal and spatial distribution of manure loads and concentrations that reach receiving waters. This will provide the basis for a field sampling regime to determine actual conditions of water quality and fish communities at stream sites selected to represent a range of calculated manure pollutant loadings. Water quality data on fecal coliform bacteria, phosphorus compounds, and ammonia, among others, will be evidence concerning actual loading of manure material. Ecological impact of the pollution will be evaluated by the developed immunological assays performed on wild-caught fathead minnows. Statistical comparisons will be made between the calculated and measured evidence for the pollutant to determine the accuracy and reliability of the immunological approach in actual practice. As a further check on the procedure, Index of Biotic Integrity (IBI) values will be calculated based on wild fish community parameters. The IBI is a commonly used bioindicator of stream environmental quality. It serves as a summary measure of biotic community response to pollution and other forms of habitat degradation. It is being used routinely for long-term environmental monitoring programs in Iowa and other Midwestern states. This design, therefore, will allow comparisons between this established coarse-scale environmental indicator and the experimental fine-scale immunological indicator.

Principal Findings and Significance

Based on results of the performed research, fathead minnows appear to be a useful model for investigating effects of acute handling and crowding stress, chemical compound (anesthetics) application, chronic crowding and poor water quality stress, and dietary immunomodulation on neutrophil function. Widespread use of fathead minnows as laboratory animals in toxicology research, their aquacultural and ecological relevance, as well as availability of functional assays, make them an aquatic species of choice for immunological research. This research provided essential information about fathead minnow neutrophil morphology, cytochemistry, and physiology, and determined the potential for use of fathead minnow neutrophil functional assays in investigating stress conditions in the environment.

The morphology and cytochemical characteristics of granulocytes in fathead minnows were described, and quick and reliable isolation procedures were developed for obtaining neutrophil suspensions of adequate quantity and purity for functional assays. Neutrophils were identified as leucocytes that contain clear non-staining cytoplasm, moderately coarse nuclear chromatin, and reniform indented or lobulated nuclei with a moderate nuclear to cytoplasmic ratio. It was demonstrated that the fathead minnow neutrophil granules have myeloperoxidase activity, stain positively with Sudan Black B reagent, and are negative for periodic acid-Schiff and alpha naphthyl acetate esterase. The gradient separation resulted in semi-pure and viable neutrophil populations from the kidneys of fathead minnows in approximately 3 hours for functional studies to provide additional information about fish health status. This was an essential step for developing neutrophil functional assays.

Neutrophil function assays were developed and characterized for the fathead minnow neutrophil response to various stimulants *in vitro*. The cytochrome C reduction assay was used to detect release of superoxide as a measure of neutrophil respiratory burst and the assay was optimized for use with fathead minnow neutrophils. The myeloperoxidase (MPO) assay is direct, quantitative, can rapidly measure a large number of samples, and was shown to be capable of detecting the inhibition of primary granule degranulation and differences in total MPO content between populations of fathead minnow neutrophils. The kinetic study of MPO release in fathead minnow kidney neutrophils demonstrated the maximum activity of up to 80% MPO release is reached after 40-60 min when calcium ionophore (CaI) is used as a stimulant. The MPO assay was responsive to detect changes in fathead minnow neutrophils over time, and an incubation of 20 min should be used for CaI as a mid-point time period in MPO release that provides the ability to measure a decrease, as well as an increase, in exocytosis of primary granules. The described assay is a useful method of measuring neutrophil primary granule degranulation and total MPO content in the fathead minnow kidney neutrophils, and it shows the potential for assessing neutrophil activity during disease states and toxicant exposure. This was an essential step to measure changes in neutrophil function provoked by stress caused by handling or poor water quality.

The effects of acute and chronic stress on the fathead minnow neutrophil function *in vivo* were determined. The effects of handling and crowding stress with and without anesthesia on plasma cortisol concentration and neutrophil function showed that tricaine methanesulphonate did not, while metomidate and eugenol did, prevent an increase in plasma cortisol concentration and a decrease in neutrophil function. Cortisol concentration significantly correlated with a decrease in degranulation of primary granules within 24^{h} and for as long as 7 days post treatment. Since a decrease in degranulation was not observed when a known blocker of cortisol release and synthesis (metomidate) was used, we hypothesize that the degranulation decrease in stressed fish was caused primarily by an increased cortisol concentration. Likewise, fathead minnows exposed to chronic stress conditions had significantly reduced degranulation, demonstrating that the degranulation assay can be used to measure both acute and chronic stress effects on neutrophil function in this species. This step demonstrated the capability of the assay to measure reduction in neutrophil function.

Yeast glucan proved to be a strong stimulant *in vitro* and a dietary immune enhancer *in vivo*. Glucan treated, non-stressed fish showed a significant increase in neutrophil degranulation and neutrophil ratios for the duration of treatment, and they remained significantly higher than controls after exposure to acute stress. Application of dietary glucans to chronically stressed fish increased degranulation to control levels after 72^{h}, while the oxidative burst followed a pattern described in non-stressed fish (transient increase, followed by decrease). The glucan supplemented diet significantly increased neutrophil degranulation and ratios; transiently increased oxidative burst and total MPO content; and prevented a decrease in degranulation after acute handling and crowding stress. The use of ß-glucans in fish diets prior to acute stress and during chronic stress could enhance neutrophil function, and potentially increase disease resistance and survival rates after transportation or exposure to poor water quality. This step demonstrated the capability of the assays to measure increases in neutrophil function as well as measure effects of chronic poor water quality stress on neutrophil function.

Scientific background and baseline data for use of fathead minnow neutrophil function in future research and aquatic ecosystem evaluation was provided. Fathead minnows are shown to be a useful model to investigate neutrophil degranulation in fish exposed to different environmental conditions.

In summary, work performed up to this point clearly demonstrated that:

1. Fathead minnows have granulocytic cells capable of superoxide anion production and degranulation of primary granules;
2. Exposure to handling and crowding stress increased blood cortisol concentration and decreased degranulation of fathead minnow neutrophil primary granules;
3. Application of dietary ß-1, 3 – 1, 6-glucan from baker's yeast increased degranulation of fathead minnow neutrophil primary granules, and prevented decrease of degranulation in fish exposed to handling and crowding stress;
4. Exposure to chronic stress conditions decreased degranulation of fathead minnow neutrophil primary granules; and
5. Application of dietary ß-1, 3 – 1, 6-glucan from baker's yeast prevented decrease of degranulation in fish exposed to chronic stress.

Neutrophil functional assays show potential for use in studying effects of immunomodulatory compounds, as well as effects of environmental stress on fish physiology, providing us with new tools to be used in the assessment of aquatic ecosystem health.

Predicting sorption, mobility, accumulation, and degradation potential of antibiotics in Iowa's soil/water environment

Basic Information

Title:	Predicting sorption, mobility, accumulation, and degradation potential of antibiotics in Iowa's soil/water environment
Project Number:	2002IA4B
Start Date:	3/1/2002
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	Iowa 3rd
Research Category:	Biological Sciences
Focus Category:	Agriculture, Non Point Pollution, Toxic Substances
Descriptors:	Adsorption and sorption, mobility, leaching, organic compounds, manure lagoons, solute transport, degradation and biodegradation, antibiotics
Principal Investigators:	Steven Fales, David A. Laird

Publication

1. Pils, Jutta. 2005. The role of soil clays and clay-humic complexes in processes controlling colloidal stability and the sorption and degradation of tetracyclines. Ph.D. Dissertation, Dept. of Agronomy, College of Agriculture, Iowa State University, Ames, IA.
2. Pils, J.R.V., D.A. Laird, and T.B. Moorman. 2004. Degradation of Tetracycline Sorbed on K- and Ca-saturated Soils and Soil Components. Agron. Abstr. CD-ROM S11-pils5035.pdf.
3. Pils, J.R.V. and D.A. Laird. 2004. Adsorption of Tetracycline and Chlorotetracycline on K- and Ca-saturated Soil Clays and Humic Substances in 41st Annual Meeting Program and Abstracts, Clay Minerals Society, 57 pp.
4. Pils, J.R.V. and D.A. Laird. 2003. Adsorption of Tetracycline and Chlorotetracycline on K- and Ca-saturated Soil Clays and Humic Substances. Agron. Abstr. S02-pils672004-O.pdf.
5. Pils, J.R.V., V.P. Evangelou, and D.A. Laird. 2002. Smectite tactoid formation induced by confined and double layer monovalent cations. Agron. Abstr. S02-pils152704-O.pdf.

Predicting Sorption, Mobility, Accumulation, and Degradation Potential of Antibiotics in Iowa's Soil/Water Environment

Steven Fales, David Laird, Jutta Pils

Problem and Research Objectives

Approximately 31.6 million pounds of antibiotics are used in the production of poultry (10.6 million pounds), hogs (10.3 million pounds), and cattle (3.7 million pounds) in the United States each year (Mellon et al., 2001). Over three fourths of these antibiotics (24.6 million pounds) are given to healthy animals in low doses to promote growth (Levy, 1997). Most of the antibiotics given to farm animals are not metabolized *in vivo*, rather they are excreted in the active form (Lee et al., 2000). The fate of antibiotics introduced into soil and aquatic environments with manure and other animal wastes is largely unknown. However, there is much concern that the presence and persistence of low levels of antibiotics in soil and aquatic environments could encourage the buildup of existing, and the development of new, antibiotic-resistant bacterial populations (Henry, 2000).

In Iowa, Earthen Waste Storage Structures (lagoons) are widely used for temporary storage of liquid animal wastes with the intent of protecting surface and ground water from contamination and allowing farmers to use the wastes in a timely fashion. Liquid animal wastes are generally spread on agricultural soils both as a means of disposal of the wastes and as a nutrient source for crop production. The Iowa Dept. of Public Health (1998) found relatively high concentrations of chlorotetracycline (11 to 540 µg/L) and erythromycin (10 to 275 µg/L) in such liquid animal wastes. The report also indicated that many of the 18 *E. coli* isolates, all three Salmonella species, and an isolate of Enterococcus demonstrated resistance to one or more of the antibiotics.

The antibiotics most commonly added to livestock feed as growth promoters (1 to 100 mg per head per day) are chlorotetracycline (Aureomycin), oxytetracycline (Terramycin) and macrolide (erythromycin) (Sewell, 1993; FAC, 1998; Herman et al., 1995). The fate of these compounds in Iowa soils depends on sorption and desorption of the antibiotics on soils, leaching, and the rates of chemical, photochemical, and microbial decomposition of the antibiotics. The basic hypothesis of the study is that the fate (sorption/desorption, leaching, and decomposition) of antibiotics in soil environments is strongly influenced by the chemical reactions between the antibiotics and soil constituents.

Specific Objectives:

1. Characterize three common Iowa soils and isolate and characterize reactive soil components (clay-humic complexes, clay minerals, and humic materials) from these soils;
2. Quantify sorption of tetracycline and chlorotetracycline on the soils and soil components;
3. Determine the effects of saturating cation (Ca vs. K) and ionic strength (I=0.05 and I=0.005) on sorption of tetracycline and chlorotetracycline on the soils and soil components; and
4. Quantify the influence of sorption on tetracycline and chlorotetracycline degradation rates.

Methodology

Soil samples, surface (0-15 cm) and subsurface (≥ 15 cm), were collected from three sites representing three different soil series and a range of soil physical and chemical properties. Both the studied soils and the general sampling locations had been previously characterized (McBride et al., 1987). Based on interviews with the landowners or operators, specific sampling sites that had never received manure applications were selected. The soils were characterized using standard analytical procedures to determine pH in $CaCl_2$, pH in KCl, pH in water, organic C, organic H, organic N, % sand, % coarse silt, % fine silt, % clay and extractable cations (Ca, Mg, Na, and K).

Soil components were physically and chemically separated from the soils and prepared for the sorption and degradation studies. Clay-humic complexes were isolated from the soils by sedimentation (<2 µm e.s.d.). Portions of the clay-humic complexes were K- or Ca-saturated by washing in 1M KCl or 0.5 M $CaCl_2$ and then dialyzed against distilled water and freeze-dried. Other portions of the clay-humic complexes were treated with 30% H_2O_2 for removal of the humic materials before being K- and Ca- saturated, dialyzed against distilled water and freeze-dried. Humic materials were separated from the three soils by hydrolyzing Na-saturated samples in 0.1 M NaOH under and N_2 purge. After the hydrolysis the humic materials were separated by centrifugation, neutralized to pH 7, K- or Ca-saturated, dialyzed and freeze-dried.

A batch equilibration technique was used to measure sorption of tetracycline and chlorotetracycline on the various soils and prepared soil components. HPLC was used to quantify tetracycline and chlorotetracycline in the supernatant solutions and sorption was determined by difference. Variables tested include soil components (clay-humic complexes, clay minerals, and humic substances), saturating cation (K vs Ca), and ionic strength (I=0.05 and I=0.005).

The degradation of tritium-labeled tetracycline in both aqueous and colloidal systems was quantified under both biotic and abiotic conditions. The colloidal systems included soil clays and soil clay-humic complexes that were both K- and Ca-saturated. During the incubations (149 days), we quantified both the disappearance of tetracycline from the aqueous phase by HPLC and total tritium activity in the aqueous phase using a liquid scintillation counter. Bioavailability of adsorbed tetracycline was assessed using an agar plate technique.

Principal Findings and Significance

Tetracycline (TC) and chlorotetracycline (CTC) are very strongly sorbed on soil clays, soil humic substances, and soil clay-humic complexes. In agreement with previous studies, sorption of TC and CTC was found to increase with decreasing pH and to be greater in Ca-systems compared to K-systems. Also in agreement with previous studies, we found higher sorption of CTC compared to TC, most likely due to the lower solubility of CTC. An important new finding is that TC and CTC are more strongly sorbed on soil clays than on soil humic substances, and that interactions between clays and humic substances significantly diminish sorption of TC and CTC on soil clay-humic complexes. Although TC and CTC are strongly sorbed by soil clays, humic substances, and clay-humic complexes, a small portion of sorbed TC and CTC is released back into an aqueous solution through desorption. Desorption increased with increasing pH and for K-systems relative to Ca-systems. Desorption of TC was greater than desorption of CTC. Desorption of TC and CTC from the clay-humic complexes was substantially greater than desorption from either the humic substances or the soil clays. The results demonstrate that interactions between soil clays and humic substances significantly influence both the sorption and desorption of TC and CTC from soil components. One possible explanation is that humic substances compete with TC and CTC for sorption sites on soil clays.

Despite significant effort, we were not able to find an extraction scheme that would remove more than a small fraction of the adsorbed TC from soil clays and clay-humic complexes. This precluded our ability to directly quantify degradation of adsorbed tetracycline. Also, because TC was so strongly adsorbed on soil clays and clay-humic complexes, it became apparent that there was little likelihood of our being able to successfully quantify the mobility of TC in intact soil columns. Therefore, we switched strategies and used tritium-labeled TC to quantify release of TC degradation products from clays and clay-humic complexes under both biotic and abiotic conditions during long-term (149 days) incubations. The results for abiotic aqueous systems indicated that about 30% of the added TC was transformed into 4-epitetracycline, but, otherwise, there was no degradation of TC during a 21-day incubation. In contrast, during the same period all of the TC in aqueous biotic systems was degraded. In the colloidal systems, all of the TC and 4-epitetracycline disappeared from the aqueous phase after 40 days for both the biotic and abiotic systems. Tritium concentrations in the aqueous phase increased during the first 30 days of the incubation but stabilized thereafter. Both the rate of tetracycline disappearance from the aqueous phase and the rate of tritium appearance in the aqueous phase were only slightly larger for the biotic systems relative to the abiotic systems. Tritium release increased for whole soils < clay-humic complexes < clays.

The results of these studies indicate that TC is very strongly adsorbed on soils and soil components. And, once adsorbed, only small amounts of TC are desorption from the solid phase to the aqueous phase. Although soil clays adsorb more TC than whole soils or soil clay-humic complexes, the TC that is adsorbed to soil clays is more labile than the TC that is adsorbed on whole soils or clay humic complexes. Up to 16% of the tetracycline that was added to the soil clay systems was degraded during the 149-day incubation. In contrast, only about 4% of the tetracycline that was added to the whole soil systems was degraded during the incubations. The results indicate that TC in soil systems will be subject to both biodegradation and surface catalyzed abiotic degradation. TC interacts so strongly with soil components that there is little likelihood for significant leaching of TC in soils.

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Information Transfer Program

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	4	8	0	0	12
Masters	5	2	0	0	7
Ph.D.	2	3	0	0	5
Post-Doc.	0	0	0	0	0
Total	11	13	0	0	24

Notable Awards and Achievements

2005--E. Pasco and A. Schwemm received an award for the Best Graduate Student Paper titled "Iron and acetate enhance phosphorus sequestration in wetland sediments" at the Sigma Xi Annual Meeting, University of Northern Iowa, Cedar Falls, IA.

2005--Ann Schwemm, Biology undergraduate honors thesis "The extent of phosphorus removal by wetland sediments," University of Northern Iowa, Cedar Falls, IA.

Dusan Palic received the Graduate Research Excellence Award, Iowa State University, Ames, IA, 2005.

Dawn Herolt and Dusan Palic, Iowa State University, were recipients of the 2005 Second Best Poster Award at the Student American Veterinary Medical Association Symposium, College Station, TX, March 10-12, 2005.

Dawn Herolt and Dusan Palic, Iowa State University, were recipients of the 2004 Best Poster Award at the American College of Veterinary Pathologists Annual Meeting, Orlando, FL, November 13-17, 2004.

Jutta Pils passed her final oral exam on May 16, 2005, and will officially graduate from Iowa State University with a Ph.D. in Agronomy, emphasizing soil chemistry, in August 2005.

Jutta Pils, Iowa State University, was invited (expenses paid) to present a talk entitled "Sorption of Tetracycline and Chlorotetracycline on K- and Ca-saturated Soil Clays and Humic Substances" as part of a special symposium honoring Dr. A.D. Karathanasis' achievements and his selection for the Heick Professor Fellowship, Lexington, KY, April 2004.

Jutta Pils, Iowa State University, was awarded Sixth Place for an oral presentation at the Annual Meeting of the Soils Science Society of America, Indianapolis, IN, 2002.

Ashley Mordasky, University of Iowa, received the Best Poster Award at the 2005 Annual Meeting of the Iowa Groundwater Association, Coralville, IA, November 9-10, 2004.

2004--Ceyda Polatel was awarded the Anne Cleary International Research Fellowship, University of Iowa. The fellowship was awarded as a partial funding for a four-month dissertation enhancement research at the University of Karlsruhe, Germany. The research focused on the Large Eddy Simulation of the experimental flow cases proposed by the project, to support and enhance the experimental findings.

2005--Ceyda Polatel received The University of Iowa Engineering Research Open House Best Poster Award for a poster based on the results of the research project showing the flow structure over a two-dimensional sand dune.

A.C. Kolz, T.B. Moorman, S.K. Ong, and K.D. Scoggin, Iowa State University, were awarded Second Place for their poster presented at the Water Environment Federation Technical Conference, New Orleans, LA, October 4-7, 2004.

Publications from Prior Projects