

# Nebraska Water Resources Center

## Annual Technical Report

FY 1999

### Introduction

**Problem and Research Objectives:** Most Nebraska communities rely on groundwater as a source of drinking water. Until recently, it has been assumed that groundwater is free of pathogens due to the natural filtration provided by the soil. Data from some other states seems to indicate that groundwater in some aquifers, notably those in karst formations, may be vulnerable to contamination and may contain pathogens. Nebraska does not have karst geology or other formations which would seem to be vulnerable to contamination, but, the presence of human pathogens such as viruses in well waters has not been studied sufficiently. To assess the vulnerability of Nebraska drinking water wells to pathogen contamination, a study of well integrity factors or "well vulnerability" is being performed. In this study, only small (<10,000 population) Nebraska communities which do not currently disinfect or treat their drinking water are being studied. There are 608 small community water systems in Nebraska, most of which do not currently disinfect or treat their drinking water. In addition there are 719 non-community water systems. The overall goal of the proposed research is to determine the relationship between the microbial quality of groundwater and the well, water system, and surrounding environment. In this project a total of eight small community wells are being studied; the wells selected for study are believed to be among the most vulnerable to microbial contamination in Nebraska. This is a descriptive study focused on understanding how vulnerability to microbial contamination is the "most vulnerable" community wells in the state. For these eight wells, the following information is being collected:

- General water quality data.
- Microbial and Viral testing of the well water quality (five times during a eight month period).
- Perform small modeling studies to determine travel times from nearby contamination sources.
- Summarize data and methodology approach, as a basis for future research projects.

It is anticipated that future projects will be initiated using other funding sources. The work described in this proposal is considered to be "Phase I" of a larger course of study. A second, larger study will be needed to provide sufficient data for statistical analysis. Other funding opportunities will be pursued for "Phase II" of the research. Training potential

This project represents an excellent opportunity for students with a technical background to expand their understanding of social and regulatory issues associated with the drinking water industry. In contrast to many research projects which provide students with an in-depth knowledge of an obscure technical process or model, this project will require students to work with regulatory and community water system personnel, and to integrate their technical background into a broader experience with small communities. At the same time, the required data collection and analysis, and the laboratory work associated with the water analyses dictate that the student maintain and further develop strong technical and analytical skills. Two students will be employed on this project, a graduate research assistant (Ms. Julie Fisher) and an under-graduate research assistant (Ms. Anne Stephens). Ms. Fisher is a graduate student in the Environmental Engineering program and Ms. Stephens is an undergraduate in Civil Engineering. This project will be the basis of a Master of Science thesis for Ms. Fisher. Ms. Fisher's salary is paid for through a project match by the UNL Center for Infrastructure Research.

### Research Program

**Methodology: Selection of Community Wells:** The community wells chosen to participate in the virus study were

selected based on several criteria. The first criteria considered was the location of the well. All the wells that were considered were located within the town. Hence, the wells have a higher possibility of (human) virus contamination from leaky sewers, sewer connections or septic systems. The next criteria considered were the depth of the wells. All the selected communities had to have shallow wells; for Nebraska communities a relatively shallow well is one less than 200 feet (which is not particularly shallow). Then, the communities' setback distances from possible sources of contamination were also used as a criterion. If the community had a violation or was close to the setback distance they were considered high probability for virus contamination. The last criteria used were the concentration of Nitrate/Nitrite and the total coliform bacteria. High Nitrate/Nitrite and total coliform bacteria are considered as possible indicators for virus. Thus communities with high Nitrate/Nitrite and total coliform bacteria were considered to have a high probability for virus contamination. Overall, the communities selected were considered the worst case wells within Nebraska. The selected communities can be seen in the table below.

Community	Well ID	Well Depth (ft)
Rank City	NDHS Reg # 61-1	137
Prague	61-1	137
Bradshaw	71-1	147
Hampton	84-1	214
Platte Center	37-1	100
Waco	72-1	276
Bellwood	82-1	128
Valparaiso	85-1	126
Staplehurst	82-1	116
Goehner	87-1	230
Benedict	95-1	240

Water Sampling and analysis will generally follow procedures in Standard Methods for the Examination of Water and Wastewater (1995). Virus analyses are not included in Standard Methods, but will be conducted by the University of Nebraska Medical Center Virology laboratory certified by the US EPA to conduct virus analyses. Other water quality parameters that are being evaluated include: metal concentrations (calcium, magnesium, iron, and manganese) by atomic adsorption spectrophotometry, common anions (chloride, nitrate, phosphate, and sulfate), alkalinity, pH, dissolved oxygen, UV-254, and total coliform. These parameters are being measured in samples taken at the point of collection for the virus samples. Additional total coliform samples are being measured by the Nebraska Department of Health and Human Services Regulation and Licensure, as part of the routine regulatory activities for each community. With the exception of virus and coliform testing, all water analyses is being conducted in the Environmental Engineering Laboratory in Walter Scott Engineering Center, located at the University of Nebraska. Equipment that is available for use on this project includes: atomic adsorption spectrophotometer, ion chromatograph, TOC analyzer, UV-vis spectrophotometer, pH meters, dissolved oxygen meters, and a variety of routine glassware and small equipment.

**Groundwater Modeling** The groundwater modeling will be conducted with the computer program WhAEM (Well Head Analytic Element Model), distributed by the Environmental Protection Agency (Bakker, 1994). This program is currently used by the Nebraska Department of Environmental Quality for the construction of well head protection areas for all municipal supply wells in the state of Nebraska. Shortest travel times from the surface to the well screen will be estimated with the program Gflow, which allows for the exact specification of the well screen in the aquifer (Haitjema, 1995).

**Principle Findings and Significance** This project currently is less than half way to completion. At the moment there are no preliminary or final findings. This project will be of national interest and benefit to the drinking water industry. Research on the presence of viruses in groundwater is limited, and has generally not focused on specific geological formations, but instead has tended to be 'survey' research which is of little value in understanding the complexities of groundwater systems (e.g., Abbaszadegan et al., 1998). Due to the lack of focus of the available research, very little attempt has been made to correlate the presence of viruses with specific features of the water system or well, or with controllable environmental factors (such as the proximity of waste treatment facilities.) Without sound scientific data that can be used to characterize water systems which may be at risk, public health authorities will be forced to implement very conservative groundwater disinfection regulations that will require disinfection (and the associated capital and operation and maintenance costs) in communities where disinfection is not truly needed to protect public health. The current project will also provide valuable information for the State of Nebraska. Information is needed for researchers studying small community planning, water resources, groundwater, water treatment, and waste treatment. The current project is nearing a mid-point where actual data will be available. The main finding to this point is that Nebraska's small communities have surprisingly well located

Publications: Fisher, J. (2000) "An Assessment of Well Vulnerability to Viruses in Nebraska", presentation at the Annual Conference of the Nebraska Water Environment Federation in Kearney, NE, Nov. 3, 2000.

## Basic Project Information

Basic Project Information	
Category	Data
<b>Title</b>	Field Verification of the Dipole Flow Test: A New Approach for the In-situ Determination of Transport Parameters
<b>Project Number</b>	C-44
<b>Start Date</b>	08/01/1996
<b>End Date</b>	08/01/1999
<b>Research Category</b>	Ground-water Flow and Transport
<b>Focus Category #1</b>	Methods
<b>Focus Category #2</b>	Groundwater
<b>Focus Category #3</b>	Solute Transport
<b>Lead Institution</b>	Nebraska Water Resources Center

## Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
Vitaly Zlotnik	Professor	Univ. of Nebraska City Campus	01
James Butler, Jr.	Professional Staff	Kansas State University	02
Dean E. Eisenhauer	Professor	Univ. of Nebraska City Campus	03

## Problem and Research Objectives

Many important aquifers consist of unconsolidated alluvium lying in major river valleys. The purpose of this project is to explore a promising approach, the dipole flow test (DFT), for characterization small-scale heterogeneities of aquifer hydraulic conductivity (K), which control the contaminant transport. The primary research objectives include a thorough field assessment of the dipole probe developed at the University of Nebraska-Lincoln at two thoroughly studied sites in Nebraska and Kansas, a detailed comparison of this new methodology with currently available approaches for aquifer characterization (the multi-level slug test and the borehole flowmeter test), and the development of practical guidelines for the performance and interpretation of the DFT. INFORMATION TRANSFER. Results were presented at two national meetings (American Geophysical Union, Spring 1998, Boston, National Groundwater Association, 1998, Las Vegas) and several seminars (U. of Arizona, 1997; Swiss Federal Institute of Technology, Zurich, Switzerland, 1997; U. of Tuebingen, Germany, 1997; CSIRO, Australia, 1999). The techniques were included into the class "Field Techniques in Hydrogeology", Spring 1998, University of Nebraska-Lincoln. STUDENT SUPPORT. One M.S. student and one Ph.D. student were partially supported from the grant in Geosciences Department, UNL. In addition, summer support is provided for the undergraduate student at the University of Kansas (KU). The results of this

research were incorporated into courses in hydrogeology that are offered at the UNL and KU

## **Methodology**

A new UNL dipole probe has been tested at two sites in Nebraska and Kansas where hydraulic parameters have previously been determined using core analyzes, and various types of well tests (slug, pumping, and tracer tests). The procedures for the field component of the research were as follows: (a) two 4" diameter wells were installed at the MSEA site (Nebraska) using the hydraulic reverse rotary drilling method, and two wells were installed at the GEMS site (Kansas) using the hollow stem auger; (b) profiles of K versus depth were obtained from the steady-state DFT using the dipole probe using several different recirculation rates and the dipole probe configurations; (c) multi-level slug tests and the borehole flowmeter test were used to establish profiles of K from the Springer-Gelhar method and compare with results of the DFT; (d) the theory for interpretation of the steady-state was applied for interpretation of the DFT; and (e) analysis of the effects of well construction, development, and deterioration on the DFT and other hydraulic testing methods was performed.

## **Principal Findings and Significance**

At both sites (MSEA, Nebraska, and GEMS, Kansas), the DFTs were performed, and K values were collected at each well at approximately 20 elevations. These measurements were repeated with several dipole probe configurations and/or recirculation regimes at both sites. Total number of the DFT experiments was on the order of 500. It has been demonstrated that the dipole probe and a steady-state DFT yield valuable data on variations of K in highly conductive unconsolidated sediments, where K is as high as 300 m/day. The profiles of K obtained from the multi-level slug tests and the electromagnetic borehole flowmeter tests exhibit a very strong correlation with the profiles from the DFT. The DFT has potential for more detailed interpretation of K. Interpretation of the steady-state DFT indicates that this technique provides reliable, fast, and simple estimates of the vertical variations of hydraulic conductivity. Other methods of the DFT use based on the transient response or chamber-by-chamber interpretation can enhance the potential use of the DFT. Experiments with well development at the both sites and repetitive measurements for monitoring of well deterioration due to extensive well flushing testing indicate that the well development and well drilling technique play the paramount role in quality of data collected by the DFT, and special care must be taken in designing wells for the DFT. The significance of this work is three-fold. Firstly, the experimental framework of this study is quite unique: three various hydraulic testing techniques were tested and successfully compared in field conditions. Secondly, the DFT proved to be practical, accurate, and reliable technique, and a set of guidelines for its wide use was proposed. And lastly, a significant potential exists for further development and applications of this technique, including data collection and interpretation.

## **Descriptors**

Aquifer Parameters, Groundwater Movement, Hydrogeology

## **Articles in Refereed Scientific Journals**

Zlotnik, V.A., and Zurbuchen, B.R., 1998, Dipole probe: design and field applications of a single-borehole device for measurements of vertical variations of hydraulic conductivity, *Ground Water*, 36(6), 894-893.

## **Book Chapters**

V.A. Zlotnik and B.R. Zurbuchen, Support Volume and Scale Effect in Hydraulic Conductivity: Experimental Aspects, 2000, in Dongxiao Zhang and C.Larry Winter, eds., Theory, Modeling, and Field Investigation in Hydrogeology: A Special Volume in Honor of Shlomo P. Neuman's 60th Birthday: Boulder, Colorado, Geological Society of America Special Paper 348.

### Dissertations

B. Zurbuchen, 1996, The dipole probe development and dipole flow test applications in sand and gravel aquifer (MSEA site, Shelton, Nebraska), M.S. Thesis, University of Nebraska-Lincoln, Lincoln, Nebraska, v. 1 (100 p.), v.2 (280 p.) B. Zurbuchen, in progress, Evaluation of hydraulic techniques to characterize hydraulic conductivity and its vertical variability in sand and gravel aquifers: double-packer slug test,, dipole flow test, and borehole flowmeter test. Ph. D. Dissertation.

### Water Resources Research Institute Reports

### Conference Proceedings

### Other Publications

Zurbuchen, B.R., Zlotnik, V.A., Butler, J.J., Jr., Healey, J., and Ptak, T., 1998, Steady-state dipole flow tests in sand and gravel aquifers: summary of field results. GSA Abstracts with Programs, Toronto, Ontario, October 26-29, p. A226. Butler, J. J., Jr., Zlotnik, V.A., Zurbuchen, B.R., and Healey, J. M., 1998, Single-borehole hydraulic tests for characterization of vertical variations in hydraulic conductivity: A field and theoretical assessment, Proc. of Technical Program for the NGWA 50th National Convention and Exposition, Dec. 13-16, 1998, Las-Vegas, 94-95. V. Zlotnik, B. Zurbuchen, J.J. Butler, Jr., and J. Healey, 1998, Field comparison of single-borehole hydraulic testing methods for estimating vertical K-profiles in highly permeable aquifers: Preliminary results, EOS Transactions, American Geophysical Union, AGU Spring Meeting, Boston, Abstracts, 79(17), S153. Butler, J.J., Jr., Healey, J.H., Zlotnik, V.A., and B.R. Zurbuchen, 1998, The dipole flow test for site characterization: Some practical considerations, EOS Transactions, American Geophysical Union, AGU Spring Meeting, Boston, Abstracts, 79(17), S153. Butler, J.J., Jr., and J.M. Healey, The influence of test method on hydraulic conductivity estimates: Implications for studies of scale dependence (invited abstract), GSA 1999 Annual Meeting Abstracts with Program, v. 31, no. 7, p. A212, 1999.

### Basic Project Information

Basic Project Information	
Category	Data
Title	Advanced Assessment for Spot Spraying Plants to Reduce Chemical Input and Improve Water Quality
Project Number	C77
Start Date	10/01/1996
End Date	09/30/2000
Research Category	Engineering
Focus Category #1	Water Quality

<b>Focus Category #2</b>	Non Point Pollution
<b>Focus Category #3</b>	Management and Planning
<b>Lead Institution</b>	University of Nebraska, East Campus

## Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
George E. Meyer	Professor	University of Nebraska, East Campus	01
Thomas G. Franti	Associate Professor	University of Nebraska, East Campus	02
David A. Mortensen	Professor	University of Nebraska, East Campus	03

## Problem and Research Objectives

The premise of these studies is that reduction in the use of chemicals can be achieved by selectively and intermittently applying chemicals to the plants themselves and not the soil, thus reducing chemicals in runoff water and infiltration into the groundwater. Initial estimates are that 15-65% of current applications could be eliminated while maintaining crop yields. This premise will be tested by the following objectives:

1. Develop and test an advanced machine vision-based assessment and plant mapping system to evaluate optical sensor controlled spot sprayers under field conditions.
2. Analyze both plant spatial distributions and spot sprayer performance to evaluate the efficacy, efficiency, and economics of intermittent chemical applications.
3. Use the performance data from Objectives 1-2 to simulate and study the impact of spot spraying on surface water quality.

## Methodology

Objective 1. Machine Vision Assessment using electronic images of crop and weeds in the field will provide location of plants, plant type, and chemical coverage of leaves. By using and testing various segmentation methods, plant regions will be separated from backgrounds in these images. Once located, further image analysis will result in plant size, shape and type (monocot or dicot), numbers of clusters, wetting of leaves by the chemical and plant distribution. Genetic and inductive textural algorithms will assist in plant species identification. Objectives 2. UNL has been a pioneer by building a field scale prototype optical sensor controlled spot sprayer as a research tool. Weed threshold information for economic and environmental considerations will assist in describing the performance characteristics of spot spraying. These data will be used to calculate (a) how much chemical application is reduced through spot spraying, (b) how effective was the chemical application control using spot spraying. Follow-up video assessment will show which plants died. Plant type and distribution data will be further analyzed using geographic information system and geostatistics software. Using these software, the spatial variability of plants (crop and weeds) will be analyzed. We will also determine spatial criteria for improved sampling procedures. These data will essentially tell us if selected plants were sprayed or missed and why. Objective 3. The plant distribution and chemical use reduction data collected will be used in two water quality models, the Agricultural Nonpoint Source (AGNPS) surface water quality model and the Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) pesticide runoff model. These will be used to model field-scale runoff (GLEAMS) and watershed-scale runoff (AGNPS) to determine the long-term impacts of improving

chemical management on reducing pesticide runoff losses. Simulations of runoff events will be performed using synthetic rainfall data and with atrazine and alachlor as the subject pesticides. Typical corn production at a central Nebraska location will be modeled on a field scale with GLEAMS and a typical 800-acre watershed in central Nebraska will be used for the AGNPS modeling. Pesticide management alternatives evaluated will include spray application using conventional spray (broadcast and banded), with and without incorporation versus intermittent sprayer technology, and timing of application, e.g. preemergent herbicide application (standard) versus postemergent with spot spraying.

## **Principal Findings and Significance**

### **Annual Update - June 29, 2000**

#### **Summary of Results**

There are two approaches to controlling weeds using electro-optical sensors or machine vision and variable-rate application technology. The first real time method uses a sprayer mounted sensor which must detect and process weed information quickly followed by delivery of herbicide to the spotted location. Detection and processing speed depend on sprayer ground speed, background lighting, and roughness of the terrain. The second method uses aircraft over flight and digital photography over large field areas, followed by post flight processing of image data and development of a prescription map of the field. Coordination of weed locations is accomplished by a global positioning system on both the aircraft and the variable rate applicator using the prescription map. Image resolutions can achieve + 1 cm per pixel with either method. Satellite imagery will probably not be to provide the needed resolution at this time.

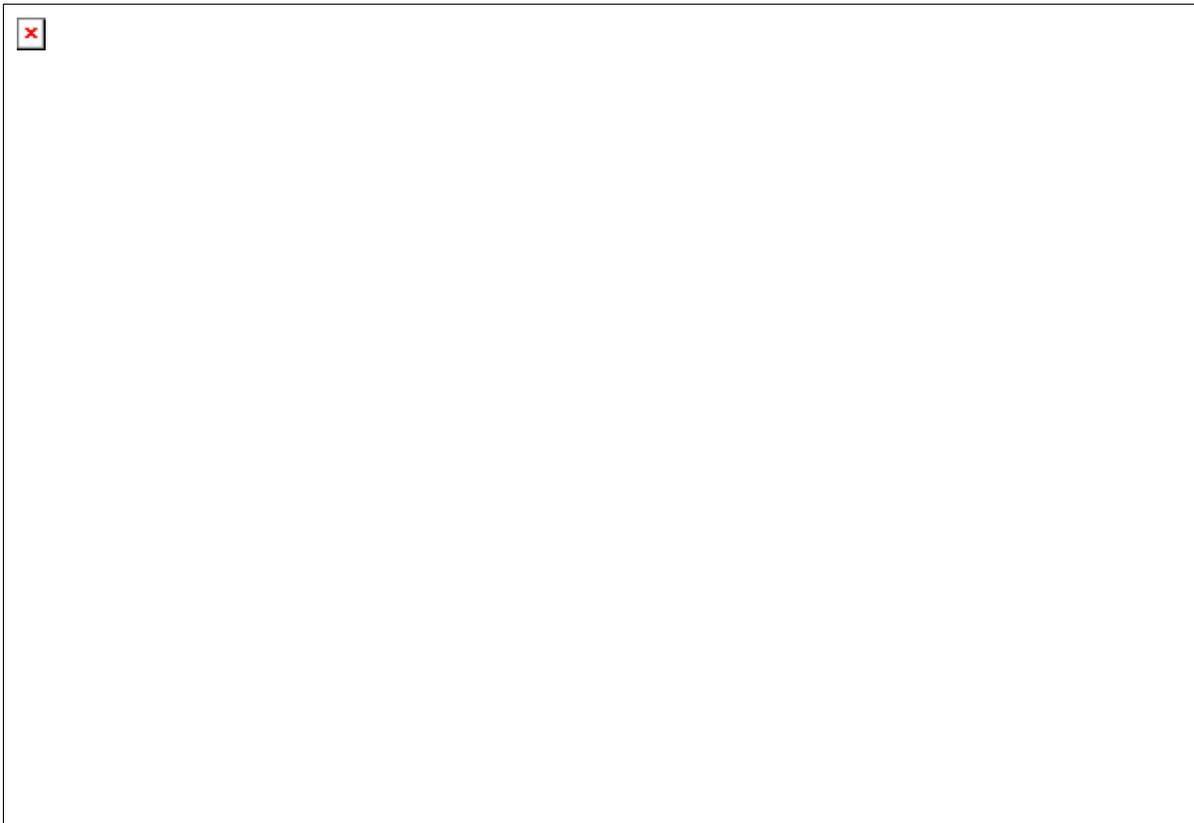
#### **Machine vision detection of weeds**

Under objective 1, image analysis appears to offer the best approach for discriminating between crop and weeds. Efforts during this project have focused on improving machine vision and software techniques for identifying, counting, and identifying weed types. Weed identification for potential spot spraying is based on weed seedlings of three weeks of age or less using post-emergence application of chemicals. It is during these growth periods, that the highest probability exists for identifying the species of weed according to basic botanical keying and imaging methods. The principal image analysis software packages used were Image-Pro and Visual Basic with Windows. Image-Pro has built-in shape feature analysis under the menus. The textural feature analysis utility of Image-Pro is expanded with Visual Basic script. The combined use of these two software packages provides the image analysis tools needed for weed identification, based on canopy structure and individual leaf venation and shapes. However, the principle significant problem is to find plant objects and distinguish it from the background in color images. This process is called image segmentation. It depends primarily on image quality or tonal value. Unfortunately, traditional film photography and even modern digital photography can create highly variable tonal quality in images.

Color (Red-Green-Blue) images were used to detect and identify weed plants. Several manufacturers produce some very useful digital cameras. Kodak did produce an experimental color infrared camera, which could be used to NIR spectral bands, but it is our conclusion that plants can also be detected solely with RGB. In most cases, digital cameras running under automatic exposure and focus produce superior images with the maximum tonal information needed. The only problem is that the color temperature and illuminance intensity of background lighting may change the RGB balance. Canopy lighting affects the degree of light and dark transitions, edginess, and feature detail. Color temperature varies from full shade / clear sky (12,000 K), full sun / clear sky (5700 K), cloudy sky (5900 K), all the way to incandescent lights at 2800 K. This was the major source of segmentation error. A model for this

way to incandescent lights at 2000 K. This was the major source of segmentation error. A model for the RGB balance must be developed. A one megapixel Kodak DC 120 digital camera was the primary tool for obtaining electronic images of various plant species in this project. Plants were grown in the plant growth chamber, the greenhouse, and in field plots near the campus. The DC-120 camera was focused to include entire plants within the camera's field of view. Different natural and background lighting conditions were tested, forward lighting with soil background and back lighting without soil background. The DC 120 camera was found very versatile for most lighting conditions. It automatically adjusts for light quality within certain limits. We are also testing the camera with manual settings with plants under different lighting sources, described by light intensity and color temperature.

Using the Kodak software provided with the digitized camera, digitized images are transferred to either a 400 or 700 MHz Pentium computers with 128/256 megabytes memory, respectively for analysis. Digital resolution is 25 dots/inch, with a width of 1280 pixels and height of 960. All electronic images were saved in a 24-bit color format (JPEG) on CD-ROM. It was found that one megapixel was too much data to handle in subsequent analyses. Digitally scanned pictures were then resized during pre-processing to a width of 240 pixels and a height of 180 pixels sort of a television-like analysis. Figure 1 shows the overall image preprocessing and model development activities.

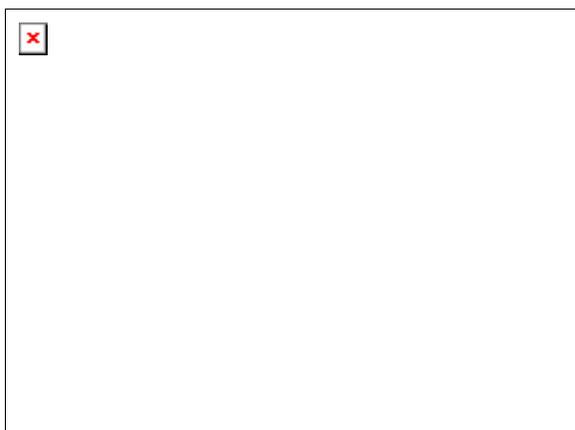


**Figure 1.** Plant and Weed Machine Vision, Fuzzy Neural and Statistical Analysis.

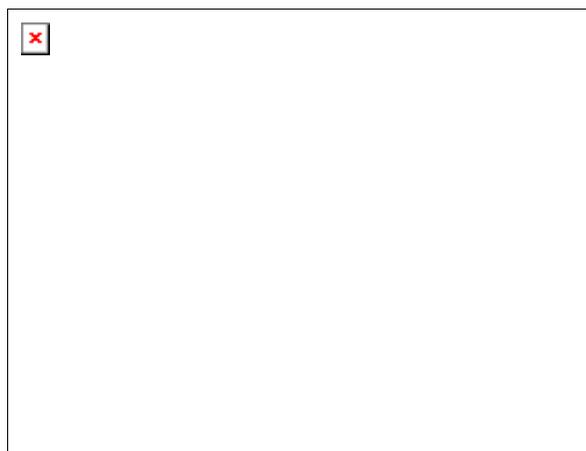
As previously mentioned, the most critical processing step is the segmentation of plant regions from background regions. If this step is not done correctly, subsequent shape and textural feature analysis will not work. Several approaches to segmenting the plant from the soil background have been tested. The simplest method is to use a threshold value such that all pixels with greater value are selected as leaf (white) and all pixels with less value were taken as soil background (black). This is usually done after analyzing a histogram. However, the threshold method always brings in background errors that make subsequent shape and textural feature analysis of the plant difficult. Pixel intensity values at some places in the soil background image part may be at the same level as or higher than that of leaf. This causes

errors in the computation of textural co-occurrence matrices since the algorithm will use those tonal areas as well. These errors will show up on a grayscale as well as any color raster of a red-green-blue (RGB) or hue-saturation intensity (HSI) image. We saw no advantage of using HSI as suggested by Shearer of Kentucky.

Another approach to segmenting plants from soil background uses a variance-based object detection method. With this approach, graphical outlines of all candidate plant areas are identified. Generally, edge detection techniques will create a number of boundaries of objects found within an image. These boundaries are then investigated to determine which ones have the highest probability of being plant and then must be confirmed by subsequent feature analyses. The selected plant outlines are then painted or filled (cleaned up) using application programming interface (API) graphics functions from Visual Basic. A comparison of the original and cleaned up binary files are shown in Figures 2a and b.



**Figure 2a.** Cluttered Binary Image



**Figure 2b.** Uncluttered Binary Image

Once a clean binary template image is processed, excellent algorithms for plant feature analyses, counting or enumeration algorithms are available. Shape feature parameters such maximum ferret, minimum ferret, perimeter, area of the leaf, maximum length, maximum width, aspect ratio and roundness can be used to calculate other complex shape factors were obtained from the template image. Dimensionless shape features independent of size and orientation, identified by Yonekawa et al, (1996) are currently being investigated. Texture features of angular second moment, local homogeneity, inertia and entropy are computed, based on the co-occurrence matrices of the original gray scale images at all four directional orientations: Feature data is currently put into a large Access database for further analysis. The binary template has been shown to reduce the errors brought about by background segmentation noise, (Mehta, et. al, 1998). Statistical analyses and hypothesis testing are performed using SAS Canonical Discriminant Analysis. Results by Meyer et al (1999) support that methodology for identification of individual plant species based on leaf shape and textural analysis.

A third but very new segmentation approach tested was to integrate colors and textures into a sophisticated rule-based model. Essentially, human vision uses color and texture together to separate natural and man made objects. The human process is not easily modeled with ordinary mathematical methods. Fuzzy set theory is a mathematical system derived from basic set theory, with sets or classes of objects with unsharp boundaries and uncertainty. Fuzzy logic with neural networks on high-speed computers allows approximate interpolation between uncertain observed input and output data with fundamental mathematical support (Ross, 1995). Fuzzy logic rules or fuzzy logic models was developed with an artificial neural network (ANN). Fuzzy logic has already been applied to a variety of agricultural, biological, and environmental systems. This method simulates human decision-making processes based on imprecise criteria. using a set of linguistic variables to define a degree of membership for each object

in a set. Fuzzy logic models have been developed for a set of single-background images under a range of uniform illumination conditions. Target backgrounds included green turfgrass, bare soil, weathered corn stalks, and weathered wheat straw. Both natural and controlled artificial light sources, including fluorescent, incandescent, and halogen sources, were used. Average red, green, and blue (RGB) pixel values were calculated for each image. These average values, along with camera exposure time, light source illuminance, and apparent source color temperature, were used as inputs to train a Sugeno-type fuzzy inference system (FIS).



**Figure 3.** Fuzzy logic discrimination vs. SAS discriminant analysis.

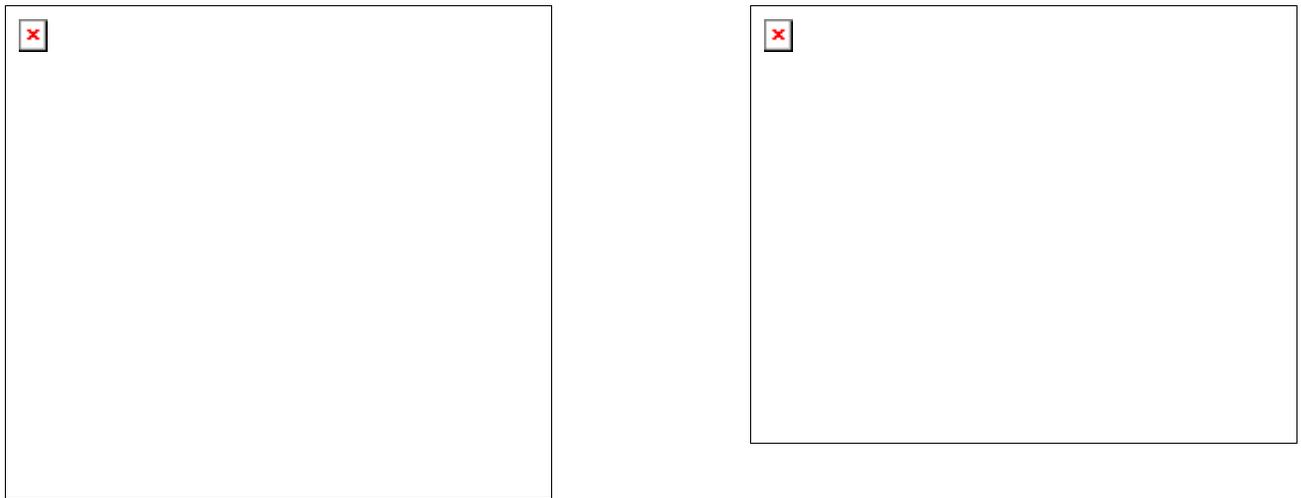
The initial fuzzy logic plant segmentation models of the original images developed to date resulted in correct classification rates of up to 94%, compared to 56.3% for SAS discriminant analysis (Figure 3 and Tables 1 and 2). Similar results were obtained using hue, saturation, and intensity (HSI) values and calculated excess green and excess red plant segmentation indices. Work is currently on going to validate these models to independent sets of plant images against bare soil, corn stalk, and wheat straw backgrounds. The neural fuzzy method is a very powerful system of correlating input and output data. What happens is that the system when allowed to process indefinitely, develops rules for every generalization and special case condition. The next critical step is the post rule evaluation to determine the quality and impact of specific rules on the prediction process.

### **Evaluation of electro-optical, single element sensor - prototype spot sprayer**

A prototype electro-optical single element sensor - spot sprayer was developed prior to this project, but was not thoroughly tested at that time. Under objective 2, Raemakers, et al reported that the use of single element plant (non-imaging) sensors using narrow spectral bandwidths of reflected natural red and near-infrared (NIR light). These bandwidths were combined into a Normalized Difference Index ratio (NDI). Such sensors may only work to detect weeds under good lighting conditions. The NDI method was only found capable of detecting small plants using a high level of operator supervision. Moreover, the NDI plant detection threshold was found to be unstable over extended time periods ( 1 hour), resulting in the spray operator constantly needing to make gain and timing adjustments to the system to

achieve a desired performance level.

There is a strong shadow effect with the NDI method where shadows can occur during any period of high available light energy as shown in Figure 4.



**Figure 4.** Shadows generated by sensing head (Ramaekers, et al)

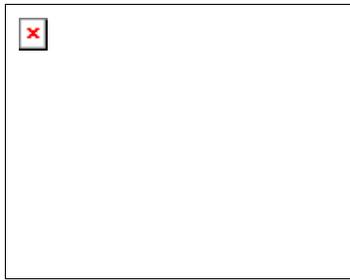
A weed detection sensor-control system that utilizes NDI will need a continuous readjustment of the threshold NDI. Table 3 shows experimentally obtained thresholds. These thresholds change with both plant and environmental conditions. In all probability, the single element system is too sensitive to reliably perform a real time spot spraying operation over a daylong period.

Under objective three, Ramaeker's intermittent sprayer evaluation model was based upon one herbicide application to control weeds. Dividing the sensors spot area in half allows for greater resolution and a possible smaller spray area/weed. The smaller the spray area, the greater the herbicide reduction potential. This resolution however has an increased cost associated with it. There is an optimal spray nozzle (row-unit) width that has not yet been determined. There would also be a balance between chemical savings, crop value loss due to crop/weed interaction (if applicable), repeat applications, and additional herbicide costs.

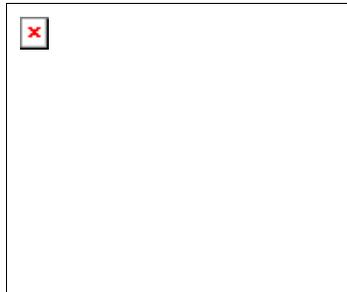
The estimated field herbicide reduction for intermittent spraying was 98.2%, 90.8%, and 83.5% (Table 4) respectively for low, medium, and high weed densities shown in the weed maps in Figure 5a,b,c. One reason the estimated herbicide reductions were greater than Johnson et al. (1995) was the size of the area sprayed per individual weed. These reduction values are more optimistic than Hanson and Wick (1992). Repeat chemical application could be needed to control small-undetected weeds and would reduce the overall herbicide savings. The sprayer sizes chosen are based on popular row crop machinery sizes. The cost of retrofitting a conventional sprayer for intermittent sprayer approximately \$1500/m (\$455/ft). There is no large difference in sprayer per unit of width as size changes.

The average herbicide cost reductions ranged from \$24.10/ha. (\$9.75/a) for the high weed density field to \$28.40/ha (\$11.50/a) for the low weed density field. The 4.6 m (15 ft) wide sprayer would require 100 ha (250 acres) of annual use to recover the addition fixed costs). The 6.1m (20 ft) and 9.1 m (30 ft) wide sprayer would break even at 200 ha (500 acres) of annual use. At an annual use of 300 ha (750 acres) the 12.2 m (40 ft) sprayer would break even. All sprayers sizes would break-even at an annual use rate of less than 400 ha (1000 acres). The timeliness of the application operation at the sprayer beak-even points was not assessed.

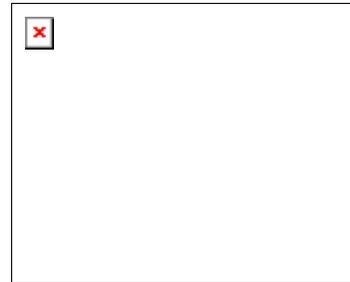
Break-even usage for all sprayer sizes could be less. The high weed density field was used for analysis and would be a worse case scenario in terms of herbicide reduction in the simulation. Actual field weed densities would occur over a range from the low to high weed densities. The break-even annual usage would dependent upon a composite of numerous field weed densities in actual field usage. The lower the average weed density, the greater the chemical savings, and the lower the break-even usage.



**Figure 5a**



**Figure 5b**



**Figure 5c**

### **Impact of Fixed and Variable Application Dates on Runoff Losses of Post-Emergent Herbicide**

The use of spot-spraying techniques will require identification and herbicide application to emerged weeds. The dates at which the herbicide can be applied will depend on planting dates and weed growth rates. To assess the potential impact of spot spraying on herbicide runoff an assessment was conducted to determine the impact of fixed and variable application dates on runoff losses.

Whenever herbicides are used, a portion of the applied dose will reach the soil. An important aspect of the subsequent herbicide fate is loss to surface and subsurface water. Surface runoff is a dominant pathway for losses for moderately adsorbed herbicides commonly used with corn production. Some chemicals are lost more in subsurface flow. To make the fullest use of herbicide and reduce impacts on water quality, we should decrease the losses in runoff events.

In order to study the impact of application dates on runoff losses of post-emergent herbicide, we did trial computer simulations using GLEAMS (Groundwater Loading Effects of Agricultural Management Systems, 2.10) (Leonard et al., 1987) to test two methods to select application dates. The following methods were evaluated:

1. Application on five fixed dates each year for 50-year period.
2. Applications on different dates around the previous schedule every year.

Using the first method, we chose May 25, May 30, June 5, June 10, and June 15 as application dates. Using the second method, we checked the precipitation record first and then selected five dates each year around May 25, May 30, June 5, June 10, respectively, according to the criteria, with  $D_e$  = Date application expected

1. If no rain on  $D_e$  and 1 day before, then apply on  $D_e$ .
2. If rain on  $D_e$  or one day before, then apply on first day following or 2 days without rain (ignore rainfall when it is less or equal 0.25 in.).

Four locations: York, Otoe, Dodge, Scotts Bluff County, Nebraska were used for this evaluation.

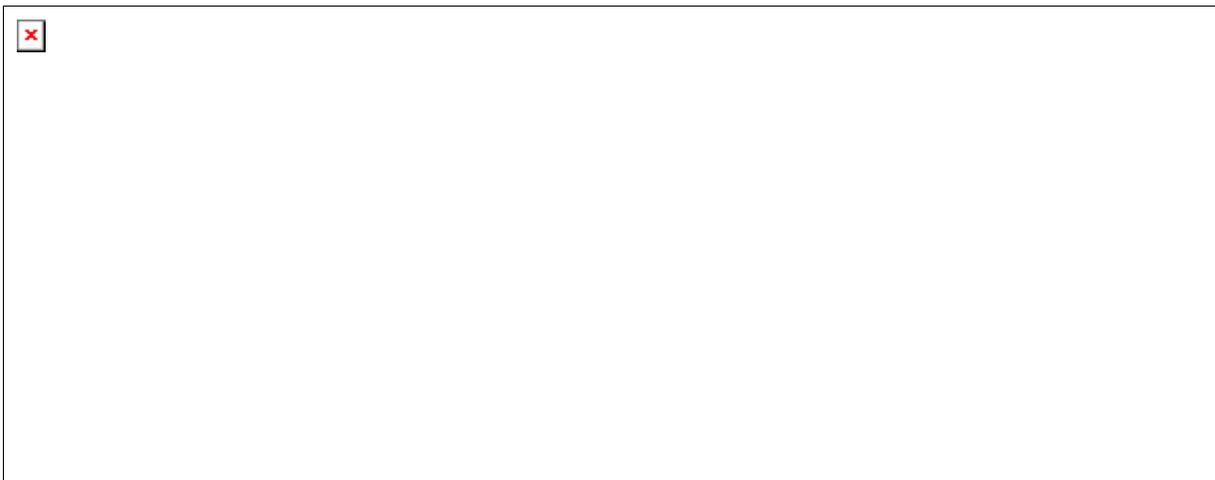
From the results (Table 5), obvious differences can be seen between the two methods for Otoe and York County. The variable method results in loss for these two counties with difference in the mean loss ranging for 0.0% on June 15 York, to -21% on May 25 Otoe. But for Scotts Bluff County, it even increases the pesticide losses. The reason is because of the variable method's application date selection criteria. When it rained on the proposed day, that day was moved forward until no rain for two continuous days. For instance, the precipitation data of Scotts Bluff and following days May 30 1954 are 0.48 in., 0.26 in., 0.00, and 0.00 in. An application was planned on day 1, with 0.48 inches rainfall, but because of the rain; we applied three days later. The result in the losses changed from 17.87 g/ha to 23.65 g/ha. Although it has rain on the expected day, it may be not enough to make the soil saturated. If the application were applied on the following day, though there is no rain on that day, the previous two-day rainfall is enough to cause runoff.

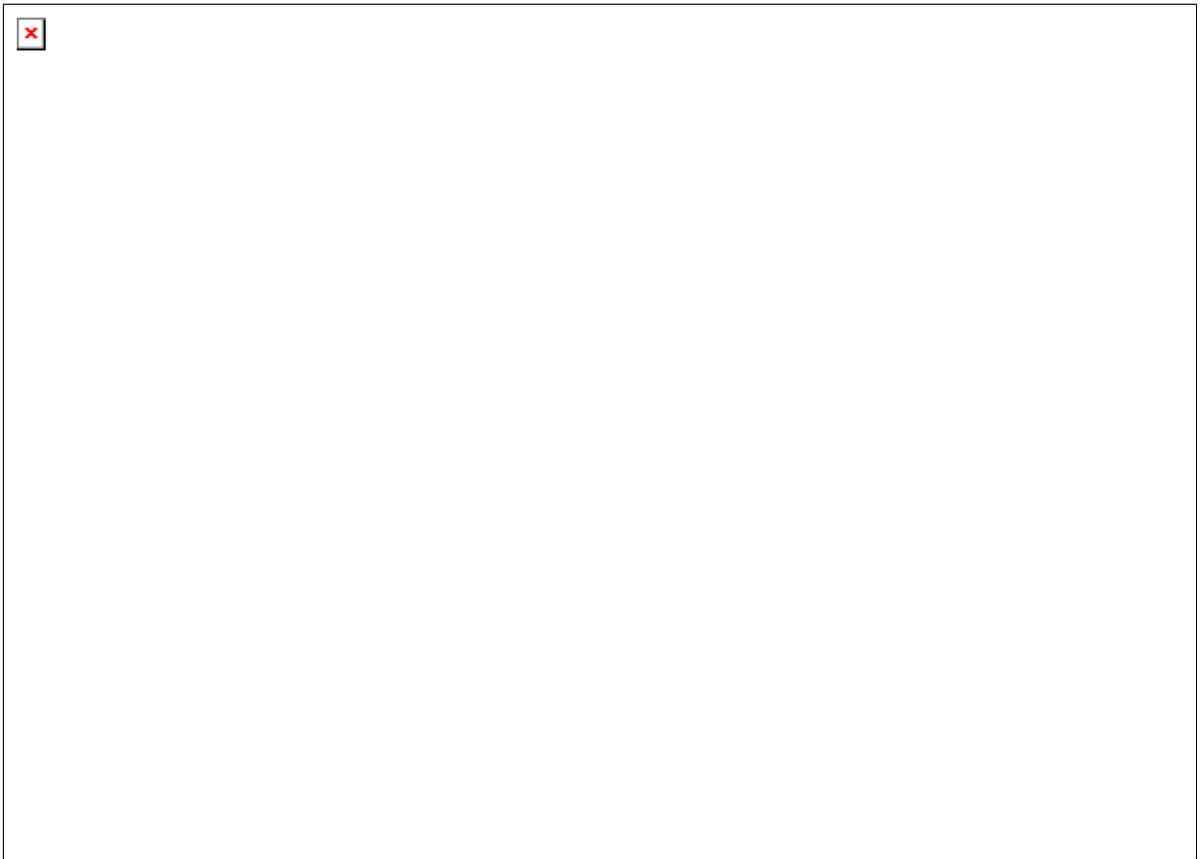
After these simulations we conclude the following:

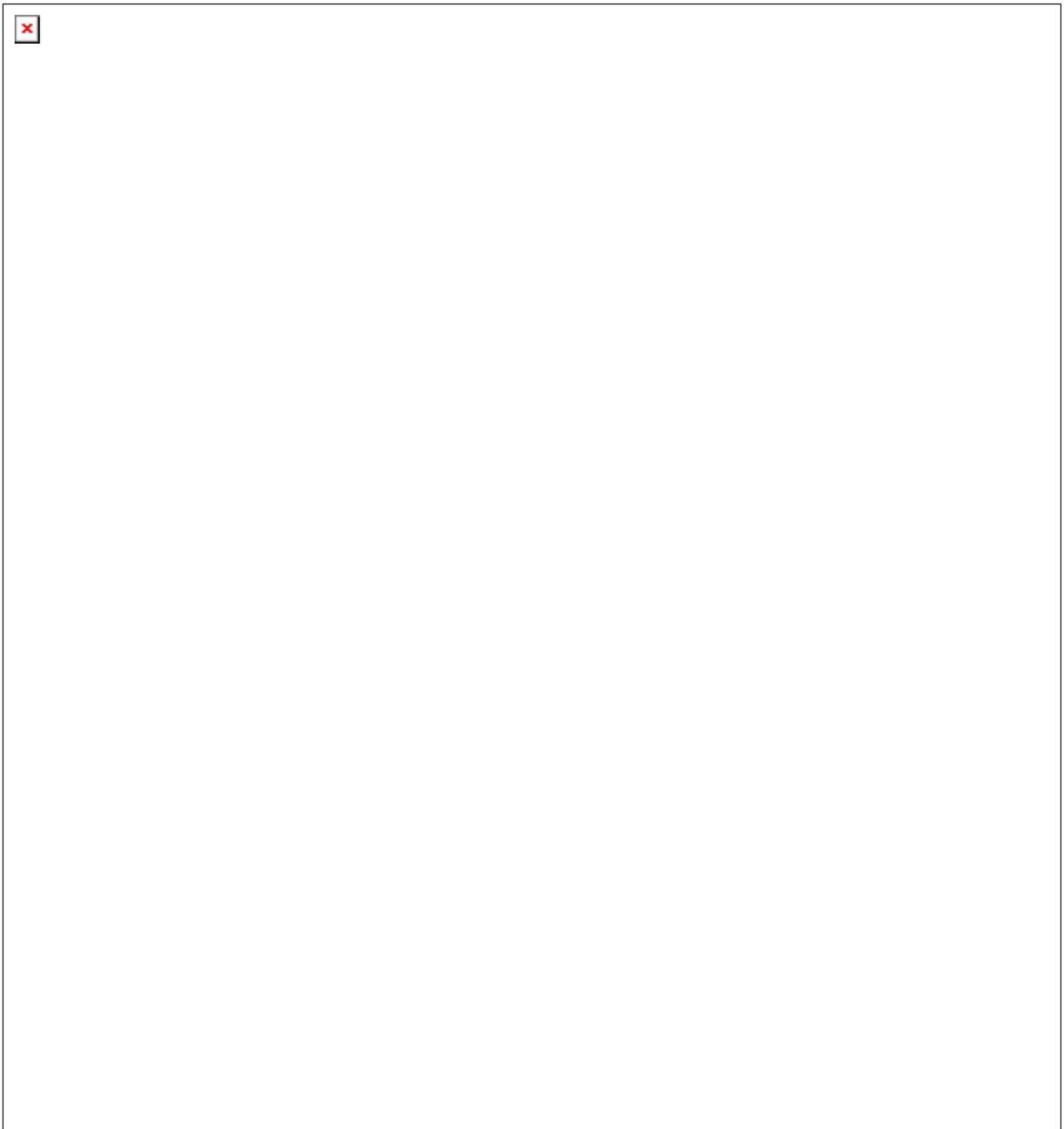
If the soil is unsaturated, the rain cannot run off. After the soil is saturated, the rain will cause runoff and it will result in potential significant pesticide losses depending on the amount of previous rainfall.

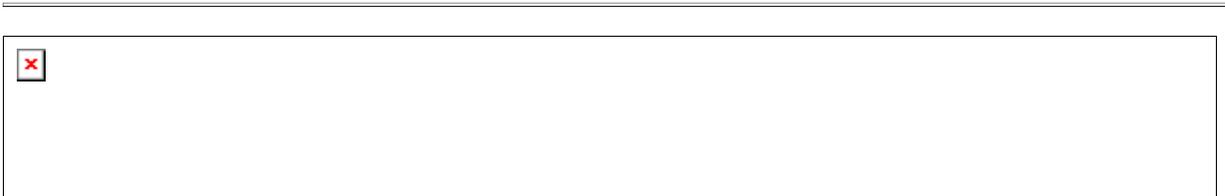
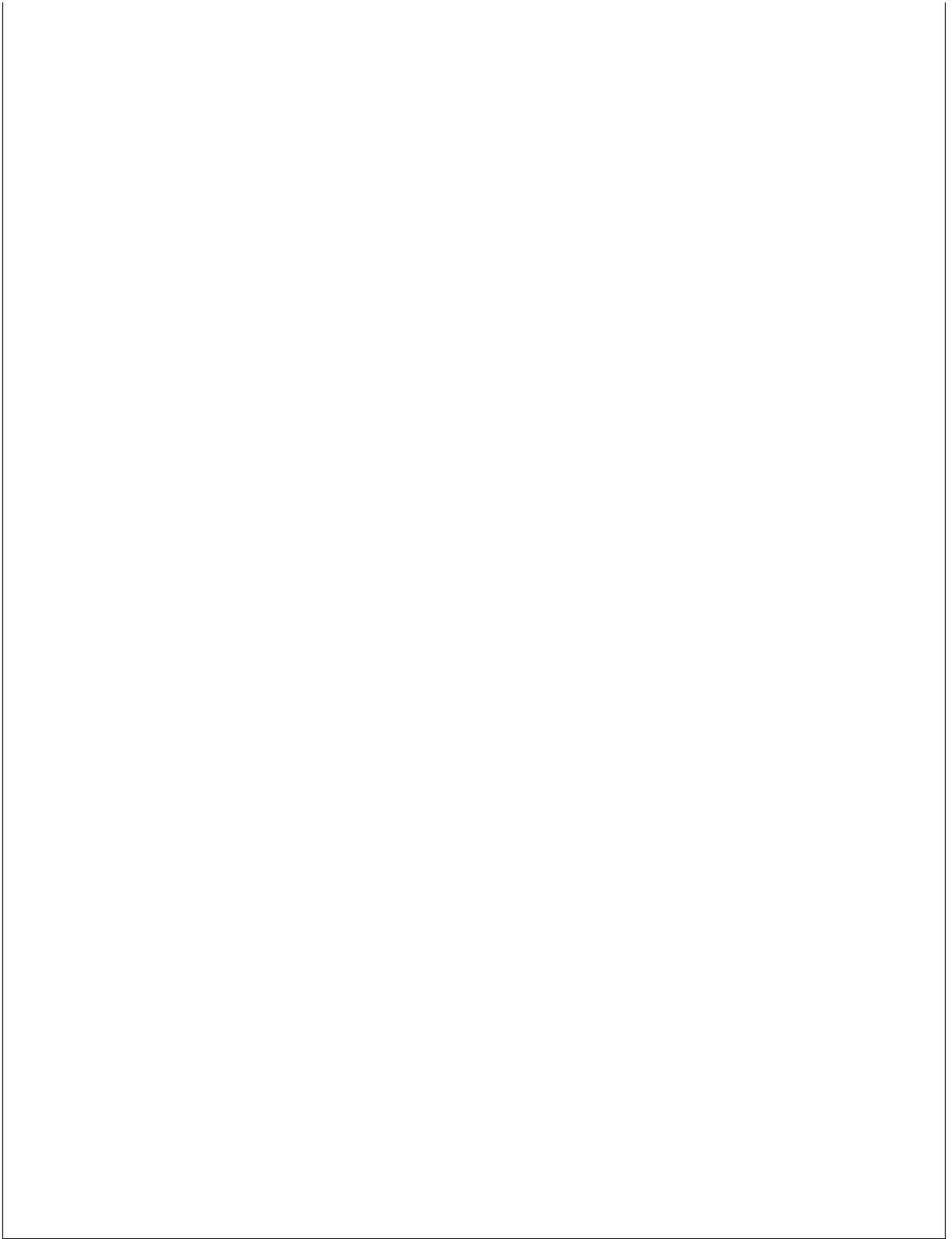
1. If an application date is chosen at the end of a long dry period, there are only little losses. If there is no rain, then there is no run off, resulting in no herbicide losses.
2. However, if the application date that is chosen after several wet days, it may cause great losses. For example, the loss of Otoe County May 25, 1956 is 130.8 g/ha. There was 0.17, 0.15, 0.34, 0.00, 0.07, 0.27 in. rainfall on the previous days respectively.
3. If significant rain is on the previous day, even if no rain on the day of application, there are still large losses. If only a little rain, the losses would not be great.
4. The variable method can make a big difference on herbicide losses, but it is only for the locations with a relatively large loss. If the location has small losses, such as Scotts Bluff, this method has less impact.

A statistical evaluation was performed. The herbicide losses data obtained by GLEAMS are not harmonious. For instance, the data for Dodge County May 30 (application date is May 30) comes either from normal or gamma distribution; the data for Otoe County June 5 comes only from gamma, but not normal distribution. There remains an unsolved problem: Is there a significant difference in mean losses for each location and each application date?

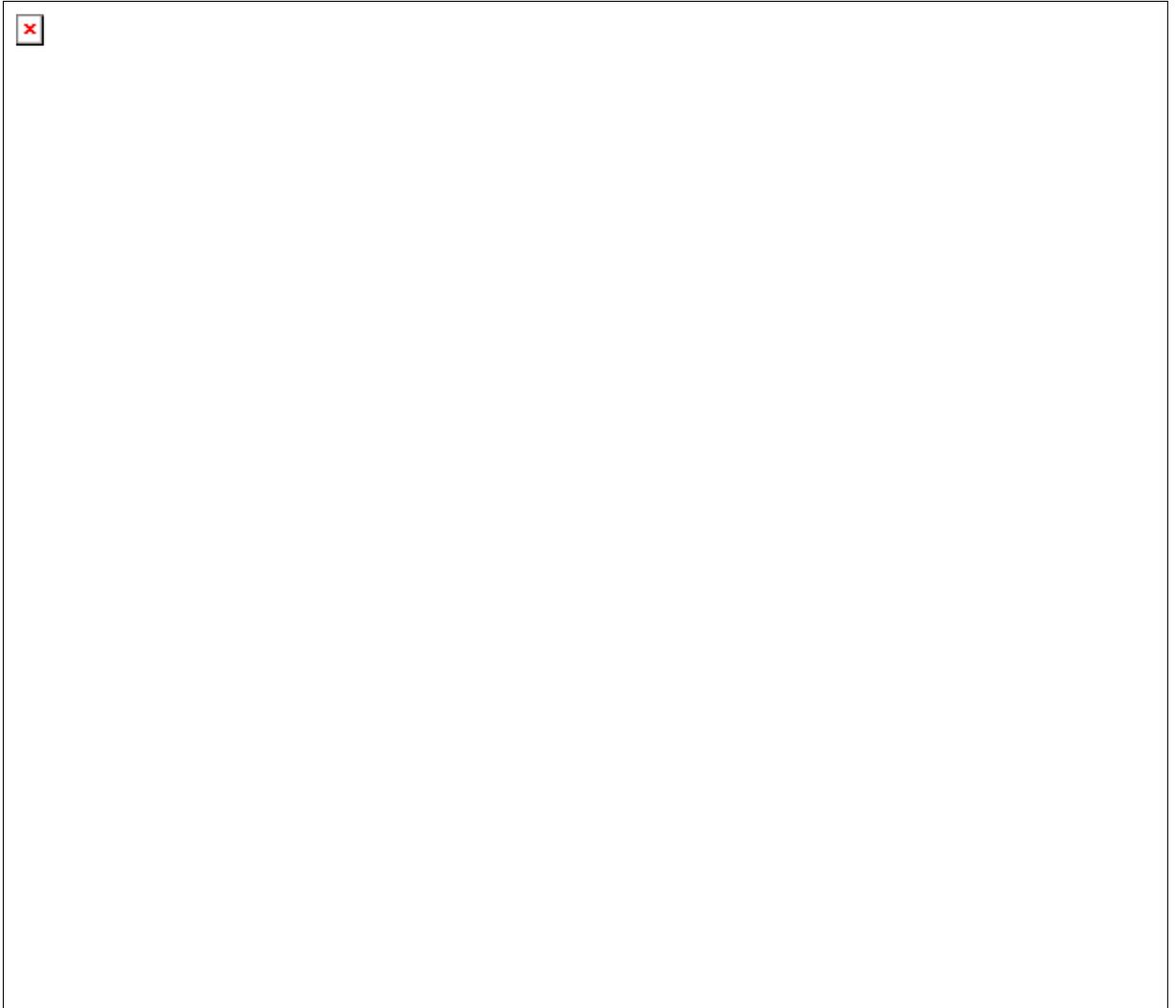














## **Descriptors**

Pesticides, Spot Spraying, Machine Vision, Spatial Variability, Water Quality Assessment.

## **Articles in Refereed Scientific Journals**

Meyer G.E., T.G. Franti, and D.A. Mortensen. 1997. Seek and Destroy Machine vision identifies weeds for spot spraying. Resource Magazine, Engineering and Technology for a Sustainable World. ASAE 4 (12):1314. Meyer G.E., T. Mehta, M. F. Kocher., D. A. Mortensen, and A. Samal.1998. Textural Imaging and Discriminate Analysis for Distinguishing Weeds for Spot Spraying. TRANSACTIONS of ASAE, 41 (4): 1189-1197. Ramaekers, B. P. ,G.E. Meyer, K. Von Bargen, and D.A. Mortensen. A Plant Detection System Performance Evaluation Applied Engineering in Agriculture, in review.

## **Book Chapters**

## **Dissertations**

## **Water Resources Research Institute Reports**

## **Conference Proceedings**

Meyer G.E and, J.A. DeShazer. 1997. ( Chairs/Editors). Optics in Agriculture, Forestry, and Biological Processing II. SPIE--The International Society for Optical Engineering, Bellingham, WA.. (ISBN: 0819423092) 2907: 284 pp. Meyer G.E, T.W. Hindman, and M.Schultz. 1997. Simulation Tools for Evaluating Optical Plant Sensors for Variable-Rate Application Technologies. In Meyer G.E and, J.A. DeShazer. Optics in Agriculture, Forestry, and Biological Processing II. SPIE--The International Society for Optical Engineering, Bellingham, WA.. 2907:139-150. Meyer, G.E. and J.A. DeShazer (Chairs/Editors) 1998. Precision Agriculture and Biological Quality. Proceedings of SPIE -- The International Society for Optical Engineering, Bellingham, WA. (ISBN: 0819431559) 3543: 390 pages Meyer, G.E, .T.W. Hindman, and K. Laksmi 1998. Machine vision parameters for plant species identification. In Meyer, G.E. and J.A. DeShazer, Precision Agriculture and Biological Quality. Proceedings of SPIE -- The International Society for Optical Engineering, Bellingham, WA. 3543: 327-335. Hindman, T.W., and G E. Meyer. 1999. Fuzzy Logic Detection Parameters for Plant Species Identification. EUFIT '99 - Proceedings of the 7th European Congress on Intelligent Techniques and Soft Computing on CD-ROM, Verlag Mainz Publishers, Aachen Germany, 3:1-8.

## **Other Publications**

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## Basic Project Information

Basic Project Information	
Category	Data
<b>Title</b>	Site-Specific Management Strategies for Improving Nitrogen use Efficiency Under Furrow Irrigation
<b>Project Number</b>	C-22
<b>Start Date</b>	09/01/1997
<b>End Date</b>	08/31/2000
<b>Research Category</b>	Water Quality
<b>Focus Category #1</b>	Nitrate Contamination
<b>Focus Category #2</b>	Irrigation
<b>Focus Category #3</b>	Methods
<b>Lead Institution</b>	Nebraska Water Resources Center

## Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
Gary W. Hergert	Professor	Nebraska Water Resources Center	01

## Problem and Research Objectives

Richard B. Ferguson, Professor, UNL-SCREC and Brian L. Benham, Assistant Professor, UNL-SCREC, Clay Center, NE 68933 Charles A. Shapiro, Associate Professor, UNL-NEREC and William L. Kranz, Assistant Professor, UNL-NEREC, Concord, NE 68728 C. Dean Yonts, Associate Professor, UNL-PREC and Jurg Blumenthal, Assistant Professor of Agronomy, UNL-PREC, Scottsbluff, NE 69361 Current best management practices (BMPs) for nitrogen and irrigation used by most producers and Natural Resource Districts in Nebraska have been developed primarily from University of Nebraska research. Additional research is required to provide next generation BMPs which will continue to reduce nitrate-N loss. Although there has been a transition to sprinkler irrigation during the past 25 years in the central Great Plains, large areas of cropland are still furrow irrigated (50% in Nebraska). Changing to sprinkler irrigation is expensive and offers no immediate economic returns other than labor savings for irrigated land in river valleys. Furrow irrigation will continue to be a major factor influencing N management and leaching although the impact of alternate row irrigation and N application has not been thoroughly investigated. Increasing levels of nitrate in groundwater have been observed in some river valleys in Nebraska since the mid-1950's. In the most recent statewide evaluation of groundwater nitrate and pesticide levels, over half of the wells in the state testing higher than 10 ppm NO<sub>3</sub>-N were in irrigated river valleys. A significant number of wells exceed 10 ppm NO<sub>3</sub>-N in southern Phelps and southwestern Kearney counties, an irrigated corn producing area of fine-textured soils with depths to

ground water between 15 and 30 m. Other research has shown that nitrate has moved down at least 18 m in 15 years under furrow-irrigated research plots on a silt loam soil. This situation may also be representative of most furrow irrigated areas from the arid west to the corn belt. A more recent concern about agriculture's impact is the hypoxia question in the Gulf of Mexico. Many sources of N contribute to increased stream flow nitrate, but crop land N management can have an influence. Improvements in N use efficiency in all parts of the Mississippi watershed will be required if agriculture is part of the hypoxia cause. The objectives of the project are to: 1. Compare spatial nitrogen use efficiency and N balances for alternate row irrigation and alternate row N application versus every row N application and irrigation for variable rate and fixed rate side-dressed anhydrous ammonia. 2. Compare spatial nitrate-N movement of the four methods using a conservative (KBr) tracer. 3. Correlate spatial N leaching to crop and soil parameters including grain yield, N applied, field position and conservative tracer leaching. 4. Compare systematic soil sampling strategies for the 4 management schemes that will provide the best estimate of residual nitrate N that will be used in N recommendation algorithms for the next corn crop.

**INFORMATION TRANSFER PROGRAM:** Information on improving nitrogen and irrigation management has been presented at various Extension forums during the fall and winter of 1999-2000 (field days and workshops). In addition, results from the study were presented at the 1999 Meetings of the American Society of Agronomy. Research findings will be presented at the 5th International Conference on Precision Agriculture, Minneapolis, MN, July 16-19, 2000, and the 4th Decennial National Irrigation Symposium, Phoenix, AZ, November 14-16, 2000. Primary audiences included researchers, producers, crop consultants and fertilizer dealers.

**STUDENT SUPPORT:** Four undergraduate students were hired to provide assistance for the project during summers of 1998 and 1999, and two in 2000.

## Methodology

This project was conducted at 3 locations across Nebraska in 1999 representing the major corn production areas--Western NE near Scottsbluff, West Central NE near North Platte, and South Central NE near Clay Center. Treatments within the 4 management schemes were combine-width (6 to 8 rows) by full field length (usually 300-400 m). This required large experiment areas (15-20 acres or 6-8 ha) to sufficiently measure treatment effects and to compare soil sampling schemes. The four management schemes being compared were: 1. Every furrow application of anhydrous ammonia (EFI) (fixed rate based on average soil nitrate, average organic matter and average expected yield) and every furrow surge irrigation. 2. Every furrow application of anhydrous ammonia (EFI) (variable rate based on spatial soil nitrate, spatial organic matter and average expected yield) and every furrow surge irrigation. 3. Every other furrow application of anhydrous ammonia (AFI) (fixed rate based on average soil nitrate, average organic matter and average expected yield) and every other furrow surge irrigation in the non-N application furrows. 4. Every other furrow application of anhydrous ammonia (AFI) (variable rate based on spatial soil nitrate, spatial organic matter and average expected yield) and every other furrow surge irrigation in the non-N application furrows. Anhydrous ammonia was applied at the 4 to 8 leaf stage corresponding to current BMP suggestions. Treatments were replicated 4 to 5 times. Anhydrous ammonia application was made with a variable rate applicator (VRA) owned by the investigators. Grain yields were determined with a conventional 6 or 8 row combine equipped with a GPS and a yield monitoring system or a plot combine. Preplant soil nitrate samples were taken and logged with a GPS. During harvest, samples of grain were taken at the previously logged soil sampling locations and analyzed for N content. Post-harvest soil samples for nitrate were taken from the previous soil and grain sampling sites. The information on preseason nitrate, grain N removal, post season nitrate and N applied will be used to calculate a spatial N balance and apparent nitrogen use efficiency calculation for the management schemes. Mini-plots of KBr (30 cm x 120 cm) were spaced along the length of furrows from the upper to lower end of the field (5 to 6/furrow depending on furrow length) in irrigated and

non-irrigated furrows. KBr was applied within several days after N application (200 kg/ha Br watered in with 1 ha-cm of water) but before irrigation began. Two in-season and one post season sampling was used to determine Br and NO<sub>3</sub>-N movement and distribution in the root zone. Nitrogen unaccounted for calculated from the N balance under Objective 1 will be correlated with other parameters listed. A paired sample grid with individual 5 cm cores taken on the furrow shoulder was used on adjacent rows of the alternate furrow N application and irrigation treatments. Sites were sampled for residual nitrate and soil organic matter. The spatial data for organic matter and nitrate were used to develop spatial N rate recommendations using the University of Nebraska N recommendation algorithm for corn. This data was kriged to develop N rate application maps. N was sidedressed in early to mid-June each year.

## Principal Findings and Significance

Objectives 1 and 4: There was significant spatial variability in soil parameters (soil organic matter and residual nitrate-N) that influenced N dynamics at all three locations. At Clay Center, soil organic matter levels varied from about 10 g/kg in an area where topsoil had been removed to facilitate irrigation, to 30 g/kg in better areas of the field. At all locations, and in all years, yield from treatments that received no N fertilizer (control treatments) were significantly lower than those that received N. Grain yield was not significantly affected by N application method (variable versus uniform rate). These results are consistent across locations and with previous studies in Nebraska, and show that variable rate N application provided no field-wide yield advantage compared to uniform N application. While rates varied within the variable rate application treatment, the average treatment N rate was within 11 kg/ha of the uniform rate at each site. The lack of yield difference between variable and uniform N rates indicates that organic matter and residual nitrate-N were not so variable that the uniform application significantly under-applied N to a large area of the field. This is consistent with the hypothesis that the University of Nebraska recommendations are near the maximum of the response function and the N response function is either quadratic or linear-plateau. In addition, there were no significant differences in end-of-season residual nitrate-N between uniform and variable N treatments at the North Platte and Clay Center locations. At the Scottsbluff site, for the AFI treatments, the uniform application had greater residual nitrate-N than the variable rate treatments. Corn grain yields for both AFI and EFI were the same at Clay Center and North Platte. The AFI treatment had an average of 72 mm less irrigation water applied per season at these locations. As was the case at Clay Center and North Platte, application of N fertilizer at Scottsbluff increased corn yield for both uniform and variable N applications. In contrast to the other two locations, grain yield at Scottsbluff was significantly lower for the AFI treatment compared to EFI. Factors influencing the potential for AFI to reduce yield include soil water holding capacity and mean annual water balance - both of which are lower at Scottsbluff than the other two locations. With reduced precipitation the non-irrigated furrow may have insufficient moisture to allow either the N to move to the roots or root development to occur towards N bands. Summary Theoretically, reduced leaching of fertilizer N with alternate furrow application should result in greater N use efficiency making it possible to produce similar grain yields using less fertilizer N than with very furrow application. Moreover, alternate furrow application of irrigation water should result in more efficient use of irrigation water since less of the soil volume is wetted during irrigation and more precipitation can be captured and utilized by the crop as compared to every furrow irrigation. At the Scottsbluff site, with a greater mean annual water deficit, alternate furrow irrigation resulted in reduced yield potential and N use efficiency. Results of this study suggest that alternate furrow application of N fertilizer and irrigation water is a viable management practice in central and west-central Nebraska. Alternate furrow application of N and irrigation water may not be as effective in dryer climates where insufficient moisture in the furrow where N is applied may reduce availability of N to the plant. Variable rate N application did not significantly influence grain yield, relative to uniform application. Variability in soil residual nitrate-N was reduced with variable rate application, and variable rate application

resulted in significantly less soil residual nitrate-N at the Scottsbluff location. Objectives 2 and 3: Spatial nitrate-N movement and correlation of spatial N leaching to crop and soil parameters. These objectives, which include the use of a bromide tracer to model nitrate movement, are part of the PhD project of a graduate student working under the direction of Dr. Charles Shapiro and Dr. Gary Hergert at the WCREC in North Platte. The summary of these data are unavailable at the present time pending the completion of the graduate student's dissertation.

## Descriptors

Irrigation management, nitrogen, fertilizers, leaching, water quality management, water use efficiency

## Articles in Refereed Scientific Journals

## Book Chapters

## Dissertations

## Water Resources Research Institute Reports

## Conference Proceedings

Benham, B.L., J. Blumenthal, R.B. Ferguson, G.W. Hergert, W.L. Kranz, C.A. Shapiro, W.B. Stevens and C.D. Yonts. 2000. Crop Response and Nitrogen Availability as a Function of Climate, Variable-Rate Nitrogen Application and Every- and Alternate-Furrow Irrigation. in Proceedings of the 4th Decennial National Irrigation Symposium, November 14-16, 2000, Phoenix, AZ. American Society of Agricultural Engineers. Shapiro, C.A., W.L. Kranz, J. Blumenthal, C.D. Yonts, B.L. Benham, R.B. Ferguson, G.W. Hergert, W.B. Stevens, and W.J. Waltman. 2000. Site-Specific Nitrogen and Irrigation Management Across Nebraska Agro-Ecological Zones in Proceedings of the 5th International Conference on Precision Agriculture, July 16-19, 2000, Minneapolis, MN. American Society of Agronomy.

## Other Publications

Echavaria, F., C.A. Shapiro and G.W. Hergert. 1999. Bromide Movement under Alternate Irrigation and Fertilization. Agronomy Abstracts, pg 345, 91st Annual Meeting, ASA-CSSA-SSSA, Madison, WI. Shapiro, C.A., J.M. Blumenthal, B.L. Benham, R.B. Ferguson, G.W. Hergert, W.L. Kranz, W.B. Stevens and C.D. Yonts. 1999. Site-Specific Nitrogen and Irrigation Management across Nebraska Agro-Ecological Zones. Agronomy Abstracts, pg 319, 91st Annual Meeting, ASA-CSSA-SSSA, Madison, WI.

## Basic Project Information

Basic Project Information	
Category	Data
Title	Herbicide Effects on Water Quality in the Great Plains: Mechanisms of Selective Toxicity in Freshwater Algae
Project Number	C-33
Start Date	09/01/1997

<b>End Date</b>	08/01/1999
<b>Research Category</b>	Water Quality
<b>Focus Category #1</b>	Water Quality
<b>Focus Category #2</b>	Toxic Substances
<b>Focus Category #3</b>	None
<b>Lead Institution</b>	Nebraska Water Resources Center

### Principal Investigators

<b>Principal Investigators</b>			
<b>Name</b>	<b>Title During Project Period</b>	<b>Affiliated Organization</b>	<b>Order</b>
Kyle D. Hoagland	Professor	University of Nebraska, East Campus	01
Blair D. Siegfried	Professor	University of Nebraska, East Campus	02

### Problem and Research Objectives

It has recently been shown that different divisions of freshwater algae and even clones of the same algal species may exhibit differential responses to atrazine exposure. In the agricultural Midwest where even higher order streams such as the Platte River have detectable levels of atrazine virtually year-round, it is clearly important to understand how these toxicants currently affect community structure and biomass production. Because many aquatic systems in North America receive inputs of atrazine and other soluble herbicides, this study addressed a potential problem of significant proportion. The overall goal of this research was to determine the ecotoxicological effects of atrazine on attached algal communities in freshwater ecosystems in the Midwest. The primary objective was to determine the relative tolerance to atrazine exposure in representative species of five major algal Divisions from several streams and rivers throughout the Region. Thus, the principal aim of the study was to provide a much more environmentally realistic assessment of the effects of atrazine, and by implication other commonly occurring herbicides, on surface water quality in the agricultural Midwest. Student Support One Master's student (Christine King)

### Methodology

The proposed project consisted of three major tasks, namely the isolation and culturing of representative algal taxa from five algal Divisions, acute bioassays to determine relative toxicities, and determination of photosynthetic inhibition at the population level. Nine species of freshwater algae, from five algal divisions were exposed to concentrations of 0.01 to 1000 µg/L atrazine. Growth was monitored for a period of two weeks using fluorometric detection of chlorophyll a. Percent inhibition values, relative to controls were calculated.

### Principal Findings and Significance

The optimum time to compare growth rates was day five, when atrazine exposure was sufficient to

exhibit an effect yet nutrients were not limiting. Although low atrazine had a stimulatory effect, selective toxicity was clearly evident, especially at 100 µg/L. Inhibition values relative to control treatments ranging from most to least sensitive were: green algae (40.5 - 75.0%), blue-green algae (26.9 - 33.6%), cryptomonad (15.8%), diatoms (13.0 - 19.4%), and the euglenoid (-3.1%). Cell volumes varied widely, ranging from 2.52 to 3764.4 µm<sup>3</sup>, and the correlation to percent inhibition was low. These results suggest that algal division is a better predictor of algal sensitivity than cell size. The broad range of sensitivities to atrazine among the algae shown here indicates that atrazine in streams and lakes will likely reduce algal diversity and shift species composition. Algae form the base of aquatic food webs, thus inputs of atrazine to surface waters may impact higher trophic levels as well.

## **Descriptors**

Pesticides, atrazine, water quality, algae, streams

## **Articles in Refereed Scientific Journals**

## **Book Chapters**

## **Dissertations**

## **Water Resources Research Institute Reports**

## **Conference Proceedings**

King, C.A., K.D. Hoagland and B.D. Siegfried. 1999. Selective atrazine toxicity in freshwater algae. Society for Environmental Toxicology and Chemistry meetings, Philadelphia, PA. Abstract, p. 301.  
King, C.A., K.D. Hoagland and B.D. Siegfried. 1999. Selective atrazine toxicity in freshwater algae. Seventh Symposium on the Chemistry and Fate of Modern Pesticides, Laurence, KS.

## **Other Publications**

Hoagland, K.D., S. A. Matteen, J.-X. Tang and B.D. Siegfried. (in press) Pesticide effects on diatom communities: differential toxicity of atrazine metabolites. International Diatom Symposium. Nelson, K.J., K.D. Hoagland and B.D. Siegfried. 1999. Chronic effects of atrazine on tolerance of a benthic diatom. *Environmental Toxicology and Chemistry* 18:1038-1045. Carder, J.P. and K.D. Hoagland. 1998. Combined effects of alachlor and atrazine on benthic algal communities in artificial streams. *Environmental Toxicology and Chemistry* 17:1415-1420. Tang, J.-X., B.D. Siegfried and K.D. Hoagland. 1998. Glutathione-s-transferase and in vivo metabolism of atrazine in freshwater algae. *Pesticide Biochemistry and Physiology* 59:155-161. Tang, J.-X., K.D. Hoagland and B.D. Siegfried. 1998. Uptake and biocentration of atrazine by selected freshwater algae. *Environmental Toxicology and Chemistry* 17:1085-1090.

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## **Basic Project Information**

<b>Basic Project Information</b>	
<b>Category</b>	<b>Data</b>
<b>Title</b>	Hydraulic Characterization of the Stream-Aquifer Interface: Theory, Field Implementation, and Practical Ramifications - a Multi-state Proposal
<b>Project Number</b>	C-66
<b>Start Date</b>	09/01/1998
<b>End Date</b>	08/01/2001
<b>Research Category</b>	Climate and Hydrologic Processes
<b>Focus Category #1</b>	Groundwater
<b>Focus Category #2</b>	Methods
<b>Focus Category #3</b>	Water Quantity
<b>Lead Institution</b>	Nebraska Water Resources Center

### Principal Investigators

<b>Principal Investigators</b>			
<b>Name</b>	<b>Title During Project Period</b>	<b>Affiliated Organization</b>	<b>Order</b>
Vitaly Zlotnik	Professor	Univ. of Nebraska City Campus	01
James Butler, Jr.	Professional Staff	University of Kansas	02

### Problem and Research Objectives

Surface-ground water interactions are often a key component of the hydrologic budgets of aquifers and streams. In Nebraska and Kansas, as well as many other areas in the Great Plains and elsewhere in the United States, these interactions have very significant socio-economic and political ramifications. As illustrated by the numerous interstate conflicts that have arisen from disagreements concerning the impact of groundwater pumping on stream flow, there is a critical need to quantify the volumes involved in water exchanges between streams and aquifers. Given the potential magnitude of the financial stakes, it is imperative that this quantification be founded on methodology with a sound scientific basis. A key element of efforts to quantify stream-aquifer interactions is the estimation of the impact of pumping from alluvial aquifers on stream flows. Although several methods for estimation of pumping-induced water transfers have been developed over the last 50 years, these methods are based on mathematical models of hypothetical flow systems that often bear little resemblance to stream-aquifer systems in the Great Plains. Recent work has shown that these simplistic models can introduce significant errors into estimates of the impact of groundwater pumping on stream flows as a result of their neglect of critical aspects of the stream-aquifer interface, specifically the near-stream channel. Clearly, there is a pressing need to develop field and modeling methods that can result in estimates of

pumping-induced water transfers that are based on more realistic representations of the stream-aquifer interface. The development of such methods is the primary purpose of this research. INFORMATION TRANSFER. Results were presented at two international meetings (Congress of International Association of Hydro geologists: Gambling with Groundwater: Physical, Chemical, and Biological Aspects of Aquifer-Stream Relations", Las Vegas, Nevada, Sept. 27-Oct.2, 1998; Joint Congress, Water 99, Brisbane, Australia, July 6-8, 1999), two national meetings (American Geophysical Union, Spring 1999, Boston, Spring 2000, Washington, D.C.). Results were also presented to the state Central Platte state users: Natural Resources District, Nebraska in 1999 and 2000, and at the 17th Annual Water and the Future of Kansas Conference, March 1, 2000, Manhattan, Kansas. The web site was set up in Kansas Geological Survey - [www.kgs.ukans.edu/StreamAq](http://www.kgs.ukans.edu/StreamAq) - for rapid and direct dissemination of information. Downloading of reports and computer program is available on the Internet. The materials were taught at the seminar "Modern Problems of Hydrogeology", Spring 1999, University of Nebraska-Lincoln. STUDENT SUPPORT. Two M.S. students and one Ph.D. student were partially supported from the grant in Geosciences Department, UNL. Total number - 3 students.

## **Methodology**

Methodology includes field and modeling studies at two sites in Nebraska and Kansas. Field studies involve development of networks of observation wells at the selected sites and stream gauging stations. These wells will be used for measurements of head changes invoked by pumping from irrigation wells and varying in time stream stages. In addition, small-scale hydraulic methods for aquifer characterization (borehole flowmeter, multi-level slug test, dipole-flow test) will be used for independent estimation of hydraulic conductivity of the aquifer and stream-aquifer interface zone. Transient head changes will be interpreted in terms of aquifer properties and characteristics of the stream-aquifer interface. New and improved mathematical models of head changes invoked by pumping and stream stage fluctuations will be developed. Based on these solutions, new procedures will be developed for analysis of the head data. The obtained results will be compared with other hydraulic methods used for assessment of aquifer and stream-aquifer interface properties. This study will result in analytical and numerical methods for assessment of stream depletion.

## **Principal Findings and Significance**

Theoretical investigations in this study lead to the development of accurate two-dimensional models of stream depletion and drawdown near the shallow, partially penetrating streams of a finite width. These models explicitly consider conditions of the shallow penetration and low-permeable streambed sediments common to the Great Plains and many other areas of the United States. Three major results include: (1) aquifer response to stream stage fluctuations, (2) stream depletion, and (3) head drawdown under pumping conditions near partially penetrating streams. Results were compared to the previously known models of stream depletion including finite-difference numerical models. It has been shown that the new models offer significant conceptual and quantitative improvement over the previous models. This work has resulted in peer-reviewed publications and conference presentations. Currently, research emphasis shifted towards fields studies. In Nebraska, screening of more than twenty potential sites on Prairie Creek watershed (Platte River tributary) yielded two potential sites with saturated thicknesses of 8 ft and more than 60 ft, respectively. These sites are located on privately owned land and have existing pumping wells (capacities 200 gpm and 1200 gpm). At each site a two-well transect was installed and tested by pumping. It has been established by pumping tests that the drawdown on the opposite side of the stream from the irrigation wells is detectable by the pressure transducers after one-day pumping, and the drawdown is larger at the site with 1200 gpm. Both sites have 4" wells designed for hydraulic testing of the aquifer. Geological conditions and infrastructure at the site near town of Silver Creek near

the Prairie Creek watershed were the final arguments in favor of this site. In the future, research efforts in Nebraska will be concentrated at one site. Network of observation wells has been installed and instrumented with the pressure transducers. Data base on well construction characteristics and topography is being developed. During Spring 2000, the first pumping test with pumping rate 1,200 gpm was performed. Preliminary data indicate that the local drawdown and other test characteristics generally comply with the previously developed theoretical concepts and can be used for characterization of the stream depletion. Weather conditions on the watershed were found to be a significant factor in the dynamics of groundwater-surface water interactions. In Kansas, research efforts are concentrated on the search for the appropriate sites and exploring the potential of the "direct push" methodology. This methodology will replace the conventional drilling for installation of the near-stream piezometers and improve the methodology of the aquifer characterization. Current experience indicates that a combination of drilling and direct push techniques may be the most efficient strategy for site instrumentation and exploration.

## **Descriptors**

Surface-Groundwater Relationships, Groundwater Movement, Streams, Groundwater Hydrology

## **Articles in Refereed Scientific Journals**

Zlotnik, V.A., and Huang, H., 1999, Effect of partial penetration and streambed sediments on aquifer response to stream stage fluctuations, *Ground Water*, 37(4), 599-605. Butler, J.J., Jr., Zlotnik, V.A., and M.-S. Tsou, in review, Drawdown and stream depletion produced by pumping in the vicinity of a partially penetrating stream, *Ground Water*.

## **Book Chapters**

## **Dissertations**

Huang, Huihua, in preparation, "Evaluation of stream-aquifer interactions considering streambed sediments and partial penetration effects", M.S. Thesis, Department of Geosciences, University of Nebraska-Lincoln, Lincoln, Nebraska.

## **Water Resources Research Institute Reports**

## **Conference Proceedings**

Zlotnik, V., Huang, H., and Butler, J.J., Jr., 1999, Evaluation of stream depletion considering finite stream width, shallow penetration, and properties of streambed sediments, in "Proceedings of Joint Congress, Water 99, Brisbane, Australia, July 6-8, 1999", 221-226. Zlotnik, V.A., and Huang, H., 1998, An analytical model of aquifer response to stream stage fluctuations: Effect of partial penetration and streambed sediments, in "Proceedings of XXVIII Congress of International Association of Hydrogeologists: Gambling with Groundwater: Physical, Chemical, and Biological Aspects of Aquifer-Stream Relations", Las Vegas, Nevada, Sept. 27-Oct.2, 1998, ed.: V.Brahana, Y.Eckstein et al., 297-304.

## **Other Publications**

Butler, J.J., Jr., Tsou, M.-S., Zlotnik, V.A., and H. Huang, Drawdown and stream depletion produced by pumping in the vicinity of a finite-width stream of shallow penetration (abstract), *EOS, Transactions*,

American Geophysical Union 1999 Spring Meeting, v. 80, no. 17S, p. S137, 1999. Butler, J.J., Jr., Tsou, M.-S., Zlotnik, V.A., and H. Huang, Drawdown and stream depletion produced by pumping in the vicinity of a finite-width stream of shallow penetration, Kansas Geological Survey Open-File Report 99-16, 22 pp., 1999. Butler, J.J., Jr., and M.-S. Tsou, The StrpStrm model for calculation of pumping-induced drawdown and stream depletion (version 1.0), Kansas Geological Survey Computer Series Report 99-1, 1999 (executable code and sample input/output files available at [www.kgs.ukans.edu/StreamAq](http://www.kgs.ukans.edu/StreamAq)). Butler, J.J., Jr., and M.-S. Tsou. 2000. Mathematical derivation of drawdown and stream depletion produced by pumping in the vicinity of a finite-width stream of shallow penetration. Kansas Geological Survey Open-File Rept. 2000-8 (also available at [www.kgs.ukans.edu/StreamAq](http://www.kgs.ukans.edu/StreamAq)). Butler, J.J., Jr., and M.-S. Tsou, 2000, Stream-Aquifer Interactions - A new model for prediction of pumping-induced drawdown and stream depletion, 17th Annual Water and the Future of Kansas Conference, March 1, 2000, Manhattan, Kansas. Butler, J.J., Jr., and M.-S. Tsou, 2000, Aquifer response to stream-stage fluctuations in a partially penetrating stream (abstract), Spring 2000 Meeting of the American Geophysical Union, May 31, 2000, Washington, D.C.

### Basic Project Information

Basic Project Information	
Category	Data
<b>Title</b>	Determination of Aquifer and Aquitard Hydraulic Properties and Their Role in Streamflow Depletion
<b>Project Number</b>	C-88
<b>Start Date</b>	09/01/1998
<b>End Date</b>	02/28/2001
<b>Research Category</b>	Ground-water Flow and Transport
<b>Focus Category #1</b>	Groundwater
<b>Focus Category #2</b>	None
<b>Focus Category #3</b>	None
<b>Lead Institution</b>	Nebraska Water Resources Center

### Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
Xun-Hong Chen	Associate Professor	Univ. of Nebraska City Campus	01
James Goeke	Professor	Univ. of Nebraska City Campus	02
Robert F. Diffendal, Jr.	Professor	Univ. of Nebraska City Campus	03

### Problem and Research Objectives

Problem: Streamflow depletion caused by groundwater withdrawal. Objectives: 1) to apply new methodologies for collecting high quality pumping and recovery test data and for determination of reliable hydraulic properties of aquifers and aquitards; and 2) to analyze the role of aquifer and aquitard hydraulic conductivity in streamflow depletion due to groundwater pumpage. INFORMATION TRANSFER PROGRAM Central Platte Natural Resource District in Nebraska participated in the aquifer tests conducted in the Platte River valley. Preliminary results of aquifer tests were presented to a group of people from State and local agencies in Nebraska who had been looking for aquifer hydraulic properties for their groundwater modeling project along the Platte River valley to analyze stream-aquifer interactions. STUDENT SUPPORT A graduate student was hired to develop computer programs for the analysis of well hydraulics and the design of monitoring wells.

## **Methodology**

Design and construction of monitoring wells in alluvial aquifers, which connects to streams; Long-term groundwater level monitoring for determination of recharge and the responses of aquifer to groundwater pumping; Conducting pumping tests; Determination of aquifer and aquitard hydraulic properties; Analysis of the role of aquifer and aquitard hydraulic properties in streamflow depletion using numerical modeling analysis.

## **Principal Findings and Significance**

The research was in its second year and will continue to 2002. Between March 1, 1999 to February 28, 2000, we examined the log records of test holes and irrigation wells in the Platte River valley, Nebraska and analyzed regional hydrostratigraphic features. We identified two study sites in the Platte River valley, one near Shelton and the other near Woodriver, Nebraska. The Shelton site contains aquifer and aquitard units and the Woodriver site contains an alluvial aquifer. Twelve monitoring wells were constructed at each study site. Monitoring wells were constructed in the shallow and deep aquifer units and the aquitard in the Shelton site. All 12 monitoring wells were constructed in the same aquifer unit in the Woodriver site. The depth of the monitoring wells range from 30 to 110 feet. During well construction, drilling cuttings were collected as samples of aquifer and aquitard materials and lithology was recorded for each well bore-hole. Single-point resistance logs were also made to examine the variation in lithology of the aquifer and aquitard systems. Aquifer tests were conducted at both sites. At each test, pumping lasted about 24 hours followed by a 24-hour recovery test. At the Shelton site, a deep and a shallow well were used for separate pumping tests. Changes in groundwater levels during pumping and recovery tests were recorded using pressure transducers. In addition to aquifer tests, two transducers remain at each site to monitoring long-term variations in groundwater levels. A method was developed to measure in-situ hydraulic conductivity and anisotropy of stream bed.

## **Descriptors**

Aquifer parameters, Conjunctive use, Groundwater modeling, Surface-groundwater Relationships, Well hydraulics

## **Articles in Refereed Scientific Journals**

Chen, X. H., 2000. Measurement of streambed hydraulic conductivity and its anisotropy. *Environmental Geology* (in press). Chen, X. H., and Y. Yin, 2000. Streamflow depletion: modeling of reduced baseflow and induced stream infiltration from seasonally pumping wells. *Journal of American Water*

Resources Association (in press). Chen, X. H., 2000. Can storage coefficient be neglected in the estimation of unconfined aquifer parameters? Environmental Geosciences, (in press).

**Book Chapters**

**Dissertations**

**Water Resources Research Institute Reports**

**Conference Proceedings**

Chen, X.-H. and Y. Yin, 1999. Modeling of Stream-aquifer interactions in the Republican River valley, Nebraska. Abstract for the 19th Annual Hydrology Days, August 16-20, 1999. Colorado State University, Fort Collins, Colorado. Chen, X. H. 1999 (invited). Using three-dimensional mathematical model for the analysis of stream-aquifer interactions. Symposium on the Hydrological Sciences in China: New Problems, New Technology, and New Methods in the 21st Century, Dec. 21-23, 1999, Hong Kong.

**Other Publications**

**Basic Project Information**

<b>Basic Project Information</b>	
<b>Category</b>	<b>Data</b>
<b>Title</b>	AN ASSESSMENT OF FACTORS INDICATING WELL VULNERABILITY IN NEBRASKA
<b>Project Number</b>	C24
<b>Start Date</b>	03/01/1999
<b>End Date</b>	02/28/2001
<b>Research Category</b>	Engineering
<b>Focus Category #1</b>	Groundwater
<b>Focus Category #2</b>	Water Quality
<b>Focus Category #3</b>	Water Supply
<b>Lead Institution</b>	Nebraska Water Resources Center

**Principal Investigators**

<b>Principal Investigators</b>			
<b>Name</b>	<b>Title During Project Period</b>	<b>Affiliated Organization</b>	<b>Order</b>
Bruce I. Dvorak	Associate Professor	Univ. of Nebraska City Campus	01
Mark Bakker	Assistant Professor	Univ. of Nebraska City Campus	02

## **Problem and Research Objectives**

Most Nebraska communities rely on groundwater as a source of drinking water. Until recently, it has been assumed that groundwater is free of pathogens due to the natural filtration provided by the soil. Data from some other states seems to indicate that groundwater in some aquifers, notably those in karst formations, may be vulnerable to contamination and may contain pathogens. Nebraska does not have karst geology or other formations which would seem to be vulnerable to contamination, but, the presence of human pathogens such as viruses in well waters has not been studied sufficiently. To assess the vulnerability of Nebraska drinking water wells to pathogen contamination, a study of well integrity factors or 'well vulnerability' is being performed. In this study, only small (<10,000 population) Nebraska communities which do not currently disinfect or treat their drinking water are being studied. There are 608 small community water systems in Nebraska, most of which do not currently disinfect or treat their drinking water. In addition there are 719 non-community water systems. The overall goal of the proposed research is to determine the relationship between the microbial quality of groundwater and the well, water system, and surrounding environment. In this project a total of eight small community wells are being studied; the wells selected for study are believed to be among the most vulnerable to microbial contamination in Nebraska. This is a descriptive study focused on understanding how vulnerability to microbial contamination is the "most vulnerable" community wells in the state. For these eight wells, the following information is being collected: ? General water quality data. ? Microbial and Viral testing of the well water quality (five times during a eight month period). ? Perform small modeling studies to determine travel times from nearby contamination sources. ? Summarize data and methodology approach, as a basis for future research projects. It is anticipated that future projects will be initiated using other funding sources. The work described in this proposal is considered to be "Phase I" of a larger course of study. A second, larger study will be needed to provide sufficient data for statistical analysis. Other funding opportunities will be pursued for "Phase II" of the research. Training potential This project represents an excellent opportunity for students with a technical background to expand their understanding of social and regulatory issues associated with the drinking water industry. In contrast to many research projects which provide students with an in-depth knowledge of an obscure technical process or model, this project will require students to work with regulatory and community water system personnel, and to integrate their technical background into a broader experience with small communities. At the same time, the required data collection and analysis, and the laboratory work associated with the water analyses dictate that the student maintain and further develop strong technical and analytical skills. Two students will be employed on this project, a graduate research assistant (Ms. Julie Fisher) and an under-graduate research assistant (Ms. Anne Stephens). Ms. Fisher is a graduate student in the Environmental Engineering program and Ms. Stephens is an undergraduate in Civil Engineering. This project will be the basis of a Master of Science thesis for Ms. Fisher. Ms. Fisher's salary is paid for through a project match by the UNL Center for Infrastructure Research.

## **Methodology**

Methodology: Selection of Community Wells: The community wells chosen to participate in the virus study were selected based on several criteria. The first criteria considered was the location of the well.

All the wells that were considered were located within the town. Hence, the wells have a higher possibility of (human) virus contamination from leaky sewers, sewer connections or septic systems. The next criteria considered were the depth of the wells. All the selected communities had to have shallow wells; for Nebraska communities a relatively shallow well is one less than 200 feet (which is not particularly shallow). Then, the communities' setback distances from possible sources of contamination were also used as a criterion. If the community had a violation or was close to the setback distance they were considered high probability for virus contamination. The last criteria used were the concentration of Nitrate/Nitrite and the total coliform bacteria. High Nitrate/Nitrite and total coliform bacteria are considered as possible indicators for virus. Thus communities with high Nitrate/Nitrite and total coliform bacteria were considered to have a high probability for virus contamination. Overall, the communities selected were considered the worst case wells within Nebraska. The selected communities can be seen in the table below. Table of Community Wells Being Sampled. Rank City NDHS Well Reg # Depth (ft) 1-6 Prague 61-1 137 1-6 Bradshaw 71-1 147 1-6 Hampton 84-1 214 1-6 Platt Center 37-1 100 1-6 Waco 72-1 276 1-6 Bellwood 82-1 128 7 Valparaiso 85-1 126 8 Staplehurst 82-1 116 9 Goehner 87-1 230 10 Benedict 95-1 240

Water Sampling Water sampling and analysis will generally follow procedures in Standard Methods for the Examination of Water and Wastewater (1995). Virus analyses are not included in Standard Methods, but will be conducted by the University of Nebraska Medical Center Virology laboratory certified by the US EPA to conduct virus analyses. Other water quality parameters that are being evaluated include: metal concentrations (calcium, magnesium, iron, and manganese) by atomic adsorption spectrophotometry, common anions (chloride, nitrate, phosphate, and sulfate), alkalinity, pH, dissolved oxygen, UV-254, and total coliform. These parameters are being measured in samples taken at the point of collection for the virus samples. Additional total coliform samples are being measured by the Nebraska Department of Health and Human Services Regulation and Licensure, as part of the routine regulatory activities for each community. With the exception of virus and coliform testing, all water analyses is being conducted in the Environmental Engineering Laboratory in Walter Scott Engineering Center, located at the University of Nebraska. Equipment that is available for use on this project includes: atomic adsorption spectrophotometer, ion chromatograph, TOC analyzer, UV-vis spectrophotometer, pH meters, dissolved oxygen meters, and a variety of routine glassware and small equipment. Groundwater Modeling The groundwater modeling will be conducted with the computer program WhAEM (Well Head Analytic Element Model), distributed by the Environmental Protection Agency (Bakker, 1994). This program is currently used by the Nebraska Department of Environmental Quality for the construction of well head protection areas for all municipal supply wells in the state of Nebraska. Shortest travel times from the surface to the well screen will be estimated with the program Gflow, which allows for the exact specification of the well screen in the aquifer (Haitjema, 1995).

## **Principal Findings and Significance**

This project currently is less than half way to completion. At the moment there are no preliminary or final findings. This project will be of national interest and benefit to the drinking water industry. Research on the presence of viruses in groundwater is limited, and has generally not focused on specific geological formations, but instead has tended to be 'survey' research which is of little value in understanding the complexities of groundwater systems (e.g., Abbaszadegan et al., 1998). Due to the lack of focus of the available research, very little attempt has been made to correlate the presence of viruses with specific features of the water system or well, or with controllable environmental factors (such as the proximity of waste treatment facilities.) Without sound scientific data that can be used to characterize water systems which may be at risk, public health authorities will be forced to implement very conservative groundwater disinfection regulations that will require disinfection (and the associated capital and operation and maintenance costs) in communities where disinfection is not truly needed to

protect public health. The current project will also provide valuable information for the State of Nebraska. Information is needed for researchers studying small community planning, water resources, groundwater, water treatment, and waste treatment. The current project is nearing a mid-point where actual data will be available. The main finding to this point is that municipal water wells in Nebraska's small communities have been constructed and located in locations that appear to make them less vulnerable to microbial contamination than wells in many other states.

### **Descriptors**

Viruses Groundwater Modeling Groundwater Movement Groundwater Quality Water Quality Monitoring

### **Articles in Refereed Scientific Journals**

Not Applicable at this time

### **Book Chapters**

Not Applicable at this time

### **Dissertations**

Not Applicable at this time

### **Water Resources Research Institute Reports**

Not Applicable at this time

### **Conference Proceedings**

Not Applicable at this time

### **Other Publications**

Fisher, J. (2000) "An Assessment of Well Vulnerability to Viruses in Nebraska", presentation at the Annual Conference of the Nebraska Water Environment Federation in Kearney, NE, Nov. 3, 2000.

### **Basic Project Information**

<b>Basic Project Information</b>	
<b>Category</b>	<b>Data</b>
<b>Title</b>	Evaluating the Effects of Pesticide Mixtures to Freshwater Algae
<b>Project Number</b>	C25
<b>Start Date</b>	03/01/1999
<b>End Date</b>	02/01/2001
<b>Research Category</b>	Water Quality
<b>Focus Category #1</b>	Toxic Substances

<b>Focus Category #2</b>	Surface Water
<b>Focus Category #3</b>	Water Quality
<b>Lead Institution</b>	Nebraska Water Resources Center

### Principal Investigators

<b>Principal Investigators</b>			
<b>Name</b>	<b>Title During Project Period</b>	<b>Affiliated Organization</b>	<b>Order</b>
Blair D. Siegfried	Professor	University of Nebraska, East Campus	01
Kyle D. Hoagland	Professor	University of Nebraska, East Campus	02

### Problem and Research Objectives

Evaluation and protection of water quality requires an understanding of the effects of contaminants on aquatic biota. While contaminants usually occur as a mixture of chemicals in surface waters, very few studies have examined the effects of such mixtures. Presently, all guidelines and standards for allowable or "safe" amounts of pesticides in surface waters are based on single toxicant studies. Therefore, to assess actual environmental effects of chemicals on aquatic ecosystems, it is necessary to begin evaluating mixtures of toxicants. Recent reviews of pesticide toxicity to aquatic organisms generally conclude that concentrations found in aquatic systems are not ecologically harmful (e.g., Solomon et al. 1996). However, the possibility that synergistic interactions can occur between agricultural chemicals, such as herbicides and insecticides, have not been thoroughly examined. To date, most investigations of pesticide toxicity to freshwater organisms involve single-species bioassays involving a single compound. Herbicides such as atrazine and alachlor are commonly used throughout the Midwest to control a variety of weed species and have been identified as relatively common contaminants of aquatic systems. Insecticides such as, chlorpyrifos, and cyfluthrin are widely used to control soil arthropods and are commonly applied during periods when herbicides are also in common use. Although many of these compounds have been shown to be relatively non-toxic at ecologically relevant concentrations, the interaction of these compounds has not been examined. Recently, it has been shown that aquatic midge larvae (*Chironomus tentans*) exposed to atrazine and several organophosphate insecticides exhibit greater than additive toxicity (Pape-Lindstrom and Lydy 1997). This study suggests that the joint action seen between atrazine and these compounds may be due to atrazine induction of detoxification enzymes involved in biotransformation of the insecticides. The synergistic effect observed in this study indicates that oxidative processes involved with activation of the OP molecule may be enhanced in the atrazine exposed midges. Since pesticides such as herbicides and insecticides are so widely used in Midwestern agricultural systems, there is a likelihood that combinations of these pesticides occur in aquatic environments. It is therefore important that interactions between compounds be examined for potential synergistic effects in aquatic organisms such as freshwater algae. Algae are the most important primary producers in aquatic systems and account for nearly the same percentage of total global net primary production of carbon annually as do cultivated plants. In addition, algae represent the basal component of aquatic food webs, since they are consumed by a variety of invertebrates or directly by fish, both of which are consumed by other fish species. Algae possess a complex system of detoxification enzymes such as glutathione-S-transferases responsible for metabolism (Tang et al. 1998) of both toxic and non-toxic xenobiotics. Therefore, compounds that are relatively non-toxic may act as inducers or inhibitors of these metabolic enzymes which could potentially affect an organism's ability to detoxify other more toxic chemicals during simultaneous exposure. The present research proposal is designed to measure the joint action of selected pesticides with different modes of action in freshwater algae. Various binary

combinations of pesticides will be tested against representative algal species common to Midwestern aquatic environments. Additionally, we will examine the effect of sublethal exposure of selected species on the activity of detoxification enzymes important to pesticide metabolism and potentially to the mechanism of joint pesticide toxicity.

## Methodology

**ALGAL BIOASSAYS** The identification of dominant algal taxa from Midwestern lakes and streams already has received considerable attention (e.g., Rosowski et al. 1979), and for the purposes of this study, selected cultures will be obtained from biological suppliers, such as Carolina Biological Supply or established culture collections (e.g., Loras College Diatom Collection). Standard soil-water extract will be used for all cultures (Hoshaw and Rosowski 1973), because it provides a well-buffered, nutrient-rich growth medium suitable for a wide range of taxa from varied environments. We have used similar techniques to culture and bioassay six different algal species and LC<sub>50</sub> values for atrazine have already been established (Tang et al. 1997). Cultures will be maintained in 250 mL flasks on a 12:12 light:dark cycle (20 W cool white fluorescent bulbs), to produce synchronous growth. Cultures will be grown in environmental chambers (Percival Model I-35L) at temperatures that simulate ambient conditions. All algal toxicity (algal growth in the presence of pesticide) experiments will be conducted using 18 x 150 mm test tubes with plastic caps (Tang et al. 1997). Binary combinations of each of the following compounds; atrazine, alachlor, chlorpyrifos, and tefluthrin will be tested using the modified toxic unit approach to model joint toxicity (Pape-Lindstrom and Lydy 1997, Marking 1985). Technical grade pesticides (>95% purity) will be obtained from commercial vendors (e.g., Chem Service Inc., West Chester, PA). Stock solutions of pesticides in acetone will be added to sterilized culture medium (1 L). Control treatments will consist of culture medium only with a similar volume of acetone. Treated cultures will be monitored 24 h, 3 d, 7 d, 10 d, and 14 d for cell densities. Growth rates will be calculated in cell doubling per day based on changes in cell densities between time intervals. Cell densities will be monitored using a Palmer counting chamber to confirm fluorometer readings obtained with a Turner fluorometer. If synergistic effects on growth rates are found, productivity measurement will be made using standard <sup>14</sup>C-upake methodology (Lind 1985). This will allow us to better extrapolate our findings to natural ecosystems.

**GLUTATHIONE-S-TRANSFERASE ASSAYS** Glutathion-S-transferase activity from the algal species used in previous bioassays will be measured to determine if sublethal exposure to pesticides results in significant induction and/or inhibition of activity using previously established techniques (Tang et al. 1998). Representative algal species will be cultured in growth media containing sublethal concentrations of each pesticide for at least 7-14 days prior to activity determinations. Cells from these cultures (9-10 day old) will be harvested by centrifugation at 4,000 g. The cell pellet will be homogenized in the presence of glass beads to insure that cell contents are released. The homogenate will then be centrifuged at 10,000 g for 20 min at 4°C and the resulting pellet discarded. The supernatant is used as a source of cell-free extract for use in enzyme activity assays. Aliquots of the extract are stored at -80°C until use. Protein concentration will be determined with the Bio-Rad (Hercules, CA) DC protein assay using bovine serum albumin as the standard according to manufacturer's instructions and adjusted to 0.1 mg/ml for all samples. GST assays will be performed according to a method modified from Grant et al. (1989) using a microtiter plate reader (Bio-Tek Instruments, Winooski, VT) which measures absorbance in all 96 wells of a microtiter plate simultaneously. GST activity will be measured with 2-chloro-3,4-dinitrobenzene (CDNB) as the substrate and reduced glutathione (GSH) as the cofactor. CDNB (30 mM) is dissolved in anhydrous ethanol, and GSH (12.5 mM) is prepared fresh daily in sodium phosphate buffer (0.01 M, pH 7.6). The reaction mixture (250 µl) consisted of GSH (5 mM) and 4 µg soluble protein in 0.01 M sodium phosphate buffer (pH 7.6). The reaction is initiated with 10 µl of 30 mM CDNB in ethanol (final concentration = 1.2 mM). The microtiter plate is immediately placed in the reader, and the change in

absorbance at 340 nm is monitored for 5 min. Slopes (i.e. rate of changes in absorbance versus time) are automatically calculated by the software program (Kineticalc) provided with the instrument. The rate of non-enzymatic conjugation will be determined from the same reaction mixture in the absence of enzyme extract.

## **Principal Findings and Significance**

During the first 10 months of this project the following tasks have been accomplished: (1) a very promising graduate research assistant (M.S. level) was recruited to conduct the research, (2) clonal cultures of three algal divisions are now in defined medium (diatoms, green algae, blue-green algae), (3) standard growth curves for each taxon have been determined under control conditions, prior to herbicide exposure, and (4) acute bioassays have been initiated for two of the species with the herbicide alachlor. EC50 values obtained for alachlor will allow experimental design for testing binary interactions of pesticide mixtures. For compounds such as atrazine, good dose-response curves already exist so that concentration ranges can be determined. Algae form the base of aquatic food webs, thus inputs of pesticide mixtures to surface waters may impact higher trophic levels as well.

## **Descriptors**

herbicides, pesticide interactions, water quality, algae, streams

## **Articles in Refereed Scientific Journals**

## **Book Chapters**

## **Dissertations**

## **Water Resources Research Institute Reports**

## **Conference Proceedings**

## **Other Publications**

Hoagland, K.D., S. A. Matteen, J.-X. Tang and B.D. Siegfried. (in press) Pesticide effects on diatom communities: differential toxicity of atrazine metabolites. International Diatom Symposium. Nelson, K.J., K.D. Hoagland and B.D. Siegfried. 1999. Chronic effects of atrazine on tolerance of a benthic diatom. *Environmental Toxicology and Chemistry* 18:1038-1045. Carder, J.P. and K.D. Hoagland. 1998. Combined effects of alachlor and atrazine on benthic algal communities in artificial streams. *Environmental Toxicology and Chemistry* 17:1415-1420. Tang, J.-X., B.D. Siegfried and K.D. Hoagland. 1998. Glutathione-s-transferase and in vivo metabolism of atrazine in freshwater algae. *Pesticide Biochemistry and Physiology* 59:155-161. Tang, J.-X., K.D. Hoagland and B.D. Siegfried. 1998. Uptake and bioconcentration of atrazine by selected freshwater algae. *Environmental Toxicology and Chemistry* 17:1085-1090. Tang, J., K.D. Hoagland, and B.D. Siegfried. 1997. Differential toxicity of atrazine to selected freshwater algae. *Bull. Env. Contam. Toxicol.* 59: 631-637.

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## Basic Project Information

Basic Project Information	
Category	Data
<b>Title</b>	A Test of Permeable Zero-Valent Iron Barriers for In-Situ Containment and Remediation of Pesticide Contamination in Unsaturated Soils
<b>Project Number</b>	C34
<b>Start Date</b>	03/01/1999
<b>End Date</b>	02/28/2000
<b>Research Category</b>	Water Quality
<b>Focus Category #1</b>	Toxic Substances
<b>Focus Category #2</b>	Solute Transport
<b>Focus Category #3</b>	Water Quality
<b>Lead Institution</b>	University of Nebraska, East Campus

## Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
Steven D. Comfort	Associate Professor	University of Nebraska, East Campus	01
Patrick J. Shea	Professor	University of Nebraska, East Campus	02

## Problem and Research Objectives

Problem and Focus A critical need in Nebraska, the Midwest and nationwide is the development of cost-effective and environmentally benign technologies for remediating pesticide-contaminated soils. Each year, leaking tanks, pesticide spills, and inadvertent discharges of agrochemicals lead to a growing number of pesticide-contaminated sites in Nebraska. These point sources of contamination are usually responsible for the highest pesticide concentrations found in ground and surface water throughout the state. It has been estimated that ground water contamination from 32 different pesticides in 12 different U.S. states can be attributed to point sources (Goodrich et al., 1991). For example, a midwest study in Wisconsin found that in 240 wells monitored for metolachlor, all water samples with a concentration greater than 1 ug/L could be related to a known or suspected point source. Identifying and remediating point-sources of pesticide contamination is a major undertaking. The Nebraska Departments of Agriculture and Environmental Quality continue to identify several pesticide-contaminated sites and are in need of alternative means of remediating pesticide spill sites. Presently in Nebraska, pesticide spills to land are often handled in one of two ways. The contaminated soil is excavated and shipped to a certified landfill or the contaminated soil is diluted with clean soil and reapplied to farmland at labeled rates.

Neither approach treats the soil on-site and both are costly and often labor-intensive. Given the success iron walls have had in remediating contaminant plumes in groundwater (Wilson, 1995), this same concept may be applicable to treating soil and contaminant solutes as they move downward in unsaturated soils. In practice, contaminated soils, such as those present at small pesticide-contaminated sites, would be removed and a layer of Fe(0) or a sand-Fe(0) mixture added to the bottom of the excavation pit. The contaminated soil, or partially treated contaminated soil, would be replaced and natural leaching and attenuation allowed to occur. Theoretically, as the contaminant desorbs from the soil matrix and migrates through the Fe layer, it would be transformed and possibly mineralized through subsequent biodegradation. Our project focuses on the development of an alternative approach for remediating point and nonpoint sources of pesticide contamination in soil and water by employing zerovalent iron [Fe(0)] and permeable Fe(0) barriers. Objectives 1. Determine the capacity of Fe(0) to remediate pesticide-contaminated soil and leachate during unsaturated transport. 2. Quantify the extent of pesticide degradation in Fe(0)-treated soil and in a Fe(0) barrier system. 3. Determine if pesticide degradation products in Fe(0)-treated soil and via transport through the Fe(0)-barriers are biodegradable. Reference Goodrich, J.A., B.W. Jr. Lykins, and R.M. Clark. 1991. Drinking water from agriculturally contaminated groundwater. *J. Environ. Qual.* 20:707-717.

## Methodology

**Destructive Capacity of the Fe(0) Barrier.** Miscible displacement experiments are being performed with 20-cm soil columns attached to vacuum chambers. Treatments include soil columns with various Fe treatments. Pesticide degradation during transport is quantified by controlling the contaminant flux rate through the columns under unsaturated flow. Pore water velocities are adjusted to vary the resident times of the contaminant in the column. By controlling the pore water velocity of the contaminant pulse and using tritiated water as a tracer for soil water movement, the residence time of the contaminant (pesticide) in the soil or Fe barrier system can be estimated and used to determine and validate relative degradation rate. In developing a successful Fe(0) barrier system, several questions need to be addressed: 1. How thick of an iron barrier is needed and how long can it be expected to last? 2. What hydraulic properties should the Fe(0) barrier have? 3. Is there an advantage to mixing surface soil with the Fe(0) barrier as a means of having a more active microbial population? 4. How much of the pesticide will be sorbed to the barrier versus that which is transformed? 5. How biodegradable will the Fe(0)-mediated transformation products be in the subsoil? 6. Will plugging become a problem with time? 7. Can various inorganic or organic amendments (e.g., pH and/or redox modifiers, carbon sources) be blended with the Fe(0) to improve destruction efficiency? **Quantification of Pesticide Degradation.** Degradation of the selected pesticides in Fe(0)-treated soil and in the iron barrier column system is being determined by measuring the loss of parent compound, and by functional group (i.e., chloride) and carbon ( $^{14}\text{C}$ -labeled) mass balance. To support the transport experiments, batch sorption and incubation experiments are conducted to determine the extent of pesticide adsorption (using  $^{14}\text{C}$ -labeled compounds) and degradation occurring Fe(0)-treated soil and in the pesticide-iron barrier system. These experiments follow procedures developed in our laboratories (Comfort et al., 1995; Singh et al., 1998a, 1998b). Concentrations of pesticides and their degradation products in the column effluent and soil are determined using HPLC, GC and GC/MS methods previously developed in our laboratories or by other researchers (Eykholt and Davenport, 1998; Monson et al., 1998; Potter and Carpenter, 1998). Chloride release and Fe(II)/Fe(III) speciation in the system is monitored using ion chromatography and spectrophotometric techniques. **Biodegradability of Fe(0) Treatment Products.** The biodegradability of Fe(0)-treated soil is determined by monitoring  $^{14}\text{CO}_2$  release during incubation of soil containing  $^{14}\text{C}$ -labeled pesticides (Singh et al., 1998a, 1998b). To determine if transformations occurring in the iron barrier result in compounds that are more biodegradable, we combine and homogenize  $^{14}\text{C}$  fractions collected from the bottom of the iron

treatment columns following the transport experiments. This solution is then added to bioreactors where cumulative  $^{14}\text{CO}_2$  was monitored with time (Singh et al., 1998c). Column effluent and soils are analyzed by HPLC, GC and GC/MS to determine the presence of degradation intermediates and end-products. References Comfort, S.D., P.J. Shea, L. Hundal, Z. Li, B.L. Woodbury, J.L. Martin, and W.L. Powers. 1995. TNT transport and fate in contaminated soil. *J. Environ. Qual.* 24: 1174-1182. Eykholt, G.R., and D.T. Davenport. 1998. Dechlorination of the chloroacetanilide herbicides alachlor and metolachlor by iron metal. *Environ. Sci. Technol.* 32:1482-1487. Monson, S.J., L. Ma, D.A. Cassada, and R.F. Spalding. 1998. Confirmation and method development for dechlorinated atrazine from reductive dehalogenation of atrazine with Fe<sup>0</sup>. *Anal. Chimica Acta* 19041:1-8. Potter, T.L., and T.L. Carpenter. 1998. Occurrence of alachlor environmental degradation products in groundwater. *Environ. Sci. Technol.* 29:1557-1563. Singh, J., S.D. Comfort, L.S. Hundal, and P.J. Shea. 1998a. Long-term RDX sorption and fate in soil. *J. Environ. Qual.* 27:572-577 Singh, J., P.J. Shea, L.S. Hundal, S.D. Comfort, T.C. Zhang, and D.S. Hage. 1998b. Iron-enhanced remediation of water and soil containing atrazine. *Weed Sci.* 46:381-388. Singh, J., S.D. Comfort, and P.J. Shea. 1998c. Remediating RDX-contaminated water and soil using zero-valent iron. *J. Environ. Qual.* 27:1240-1245.

## Principal Findings and Significance

Field Demonstration - Soil Treatment with Fe(0). A half-acre bentonite-lined lagoon was constructed in 1979 at a farm cooperative in southwestern Nebraska. The original purpose of the lagoon was to receive and contain potentially contaminated storm runoff and other excess wastewater. In 1995, an accidental release of metolachlor from a storage tank resulted in 755 gallons of unrecovered product, some of which ran into the sump that drains into the lagoon. The spill resulted in approximately 1000 cu yd of contaminated soil that was excavated from the lagoon and held for remedial treatment. The targeted contaminant was metolachlor, which was present at initial concentrations >1400 mg/kg. The soil also contained atrazine, alachlor, pendimethalin, and chlorpyrifos at concentrations exceeding 250, 90, 90, and 25 mg/kg. Due to the high concentration, natural attenuation would not proceed rapidly enough to significantly reduce the soil contamination and thus the soil represented a sustained point source of ground water contamination. In the summer of 1999, we conducted a field-scale demonstration project in which the contaminated soil was placed in windrows and amended with various treatments involving zerovalent iron. Following treatment, acetonitrile-extractable metolachlor concentrations rapidly decreased, and up to 95% destruction was achieved within 24 h. By 90 d, concentrations of metolachlor, atrazine, alachlor, pendimethalin, and chlorpyrifos were decreased by up to 99, 70, 99, 90, and 96%. Batch Experiments with Metolachlor. Batch experiments were conducted using Fe(0) - metolachlor suspensions to determine destruction kinetics and degradation products. By adding small amounts of aluminan sulfate [ $\text{Al}_2(\text{SO}_4)_3$ ] to annealed iron, we found metolachlor destruction rates were significantly enhanced and stoichiometric recovery of chloride was observed. By varying the  $\text{Al}_2(\text{SO}_4)_3$  concentration and holding the mass of Fe(0) constant, we found that the optimum percentage of  $\text{Al}_2(\text{SO}_4)_3$  needed was between one and five percent of the Fe(0) weight. Adding  $\text{Al}_2(\text{SO}_4)_3$  resulted in a high iron concentration in the aqueous system. Additional experiments indicated that metolachlor degradation was not promoted by aluminum oxide ( $\text{Al}_2\text{O}_3$ ) or aluminum hydroxide [ $\text{Al}(\text{OH})_3$ ]. The relative effect of catalysts on metolachlor degradation by Fe(0) in batch experiments was:  $\text{Al}_2(\text{SO}_4)_3 > \text{AlCl}_3 > \text{FeSO}_4 > \text{Fe}_2(\text{SO}_4)_3$ . Adding  $\text{FeSO}_4$  increased Fe(II) concentration in solution and enhanced metolachlor degradation. The same results were observed in metolachlor-soil slurries. Solution pH affected metolachlor degradation and experiments were conducted using an Eh-pH Stat to control pH. In the absence of soil, pH 5 was most effective for metolachlor degradation using annealed (heat-treated under low oxygen) iron and metolachlor was completely degraded within 6 h. A solution pH of 3 was most effective for treatment with unannealed iron in solution and in a metolachlor-soil slurry. UV spectrum and GC/MS analysis verified that the iron

treatment resulted in dechlorination of metolachlor, and subsequent experiments indicated that the dechlorinated product was about five-fold more biodegradable than metolachlor during a 90-d incubation. Permeable Iron Barrier. Although treatment with Fe(0) greatly reduced pesticide concentrations in soil at the Nebraska field site, the potential for leaching remained. To counteract this potential problem, we proposed placing a protective permeable iron barrier at the bottom of the excavated pit at the Nebraska field site before returning the treated soil. Laboratory experiments were conducted to determine the effectiveness of a permeable iron barrier to degrade residual metolachlor in leachate from soil. Transport experiments were conducted using 20-cm (5-cm diam.) columns, with and without iron barriers [Fe(0) - sand mixtures, amended with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>]. The columns were attached to vacuum chambers and run under constant matrix potential (-20 kPa) and soil-water (Darcy) flux (2 cm/d). Initial experiments used a continuous <sup>14</sup>C-labeled metolachlor pulse (1.45 mM), with tritiated water as the tracer, in columns containing 50% (w/w) Fe(0) - sand. Total <sup>14</sup>C and metolachlor were measured in effluent fractions using liquid scintillation counting (LSC) and high performance liquid chromatography (HPLC) with radioisotope detection. Break-through curves indicated complete destruction of <sup>14</sup>C-metolachlor in columns containing the sand/iron mix. Transport experiments using a 25% (w/w) Fe(0) - sand barrier demonstrated the effectiveness of adding Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> to the Fe(0) - sand mixture and the dechlorinated product was the primary degradate in the leachate. Subsequent transport experiments using untreated metolachlor-contaminated soil from the Nebraska field site indicated that the iron barrier was effective in decreasing metolachlor concentration in the leachate by >50% compared to the untreated contaminated soil, although breakthrough concentrations remained unacceptably high. Conducting similar experiments with Fe(0) - treated soils (42 d after treatment) revealed that combining soil treatment with the iron barrier significantly reduced the metolachlor concentration in the leachate. It is noteworthy that under our experimental conditions, the resident time of the solute in the barrier was less than 1 d and that longer times would likely occur in the field, resulting in more efficient destruction. Second Year Plan. Results from the first year of our project indicate that zerovalent iron [Fe(0)] promotes rapid degradation of metolachlor and several other pesticides in soil and that permeable Fe(0) barriers can effectively reduce the leaching of metolachlor through soil under unsaturated flow. We found that this process is catalyzed by adding aluminum sulfate with the iron, but optimum amendment ratios, reaction conditions and mechanisms need to be determined. While rapid initial dechlorination of metolachlor results from Fe(0) oxidation to Fe(II), oxidation of surface-bound Fe(II) can provide additional reducing power to further decrease metolachlor concentrations in water or soil. Formation and oxidation of metastable mixed Fe(II)/Fe(III) forms (green rusts and magnetite) appear to be associated with maximum metolachlor degradation, although mechanisms are not presently understood. Our subsequent research will answer these questions and provide guidance for the most effective use of iron-based treatment systems for contaminated water and soil. We plan to disseminate results of our research in professional publications and proceed with additional field demonstrations as appropriate. Compliance Advisory Services Inc., the Hastings, Nebraska consulting firm that cooperated with us in the 1999 field site, will help us identify additional field sites and assist in arranging on-site demonstrations. Dissemination of research results to the public and potential industrial users of the technology is being facilitated through Dr. Comfort's university extension position, which centers on protecting water resources in Nebraska.

## **Descriptors**

Pesticides, Soil Chemistry, Hazardous Waste, Contaminant Transport, Remediation

## **Articles in Refereed Scientific Journals**

## **Book Chapters**

## Dissertations

## Water Resources Research Institute Reports

## Conference Proceedings

Gaber, Hesham M., Steve D. Comfort, Patrick J. Shea and Thomas A. Machacek. 1999. Permeable zerovalent iron barriers for remediating pesticide-contaminated soil. Abstr. Am. Soc. Agron. 91:27.

## Other Publications

Singh, Jasbir, Steve D. Comfort and Patrick J. Shea. 1999. Iron-mediated remediation of RDX-contaminated water and soil under controlled Eh-pH. Environmental Science and Technology 33:1488-1494.

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# Information Transfer Program

## Basic Project Information

Basic Project Information	
Category	Data
Title	Information Transfer Plan
Description	Communications
Start Date	03/01/1999
End Date	02/28/2000
Type	Newsletter
Lead Institution	Nebraska Water Resources Center

## Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
Steven W. Ress	Professional Staff	University of Nebraska, East Campus	01

## Problem and Research Objectives

Not applicable.

## Methodology

Not applicable.

## Principal Findings and Significance

Not applicable.

### **Articles in Refereed Scientific Journals**

Not applicable

### **Book Chapters**

Not applicable

### **Dissertations**

Not applicable

### **Water Resources Research Institute Reports**

Not applicable

### **Conference Proceedings**

"Prioritized List of Water Management Issues from the 29th Annual Nebraska Water Conference. An eight-page synopsis of attendee voting and prioritization on 33 water issues for Nebraska's future. From the third of three "Nebraska Water 2000" conferences held in Lincoln, NE in March, 2000. Copies of the list were distributed to conference participants, to pertinent University of Nebraska departments, federal and state agencies, non-profit water and environmental organizations and to state senators. Available free. "Overview of Vision Statements Created at the 28th Annual Nebraska Water Conference;" a 15-page overview of the "Nebraska Water 2000" conference held in Kearney, NE in March, 1999. Copies were distributed to conference participants and to pertinent and interested University of Nebraska departments, federal and state agencies and non-profit water and environmental organizations. Available free. CONFERENCES, SEMINARS AND TOURS: Annual Nebraska Water Conference conducted each March, co-sponsored by the University of Nebraska Water Center/Environmental Programs, School of Natural Resource Sciences, Nebraska Department of Water Resources, Nebraska Water Conference Council and others. In 1999, the 28th annual conference was the second in a three-year series to explore the past, present and future of Nebraska water and Nebraska water issues under the collective title of "Nebraska Water 2000." The conference annually attracts 175-225 speakers and participants. News releases, brochures and a program are produced in conjunction with this event. Annual Water Resources Seminar Series is a series of 12 to 14 public lectures held from January to April each year and co-sponsored by the University of Nebraska Water Center/Environmental Programs, School of Natural Resource Sciences, and other NU departments and centers. The series may be taken for graduate or undergraduate student credit and is available on video tape for students opting for a distance learning option. Weekly attendance at the lectures is approximately 30 students and another 40 from the public at-large. News releases, mailings and brochures are produced in conjunction with this event. Fall Festival of Color is an annual summer horticulture and lawn and garden open house co-sponsored by the University of Nebraska-Lincoln Department of Horticulture, Water Center/Environmental Programs, School of Natural Resource Sciences, Cooperative Extension and Institute of Agriculture and Natural Resources. The one-day event, held at UNL's Agricultural Research and Development Center (ARDC) located between Lincoln and Omaha, attracts great media interest and is attended by more than 10,000. News releases and

newspaper advertisements are produced in conjunction with this event. Annual Summer Water Tour co-sponsored by the Nebraska Water Conference Council, Nebraska Department of Water Resources, NU Water Center/Environmental Programs and School of Natural Resource Sciences, and other public, private and commercial entities. The annual tours, normally conducted in July or August, explore current water projects, legislation, research and water-related issues in Nebraska and neighboring states. They attract educators, water users, legislators and members of the public at-large and are typically attending by approximately 100. Tours last from two to four days, depending on location. Recent tours have visited Nebraska, Colorado, Kansas and Wyoming. News releases, mailings and a brochure are produced in conjunction with this event. Water Research Forums are annual events designed to bring University of Nebraska water research faculty together with state and federal agency representatives to discuss the conduct and progress of current water resources research in Nebraska and to explore potential areas of concern, as well as concepts and ideas for future interdisciplinary research opportunities. Research funding and linkages are also discussed. Summations of these events are frequently published and distributed to attendees, as well as to university officials and state and federal government decision makers. CONFERENCES AND EDUCATIONAL DISPLAYS: The Water Center/Environmental Programs makes frequent public displays in association with conferences, symposiums, water-related trade shows and water and environmental festivals. These average eight to 10 per year. A new Downing Display highlighting the latest Water Center-sponsored research and/or programming is created approximately every 18 months. A wide variety of informational and educational materials are distributed at no charge at these events. Water Center faculty and staff also use a Groundwater Flow model to help introduce elementary and middle school science students to the concepts of groundwater and groundwater contamination issues. Presentations are scheduled on an as-requested basis.

## **Other Publications**

NEWSLETTER: The "Water Current" newsletter is in its 33rd year of continuous publication. Published in February, April, June, August, October and December. An annual reader survey is published in the April edition. Survey results help drive editorial content of the publication and overall design evolution. Each issue is eight pages in length. Research briefs and RFPs are published as inserts to the newsletter. The publication covers research, extension and outreach programming and educational efforts sponsored all or in part by the UNL Water Center/Environmental Programs unit. Distribution reaches international proportions. Subscriptions are provided at no charge to the public and there are approximately 3,550 subscribers. WETLANDS TABLOID: "Wetlands - Understanding a Resource" a 16-page newspaper tabloid on wetlands-related issues was published in May, 1998. 200,000 copies were printed and distributed to the public at-large, public and private schools; other educational programs; non-profit environmental organizations and to co-sponsoring local, state and federal agencies. This was the third in a series of water and wetlands-related tabloids that have been published by the Water Center/Environmental Programs unit since 1994. "Drinking Water - Understanding a Resource" a 16-page newspaper tabloid on Nebraska's public and private drinking water and drinking water issues was published in December, 1999. 275,000 copies were printed and distributed largely through a statewide, Sunday edition of the Omaha World-Herald newspaper. Remaining copies have been distributed to University of Nebraska programs dealing with water and environmental issues, to state and federal agencies, educational and non-profit environmental organizations and to the public-at-large. This was the fourth in a series of water and wetlands-related tabloids that have been published by the UNL Water Center since 1994. Available free. OTHER PRINTED PUBLICATIONS: "How To Access Water Resources Information," a public guide to local and internet resources on a variety of water and water-related issues. Distributed free to the public at seminars, conferences and displays and available free through the Water Center/Environmental Programs internet web site. "Nebraska Water

Resources Directory," a public guide to federal, state and local water resources agencies, organizations and educational institutions. Distributed free to the public at seminars, conferences and displays and available free through the Water Center/Environmental Programs internet web site. Water Center/Environmental Programs and School of Natural Resource Sciences informational brochures. Updated and produced annually to provide overviews of the mission and programming of these two University of Nebraska programs. Distributed free. NEWS RELEASES: The Water Center/Environmental Programs produces about 40 press releases annually based on research, cooperative extension, teaching and public outreach programming sponsored by the Water Center. Press releases receive wide publication in state newspapers, as well as in organization, trade and research journals. ELECTRONIC RESOURCES: Electronic versions of newsletters, other printed materials, RFPs, up-to-date information about the unit and its research faculty and information about the associated Water Sciences Laboratory and Pesticide Education Resources programs are available on the internet at <http://www.ianr.unl.edu/ianr/waterctr/wchome.html> The Water Center/Environmental Programs also co-sponsors four additional educational internet sites. These sites are associated with the Water Center, the Water Sciences Laboratory, the Platte Watershed Program and the UNL Horticulture Department's Festival of Color. Many free water-related print and electronic publications are available through these five sites. Addresses for the other four sites are: Water Sciences Laboratory: <http://www.ianr.unl.edu/waterscience/wsl.html> Platte Watershed Program: <http://ianrwww.unl.edu/ianr/pwp/pwp.html> Fall Festival of Color: <http://hort.unl.edu/fallfest/> Blue River Basin Water Quality Project: <http://ianrwww.unl.edu/blueriver/>

### Basic Project Information

Basic Project Information	
Category	Data
<b>Title</b>	A Test of Permeable Zero-Valent Iron Barriers for In-Situ Containment and Remediation of Pesticide Contamination in Unsaturated Soils
<b>Description</b>	
<b>Start Date</b>	03/01/1999
<b>End Date</b>	02/28/2000
<b>Type</b>	Publications
<b>Lead Institution</b>	Nebraska Water Resources Center

### Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
Patrick J. Shea	Professor	University of Nebraska, East Campus	02

### Problem and Research Objectives

A critical need in Nebraska, the Midwest and nationwide is the development of cost-effective and environmentally benign technologies for remediating pesticide-contaminated soils. Each year, leaking tanks, pesticide spills, and inadvertent discharges of agrochemicals lead to a growing number of pesticide-contaminated sites in Nebraska. These point sources of contamination are usually responsible

for the highest pesticide concentrations found in ground and surface water throughout the state. It has been estimated that groundwater contamination from 32 different pesticides in 12 different U.S. states can be attributed to point sources (Goodrich et al., 1991). For example, a midwest study in Wisconsin found that in 240 wells monitored for metolachlor, all water samples with a concentration greater than 1 ug/L could be related to a known or suspected point source. Identifying and remediating point-sources of pesticide contamination is a major undertaking. The Nebraska Departments of Agriculture and Environmental Quality continue to identify several pesticide-contaminated sites and are in need of alternative means of remediating pesticide spill sites. Presently in Nebraska, pesticide spills to land are often handled in one of two ways. The contaminated soil is excavated and shipped to a certified landfill or the contaminated soil is diluted with clean soil and reapplied to farmland at labeled rates. Neither approach treats the soil on-site and both are costly and often labor-intensive. This proposal offers the development of an alternative approach employing permeable zero-valent iron [Fe(0)] barriers to remediate point-sources of pesticide contamination in soil. The purpose of this research is to determine the appropriateness of an Fe(0)-barrier for in situ treatment of pesticide-contaminated soil. Given the success iron walls have had in remediating contaminant plumes in groundwater (Wilson, 1995), this same concept may be applicable to treating contaminant solutes as they move downward in unsaturated soils. In practice, contaminated soils, such as those present at small pesticide-contaminated sites, would be removed and a layer of Fe(0) or a sand-Fe(0) mixture added to the bottom of the excavation pit. The contaminated soil, or partially treated contaminated soil, would be replaced and natural leaching and attenuation allowed to occur. Theoretically, as the contaminant desorbs from the soil matrix and migrates through the Fe(0) layer, it would be transformed and possibly mineralized through subsequent biodegradation. This proposed treatment scheme is being experimentally tested using a soil column transport system (Comfort et al., 1995). Objectives 1. Determine the destructive capacity of permeable Fe-barriers to contain and remediate pesticide-containing leachate during unsaturated transport. 2. Quantify extent of pesticide degradation in the Fe-barrier system. 3. Determine if terminal degradates produced via transport through the Fe-barriers are biodegradable. References Comfort, S.D., P.J. Shea, L. Hundal, Z. Li, B.L. Woodbury, J.L. Martin, and W.L. Powers. 1995. TNT transport and fate in contaminated soil. *J. Environ. Qual.* 24: 1174-1182. Goodrich, J.A., B.W. Jr. Lykins, and R.M. Clark. 1991. Drinking water from agriculturally contaminated groundwater. *J. Environ. Qual.* 20:707-717. Wilson, E.K. 1995. Zero-valent metals provide possible solution to groundwater problems. *Chem. Eng. News* 73:19-22.

## Methodology

**Destructive Capacity of the Fe Barrier.** Miscible displacement experiments were performed with 20-cm soil columns attached to vacuum chambers. Treatments include columns of sand and/or soil with various zerovalent iron treatments. Pesticide degradation during transport is being quantified by controlling the contaminant flux rate through unsaturated soil columns. Pore water velocities are adjusted to vary the resident times of the contaminant in the column. By controlling the pore water velocity of the contaminant pulse and tritiated water (soil water tracer) through the soil columns, the residence time of contaminant in the column can be estimated and used to determine and validate the relative degradation rate in the Fe barrier. Several questions are being addressed: • How thick of an iron barrier is needed and how long can it be expected to last? • What hydraulic properties should the Fe barrier have? • Is there an advantage to mixing surface soil with the Fe barrier as a means of having a more active microbial population? • How much of the pesticide will be sorbed to the barrier versus that which is transformed? • How biodegradable will the Fe-mediated transformation products be in the subsoil? • Will plugging become a problem with time? • Can additives (carbon source, pH, and/or redox modifiers) be blended with the Fe to improve destruction efficiency? **Quantification of Pesticide Degradation.** Degradation of the selected pesticides in the iron barrier column system was determined through loss of

parent and by functional group (i.e., Cl-) and carbon (<sup>14</sup>C-labeled) mass balances. To support the transport experiments, batch sorption and incubation experiments are being conducted to determine the extent of pesticide adsorption (using <sup>14</sup>C-labeled compounds) and degradation occurring in the pesticide-iron barrier environment. These experiments are being conducted using procedures developed in our laboratories (Comfort et al., 1995; Singh et al., 1998a). Concentrations of a pesticides and their dechlorinated products are being determined in the column effluent using HPLC, GC and GC/MS methods previously developed in our laboratories or by other researchers (Eykholt and Davenport, 1998; Monson et al., 1998; Potter and Carpenter, 1998). Chloride release and Fe(II)/Fe(III) speciation in the system is being monitored using colorimetric and ion chromatography techniques.

Biodegradability of the Iron Treatment Products. To determine if transformations occurring in the iron barrier result in compounds that are more biodegradable, we combined and homogenized <sup>14</sup>C fractions collected from the bottom of the Fe(0)-barrier columns following the transport experiments. This solution was then added to static soil microcosms (bioreactors) where cumulative <sup>14</sup>CO<sub>2</sub> was monitored with time (Singh et al., 1998b).

References Comfort, S.D., P.J. Shea, L. Hundal, Z. Li, B.L. Woodbury, J.L. Martin, and W.L. Powers. 1995. TNT transport and fate in contaminated soil. *J. Environ. Qual.* 24: 1174-1182. Eykholt, G.R., and D.T. Davenport. 1998. Dechlorination of the chloroacetanilide herbicides alachlor and metolachlor by iron metal. *Environ. Sci. Technol.* 32:1482-1487. Monson, S.J., L. Ma, D.A. Cassada, and R.F. Spalding. 1998. Confirmation and method development for dechlorinated atrazine from reductive dehalogenation of atrazine with Fe<sup>0</sup>. *Anal. Chimica Acta* 19041:1-8. Potter, T.L., and T.L. Carpenter. 1998. Occurrence of alachlor environmental degradation products in groundwater. *Environ. Sci. Technol.* 29:1557-1563. Singh, J., S.D. Comfort, L.S. Hundal, and P.J. Shea. 1998a. Long-term RDX sorption and fate in soil. *J. Environ. Qual.* 27:572-577. Singh, J., S.D. Comfort, and P.J. Shea. 1998b. Remediating RDX-contaminated water and soil using zero-valent iron. *J. Environ. Qual.* 27:1240-1245.

## Principal Findings and Significance

Field Demonstration. A half-acre bentonite-lined lagoon was constructed in 1979 at a farm cooperative in southwestern Nebraska. The original purpose of the lagoon was to receive and contain potentially contaminated storm runoff and other excess wastewater. In 1995, an accidental release of metolachlor from a storage tank resulted in 755 gallons of unrecovered product, some of which ran into the sump that drains into the lagoon. The spill resulted in approximately 1000 cu yd of contaminated soil that was excavated from the lagoon and held for remedial treatment. The targeted contaminant was metolachlor, which was present at initial concentrations >1400 mg/kg. The soil also contained atrazine, alachlor, pendimethalin, and chlorpyrifos at concentrations exceeding 250, 90, 90, and 25 mg/kg. Due to the high concentration, natural attenuation would not proceed rapidly enough to significantly reduce the soil contamination and thus the stockpiled soil represented a sustained point source of ground water contamination. In the summer of 1999, we conducted a field-scale demonstration project in which the contaminated soil was placed in windrows and amended with various treatments involving zerovalent iron. Following treatment, acetonitrile-extractable metolachlor concentrations rapidly decreased, and up to 95% destruction was achieved within 24 h. By 90 d, concentrations of metolachlor, atrazine, alachlor, pendimethalin, and chlorpyrifos were decreased by up to 99, 70, 99, 90, and 96%. Batch Experiments with Metolachlor. Batch experiments were conducted using Fe<sup>0</sup> - metolachlor suspensions to determine destruction kinetics and degradation products. By adding small amounts of aluminum sulfate [Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>] to annealed iron, we found metolachlor destruction rates were significantly enhanced and stoichiometric recovery of Cl<sup>-</sup> was observed. By varying the Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> concentration and holding the mass of Fe(0) constant, we found that the optimum percentage of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> needed was between one and five percent of the Fe(0) weight. Addition of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> resulted in a high iron concentration in the aqueous system. Additional experiments indicated that metolachlor degradation was not promoted by

aluminum oxide ( $\text{Al}_2\text{O}_3$ ) or aluminum hydroxide [ $\text{Al}(\text{OH})_3$ ]. The relative effect of catalysts on metolachlor degradation by  $\text{Fe}(0)$  in batch experiments was:  $\text{Al}_2(\text{SO}_4)_3 > \text{AlCl}_3 > \text{FeSO}_4 > \text{Fe}_2(\text{SO}_4)_3$ . Adding  $\text{FeSO}_4$  increased  $\text{Fe}(\text{II})$  concentration in solution and enhanced metolachlor degradation. The same results were observed in metolachlor-soil slurries. Solution pH affected metolachlor degradation and experiments were conducted using an Eh-pH Stat to control pH. In the absence of soil, pH 5 was most effective for metolachlor degradation using annealed (heat-treated under low oxygen) iron and metolachlor was completely degraded within 6 h. A solution pH of 3 was most effective for treatment with unannealed iron in solution and in a metolachlor-soil slurry. UV spectrum and GC/MS analysis verified that the iron treatment resulted in dechlorination of metolachlor, and subsequent experiments indicated that the dechlorinated product was about five-fold more biodegradable than metolachlor during a 90-d incubation. Permeable Iron Barrier. Although treatment with zerovalent iron greatly reduced pesticide concentrations in soil at the Nebraska field site, the potential for leaching remained. To counteract this potential problem, we proposed placing a protective permeable iron barrier at the bottom of the excavated pit at the Nebraska field site before returning the treated soil. Laboratory experiments were conducted to determine the effectiveness of a permeable iron barrier to degrade residual metolachlor in leachate from soil. Transport experiments were conducted using 20-cm (5-cm diam.) columns, with and without iron barriers [ $\text{Fe}(0)$  - sand mixtures, amended with  $\text{Al}_2(\text{SO}_4)_3$ ]. The columns were attached to vacuum chambers and run under constant matrix potential (-20 kPa) and soil-water (Darcy) flux (2 cm/d). Initial experiments used a continuous  $^{14}\text{C}$ -labeled metolachlor pulse (1.45 mM) with tritiated water as the tracer in columns containing 50% (w/w)  $\text{Fe}(0)$  - sand. Total  $^{14}\text{C}$  and metolachlor were measured in effluent fractions using liquid scintillation counting (LSC) and high performance liquid chromatography (HPLC) with radioisotope detection. Break-through curves indicated complete destruction of  $^{14}\text{C}$ -metolachlor in columns containing the sand/iron mix. Transport experiments using a 25% (w/w)  $\text{Fe}(0)$  - sand barrier demonstrated the effectiveness of adding  $\text{Al}_2(\text{SO}_4)_3$  to the  $\text{Fe}(0)$  - sand mixture and the dechlorinated product was the primary degradate in the leachate. Subsequent transport experiments using untreated metolachlor-contaminated soil from the Nebraska field site indicated that the iron barrier was effective in decreasing metolachlor concentration in the leachate by >50% compared to the untreated contaminated soil, although breakthrough concentrations remained unacceptably high. Conducting similar experiments with  $\text{Fe}0$  - treated soils (42 d after treatment) revealed that combining soil treatment with the iron barrier significantly reduced the concentration of metolachlor in the leachate. It is noteworthy that under our experimental conditions, the resident time of the solute in the barrier was less than 1 d and that longer times would likely occur in the field, resulting in more efficient destruction. Second Year Plan. Results from the first year of our project indicate that zerovalent iron promotes rapid metolachlor degradation in soil and permeable zerovalent iron barriers can effectively reduce the leaching of metolachlor through soil under unsaturated flow. We found that this process is catalyzed by adding aluminum sulfate with the iron, but optimum amendment ratios, reaction conditions and responsible mechanisms need to be determined. While rapid initial dechlorination of metolachlor results from  $\text{Fe}(0)$  oxidation to  $\text{Fe}^{2+}$ , oxidation of surface-bound  $\text{Fe}(\text{II})$  can provide additional reducing power to further decrease metolachlor concentrations in water or soil. Formation and oxidation of metastable mixed  $\text{Fe}(\text{II})/\text{Fe}(\text{III})$  forms (green rusts and magnetite) appear to be associated with maximum metolachlor degradation, although mechanisms are not presently understood. Our subsequent research will answer these questions and provide guidance for the most effective use of iron-based treatment systems for contaminated water and soil.

## Articles in Refereed Scientific Journals

## Book Chapters

## **Dissertations**

## **Water Resources Research Institute Reports**

## **Conference Proceedings**

Gaber, Hesham M., Steve D. Comfort, Patrick J. Shea and Thomas A. Machacek. 1999. Permeable zerovalent iron barriers for remediating pesticide-contaminated soil. Abstr. Am. Soc. Agron. 91:27.

## **Other Publications**

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# **USGS Internship Program**

## **Student Support**

## **Awards & Achievements**

## **Publications from Prior Projects**

### **Articles in Refereed Scientific Journals**

### **Book Chapters**

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