

Nebraska Water Resources Center Annual Technical Report FY 2003

Introduction

Dr. Kyle D. Hoagland resumed duties as director of the University of Nebraska Water Center in August 2003, after serving 20 months as interim director of the University of Nebraska-Lincoln (UNL) School of Natural Resources. Michael Jess became Associate Director of the Water Center after serving as acting director during this time.

An innovative, comprehensive and interdisciplinary new water resources research initiative began at UNL in 2003. Initial progress includes recruitment of two new water faculty positions, approval of four others across several academic units, and initiation of an annual, national-level water law, policy and science conference, the first of which was held in March 2003. The initiative represents significant new multi-year support for water research, education and outreach programming at the University of Nebraska. Its programming focus is grounded in recognizing the critical importance of water resources in the state, the nation and globally.

Research Program

Late in 2003, an independent panel of state and federal agency representatives reviewed 11 USGS 104b proposals and recommended 3 for funding assistance. Areas of focus included irrigation use efficiency, water quality remediation, arsenic in water supply systems, river-ground water interactions, pesticide impacts on aquatic ecosystems, and nutrient management strategies.

The Water Centers associated Water Sciences Laboratory, which is a core research facility serving all water science faculty throughout the University of Nebraska system, made significant strides in improving analytical capabilities and research methodologies during 2003 with the integration of several major new pieces of analytical equipment. These improvements have been made under the management of a new director of laboratory services, Dr. Daniel D. Snow. Additional funding for new equipment is anticipated in 2004 through the water initiative, which will maintain momentum toward elevating the lab to a national-level, cutting-edge analytical facility, specializing in detection of trace organics.

Defining Dynamic Crop-Water-Stress-Index Baselines to Schedule Irrigation Using Infrared Thermometers

Basic Information

Title:	Defining Dynamic Crop-Water-Stress-Index Baselines to Schedule Irrigation Using Infrared Thermometers
Project Number:	2003NE34B
Start Date:	4/1/2003
End Date:	10/31/2004
Funding Source:	104B
Congressional District:	3
Research Category:	Not Applicable
Focus Category:	Irrigation, Agriculture, Climatological Processes
Descriptors:	Crop Water Stress Index, CWSI, Canopy Temperature, Irrigation scheduling
Principal Investigators:	Jose Oscar Payero

Publication

Current Status of Project:

During the summer of 2003 it was not possible to collect the field data required to complete this project. Consequently, a no cost extension of the funding period until October 31, 2004 was granted by the Water Center to complete this project. No expenses were therefore made during the reporting period, and no publications or extension programs have yet resulted from this project. The current plan is to collect field data during the summer of 2004. Because of the nature of this project, field data needs to be collected after the crops effectively cover the soil background. Data collection period therefore starts sometime at the end of June. So far, the necessary equipment has been ordered and will be received and installed in the field in the next two weeks. Field data will be collected until the crops mature, which usually occurs in mid September. This will provide time to have the data analyzed and final report written by the end of October. A student will be hired to assist in this project from the end of June until the end of August.

Assessing the occurrence of Arsenic in groundwater: Implications for Small Water Supply Systems in Nebraska

Basic Information

Title:	Assessing the occurrence of Arsenic in groundwater: Implications for Small Water Supply Systems in Nebraska
Project Number:	2003NE36B
Start Date:	4/1/2003
End Date:	9/30/2004
Funding Source:	104B
Congressional District:	1
Research Category:	Ground-water Flow and Transport
Focus Category:	Water Quality, Groundwater, Hydrogeochemistry
Descriptors:	
Principal Investigators:	David C. Gosselin, F. Edwin Harvey, R. Matthew Joeckel

Publication

1. Gosselin, Dave, Lynne Klawer, and Angela Noe, 2004, Arsenic in Nebraskas Groundwater and Public Water Supplies, Earth Science Notes No. 7, Conservation and Survey Division, University of Nebraska-Lincoln, 8 pages.
2. Gosselin, David C., Lynne M. Klawer, R. M. Joeckel, F. Edwin Harvey, Angela R. Noe, and Kelli J. Warren, 2004, Arsenic Variations in Rural Public Water Supplies in Nebraska: U.S.A., A Basis for Assessment, Management and Remediation, Ground Water. (In Review)

Summary:

This project is part of an on-going state-wide groundwater resource assessment that is currently focused on arsenic. The **long-term goal** of our research is to reduce the economic impact of arsenic regulations on public water supply systems by evaluating less costly options for achieving compliance with the 10 µg/L MCL. The **specific goal of this project** is to improve our understanding of As in Nebraska's groundwater and apply this knowledge to mitigating the impact of As on public water systems.

Specific Objectives: The specific objectives of this state-wide project are: 1. Determine the chemical form in which the arsenic occurs in groundwater; and 2. Determine the geological and geochemical factors that control the occurrence of arsenic.

Results - Objective 1: As part of our EPA-funded reconnaissance sampling of two wells from 10 public water supplies, we tested 20 wells two to five times for arsenate from April through August 2003. These data indicate that arsenate (As^{5+}) comprises between 70 and 90 percent of the arsenic in the following public water supplies: Anselmo, Broadwater, Cambridge, Elwood, Lodgepole, McCook, Oshkosh, and Stromsburg. The two wells at Benkelman had less than 40 percent arsenate. In Cambridge, there was about a 20 percent difference in arsenate concentration between the two wells tested. Our conclusions thus far are that Arsenic occurs primarily as As^{5+} . This form of arsenic is preferred for most treatment options. However, wells need to be evaluated on an individual basis.

Results - Objective 2: In Nebraska, arsenic in the groundwater is derived from the interaction between the water and geologic material through which it flows. Therefore, it is crucial to assess the availability of arsenic from the various geologic materials that comprise Nebraska's aquifers. We obtained two cores (~90 feet total) of unsaturated and saturated alluvial sand and gravel from Cambridge in the Republican River valley and from Oshkosh in the North Platte valley. Both of these valleys are recognized for their high arsenic levels. We have also acquired samples from the Conservation and Survey Division archive that includes: Quaternary sand and gravels, loess and glacial till, Cretaceous bedrock, and Tertiary Bedrock. To determine arsenic availability, sequential extraction procedures will be used on approximately 22 samples. We are in the process of evaluating the sequential extraction procedures of Keon and others (2001) for our use. After the extractions are completed, the solutions will be analyzed by ICP-mass spectrometry.

Results - Related EPA-funded Studies: The average concentrations for the 20 public water supplies range from 4.2 to 22.1 µg/L. Twelve of those wells have average As concentrations greater than the MCL. Only four of these (Stromsburg 1 and 3, Anselmo 871, Broadwater 551) have average As concentrations greater than 13 µg/L. An additional four wells (Benkelman 962, Cambridge 831, Lodgepole 751, Oshkosh 1741) have average concentrations between 9.3 and 9.8 µg/L, but they have values that, at times, exceed 10 µg/L. The two wells at Elwood and Shelton 49 have the lowest average As concentrations at 6.3, 5.5, and 4.2 µg/L, respectively. Wells from the same PWS which derive their water from similar geologic units can have comparable As concentrations (for example, McCook); or one well can have concentrations up to 60 percent higher than another (for example, Anselmo). Arsenic concentrations varied by as

little as 1.5 µg/L to as much as 7.0 µg/L in individual wells over the one-year study. In some cases, the apparent variation in As concentrations brings the well into compliance with the MCL. Analytical variability may be responsible for up to at least +/- 10% of the observed variation among the samples.

Our conclusions thus far are as follows: 1. Arsenic concentrations are variable in individual wells on different time scales. 2. In some cases, monthly variability is large enough to bring the As concentrations into compliance with the MCL. However, this variability is not predictable. 3. A well should be pumped for at least 30 minutes prior to sampling. Mitigating arsenic by well field management does not appear to be an adequate solution for PWS.

Information Dissemination: Project information has been disseminated through a variety of avenues including 12 newspaper articles, 10 presentations and one radio interview. The Arsenic Information System website (<http://nesen.unl.edu/nearsenic/>) was developed to inform not only the PWSs involved in the project, but also a wider audience such as educators, researchers, government agencies and the public in general.

Additional Funding

Funding from Region 7 of the U.S. Environmental Protection Agency (Federal Assistance Identifier MM-98720701-0 and X6-98728301-0).

Biodegradation of Dual-Contaminant Mixtures in Groundwater: Chlorinated Solvents and High Explosives

Basic Information

Title:	Biodegradation of Dual-Contaminant Mixtures in Groundwater: Chlorinated Solvents and High Explosives
Project Number:	2003NE41B
Start Date:	3/1/2003
End Date:	2/29/2004
Funding Source:	104B
Congressional District:	1
Research Category:	Not Applicable
Focus Category:	Treatment, Toxic Substances, None
Descriptors:	groundwater, remediation, high explosives, chlorinated solvents, biodegradation
Principal Investigators:	Matthew Morley, Daniel Davidson Snow

Publication

1. Young, Travis S.M., 2004, Anaerobic Biodegradation of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine (RDX) and Trichloroethylene (TCE): Single- And Dual-Contaminant Batch Tests, MS Thesis, Environmental Engineering, College of Engineering and Technology, University of Nebraska at Lincoln, Lincoln, NE, 140 pages.

RESEARCH: Due to its extensive use as an explosive, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is a common groundwater contaminant at many defense-related sites. Because of its wide spread use as an industrial degreasing compound, roughly fifty percent of the sites listed on the U.S. EPA National Priority List have groundwater contaminated with trichloroethylene (TCE). There are at least five sites in the U.S. that have groundwater contaminated with mixtures of high explosives and TCE. The current remediation approach is to extract this contaminated groundwater and treat it using granular activated carbon, which will be a long and costly process. Single contaminant biodegradation of TCE and RDX has been well studied and can be an effective treatment method. However, there has been no previous research examining the ability of mixed microbial consortia to biodegrade two contaminant mixtures of TCE and RDX. This research examined the ability of two separate anaerobic cultures to biodegrade single- and dual-contaminant mixtures of TCE and RDX.

Single- and dual contaminant batch tests were conducted to examine the ability of anaerobic sludge and an environmentally derived culture, to biodegrade TCE and RDX. All assays used sodium acetate as an organic carbon source. In the single component RDX batch tests, both cultures readily degraded RDX and all RDX-nitroso compounds to concentrations below minimum detection limits (MDLs). For the single component TCE batch tests, the anaerobic sludge could not biodegrade TCE, while the environmental culture transformed approximately ten percent of the initial TCE concentration to a secondary chlorinated compound. Prior to conducting the dual-contaminant batch tests, the two cultures were acclimated to TCE. Following acclimation to TCE, both cultures were able to degrade TCE to secondary chlorinated compounds during the dual contaminant batch tests. Also, during the dual contaminant batch tests, both cultures were also able to degrade RDX and RDX-nitroso compounds to concentrations below the MDLs.

Results of these experiments indicate that the two cultures examined in this research were able to biodegrade RDX, RDX-nitroso compounds, and TCE in single- and dual-contaminant mixtures. Biodegradation of TCE metabolites was more variable, with the environmental culture displaying the ability to biodegrade a wider range of metabolites.

STUDENT SUPPORT: 1 MS student (Travis Young) was supported with USGS funding.

Assessment of Source of Variation in Copper Concentrations in Nebraska Drinking Water Systems

Basic Information

Title:	Assessment of Source of Variation in Copper Concentrations in Nebraska Drinking Water Systems
Project Number:	2002NE12B
Start Date:	3/1/2002
End Date:	9/30/2003
Funding Source:	104B
Congressional District:	1
Research Category:	Engineering
Focus Category:	Treatment, Water Quality, Water Supply
Descriptors:	
Principal Investigators:	Bruce Irvin Dvorak, Matthew C Morley

Publication

1. Qiu, Junling, 2003, Impact of Phosphate Inhibitors on Copper Corrosion: Pilot Studies at Two Nebraska Water Systems, MS Dissertation, Environmental Engineering, University of Nebraska at Lincoln, Lincoln, NE, 120 pages.
2. Qiu, Junling and Dvorak, Bruce, 2004, Impact of Phosphate Inhibitors on Copper Corrosion: Pilot Studies at Two Nebraska Water Systems, Submitted to the 2004 American Water Works Association Water Quality Technology Conference, American Water Works Association, Denver, CO.

Assessment of Source of Variation in Copper Concentrations in Nebraska Drinking Water Systems

RESEARCH

Project Summary

Three bench-scaled pilot studies were conducted to investigate the impact of phosphate inhibitors on copper by-product release into water in two Nebraska water supplies. The waters in copper pipes treated by phosphate inhibitors were collected to test for copper by-product release after an 8 or 10 hours stagnation time. At the end of each study, the copper pipes were removed and the pipe scale was analyzed using a Scanning Electron Microscope (SEM). Results from three studies yield the following conclusions: 1) In all cases orthophosphate reduced copper corrosion. 2) In all cases ortho/polyphosphate increased copper corrosion. 3) For all pipes with no treatment in the first two studies, pale-green and adherent scales with malachite were formed on the inner walls of pipes that protected these pipes from further corrosion and resulted in lower copper concentrations in pipes. 4) For all pipes fed phosphate inhibitors, their surfaces appear brown and shiny and no phosphates were found on the surfaces. CuO or/and Cu₂O existed on the surfaces.

Problem and Research Objectives:

Copper is a commonly used material for water distribution piping. Although it is fairly resistant to corrosion, copper piping may corrode under some conditions, resulting in elevated copper concentrations in drinking water. In response to potential for adverse health effects at high concentrations, the EPA has established an action level of 1.3 mg/L for copper in drinking water (USEPA, 2000). The action level is the 90% percentile value for the samples collected. Because the primary source of copper in drinking water is corrosion of plumbing materials, the EPA requires treatment for corrosion control as a method for reducing copper concentrations. As of August 2001, a total of 49 drinking water systems in Nebraska exceeded the U.S. EPA's action level for copper in drinking water (NDHHS, 2001). A total of 19 of the systems in violation of the copper standard were below the copper action level in several rounds of samples between 1992 and 1999, but exceeded the action level in a round of testing in the past year. Implementation of the EPA-mandated corrosion control methods will be a significant financial impact on many of these communities.

Many of Nebraska water systems that have excessive copper levels utilize groundwater that has high alkalinity, neutral pH, and low dissolved oxygen. There is little scientific information concerning corrosion of copper by this type of water chemistry (Edwards, 2001; Schock, 2001).

For many waters, a protective scale will form on copper pipe (which significantly reduces copper corrosion) in between 1 day and 50 years, depending on a range of factors (water chemistry, temperature, water use pattern, etc.). In a few cases, a protective scale will never form. If a protective scale layer has not formed on the copper pipes, then a common method of reducing copper corrosion is to add food grade ortho- and polyphosphate inhibitors to the water at the water source. Past research has shown that orthophosphates will help form a protective CuPO₄ scale layer on the pipe. In all cases found in the literature, orthophosphates reduced copper dissolution. On the other hand, polyphosphates have been found to make copper corrosion worse.

The reason polyphosphates are often added to drinking waters is to sequester dissolved iron and manganese. In Nebraska this occurs with some high alkalinity, neutral pH, high TDS waters. Dissolved iron and manganese (in anoxic ground waters) can be oxidized in the home or distribution system by dissolved oxygen and/or chlorine and form precipitates that are observed as red or black water (and lead to staining of fixtures). The sequestering agents, such as ortho and polyphosphates, can change the iron and manganese precipitates so they form smaller, more stable particles, that result in less observed color and staining of fixtures. Past research has shown that polyphosphates are better sequestering agents than orthophosphates, but high orthophosphate concentrations can also be effective for sequestering. Also, polyphosphate will convert over time to orthophosphates in the water distribution system.

Edwards of Virginia Tech suggested in a 1999 publication a conceptual model of impact of polyphosphates on copper corrosion concentrations: $Cu \text{ increase} = [\text{Poly PO}_4] / ([\text{total PO}_4])$
Too much polyphosphates in a phosphate blend negate ability of orthophosphates to form a protective $CuPO_4$ film.

Although some phosphate vendors are very knowledgeable, many vendors are not very knowledgeable and Nebraska communities have been sold phosphate blends that are not optimal for their water chemistry. This project is focused on providing scientific data and a conceptual model to help water utilities better select phosphate blends for copper corrosion control.

Based on the initial findings of this project related to scale layers and interactions with small community water suppliers, this study has slightly redirected focus toward impact of phosphate inhibitors on variations in copper concentrations.

This study is funded by funds from three sources: USGS 104 program, Nebraska Section of the American Water Works Association (AWWA), and the Nebraska Department of Health and Human Services System (NE HHSS). Not all of the non-USGS funds are listed as an official match to the USGS 104 grant. The USGS funds have been used to pay for the initial portions of the project and the AWWA and NE HHSS funds will be used to complete the project.

The basic research objectives were to:

1. Study the impact of different mixtures of ortho- and polyphosphate concentration on copper dissolution in waters typically of Nebraska ground waters.
2. Study the pipe scales after exposure to the different waters for several months using a scanning electron microscope.
3. Examine the rate of polyphosphate conversion to orthophosphate in two Nebraska ground waters.
4. Develop a model to suggest the impact of ortho- and polyphosphate on copper corrosion in real drinking waters with high alkalinity and a neutral pH.

Methodology:

This study focused on investigating the effect on copper corrosion of adding six different mixtures of orthophosphate and polyphosphate (sodium hexmetaphosphate) to the drinking water; a no treatment option was also studied. Two Nebraska public water supplies (PWSs) were selected for study, Waverly and Eugene T. Mahoney State Park, NE based on their proximity to Lincoln, being a borderline copper exceeder, water quality and willingness to participate in this study. Table 1 lists the influent water quality of Waverly and Mahoney State Park. Both water supplies currently do not treat their water, which comes from deep groundwater wells. The study of each community lasted four months.

Table 1. Influent Water Quality of Waverly and Mahoney State Park to Apparatus

Location	Waverly	Mahoney
Parameters	Average	Average
Temp.(°F)	62.9	59.4
pH	7.15	7.16
Alkalinity (mg/L as CaCO ₃)	180	165
Phosphate (mg/L as P)	0.04	0.07
Sulfate (mg/L)	142	33.7
Dis. Oxygen (mg/L)	8.5	9.14
Cu (mg/L)	0.01	0.02
Total Organic Carbon (mg C/L)	1.3	0.95
Total Inorganic Carbon (mg C/L)	74.0	58.9
Fe (mg/L)	0.3	0.2
Mn (mg/L)	0.1	0.1
Ca (mg/L)	71	54
Mg (mg/L)	20	22
Total Dissolved Solids (mg/L)	399	285

A pilot-scale flow through apparatus was specially designed for this study. Water enters the apparatus through a rubber hose, which is directly connected to the Waverly or Eugene T. Mahoney distribution system through a faucet. Then the water flowed through different copper pipes and finally drains down to the sewer system. Water samples were collected from copper pipes after an eight or ten hours stagnation period two or three times every week. If samples were not collected, water could flow out of apparatus at the end of stagnation period. Influent water was also collected and tested every week.

During the period of three studies, total copper, particulate copper, orthophosphate, polyphosphate, total phosphate, pH, temperature, dissolved oxygen and alkalinity were measured. All analytical procedures followed Standard Method (APHA, 1998).

When the three studies were completed, copper pipes were removed from experimental apparatus and scales formed on the pipe surfaces were analyzed by scanning electron microscope (SEM). The SEM is equipped with equipped with an X-ray detector and can show the magnified scale image from 10 times to 300,000×times and identify the elemental composition of scales.

Results

Three studies were conducted during 2002 and 2003 in two Nebraska Public Water Supplies, Waverly and Mahoney State Park. Copper data and SEM analysis are presented and discussed subsequently.

Study #1- Waverly, 2002

The pilot apparatus was placed and operated in the Waverly High School for four months from July to November of 2002 to study the effect of phosphate treatment on corrosion in copper pipes. Two pairs of new and aged pipes were used to compare the different impact on copper corrosion

between new and aged pipes. The aged pipes were obtained from different businesses in central Waverly. One pair was treated with phosphate blend (0.3 mg P/L in orthophosphate and 0.3 mg P/L in polyphosphate), and yet another pair had no treatment. Phosphate blend and phosphate dosage used Study #1 were recommended by Waverly's current chemical supplier (Carus Co.); this blend includes fifty percent of orthophosphate and fifty percent of polyphosphate, but the type of polyphosphate was unknown. 0.3 mg P/L orthophosphate and 0.3 mg P/L polyphosphate refer to the initial adding dosage not phosphate residual after an 8-hour stagnation period. Since phosphate treatment may cause bacterial growth in pipes, water was chlorinated to a residual of 0.3 mg/L for pipes with phosphate treatment. During the period of study, it was observed that the temperature changed about $\pm 5^{\circ}\text{F}$ as the seasons changed. Based on analysis of copper data and pipes scales, the conclusions for this study are summarized as follows:

- (1) Within four months, similar surface scales were developed for new and aged pipes under the same treatment conditions.
- (2) Pipes with no treatment show lower copper concentrations due to the protection against corrosion by scales with malachite or copper oxides.
- (3) The phosphate blend increased copper concentration. This increase shows that the dosage and blend provided may be not sufficient to form a protective film.

Study #2 - Waverly, 2003

The apparatus was operated in the Waverly High School from late May to August of 2003 to study the effect of phosphate treatment on copper corrosion. Seven new copper pipes were used. Six of them were treated by six different ortho/polyphosphate blends, and the other one pipe was fed with untreated water. Commercial phosphate blends were not used because their composition is proprietary. Orthophosphate (Na_3PO_4) and polyphosphate ($\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$) were purchased and were used to make phosphate blends. The influent water was also chlorinated (0.7 mg/L) for pipes with phosphate treatment.

Due to fluctuations in copper concentrations, the results from Study #2 are divided into four portions. From when the study started in late May through Mid-June, the copper concentrations in pipes were observed to be dropping as the system moved toward an equilibrium state. In late June, pipes fed phosphates appeared to be reaching a steady state. Copper concentrations in seven pipes appeared very low. In July, the copper concentrations for all pipes increased. An accidentally increased flow rate that led to lower phosphate doses through the pipes may be responsible for the increasing copper concentrations. Due to increasing water demand in the middle of summer, pumps in Waverly's South Well field were operated more frequently and water pressure in system varied significantly during the day, more than during the rest of the year. Thus water flow through the apparatus also varied during the day, leading to phosphate doses to vary through the day, since phosphate doses were set just twice or three times a week (always in the late morning) by setting chemical feed pump rate to result in a constant feed. The flow rate through each pipe in July was observed sometimes up to 1.8-2.0 gallon/minute, almost twice as the design flow rate, which means the phosphate concentrations in pipes were about 50% of target concentrations.

To keep the constant flow rate and target phosphate concentration, a pressure regulator was installed in the end of July. After adding a pressure regulator, the flow rate became constant, about 1 gallon/minute. In August, the system appeared to move toward a steady state. Copper

concentrations in no treatment pipe kept constant, while copper concentrations for pipes with phosphates started to drop down to lower levels again.

Due to fluctuations in flow rate, only the data of total copper by-product release from last month (August) is provided. Differences in copper by-product release between the poly/orthophosphate blends are small and may not be statistically significant, as illustrated in the box plot of the data in Figure 1. The boundary of the box closest to zero indicates the 25th percentile total copper concentration, the light line within the box marks the median concentration, the dark line within the box represents the mean concentration, and the boundary of the box farthest from zero indicates the 75th percentile concentration.

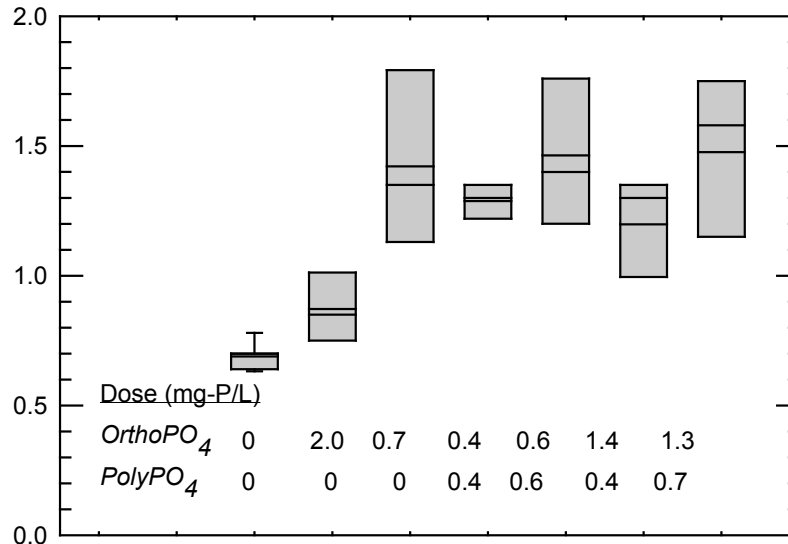


Figure 1. Box Plot of Last Month of Total Copper Data from Study #2.

Although polyphosphate is typically used for sequestering of iron and manganese, it could still serve as a corrosion inhibitor as it reverts to orthophosphate. The dosages used in this study ranged from 0.4 mg P/L to 0.7 mg/L. Also the reversion rate of polyphosphate used in this study was observed less than 10% in glass jar test over 4 days and an insignificant amount of reversion in pipes during 10-hour stagnation which means only a very small amount of orthophosphate was actually produced, although in some real systems, a significant amount of reversion of polyphosphate to orthophosphate may occur, depending on water chemistry and the contact time of the phosphates within the water before reaching home copper pipes.

After the three-month study was completed, pipes removed from the apparatus were examined and analyzed. Scales formed on the no treatment pipe appear green, adherent and uniform, and the main elemental composition of scales is copper and oxygen, very similar to those found in the pipe with no treatment in Study #1. Based on the scale color and elemental analysis, the scales found on the no treatment pipe surfaces contained malachite. Therefore, it was concluded that uniform and adherent scales with malachite protected no treatment pipe from corrosion and resulted in a lower copper concentration. For all pipes with phosphate treatment, the surfaces visually appear brown and shiny, and no scales were found on the inner wall. Even under SEM examination, phosphate films could not be detected. But the elements of copper and oxygen were found in the scale, which indicates some copper oxides, such as Cu₂O or/and CuO may present in

the scales.

Study #3 (Mahoney State Park '03)

A third study was performed in Eugene T. Mahoney State Park from early September to late November of 2003 to study the effect of phosphate treatment on copper corrosion. The same apparatus as used in Study #2 was placed in the Owen Marina of Mahoney State Park. Only new copper pipes were used for Study #3. Study #3 was very similar to Study #2, except that the phosphate blend with 0.4 mg P/L orthophosphate and 0.4 mg P/L polyphosphate in Study #2 was replaced by 3.0 mg P/L orthophosphate. There were two reasons for changing phosphate concentrations. First, it was thought the concentration of the phosphate blend used in Study #2 might be too low for water with a high hardness. Also, the pipe with 2.0 mg P/L in orthophosphate in Study #2 had a low copper byproduct release. Therefore, it was expected that a higher orthophosphate, such as 3.0 mg P/L, would have an even better effect on copper corrosion control. In the period of Study #3, small variations in temperature, pH, alkalinity and dissolved oxygen were observed in the influent water quality.

Total copper data obtained from seven pipes during a three-month period are plotted in Figure 2. The 3.0 and 2.1 mg/L-orthophosphate dosed pipes had the lowest copper concentrations by the end of the study. Copper concentrations in other five pipes were very similar. For Study #3, improvements in the apparatus design and operation lead to smaller variations in the copper concentrations, as illustrated in the box plot of the data (Figure 3).

Table 2. was created to compare the effect of different phosphate compositions on copper byproduct release. First, comparisons can be made among pipes with the same polyphosphate dose. For pipes #2, #3 and #4, no polyphosphates were added, but different (2.1, 0.7 and 3.0 mg-P/L) orthophosphate doses were given. Among these three pipes, as orthophosphate doses increased, copper concentrations decreased. For pipes #5 and #7, which had similar polyphosphate doses but different orthophosphate concentrations (1.4 and 0.7 mg-P/L), the one with higher orthophosphate dose resulted in slightly lower copper concentration. Similar, comparisons can also be made for pipes with the same orthophosphate concentration, (i.e. between pipe #3 and #5 and between pipe #6 and #7). In both cases, the pipe with lower polyphosphate resulted in a lower copper concentration, although the differences may not be statistically significant. In another comparison, a similar total phosphate concentration (2.1 mg-P/L) was added to pipes #2 and #7. Once again, the pipe with higher orthophosphate concentrations showed a significantly lower copper concentration.

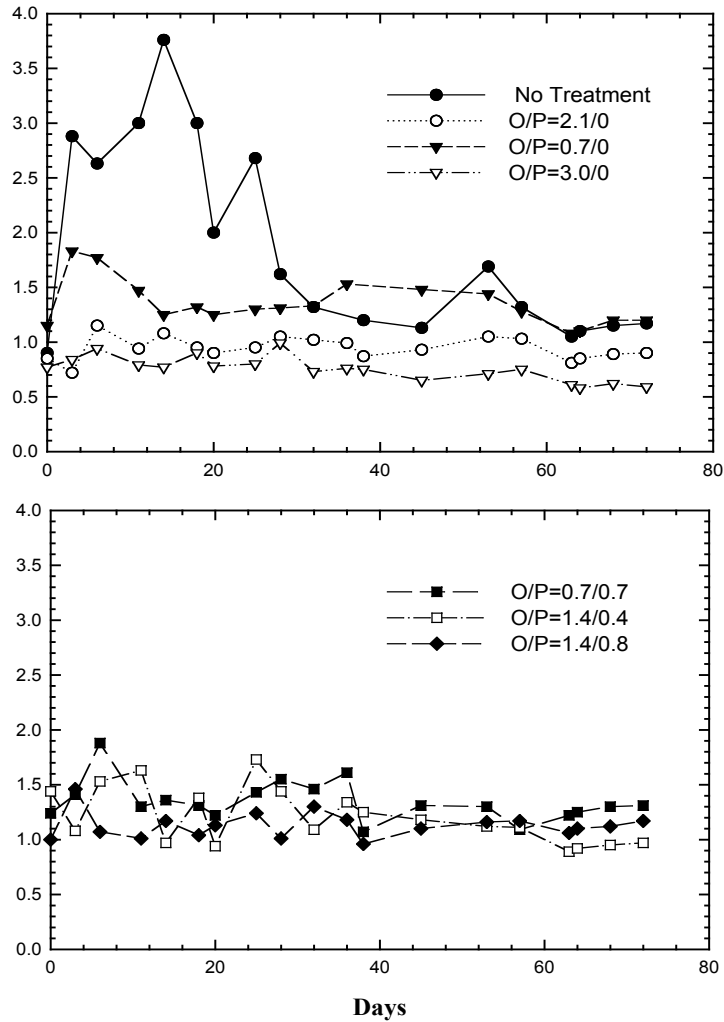


Figure 2. Copper Data from Study #3 (Mahoney Park).
(O/P=Orthophosphate (mg P/L) / Polyphosphate (mg P/L)).

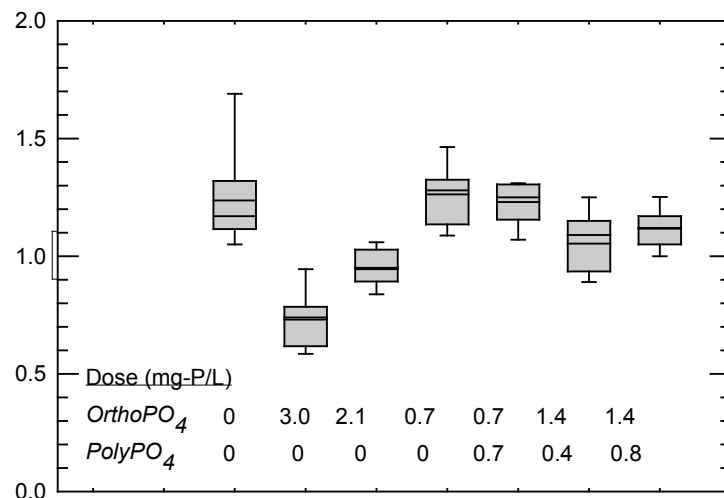


Figure 3. Box Plot of Last Month of Total Copper Data from Study #3.

Pipes removed from the apparatus were also examined and analyzed after Study #3 was completed. For the pipe with no treatment, the scales appear green, porous and non-uniform, unlike the scales found in the no-treatment pipe in Studies #1 and #2. This may explain why copper concentrations in the no-treatment pipe at Mahoney were higher than those found at Waverly under same condition. For all pipes with phosphate treatment, they looked similar to those observed in Study #2 except that Pipe #4 with lowest copper concentration (3.0 mg P/L of orthophosphate) appeared light brown and shiny, like a new pipe. Surfaces for other five pipes with different phosphate treatments except Pipe #4 visually appear brown and shiny, and no scales were found on the inner wall. Especially for pipe #4 that had the lowest copper concentration after 3 months of treatment, due to the least corrosion, the inner surface looks like a new copper pipe. Elements of copper and oxygen were detected in scales by SEM, which indicated CuO or/and Cu₂O existed in the copper surfaces. Most observations from Study #3 are similar to those obtained from Study #2 and not discussed in details in this Section.

Table 2. Comparison of Phosphate Composition on Copper Byproduct Release from Study #3 (Data from August after 10-hour stagnation time).

Comparison	Pipe #	Ortho-phosphate (mg-P/L)	Poly-phosphate (mg-P/L)	Copper Average (mg /L)	Copper Std. Dev. (mg /L)
Orthophosphate Concentration	#4	3.0	None	0.64	0.06
	#2	2.1	None	0.92	0.09
	#3	0.7	None	1.24	0.17
Orthophosphate concentration	#5	0.7	0.7	1.25	0.08
	#7	1.4	0.8	1.13	0.04
Polyphosphate Concentration	#3	0.7	None	1.24	0.17
	#5	0.7	0.7	1.25	0.08
Polyphosphate Concentration	#6	1.4	0.4	1.02	0.11
	#7	1.4	0.8	1.13	0.04
Same total phosphate concentration	#2	2.1	None	0.92	0.09
	#7	1.4	0.8	1.13	0.04

In November of 2003, after the new copper pipes had been exposed to the Mahoney water for about sixty days, a stagnation study was performed at Mahoney State Park in the same apparatus described previously. For the no treatment pipe, copper concentrations first reached a peak concentration around 10 hours, then dropped. Other researchers explain this trend as a result of the redox chemistry interactions between dissolved oxygen, metallic copper and surface oxidation products. After a range of several hours of stagnation time, dissolved oxygen levels would have dropped down dramatically. Under low dissolved oxygen, cupric ions (Cu⁺) were reduced to cuprous ions (Cu²⁺) and the surface film could be reduced to Cu (OH) or CuO by contact with pipe. As cuprous ions are less soluble than cupric ions, copper concentration in water decreased

For pipes with phosphate treatment, copper concentrations gradually reached peak and then dropped only slightly. The peak concentrations were observed for all six pipes with phosphate treatment at a range of two days (48 hours). In pipes with phosphates, the dissolved copper may tend to be sequestered in the water with the presence of phosphates, and insoluble cuprous (Cu^{2+}) forms.

Principle Findings and Significance

There are seven main findings from this study, as listed below.

- 1) Orthophosphate addition always resulted in a lower copper concentration than ortho/polyphosphate blends when the same dose (as mg-P/L) was applied.
- 2) For the phosphate blends added to the water in the copper pipes, the higher the polyphosphate concentration, the higher the concentration of the copper by-products released.
- 3) With phosphate blends, generally polyphosphate had a stronger negative impact on copper corrosion than the positive impact from orthophosphate.
- 4) The reversion rate of polyphosphate to orthophosphate was about 10% over four days for the communities studied.
- 5) For all pipes fed phosphate inhibitors, their surfaces appeared brown and shiny and no phosphates were found on the surfaces after four months. CuO or/and Cu_2O existed on the surfaces.
- 6) For the copper pipes fed the untreated water (no treatment), the peak copper concentration appeared after six to ten hours of stagnation then decreased significantly, before finally leveling off after about one day. For most pipes fed phosphates, copper concentrations gradually increased to around 48 hours.
- 7) Copper byproduct release may be sensitive to changes phosphate dosage. Decreases in phosphate inhibitor dosage resulted in increases in copper concentrations. Chemical feed systems should be designed to make it easy for operators of small systems to maintain a constant concentration in the system.

Relating landscape scale characteristics with phosphorus loss potential to surface waters

Basic Information

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PROBLEM AND RESEARCH OBJECTIVES

Animal manures offer both benefits to crop production and hazards to water quality. The application of manure at rates which exceed P removal by crops and the lack of manure incorporation into soil can result in P accumulation in the top 5 cm (2 in.) of the soil surface and subsequently lost in runoff (Smith et al., 1998; Ginting et al. 1998). Phosphorus in runoff is mainly bound to eroded soil-particulate matter (Catt et al., 1998; Simard et al., 2000), but dissolved organic and inorganic P in runoff from field are also a concern (Beauchemin et al., 1998; Chardon et al., 1997).

The effects of manure on soil P that is available to crops are commonly evaluated with standard soil P tests such as Bray-1 P, sodium bicarbonate P (Olsen-P), or Mehlich-3 P, depending on soil characteristics. Extensive research has studied the positive correlation between standard soil P tests and P in runoff (Sharpley, 1995; Sharpley et al., 1981; McDowell and Sharpley, 2001). While soil tests are part of the solution for estimating the effects of manure managements on soil nutrient status and nutrient loss in runoff, computer simulation modeling can be used to scale up the results. Despite uncertainties inherent in the modeling approach, modeling provides flexibility in evaluating and comparing a wide range of existing and potential manure management practices, and projecting the effects of these management practices into the future.

The goal of this study was to evaluate the effects of manure application on soil P levels and soil stratification and to predict long-term manure application effects on soil P dynamics and runoff P losses. The specific objectives of this study were: 1) to measure P of soils which have or have not received animal manure, using a group of standard agronomic and environmental tests; 2) to use the "Groundwater Loading Effects of Agricultural Management System" (GLEAMS) model, to simulate the dynamics of soil P status and stratification, and the effects on P in runoff water at various rates of annual manure additions; and 3) to compare GLEAMS P loss prediction with the proposed Iowa P-index. The GLEAMS model considers vertical pathways of pesticide and nutrient cycling and transformation, and estimates pesticide and nutrient loadings at edge-of-field and the bottom of root zone (Leonard et al., 1990; Knisel et al., 1993). The model includes four components: hydrology, erosion, pesticides, and plant nutrients. Field operations that modify the response of each component to climate (with updateable parameters) can be adjusted (e.g., dates of planting, harvest and crop rotation, tillage systems, etc.). Because P dynamics and loadings in runoff water and sediment were the focus of our study, only the hydrology, erosion, and nutrient components were considered.

MATERIALS AND METHOD

Characterization of Soil Phosphorus

Site Selection

Soils at the three small watersheds are Moody silty clay loams (fine-silty, mixed, mesic Udic Haplustolls). These soils are representative of soils present of areas of Nebraska where heavy concentrations of livestock production occurs such as Dixon and Cumming Counties. The Moody soils are upland soils formed in loess. The <12% slope Moody soils constitute about 15% of the area of Dixon County and 30% of Cumming County. For identification, these sites were named as Haskell, West Point, and non-manured sites. Normal mean annual precipitation for the sites is about 724 mm (28.5 in.) and 80% of the annual rainfall occurs during the growing season from April to October. The normal mean annual temperature for the sites is 9 °C (48 °F) and mean temperatures for the months of April, May, June, July, August, September, and October of 9.7, 16.1, 21.5, 24.3, 22.6, 17.1, and 10.6 °C (49.5, 61.0, 70.7, 75.7, 72.7, 62.8, and 51.1 °F), respectively.

Haskell Site. The site is located in a rolling landscape toposequence with a convex shoulder, rectilinear backslope, and concave footslope. This site was delineated from a larger area used for a manure study from 1999-2002 at the Haskell Agricultural Laboratory, Concord, NE (96° 59' W, 42° 23' N). During this prior study, the area was divided into 18 strips allocated in a randomized complete block design with three replications of site specific and uniform application of a cattle feed-lot manure (CAM) treatment,

site specific and uniform application of swine manure (SWM) treatment, uniform application of commercial N fertilizer treatment, or control (CTL) check (no manure or fertilizer). Since our interest was on manure effects on soil P dynamics, only strips with uniform application of CAM and SWM, plus the CTL, were used for this study.

The manures were applied annually either in the fall or spring before planting corn (Table 1). Manure was incorporated into soil by disking within 24 hours after application. Rate of application was based on corn N needs adjusted with 90 cm (3 ft) soil profile NO₃-N test. Rate of manure application and corresponding P applied are presented in Table 1.

West Point and non-manured Sites. The West Point site was located on a farmer's field near West Point, NE (96°66' W, 41°89' N). The field site was approximately 4 ha (9.9 A) and had received feedlot beef manure for at least five years. Manure had been surface applied and incorporated by shallow disking. Rates of manure application were not documented. The field is concave with an eroded intermittent channel in the middle extending from upper backslope to toeslope. The control is a non-manured farmer's field near West Point, NE (96°67' W, 41°88' N). The field site is approximately 5 ha and has no manure history, with a landscape form similar to the West Point site.

Characterization of Soil Phosphorus

Soil samples were collected from all sites in May 2002. At the Haskell site, soil samples were collected at three positions, the shoulder, backslope, and footslope, from each of the triplicated CAM, SWM, and CRL treatments. At each of the three positions, ten 1.8 cm (0.70 in.) diameter soil cores were collected at 0-5 (0-2 in.), 5-10 (2-4 in.), and 10-15 (4-6 in.) cm depths, and then composited by depth. At the West Point and non-manured sites, soil samples were collected in five transects, 183 m (600 ft.) long, parallel to north-south intermittent channel. Two transects were located west of the channel, one was in the channel, and the other two were east of the channel. Along each transect, soil samples were collected at the highest, middle, and lowest elevations. Soil samples were air-dried and ground to pass 2-mm mesh sieve and analyzed for total P (TP), Bray-1 P, FeO-P, and water extractable P (WP). Soil texture was determined using the pipette method (Gee and Bauder, 1986). Phosphorus analyses followed procedures outlined in the Southern Cooperative Series Bulletin No. # 396 (Southern Cooperative Research Bulletin, 2000).

Statistical Analysis

The relationships among various P forms were established with simple linear models using the REG Procedures of SAS (SAS Institute, 1989). The effects of manure on P forms were determined using a mixed model of SAS (Littell et al., 1999). At the Haskell site, the experimental design was a split plot design where manure treatment (CTL, CAM, and SWM) was the main plot and depth as sub-plot, with observations for three observations landscape positions made within each experimental unit. The fixed components were treatment, soil depth, and soil depth by treatment. The random components were replication and replication by treatment. The subject was sampling position nested within replication by treatment by depth. For the West Point and non-manured sites, the experimental design was a randomized complete block design nested within the site. Within each site, transects were regarded as replication and depth as treatment. Three sampling positions (elevations) within each transect were regarded as three observations for each experimental unit. In this case, the fixed components were site, depth, and their interactions. The random components were replication nested within site, and replication by transect by elevation nested within site.

Modeling of P dynamics and potential runoff P losses at the Haskell site

Sensitivity analysis was done using a two-step approach.

- 1) Sensitivity analysis of GLEAMS was conducted by using the documented detailed management practices and manure treatments of the Haskell site from 1999 to 2002 (Table 1). At all times during the sensitivity analysis, general or non-site specific parameters were

not changed. Site-specific variables and initial conditions were either measured and/or taken from a readily available database (Soil Survey Staff, 2003).

- 2) Variables with smallest deviations between simulated and measured soil P for all treatments during the sensitivity analysis period (1999-2002) were selected for the second step. These variables were used to predict the long-term P dynamics and its effects on runoff P losses from the field at Haskell site.

Preliminary GLEAMS simulation indicated that the P was stratified and responded to depth of manure incorporation. Therefore each soil P sampling depth (0-5, 5-10, and 10-15 cm or 0-2, 2-4, 4-6 in.) was regarded as a horizon, identified as Ap1, Ap2, and Ap3, respectively. Although this degree of horizon differentiation is not normal practice, GLEAMS was sensitive to these depth layers. The rest of the profile consists of Bt1 (15-36 cm or 6-14 in.) and Bt2 (36-110 cm or 14-43 in.) horizons. These depths of B horizons were based on the average depth of B horizons of five referenced profiles of Moody soils at various counties in northeastern Nebraska (Soil Survey Staff, 2003). Subdividing the Ap resulted in a total of 5 horizons representing the soil profile. Texture (clay, silt, and sand contents) was measured for the three Ap horizons. Other soil physical properties (porosity, bulk density, field capacity, wilting point, and evaporation constant) for all horizons were estimated using the textural information (USDA-SCS, 1984; Ritchie, 1972). Soil pH, NO₃-N, OM, total N (TN) were also measured for the Ap1, Ap2, and Ap3 horizons (Table 2). Soil pH was measured in water at 1:1 ratio (m:V), NO₃-N was extracted in 2 M KCl and measured by the flow injection Cd reduction method, OM was obtained by loss on ignition, and TN was measured by combustion on a LECO 428. Other soil chemical properties for Bt horizons were based on the NRCS database (Soil Survey Staff, 2003).

Sensitivity analyses also indicated that soil P was closely related to P inputs; thus, the effects of annual CAM application rates of 0, 10, 20, 30, and 40 dry Mg ha⁻¹ yr⁻¹ on soil P dynamics and runoff P were evaluated in a 25 yr simulation for the Haskell site. The annual P loads for the 0, 10, 20, 30, and 40 Mg ha⁻¹ (0, 4.5, 9.0, 13.5, and 18.0 T A⁻¹) application were 0, 36, 72, 108, and 145 kg P ha⁻¹, respectively, using the three year average TP concentration (3.6 g TP kg⁻¹) of the CAM at the Haskell site. Based on corn grain yield of 15 Mg ha⁻¹ (210 bu A⁻¹) and P need of 6.4 g kg⁻¹, the application rates of 0, 10, and 20 will supply 0, 37, and 74% of the P need, respectively; while the 30 and 40 Mg ha⁻¹ rates will supply 111% and 148% of the P need, respectively.

Model Input

Model inputs that were used in the GLEAMS simulations are listed in Tables 2, 3, 4, and 5. Daily climatic variables from 1 January 1982 through 31 December 2002 were obtained from the Haskell weather station, located approximately 1.6 km (1 mile) from the study site. The 1999 initial P values from CTL treatment at the Haskell site were selected as the initial P values for the A horizons (i.e., Ap1, Ap2, Ap3). Selection of initial P values was based on agreement (within 10%) between measured and predicted P values in the SWM and CAM treatments. In the sensitivity analysis, it was found that disking fits the stratification of measured soil P when depth of tillage was 5 cm (2 in.). Based on Table 1, continuous corn with no irrigation was simulated.

Model defines soil labile P as 0.55 of Bray-1 P according to Sharpley et al. (1984).

P Index

The Nebraska P-index is currently under development, thus the Iowa P-index was used to compare with GLEAMS long-term P loss simulation. The Iowa P-index integrates erosion, runoff, and subsurface drainage components to assess potential risk of P loss (Mallarino et al., 2002). The erosion component estimates sediment associated P loss and considers erosion type (e.g., sheet and rill soil erosion, ephemeral and gully erosion), sediment delivery ratio, buffer strip factor, sediment enrichment factor, and total soil P. The runoff component estimates dissolved P lost with runoff and includes runoff curve (i.e., fraction of average precipitation running off), precipitation, dissolved P concentration, and method and time of P application. The subsurface drainage component considers dissolved P loss through field drainage structures. The P-index value obtained by summing the erosion component, runoff

component, and subsurface drainage component is then categorized as very low, low, medium, high or very high potential for significant surface water contamination.

The P-index values for the Haskell site were calculated based on GLEAMS model output of Bray-1 P levels at 0-5 cm (0-2 in.) after 25 years of manure application at 0, 10, 20, 30, and 40 Mg ha⁻¹. Since P index considers the distance to concentrated water flow, the overland simulation scenario considered presence of concentrated water flow at the end of the field.

RESULTS AND DISCUSSION

Relationships Among Soil P Forms

Total P, Bray-1 P, FeO-P and water P at the West Point site was higher than that of the CAM and SWM treatments at the Haskell site due to a longer history of manure application at the West Point site (Figures 1 and 2). Due to the wider range of soil P at the West Point site, Bray-1 P explained more of the variability of TP and water P at the West Point site than the CAM at the Haskell site (Table 6). Bray-1 P explained 90% of variability in TP at the West Point site compared to 52% in the CAM at the Haskell site. Bray-1 P explained 98% of the variability of water P at the West Point site compared to 88% in the CAM at the Haskell site. Bray-1 P explained 96% and 94% of the variability of FeO-P at the West Point and Haskell sites, respectively. The slope of the regression analysis between FeO-P, water P, and TP as the dependent variables and Bray-1 P as the independent variable was also the same at both sites (Table 6). Sharpley et al. (1984) found similar slope relationships between Bray-1 P and anion exchange resin extractable labile P. Also, water P explained 95% of the variability of FeO-P at both the West Point and Haskell sites. High correlation values of the simple linear models suggested that Bray-1 P and water P are good predictors of FeO-P. Sims et al. (2002) also obtained strong correlations between Mehlich 3 soil test P and water soluble P ($r^2 = 0.68$) as well as with FeO-P ($r^2 = 0.84$) on 465 soils of the Mid-Atlantic region. McDowell and Sharpley (2001) found good correlations between soil test P (Mehlich 3 and Olsen) and water soluble soil P.

Effects of Manure on Soil P Stratification

Long term and frequent manure broadcast application has been shown to increase soil P levels with greater P stratification at the 0-5 cm (0-2 in.) depth (Andraski et al, 2003; Sharpley, 2003). This accumulation in the top soil layer is especially critical since runoff P has been shown to correlate with soil P tests in the top 0-5 cm (0-2 in.) soil layer (Sims et al., 1998; Andraski and Bundy, 2003).

The degree of P stratification, i.e., the decrease of P with soil depth, was greater in the CAM treatment than in the SWM and the CTL treatments. Total P in the CAM treatment was consistently higher than the SWM and CTL plots at 0-5 cm (0-2 in.) depth. Greater soil P in the CAM than the SWM treatment was due to higher P applied in the CAM than SWM treatments (total P load of 580 kg ha⁻¹ for CAM vs. 145 kg ha⁻¹ for SWM). Phosphorus in the CAM treatment was consistently greater than the CTL at both the 0-5 and 5-10 cm (0-2 and 2-4 in.) soil depths. Phosphorus in the SWM treatment was consistently greater than the CTL only at 0-5 cm (0-2 in.) depth.

At the 5-10 cm (2-4 in.) depth, only the CAM treatment was higher than the CTL (Figure 1a). Bray-1 P at the 0-5 cm (0-2 in.) depth was in this order: CAM > SWM > CTL (Figure 1b). At the 5-10 cm (2-4 in.) depth, Bray-1 P in soil receiving SWM was similar with the CTL and the CAM was significantly greater than both the SWM and CTL plots. Bray-1 P at 10-15 cm (4-6 in.) depth was similar among all treatments. The FeO-P and water P at 0-5 cm (0-2 in.) and 5-10 cm (2-4 in.) depths were in this order: CAM > SWM > CTL (Figures 1c and 1d). At the 10-15 cm (4-6 in.) depth, both FeO-P and water P were similar among treatments, indicating insignificant vertical mobility of P.

Total P, Bray-1 P, FeO-P, and water P at 0-5 cm (0-2 in.) and 5-10 cm (2-4 in.) was higher at the West Point site than the non-manured site (Figure 2). Concentrations of all P forms were similar between the West Point and non-manured plots at the 10-15 cm (4-6 in.) depth indicating minimal vertical movement of P. Total P, Bray-1 P, FeO-P and water P at the West Point site was higher than that at the Haskell sites due to longer manure application history at the West Point site (> 5 years of annual manure application).

Measured and Simulated Soil Bray-1 P and Simulated Runoff P Losses at Haskell Site

The Haskell site data from 1999 to 2002 were used in GLEAMS sensitivity analyses because initial conditions and field management history were well documented. The values of simulated Bray-1 P after three applications of CAM and SWM were within the range of measured values for 0-5 cm (0-2 in.) and 5-10 cm (2-4 in.) depth. The model over-predicted mean Bray-1 P for both the CAM and the SWM treatments for the 10-15 cm (4-6 in.) depth by 50% and 73%, respectively (Table 7). On the 0-15 cm (0-6 in.) basis, the simulated Bray-1 P values were within the range of observed Bray-1 P and the deviation from the observed mean values were within 8.3 and 3.1%, in the CAM and SWM treatment, respectively. In general the model predicted well soil Bray-1 P and Bray-1 P stratification in the upper 10 cm (4 in.). This is important for application of soil predictive models for runoff P, because soil labile P at the 0-5 cm (0-2 in.) depth is one of the main factors that controls P loss.

Long-term Simulation of Manure (CAM) Rate Effects on Soil P and Runoff P

Simulated soil P and runoff P were sensitive to manure P input rate. The change of simulated soil labile P (defined as 0.55 of Bray-1 P) at 0-1 cm (0-0.4 in.) and 1-5 cm (0.4-2 in.), 5-10 cm (2-4 in.) and 10-15 cm (4-6 in.) are presented in Figure 3. Changes that occurred only within the top 5 cm (2 in.) depth were due to manure incorporation effectively mixing the 5 cm (2 in.) depth. Changes in soil labile P were consistent with manure rates only within 0-1 cm (0-0.4 in.) and 1-5 cm (0.4-2 in.) depths (Figure 3). A steep increase in soil labile P at the 0-1 cm (0-0.4 in.) and 1-5 cm (0.4-2 in.) depths occurred after 5 to 7 years of annual manure application, suggesting build-up of excess P (data not shown). On average, simulated soil labile P at 0-1 cm (0-0.4 in.) depth increased 5.2, 7.8, 14.4, and 21.9 mg P kg⁻¹ yr⁻¹ for manure application rate of 10, 20, 30, and 40 Mg ha⁻¹, respectively. At 1-5 cm (0.4-2 in.) depth, the increase was 2.4, 5.2, 10.8, and 17.4 mg P kg⁻¹ yr⁻¹, respectively. Over the 25 year simulation, soil labile P at 0-1 cm (0-0.4 in.) depth in the control treatment decreased from 32 to 0.67 mg P kg⁻¹ and at 1-5 cm (0.4-2 in.) from 76 to 34 mg P kg⁻¹. Manure application increased soil labile P at 5-10 cm (2-4 in.) and 10-15 cm (4-6 in.) only slightly over the zero manure rate in the 25 years simulation (Figure 3).

Simulated runoff labile-P concentration had a strong linear relationship with simulated soil labile P at 0-1 cm (0-0.4 in.) and 1-5 cm (0.4-2 in.) soil depths (Figures 4a and 4b). The slope indicated that for 1 mg P kg⁻¹ increase in soil labile P at 0-1 cm (0-0.4 in.) depth, the runoff labile P concentration increased 5.3 g L⁻¹. For a 1 mg P kg⁻¹ increase in soil labile P at 1-5 cm (0.4-2 in.) depth, the runoff labile P concentration increased 7.4 g L⁻¹. Under a rainfall simulation study, Pote et al. (1996) found a 9 g L⁻¹ increase in runoff FeO-P for every 1 mg P kg⁻¹ increase in soil FeO-P of the 0-2 cm (0-0.8 in.) soil layer. Pote (1996) also showed a 13.6 g L⁻¹ increase in runoff dissolved reactive P (DRP) for every 1 mg P kg⁻¹ increase in water extractable soil P. In other rainfall runoff studies, Pote et al. (1999) found runoff DRP increases 5.5 g L⁻¹ to 10.7 g L⁻¹ for every 1 mg P kg⁻¹ increase in water extractable P of soil at the 0-2 cm (0-0.8 in.) depth. Thus, the GLEAMS model prediction results in our study on the relationship of labile soil P to runoff labile P is well within the range observed under field conditions. The lack of relationship between runoff labile P concentration and soil labile-P at 5-10 cm (2-4 in.) depth (Figure 4c, r² = 0.63) and 10-15 cm (4-6 in.) (data not shown, r² = 0.49, slope = -140 g L⁻¹) indicated that surface runoff labile-P concentration was affected only by soil labile P at 0-5 cm (0-2 in.) depth.

The 25-year cumulative runoff labile P in the 0, 10, 20, 30, and 40 Mg ha⁻¹ CAM treatments was 0.22, 6.51, 9.09, 14.2, and 20.5 kg P ha⁻¹ (0.20, 5.81, 8.12, 12.7, and 18.3 lbs A⁻¹) (Figure 5). The cumulative loss of labile P in runoff was very small compared to the cumulative sediment associated P (Figure 5). Cumulative 25 yr sediment associated TP loss was 38, 84, 124, 174, and 227 kg ha⁻¹ (34, 75, 111, 155, 203 lbs A⁻¹), and was 93 to 99% sediment associated organic P.

Comparison of GLEAMS TP loss prediction with the P-index

On the basis of the Iowa P index, the P loss risk rating was low for the 0 Mg ha⁻¹ treatment, high for the 10, 20, 30 Mg ha⁻¹, and very high for 40 Mg ha⁻¹ treatments after 25 years (Table 8). The P-index did show high P loss risk for the manure treatments because of the large increase in Bray-1 P. The

GLEAMS model predicted a 48%, 107%, and 170% increase in cumulative TP loss for the 20, 30, and 40 Mg ha⁻¹ manure treatment over the cumulative TP loss from that of the 10 Mg ha⁻¹ manure treatment. However, the P-index rating did not discriminate among the manure treatment rates. Under the set conditions of the Haskell site, a soil test P level (Bray-1 P) of 300 mg kg⁻¹ or higher at the 0-5 cm (0-2 in.) depth will result in a high potential risk for P loss. In the 25 years model simulation, soil Bray-1 P for 20, 30, and 40 Mg ha⁻¹ exceeded the 300 mg kg⁻¹ threshold level within the first eight years of manure application. Although P-index is a very useful management tool to qualitatively assess risk of P loss from fields, it can further be refined if combined with a physical-based-model, such as GLEAMS, to quantitatively predict potential P loss under different management scenarios and provide an approach for the development of total maximum daily loads (TMDLs) in surface water.

CONCLUSIONS

Differences among cattle manure, swine manure, and the non-treated control in soil TP and soil Bray-1 P occurred mainly in the 0-10 cm (0-4 in.) depth. In the manure-treated plots, the difference in soil Bray-1 P and soil TP between 0-5 cm (0-2 in.) depth and 5-10 cm (2-4 in.) depth was much larger than between 5-10 cm (2-4 in.) depth and 10-15 cm (4-6 in.) depth, indicating higher P stratification in the shallow soil depth. Higher P input in the cattle manure treatment resulted in greater degree of soil-P stratification as compared to that of the swine manure treatment.

The GLEAMS model simulated soil Bray-1 P well within the 0-5 cm (0-2 in.) and 5-10 cm (2-4 in.) depths for both the cattle manure and swine manure treatments. On a 0-15 cm (0-6 in.) depth basis, GLEAMS model predicted soil Bray-1 P within less than 10% of the measured Bray-1 P in the cattle and swine manure amended soil. GLEAMS simulation indicated that runoff-water labile P loss or runoff-sediment P loss were closely related with soil labile P at the 0-1 cm (0-0.4 in.) and 1-5 cm (0.4-2 in.) depths but not with P at deeper depths.

Since long-term measurements of surface runoff are costly, modeling efforts using existing soil databases and routine soil tests can be useful for predicting potential P losses by runoff from the field. The simulation results would be applicable to farmers' field with large annual inputs of cattle manure under similar soil, landscape characteristics, and climatic conditions.

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Table 1. Major field operations at Haskell Site.

Activities	DOY†	Date and Description
<u>1999</u>		
Spring manure and tillage	90	31 Mar -1 Apr; swine 56 m ³ ha ⁻¹ ; Cattle 78.4 Mg ha ⁻¹ , disked
Field cultivate and planting	120	30 Apr., 54 000 seeds ha ⁻¹
Field cultivation	165	14 June; field cultivation on all plots
Harvesting	277	4 Oct.; corn residue left in the field
Autumn manure applied	319	15-16 Nov.; Swine 12 m ³ ha ⁻¹ ; Cattle 78 Mg ha ⁻¹
P load		Swine: 82 kg ha ⁻¹ ; Cattle: 184 kg ha ⁻¹
Autumn tillage	320	16-17 Nov.; Disked the manure plots
<u>2000</u>		
Spring tillage	110	26 Apr.; Pre-plant cultivation on all field
Corn planting	122	1 May
Corn harvest	251	7 Sep.
<u>2001</u>		
Cattle manure and tillage	109	19 - 20 Apr.; Manure application followed by disking
P load		242 kg ha ⁻¹
Swine manure and tillage	117	27 and 28 Apr.; Manure application followed by disking
P load		17 kg ha ⁻¹
Field cultivation	129	9 May; pre-plant cultivation on all plots
Corn planting	130	10 May
Corn harvest	263	20 Sep.
Cattle manure and tillage	312	8 Nov, 76 Mg ha ⁻¹ , disked
P load		154 kg ha ⁻¹
Swine manure and tillage	319	15-16 Nov, 43 m ³ ha ⁻¹ , disked
P load		47 kg ha ⁻¹
<u>2002</u>		
Spring tillage & Planting	136	16 May, Disking
Soil Sampling for model sensitivity analysis	137	17 May
Harvest	254	11 September

† Day of the year.

Table 2- Initial soil chemical variables used in GLEAMS model. †, ††

Horizon	bottom of horizon depth	pH	NO ₃ -N	Bray-1 P	TN	TP	OM	PMN
	cm		mg kg ⁻¹			g kg ⁻¹		kg ha ⁻¹
Ap1	5	6.5	7.0	143.5	1.9	0.991	34	126
Ap2	10	6.3	6.6	25.3	1.5	0.486	28	98
Ap3	15	6.2	6.7	12.7	1.2	0.471	26	83
Bt1	36	6.2	20.0	34.5	1.5	0.300	25	182
Bt2	110	6.9	10.0	42.0	0.5	0.200	9.8	196

† pH, NO₃-N, Bray-1 P, TN, TP, and OM measured for the Ap1, Ap2, and Ap3 horizons in 2002.

†† PMN estimated by GLEAMS following the method of Smith et al. (1980).

Table 3- Hydrological input variables used in GLEAMS model.

Drainage area†	2.6 ha
Hydraulic slopes†	0.06 cm cm ⁻¹
Field length: width ratio†	1.4
Effective saturated conductivity††	12.6 mm h ⁻¹ for the Ap horizons 7.6 mm h ⁻¹ for the Bt horizons
Effective rooting depth††	110 cm
Runoff curve for straight row crops †††	78

† Derived from topographic measurements.

†† Estimated from the Dixon County Soil Survey (USDA-SCS, 1978)

††† GLEAMS manual (Knisel, 1993).

Table 4- Erosion input variables used in GLEAMS model.

Erosion type†	Overland
Soil erodibility††	0.29
Erosion Practice factor (P) †	1.0 (no practice)
Crop factor (C) †	0.23, after harvest with corn residue on surface 0.31, disking for manure incorporation 0.55, field cultivation prior to planting
Hydraulic roughness or Manning's "n" †	0.04, after harvest with corn residue on surface 0.046, disking for manure incorporation 0.014, field cultivation prior to planting

† GLEAMS manual (Knisel, 1993). †† Estimated from an erodibility nomograph.

Table 5- Nutrient input variables used in GLEAMS model.

Initial crop residue†	5.5 Mg ha ⁻¹ (~80% residue cover)
Yield goal††	15 Mg ha ⁻¹
Number of annual manure application	1
Dry matter ratio †† (ratio of total dry matter production to grain)	2.5
Crop C:N ratio††	40
Crop N:P ratio††	5.0
Cattle manure total P concentration	3.6 g TP kg ⁻¹
N concentration in rainfall†††	2.3 mg L ⁻¹

†Based on RUSLE. †† Based on continuous corn experiments in eastern NE (Dobermann, Pers. Comm., 2004). ††† From Chapin and Uttomark (1973).

Table 6. Linear relationships among Bray-1 P, Water P, FeO-P and TP.

Variables		Haskell			West Point			Haskell and West Point combined		
Independent	Dependent	Intercept	slope	r ²	Intercept	slope	r ²	Intercept	slope	r ²
Bray-1 P	TP	589	2.00	0.52	523	2.09	0.90	550	2.06	0.85
Bray-1 P	FeO-P	1.70	0.50	0.94	3.47	0.50	0.96	2.97	0.50	0.95
Bray-1 P	Water-P	-2.23	0.18	0.88	-1.94	0.21	0.98	-2.77	0.21	0.97
Water-P	FeO-P	9.62	2.70	0.95	8.84	2.34	0.95	10.4	2.35	0.95
Water-P	TP	621	10.5	0.53	543	9.90	0.90	580	9.70	0.85

Table 7. Observed and simulated Bray-1 P after four year of cattle and swine manure treatment at Haskell site.

Depth, cm	Observed				Simulated
	Mean	Max.	Min.	Median	
	mg kg^{-1}				
	CAM†				
0-5	222	291	73.9	240	198
5-10	70.5	141	31.4	69.2	44.1
10-15	24.3	46.4	6.30	21.0	48.9
0-15	106	159	37.2	110	97.1
	SWM††				
0-5	148	223	86.0	149	101
5-10	41.5	72.5	0.92	43.6	45.9
10-15	13.6	34.1	0.46	12.1	49.6
0-15	67.6	110	29.1	68.4	65.5

† Cattle manure. †† Swine manure.

Table 8. Comparison of the Iowa P-index rating with GLEAMS simulated cumulative total P loss after 25 years of annual manure application at the Haskell site.

Manure Rate	P-index				GLEAMS Simulated Cumulative TP loss
Mg ha ⁻¹	Erosion Factor	Runoff Factor	P-rating	Category	kg ha ⁻¹
0	1.4	0.4	1.8	Low	38
10	2.9	3.0	6.0	High	84
20	3.8	5.2	9.1	High	124
30	5.7	8.3	14.1	High	174
40	8.0	11.8	19.9	Very High	227

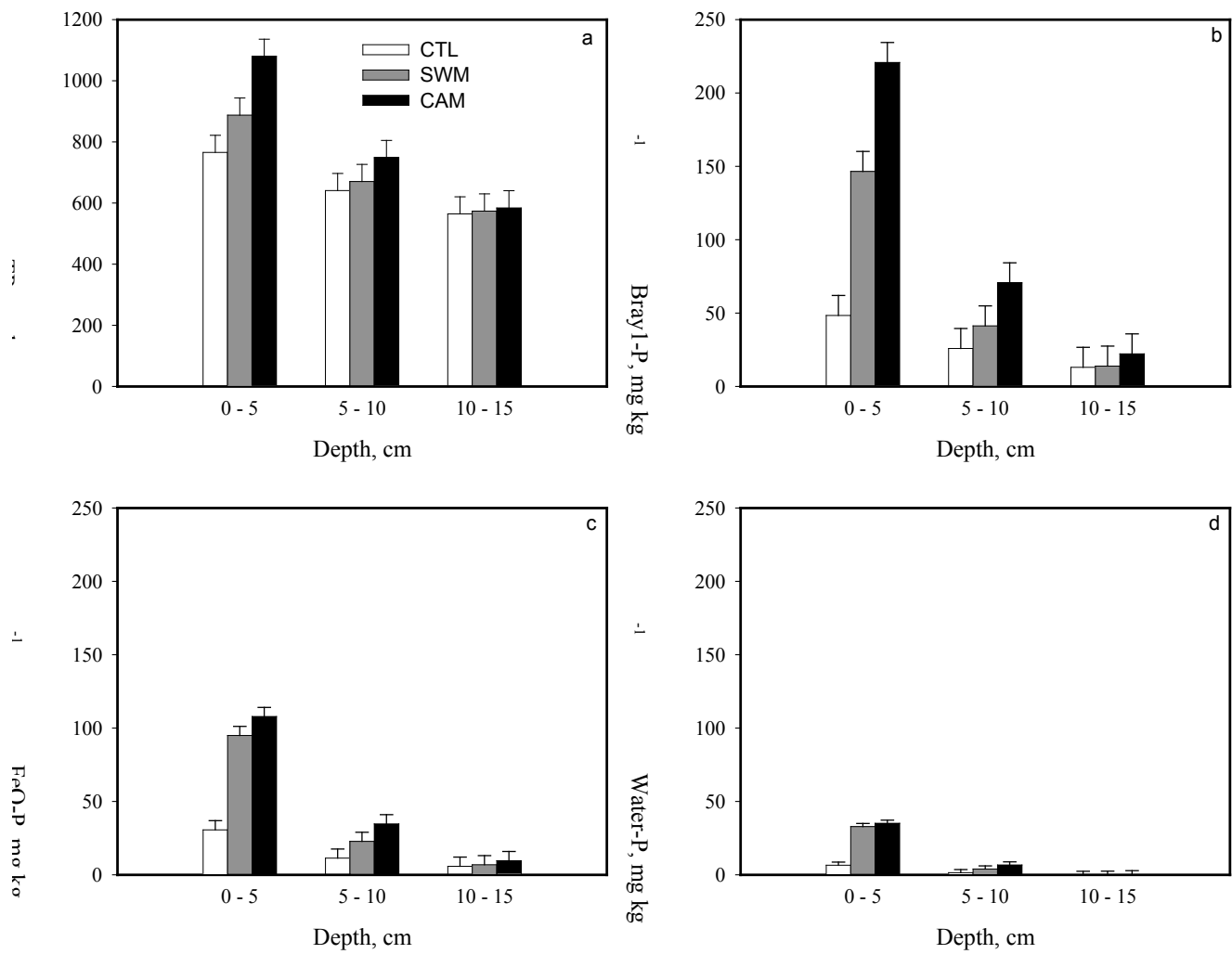


Figure 1

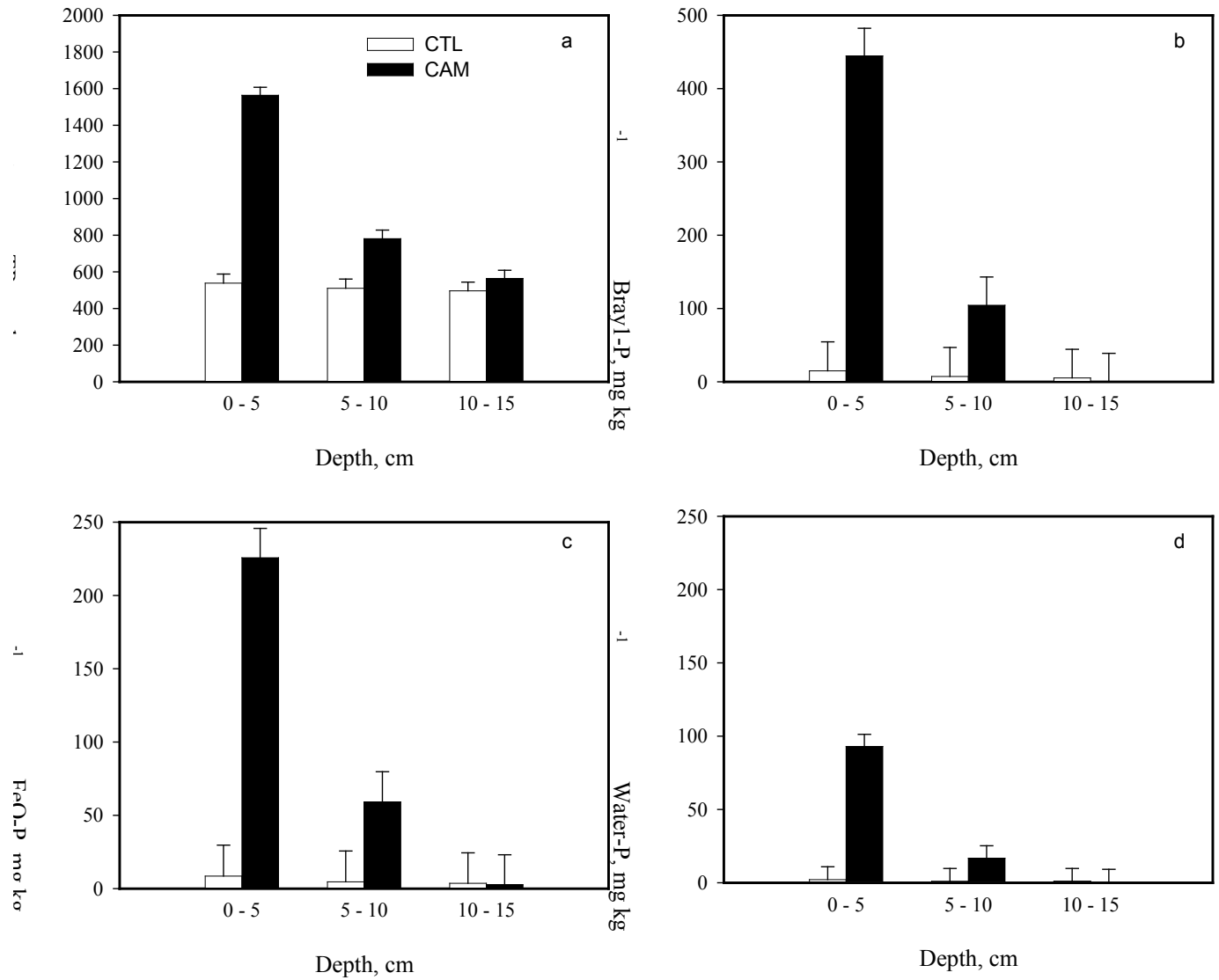


Figure 2

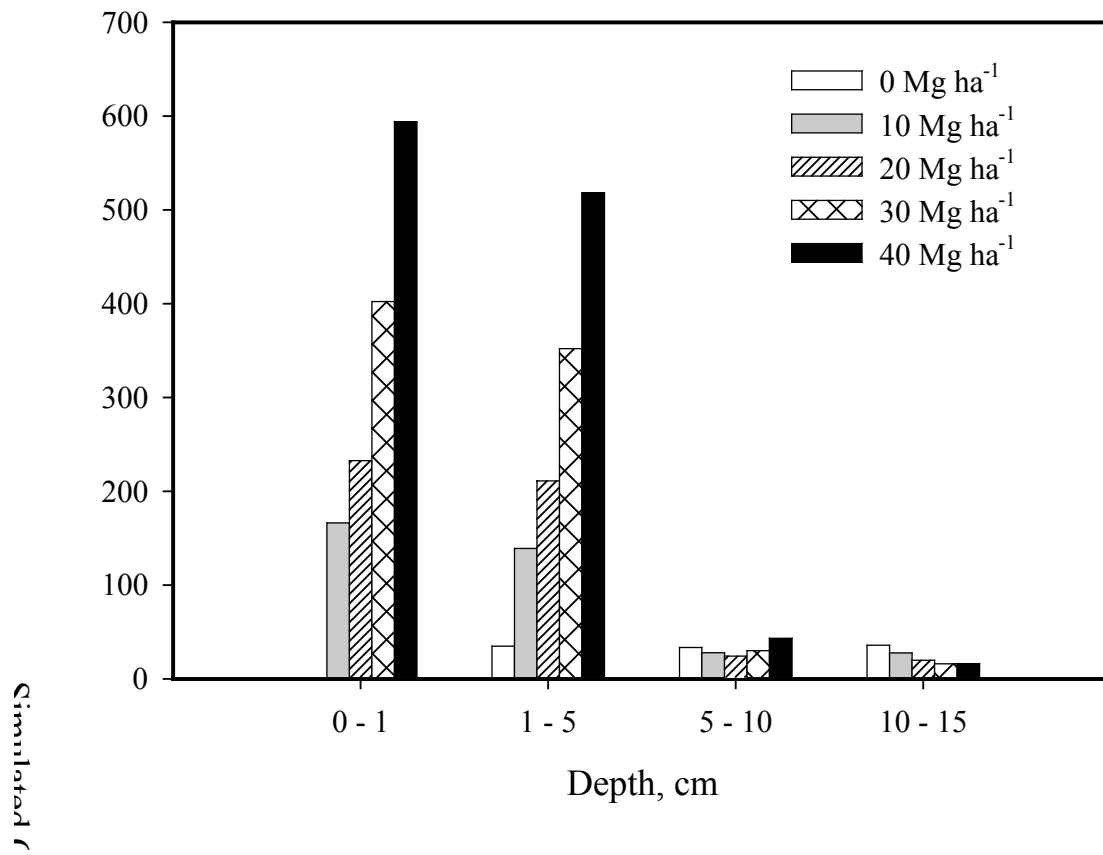


Figure 3

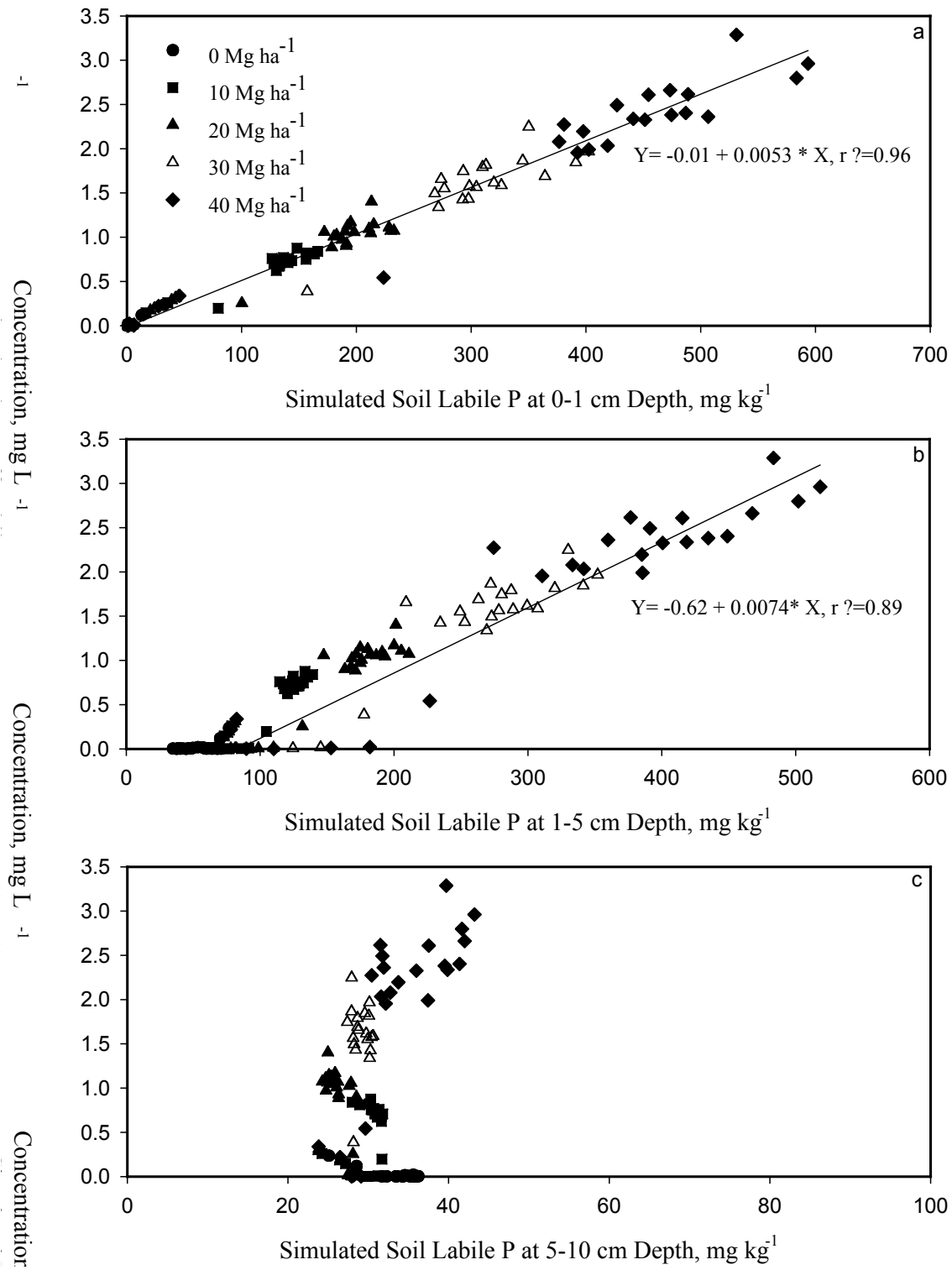


Figure 4

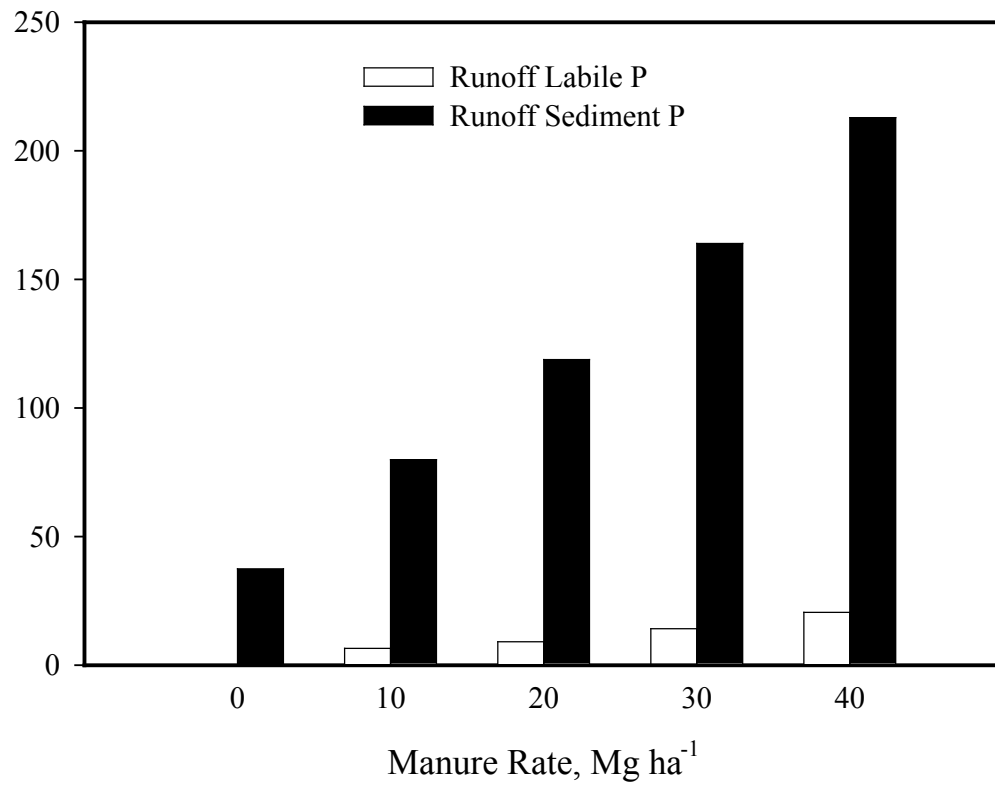


Figure 5

Information Transfer Program

The University of Nebraska Water Center has a long and productive tradition of vigorous information transfer programming utilizing USGS funding assistance. The programming supports a variety of research, extension, outreach and education programs sponsored or co-sponsored by the Water Center and UNL's School of Natural Resources. The overall program is grounded in dedication to making the Water Centers critical research work in the areas of state and regional water quality and quantity available to and understood by the public we serve.

A variety of vehicles and services are used to convey this information, including print, broadcast and electronic media, as well as conferences, symposia, lecture series, tours and other public events. Print and online newsletters, brochures, conference and symposium proceedings, web sites, educational newspaper tabloids, news releases, radio recordings and videotapes are all utilized.

During the reporting period, the Water Centers information transfer program has paid increasing attention to utilizing online resources and targeted publications to support general and specific programming areas, as well as increasing use of conferences, lectures and tours to involve and educate the public on Water Center-sponsored activities.

The securing of a Water Resources Research Initiative in 2003 represents significant new multi-year support for water research, education and outreach programming throughout the University of Nebraska system and has provided the Water Centers information transfer program with additional requirements and resources for promoting the Centers work to recognize the critical importance of water resources in the state, the nation and globally. Initially, this resulted in inaugurating an annual, national-level water law, policy and science conference, the first of which was held in March 2003.

The University of Nebraska Water Center also publishes one of the oldest, continuously produces newsletters of any of the Water Resources Research Institutes nationwide. The Water Current is in its 35th year of continuous publication, having been transformed into a full-color publication during the reporting period, as well as being offered in an online format.

Water Center Educational Materials

Basic Information

Title:	Water Center Educational Materials
Project Number:	2002NE33B
Start Date:	3/1/2003
End Date:	2/28/2004
Funding Source:	104B
Congressional District:	1
Research Category:	Not Applicable
Focus Category:	Education, None, None
Descriptors:	
Principal Investigators:	Steven W. Ress, Michael Jess

Publication

INFORMATION TRANSFER PROGRAM:

2003 USGS ANNUAL REPORT **UNL WATER CENTER**

NEWSLETTER:

The *Water Current* newsletter is in its 35th year of continuous publication. In June 2002 we began publishing it as a quarterly, rather than six times per year. This saves production and postage costs, while not reducing coverage (due to more pages being published in most issues). The newsletter is now published in the spring, summer, fall and winter. It has a free distribution of approximately 3,000 copies per issue, more than 95 percent of which represent requested subscriptions. An annual reader survey is published in the spring issue. Water-related research and extension faculty are featured in each issue. Guest columns are normally published in each issue. Area water-related professionals and educators write these on a wide variety of topics and points of view. Individual issues are normally 16 pages in length. Virtual copies of the newsletter are available on-line in PDF format and are archived at <http://watercenter.unl.edu>

The UNL Water Center is also a primary contributor to the UNL School of Natural Resources' *Resource Links* newsletter, which also is published as a quarterly, as well as the twice-annual NU Agricultural Research Division's *Research Nebraska!* magazine.

OTHER PRINT RESOURCES:

Water Center informational brochures. Updated and produced annually. Overviews of the mission and programming of the UNL Water Center, Great Plains CESU, EEAI unit, Water Resources Research Initiative (WRRI), UNL School of Natural Resources and other centers and units affiliated with the Water Center. Distributed free.

Water Center Pocket Directory. A pocket-size brochure listing key NU, federal, state and local water resource agencies and points of contact.

Newspaper tabloids on wetlands and drinking water issues respectively published in 1997 and 1999. These continue in use by a variety of university programs, 4-H, FFA, state agencies and the public schools within natural science curriculums and educational programs. Distributed free (in quantity).

Pocket cards. Credit card-size. Explain commonly used terms such as "cubic feet per second (CFS)," acre-feet, gallons per minute, etc.

A range of publications produced outside the UNL Water Center, particularly fact sheets and other print materials from the USGS, are made available through the Water Center's web site.

NEWS RELEASES:

The Water Center produces about 20 to 25 press releases annually. Most of these are based on research, cooperative extension, teaching and public outreach programming involving the

Water Center. They are also used to announce conferences, seminars, tours, pesticide collections, pesticide container recycling efforts and other activities involving the Water Center or UNL School of Natural Resources. These are widely published in state newspapers, as well as in organizational, trade and professional journals. The releases support a wide variety of UNL water-related research and programming that crosses departmental and disciplinary lines.

ELECTRONIC RESOURCES:

Electronic versions of newsletters, print materials, information about the Water Center and Water Sciences Laboratory and course information for graduate and undergraduate students enrolling in water-related courses of study are available at <http://watercenter.unl.edu>. The Water Center co-sponsors these additional sites, each of which is program specific:

Water Sciences Laboratory:

<http://waterscience.unl.edu>

Platte Watershed Program:

<http://ianrwww.unl.edu/ianr/pwp/pwp.html>

Groundwater Chemistry Laboratory:

<http://csd.unl.edu/csd/staff/harvey/lab.html>

Great Plains Cooperative Eco-Systems Studies Unit (CESU):

<http://greatplains.cesu.unl.edu/>

The Water Center's web site was redesigned and upgraded in 2003.

CONFERENCES, SEMINARS AND TOURS:

Nebraska Water Conference is normally conducted each March. Co-sponsored by the Nebraska Water Conference Council and other academic, commercial and non-profit organizations. The conference attracts about 100 to 200 participants. News releases, brochures a program and web-based information are produced for this event.

Water and Natural Resources Seminars. A series of 12 to 14 public lectures from January to April each year. Co-sponsored by other NU departments and units. The series may be taken for student credit or as a free public lecture series. Each lecture typically attracts an audience of 60-100, as well as approximately a dozen for-credit students. News releases, mailings, brochures, posters and web-based information are produced in conjunction with this event.

Platte Watershed Symposium is co-sponsored by the Water Center and other NU departments and centers, as well as by the U.S. Environmental Protection Agency and the U.S. Fish and Wildlife Service. The bi-annual symposium explores research and educational programming related to the ecology of the Central Platte River Basin area of Nebraska. Approximately 200 attend. News releases and brochures are produced in conjunction with this event, along with web-based information.

Summer Water and Natural Resources Tour. Co-sponsored by the Nebraska Water Conference Council and other NU, public, private and commercial entities. The annual three-day tour is conducted in July and is used to educate and inform on current water and natural resource issues effecting Nebraskans. About 100 water users, legislators, ag

producers and members of the public attend. News releases, mailings and a brochure are produced in conjunction with this event.

Fall Research Colloquium. A new event held in conjunction with UNL's School of Natural Resource Sciences. Brings water and natural resource researchers and students together for a one-day symposium to share research results and progress. This year's event attracted about 75 faculty members and students.

EDUCATIONAL DISPLAYS:

The Water Center makes frequent public displays in association with conferences, symposiums, water-related trade shows, educational open houses and water and environmental festivals.

In addition, Water Center staff present at such educational festivals as The Groundwater Foundation's "Children's Groundwater Festival," NU's "Earth Wellness Festival," "Husker Harvest Days" and others.

PROMOTIONAL ITEMS:

Inexpensive promotional items such as coffee mugs, key chains, lanyards, etc. imprinted with the Water Center's new bi-color logo, web address and telephone numbers are produced for distribution in conjunction with educational programs/displays, student recruitment seminars, conferences and tours.

UNL PESTICIDE EDUCATION OFFICE:

The Water Center helps with publicity and press relations for programs conducted by the UNL Pesticide Education Office, which is part of the UNL Department of Agronomy and Horticulture. This includes press releases supporting pesticide container recycling and waste pesticide collection programs.

PRIMARY INFORMATION DISSEMINATION CLIENTELE:

U.S. Department of Agriculture
U.S. Environmental Protection Agency
U.S. Geological Survey
U.S. Bureau of Reclamation
Nebraska Department of Natural Resources
Nebraska Department of Agriculture
Nebraska Department of Health and Human Services System
Nebraska Department of Environmental Quality
Nebraska Environmental Trust
Nebraska Association of Resources Districts (and individual NRDs)
Nebraska Congressional delegations
Public and private power and irrigation districts
National Audubon Society
The Nature Conservancy
Nebraska Alliance for Environmental Education
Nebraska Earth Science Education Network
Other state Water Centers
University and College researchers and educators

NU students
Public and parochial science teachers
Farmers
Private citizens

COOPERATING ENTITIES:

In addition to primary support from the USGS, the following agencies and entities have helped fund information dissemination activities by the UNL Water Center during the past year.

U.S. Environmental Protection Agency
USDA-Forest Service,
U.S. Bureau of Land Management
Nebraska Department of Environmental Quality
Nebraska Research Initiative
Nebraska Game and Parks Commission
Central Platte Natural Resources District
National Institutes for Water Resources
Nebraska Water Conference Council

Student Support

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

Notable Awards and Achievements

Publications from Prior Projects