Missouri Water Resources Research Center
Annual Technical Report
FY 2004

Introduction

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WATER PROBLEMS AND ISSUES OF MISSOURI

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

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

B>Water Quantity : Missouri has a history of either inadequate amounts of rainfall, or spring floods. Because of the 1987-1989 drought years, and the flood of 93 and 95, water quantity has become a major topic of concern. Research is needed to better understand droughts and flood conditions.

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

SUMMARY OF ADVISORY COMMITTEE ACTIVITIES

The following individuals have participated in the selection and development of our 2004 research program.

UNIVERSITY OF MISSOURI FACULTY ADVISORY COMMITTEE

1. Craig Adams, University of Missouri-Columbia, I-29 Agriculture Building, Columbia, MO. 2. Steven Anderson, University of Missouri-Columbia, 302 Abnr Bldg-Soil Sci, Columbia, MO. 3. Dr. Patrick Osbourne, University of Missouri-St. Louis, 224, Research Building, St. Louis, MO 63121. 4. Dr. Jerry Richardson, University of Missouri-Kansas City, 00126 RHFH, 574, Kansas City, MO.

STATE OF MISSOURI ADVISORY COMMITTEE MEMBERS

1. Dr. John Madras, Department of Natural Resources, Water and Pollution Control, PO Box 176, Jefferson City, MO 65102. 2. Dr. Russell Rhodes, Southwest Missouri State University, 901 South National, Springfield, MO 65802. 3. U.S. Geological Survey, 1400, Independence Road, Rolla MO 65401 4. Dr. Steve McIntosh, Water Resources Program, Department of natural Resources, PO Box 176, Jefferson City, MO. 5. Dr. Hamed Mubarak, State Water Resources Economist, Department of Natural Resources, 205 Jefferson Street, Jefferson City, MO 65101. 6. Jim Czarneszki, Fisheries & Wildlife, Department of Conservation, 1110 South College Avenue, Columbia, MO 65201. 7. Becky Shannon, Missouri Departmental of Natural Resources, PO Box 176, Jefferson City, MO 65102.

Research Program

PROGRAM GOALS AND PRIORITIES

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

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

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

Research Program

Use of Excitation/Emission Matrix Fluorescence

Basic Information

Title:	Use of Excitation/Emission Matrix Fluorescence
Project Number:	2004MO31B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	9th
Research Category:	Water Quality
Focus Category:	Treatment, Models, Water Quality
Descriptors:	
Principal Investigators:	Baolin Deng, Baolin Deng

Publication

An annual report submitted to Missouri Water Resources Research Center/USGS

Use of Excitation/Emission Matrix Fluorescence for Wastewater Sources Identification

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ABSTRACT

Water contamination can come from different sources, including wastewater treatment effluent, landfill leachate, agricultural runoff, and a wide variety of industrial sources. Identifying and differentiating these sources are needed to effectively manage the water pollution issues and enforce the environmental regulation. The objective of this project is to establish a fluorescence excitation/emission matrix database for different types of water and to develop a mathematical procedure/computer model to identify the source of unknown water samples. The research tasks include: (i) collections of substantial numbers of water samples from various known sources, (ii) analysis of water samples for excitation/emission spectra, and (iii) development of a mathematical/ computer model that can be used to identify different sources of water. In this project period, we have made significant progress on tasks (i) and (ii), including procurement, installation, and testing of the a Hitachi F-4500 fluorescence spectrophotometer; analysis of pure water samples and individual chemical dissolved in water; and analysis of 60 Missouri water samples from various lakes and water supplies.

Introduction

Molecular fluorescence spectroscopy is an analytical technique based on emission of fluorescence from a molecule upon excitation by irradiation. It is a rapid and inexpensive way of wastewater identification and quantification, in particular, when excitation/emission matrix spectra (EEMS) in a wide range of wavelength are collected. Compounds containing aromatic rings normally give the most intense molecular fluorescence emission, including benzene, toluene, phenol, quinoline, and many fused ring aromatic compounds. A small number of aliphatic and alicyclic carbonyl compounds with highly conjugated double-bound structures also fluorescence. Since fluorescence spectroscopy is much more sensitive than absorption spectroscopy, it is particularly suitable for trace amounts of contaminant detection.

The objective of this project is to establish a fluorescence EEMS database for different types of water in the state of Missouri and develop a mathematical procedure/computer model to identify the source of unknown water samples. Different types of waters have their own fluorescence features as they contain various fluorescence species. The fluorescence characteristics of river water (Yan et al., 2000), seawater (Coble et al., 1990; Coble, 1996), groundwater (Baker and Genry, 1999; Baker and Lamont-Black, 2001), sewage, and sewage-impacted river water (Reynolds and Ahmad, 1997; Baker, 2001, 2002) have been documented separately. However, by now, there is no database that provides comprehensive fluorescence spectra for various types of water. This research aims to fill the data gap by building a much more comprehensive database critical for the source identification of the unknown wastewater samples.

Experimental Section

1. Instrument Description and Parameters for Data Collection

We have acquired a Hitachi F-4500 fluorescence spectrophotometer for the current study. This is a research grade, easy to use fluorescence spectrophotometer with its FL Solutions$^{®}$ software for rapid data acquisition (2400nm/min-30,000 nm/min).

Instrument Features (Courtesy of Hitachi)

- Three-dimensional contour plots provide maximum spectral information and can be acquired and displayed in less than one minute.
- Phosphorescence is built-in as standard and allows lifetime measurements from 1 ms to address the widest range of samples.
- In addition to fluorescence and phosphorescence measurements, luminescence is included as standard. The high energy throughput and signal-to noise of the system allow measurements of chemiluminescent and bioluminescent compounds.
- The intense 150 watt xenon source provides maximum light energy over the entire 200-900 nm wavelength range of the spectrophotometer. A rhodamine B quantum counter is used to determine the correction factors for true instrument response to assure spectral accuracy.

- Unique horizontal beam geometry of the excitation and emission beams increases sensitivity and requires only 0.6 mL of sample in a standard 10mm cuvette.

- Automatic shutter control protects photo sensitive samples from degradation.

The following parameters, as illustrated in Table 1, were set before using the instrument for measurement of excitation and emission spectra. The excitation wavelength was set from 200 to 400 nm and emission wavelength from 250 to 550 nm on 12000nm/min and 30000nm/min scan speed.

Table 1: Calibration set for scanning

Information about sample/instrument		Calibration set for instrument	
Report Date:	5/19/2005 22:11	EX End WL:	400.0 nm
Sample:	Watkins Mill(#74)	EX Sampling Interval:	2.0 nm
File name:	Missouri Water Samples004.FD3	EM Start WL:	250.0 nm
Run Date:	3/11/2005 9:36	EM End WL:	550.0 nm
Operator:	Owner	EM Sampling Interval:	3.0 nm
Comment:	Collected @ 08/09/04	Scan speed:	12000 nm/min
Instrument Model:	F-4500 FL Spectrophotometer	EX Slit:	5.0 nm
Serial Number:	1606-005	EM Slit:	10.0 nm
ROM Version:	4000 05	PMT Voltage:	700 V
Measurement type:	3-D Scan	Response:	Auto
Data mode:	Fluorescence	Corrected spectra:	On
EX Start WL:	200.0 nm	Shutter control:	On

2. Analysis

To establish a database for water source identification, we need to collect water samples from various known sources and analyze the samples for excitation/emission matrix spectra. Up to now, 60 water samples collected from major lakes and water treatment plants and were analyzed. The Milli-Q deionized water and tap water, as well as solutions of individual chemicals with various functional groups were also scanned for excitation and emission spectra to understand the fluorescence characteristics and pattern and intensities. Fluorescence data were collected in the excitation wavelength from 200 to 400 nm and emission wavelength from 250 to 550 nm with 2 and 3 nm intervals respectively.

1. Tap & D.I Water Samples:

Several deionized water samples and tap water from University of Missouri Campus were scanned for excitation and emission matrix spectra. Following are the 3-D scan of each of them. The former shows no fluorescence and latter has some degree of intensity and fluorescence possible because of natural organic matter.

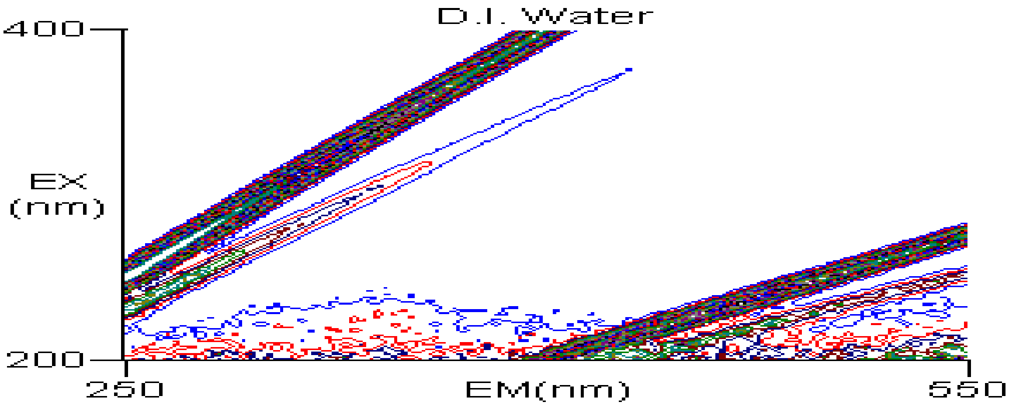

Figure 1

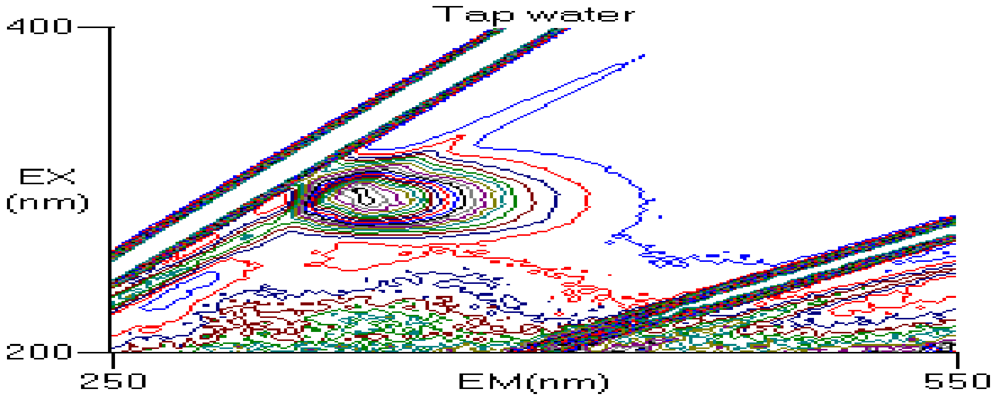

Figure 2

2. Water Samples for Individual Chemicals:

Eighteen chemicals, as listed in Table 2, were scanned at a concentration of 10 ppm for each.

Table 2: List of chemicals and water samples

S.N	Sample Name	Volume (ml)	Conc. (g/l)	Weight(g)
1	Benzoic Acid	50	5	0.25
2	Glutamic Acid	50	5	0.25
3	Hydroxybenzoic Acid	50	5	0.25
4	Phenol	50	5	0.25
5	D-Glucose	50	5	0.25
6	4-amino- Pyrine	50	5	0.25
7	1,2 cyclohexylene-dinitrilo tetracetic acid	50	5	0.25
8	Cosmic acid	50	5	0.25
9	5’-5’’-Dibromo-O- creasolesulfonephthalein	50	5	0.25
10	Dimythylamino azobenzene	50	5	0.25
11	1-5 Diphenylcarbazide	50	5	0.25
12	ADA,N(2-Acetamido) Iminodiacetic Acid	50	5	0.25
13	Oxalic Acid	50	5	0.25
14	3-(4-Morpholino)-Propanesulfonic Acid	50	5	0.25
15	2-(4-Morpholino)-Ethanesulfonic Acid	50	5	0.25
16	1,10 Phenanthroline	50	5	0.25
17	Peptone	50	5	0.25
18	2-(2-Thiazolylazo)-p-Cresol	50	5	0.25

The data collected could be visualized by 3-D contour map and Bird’s eye view, as illustrated by Figure 3-6 for hydroxybenzoic acid and D-glucose.

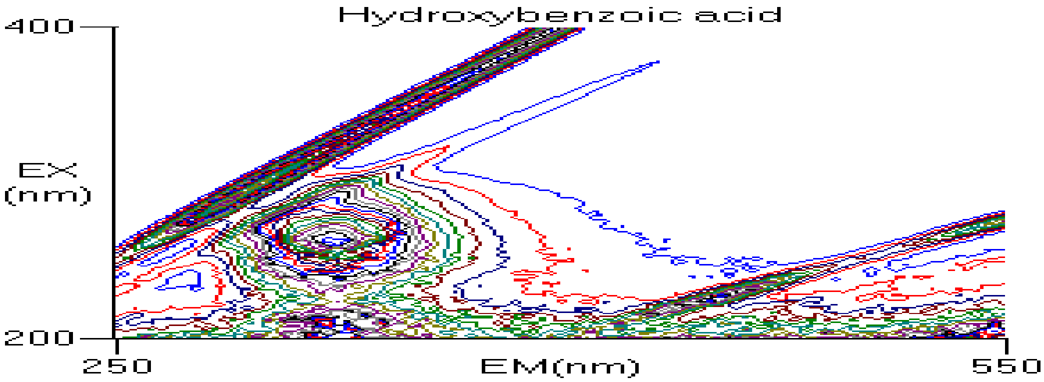

Figure 3: Contour and spectrum of hydroxybenzoic acid

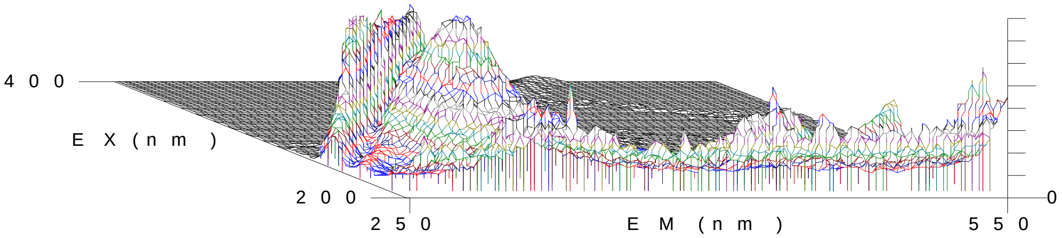

Figure 4: Bird's eye view of Hydroxybenzoic acid

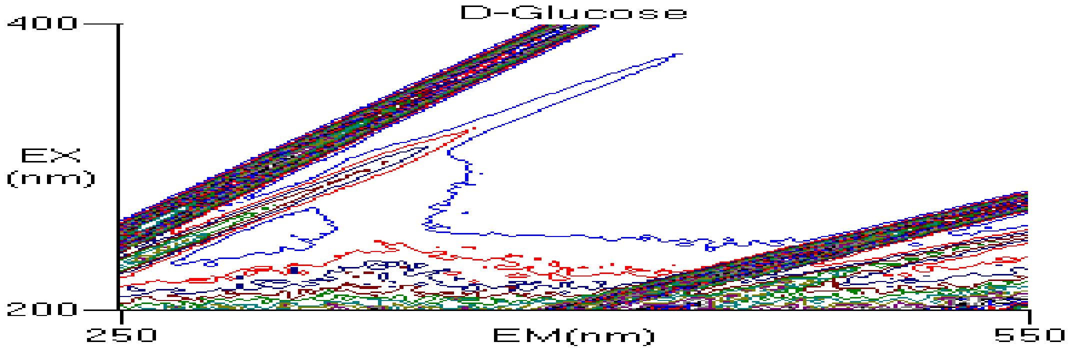

Figure 5 D-Glucose

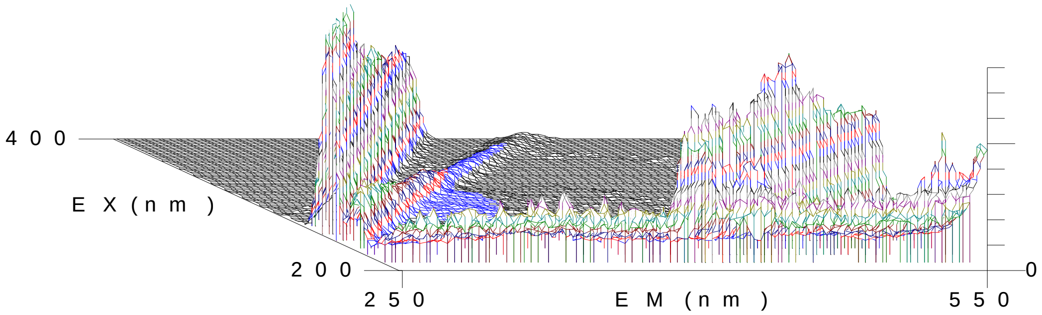

Figure 6: Bird's eye view of D-Glucose

3. Missouri Water Samples

A total of sixty (60) samples were collected through Missouri Water Resources Research Center and scanned for excitation and emission spectra. The samples represent the different rivers, lakes, creeks in the State of Missouri. Table 4 lists the samples scanned for the fluorescence intensity and some EEMS are illustrated in Figures 7-14. .

Table 4: A list of water samples collected for fluorescence analysis

S.N	Collected Date	CE Bottle #	Sample Name	Sample#
1	7/27/2004	7/27-1	Miller Community Lake	35
2	7/27/2004	7/27-3	Clearwater Lake	36
3	7/27/2004	7/27-5	Wapapello Lake	30
4	7/27/2004	7/27-7	Lake Girardeau	28
5	7/27/2004	7/27-9	Boutin Lake	27
6	7/27/2004	7/27-11	Bella Vista Lake	26
7	7/27/2004	7/27-13	Fredericktown City Lake	24
8	7/28/2004	7/28-15	Anne	22
9	7/28/2004	7/28-17	Capri	18
10	7/28/2004	7/28-19	Shane	112
11	7/28/2004	7/28-21	Bismark	186
12	7/28/2004	7/28-23	Council Bluff	39
13	8/3/2004	8/3-1	Monroe Lake	60
14	8/3/2004	8/3-3	Lake Hunnewell	115
15	8/3/2004	8/3-5	Henry Sever	114
16	8/3/2004	8/3-7	LaBelle City	129
17	8/3/2004	8/3-9	Deer Ridge	57
18	8/3/2004	8/3-11	Fox Valley	182
19	8/3/2004	8/3-13	Lancaster City	132
20	8/4/2004	8/4-15	LaPlatta Lake	130
21	8/4/2004	8/4-17	Longbranch	48
22	8/4/2004	8/4-19	Thomas Hill Reservoir	46
23	8/4/2004	8/4-21	Tri-CityCommunity Lake	42
24	8/4/2004	8/4-23	Little Dixie	117
25	8/9/2004	8/9-1	Pape Lake	113
26	8/9/2004	8/9-2	Higginsville	121
27	8/9/2004	8/9-3	Hazel Hill	183
28	8/9/2004	8/9-4	Odessa Lake	64
29	8/9/2004	8/9-5	Watkins Mill	74
30	8/9/2004	8/9-6	Smithville Lake	72
31	8/9/2004	8/9-7	Belcher Branch	187
32	8/10/2004	8/10-8	Raintree	118
33	8/10/2004	8/10-9(not filtrated)	Holden City	157
34	8/10/2004	8/10-10(not filtrated)	North Lake	70
35	8/10/2004	8/10-11(not filtrated)	Butler City	189
36	8/10/2004	8/10-12(not filtrated)	Atkinson	91
37	8/10/2004	8/10-13(not filtrated)	Bushwacker	161
38	8/10/2004	8/10-14(not filtrated)	Stockton	93
39	8/10/2004	8/10-15(not filtrated)	McDaniel	95
40	8/10/2004	8/10-16(not filtrated)	Fellows	96
41	8/11/2004	8/11-17(not filtrated)	Pomme De Terre	92
42	8/11/2004	8/11-18(not filtrated)	Truman	89

43	8/11/2004	8/11-19(not filtrated)	Lake of the Ozarks	149
44	8/11/2004	8/11-20(not filtrated)	Manito	184
45	8/11/2004	8/11-21(not filtrated)	Binder	13
46	8/17/2004	8/17-1	Sterling	119
47	8/17/2004	8/17-2	Nehai Tonkyea	45
48	8/17/2004	8/17-3	Marceline-2	88
49	8/17/2004	8/17-4	Marceline-1	139
50	8/17/2004	8/17-5	Brookfield	87
51	8/17/2004	8/17-6	Hazel Creek	131
52	8/17/2004	8/17-7	Forest	133
53	8/17/2004	8/17-8	Green City	137
54	8/18/2004	8/18-9	Marie	85
55	8/18/2004	8/18-10	Paho	84
56	8/18/2004	8/18-11	New Bethany	83
57	8/18/2004	8/18-12	Harrison Co.	185
58	8/18/2004	8/18-13	Mozingo	181
59	8/18/2004	8/18-14	Nodaway	179
60	8/18/2004	8/18-15	Bilby Ranch	180

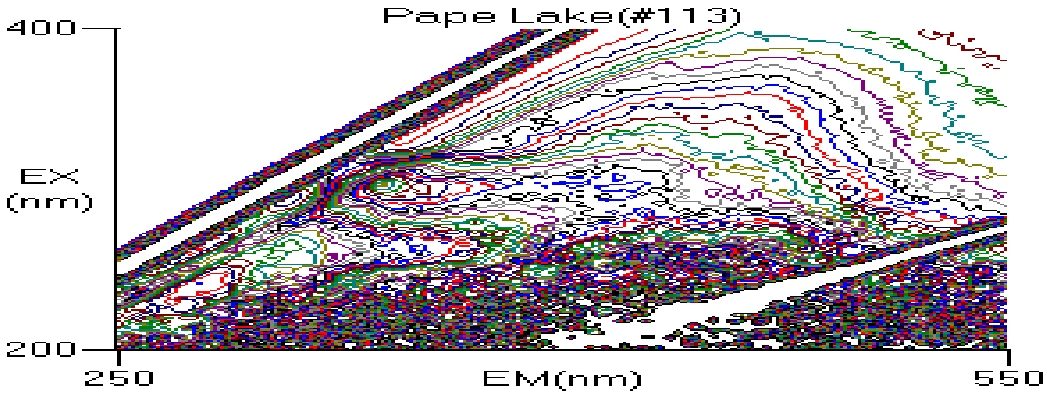

Figure 7

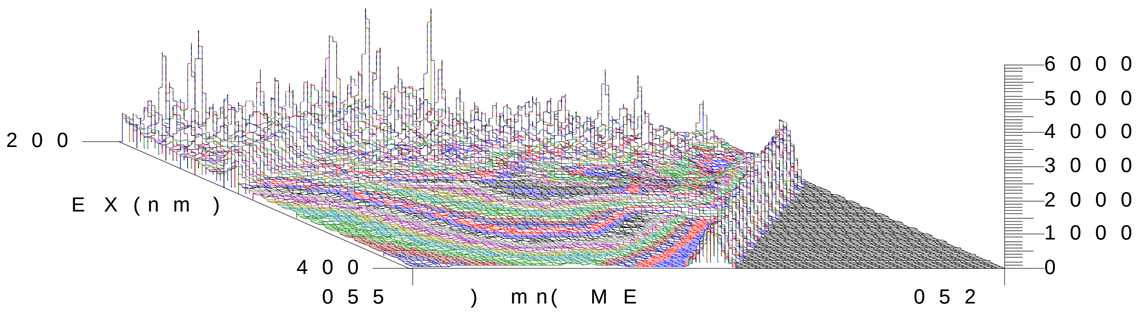

Figure 8

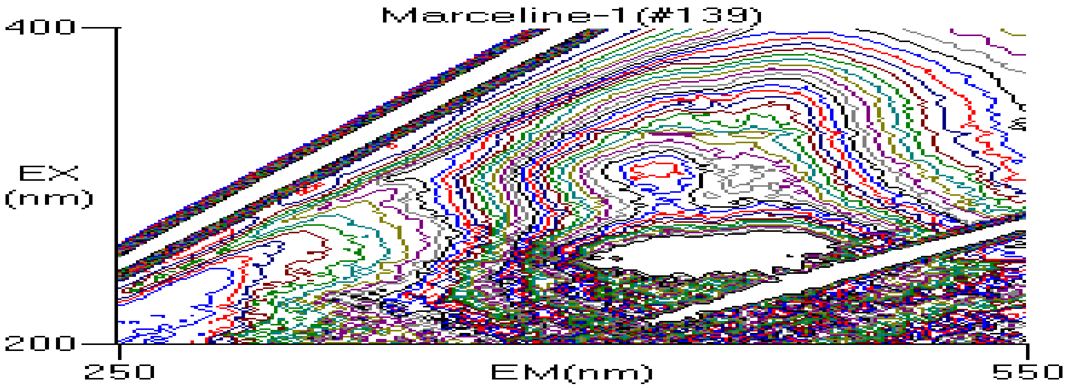

Figure 9

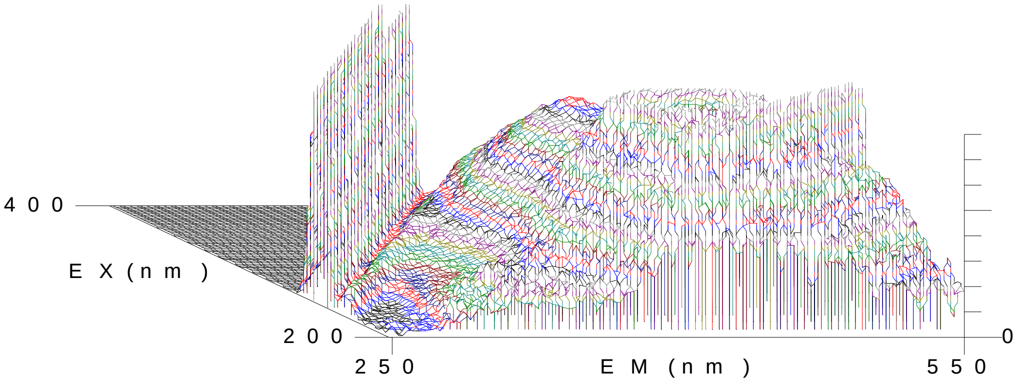

Figure 10

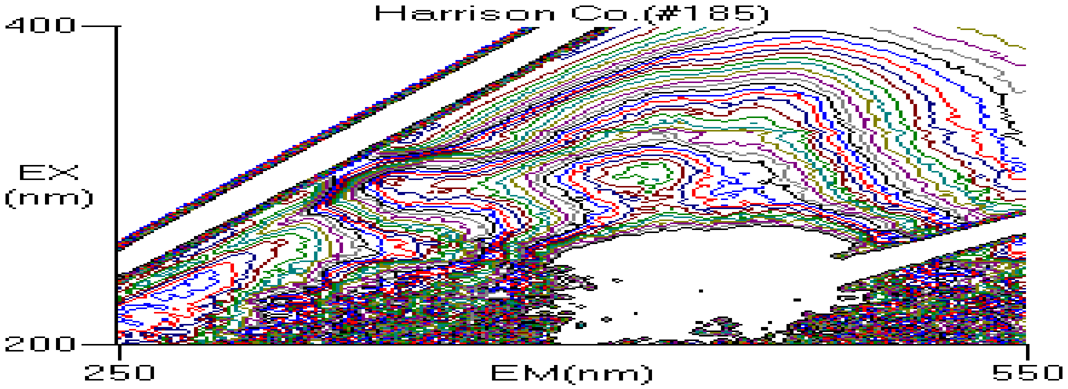

Figure 11

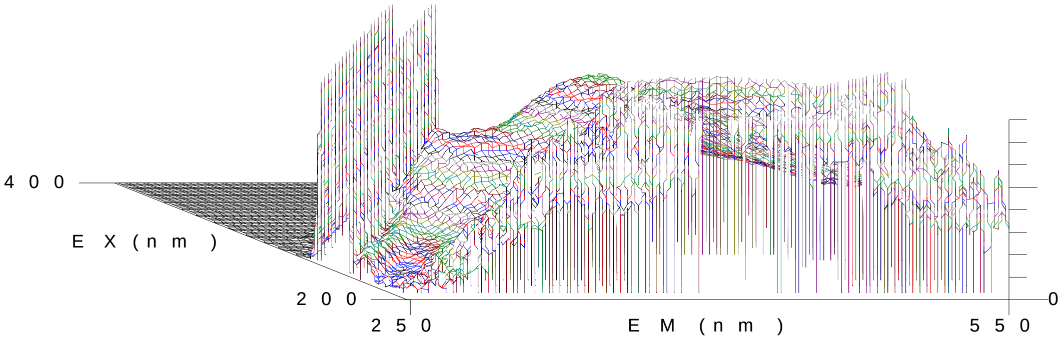

Figure 12

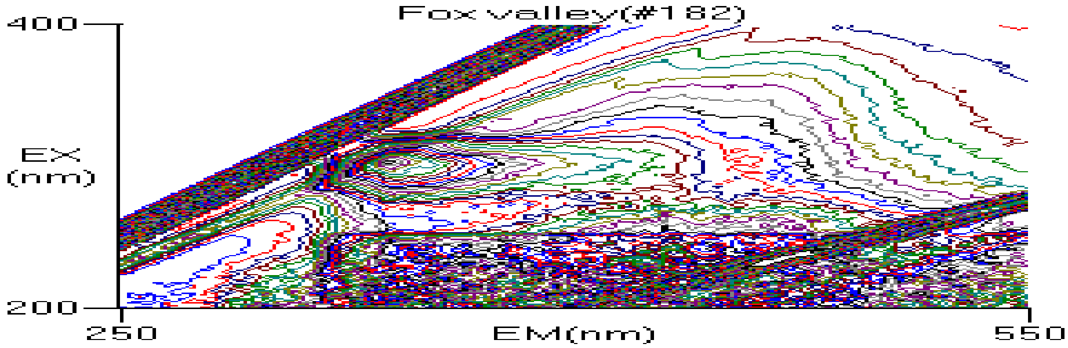

Figure 13

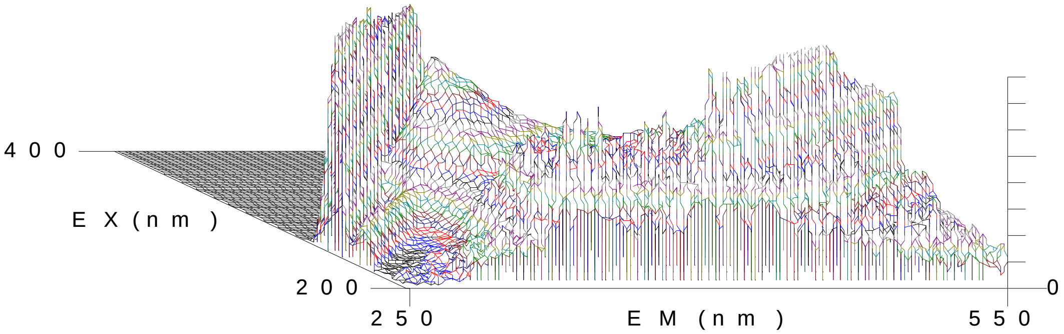

Figure 14

Summary

We have made significant progress in the first stage of this research, including (i) procurement, installation, and testing of the a Hitachi F-4500 fluorescence spectrophotometer; (ii) analysis of pure water samples and individual chemical dissolved in water; and (iii) analysis of 60 Missouri water samples from various lakes and water supplies. Different chemicals show substantially different characteristics of fluorescence spectra. Water samples also show different characteristics. Further research is under way to establish the relationship between the fluorescence features of individual chemicals and natural water samples, and between fluorescence features of natural water samples and water quality parameters such as NDMA formation potentials.

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The Leaching Behavior of Arsenic and Selenium from Fly Ash and Their Potential Impact on Water Quality

Basic Information

Title:	The Leaching Behavior of Arsenic and Selenium from Fly Ash and Their Potential Impact on Water Quality
Project Number:	2004MO34B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	8th
Research Category:	Water Quality
Focus Category:	Toxic Substances, Water Quality, Models
Descriptors:	
Principal Investigators:	Jianmin Wang, Joel Burken

Publication

1. Wang, T., Wang, J., Chusuei, C., and Ban, H. (2005) Release of Arsenic from Coal Fly Ash Surface. 229th ACS San Diego National Meeting, San Diego, California, USA (March, 2005).
2. Wang, T., Wang, J., Burken, J., and Ban, H. The Leaching Behavior of Arsenic from Fly Ash. 2005 World of Coal Ash, Lexington, Kentucky, USA (April, 2005).

The Leaching Behavior of Arsenic from Fly Ash

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KEYWORDS: arsenic, fly ash, leaching

ABSTRACT

The Maximum Contaminant Level (MCL) for arsenic in drinking water will be reduced to 10 ppb from the current 50 ppb level effective January 2006. Fly ash contains arsenic and could be a potential source of arsenic release to the environment. Understanding the leaching behavior of arsenic from fly ash is significant in predicting the arsenic impact on the drinking water quality and in developing innovative methods to prevent arsenic leaching.

The physical-chemical characteristics of three bituminous coal fly ashes (AN/Col #1, AN/Col #2 and AN/NRT #2) were studied using titration method and XPS analysis. AN/Col #1 and AN/Col #2 were obtained from different units burning the same coal. AN/Col #1 employed SNCR (selective non-catalytic reduction) for NOx control, and AN/Col #2 did not. AN/NRT #2 was collected from the same unit as AN/Col #2, but a different, higher calcium coal. Three acid sites were found on the surfaces of the fly ash, but only the first acid site, site α, was considered to be responsible for arsenic adsorption. XPS data indicated that the major elements on ash surface are C, O, Al and Si. Minor and trace elements Ca, As, and Se were also detected. Batch results indicated that pH has significant effect on arsenic leaching. Between pH 3 and 7, arsenic leaching is at a minimum. When pH was less than 3 or greater than 7, a significant amount of arsenic was leached from fly ash. More arsenic was leached out from ash AN/NRT #2 than ashes AN/Col #1 and AN/Col #2. However, the arsenic leaching from AN/NRT #2 was reduced when pH was greater than 9, which may be caused by the precipitation with calcium and other cations. We developed an arsenic adsorption model based on chemical reactions among different arsenic species and surface sites to quantify arsenic partitioning in fly ash. The pH-independent adsorption constants (log K_s) for $H_2AsO_4^-$ and $HAsO_4^{2-}$ were determined to be 2.6 and 6.2 respectively. The approach developed in this research is useful for understanding and predicting the release of arsenic from fly ash and other solid materials.

INTRODUCTION

The USEPA has recently reduced the Maximum Contaminant Level (MCL) for arsenic in drinking water to 10 ppb from 50 ppb, and all drinking water systems must comply with this new standard by January 2006.[1] Fly ash contains various levels of elements including arsenic.[2,3] For bituminous coal fly ash, the arsenic concentration can range from 1 to 1000 ppm, depending on coal source and combustion technology.[4] In 2003, a total of 122 million tons of Coal Combustion Products (CCPs) were generated in the US, and 58% of the CCPs were fly ash.[5] The release of arsenic from fly ash could lead to concentrations in drinking water that are above the new MCL. Understanding the leaching behavior of arsenic from fly ash is significant in understanding the potential arsenic impact on the drinking water quality, and in developing innovative methods to prevent arsenic leaching.

According to previous research with leaching tests and XPS analysis, arsenic was confirmed to be enriched on ash surface.[6,7] Both As(III) and As(V) were detected in ash, but the latter was present in a much higher fraction.[7,8] Various leachants, including HNO_3, H_2SO_4, sodium citrate, geopolymer, and EDTA were used to leach the arsenic from fly ash.[7,9,10,11] It was reported that 78-97% of the total As can be removed from fly ash by leaching with 0.5 N H_2SO_4 or a 1 M sodium citrate at pH 5.[7]

Many factors can influence the leaching of arsenic from fly ash, including pH, solid to liquid ratio, leaching time, temperature, etc.[11,12] Research also suggested that $H_2PO_4^-$ can displace arsenate in fly ash and increase arsenic concentration in leachate.[13]

Several mechanisms were proposed to interpret arsenic interactions with fly ash and the surrounding environment. Van der Hoek et al. reported that the leaching of As from acidic ash was sorption controlled and that iron hydroxide was the probable controlling sorbent.[14] However, other study suggested that calcium arsenate is a probable host for arsenic in fly ash.[15]

A surface complexation model was used to quantitatively describe the adsorption of arsenic on acidic fly ash.[16, 17] However, the modeling results were strongly dependent on the initial assumptions, and only amorphous iron hydroxide was considered in modeling. These factors limited the application potential of the model on fly ash.

The objectives of this study are to investigate the physical-chemical characteristics of fly ash, evaluate the leaching behavior of arsenic from fly ash, demonstrate the relationship between the surface characteristics and arsenic adsorption, and quantify the arsenic adsorption behavior by fly ash.

THEORETICAL ASPECTS

Ash Surface Speciation

According to Wang, et al.,[18] there are three types of weak acid sites on the fly ash surface. The protonated form of the first acid site, site α, which has the lowest pK_a value, is positively charged. Therefore, protonated form of the site α is most likely the one to adsorb anionic metal ions. The speciation of this acid site can be expressed as:

$\underline{S}OH_2^+ = \underline{S}OH + H^+; K_H$ (1)

where K_H is the acidity constant of the surface site $\underline{S}OH_2^+$.

The positively charged surface site concentration can be expressed as:

$$[\underline{S}OH_2^{\ +}] = \alpha_+ S_T \quad (2)$$

where S_T is the total site α density, and $\alpha_+ = \dfrac{[H^+]}{[H^+] + K_H}$

As(V) Speciation

In water solution, As(V) may exist as the following species:

$H_3AsO_4 = H_2AsO_4^- + H^+$; $pK_{a1} = 2.26$; $[H_2AsO_4^{\ -}] = \alpha_1[As(V)]_D$ (3)
$H_2AsO_4^- = HAsO_4^{2-} + H^+$; $pK_{a2} = 6.76$; $[HAsO_4^{\ 2-}] = \alpha_2[As(V)]_D$ (4)
$HAsO_4^{2-} = AsO_4^{3-} + H^+$; $pK_{a3} = 11.29$; $[AsO_4^{\ 3-}] = \alpha_3[As(V)]_D$ (5)

Where α_1, α_2 and α_3 are the fractions of As(V) as $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}, respectively. $[As(V)]_D$ is the total dissolved As(V) concentration.

As(V) Adsorption Reactions

Assuming that only the negatively charged arsenic species are adsorbed on the positively charged ash surface sites:

$\underline{S}OH_2^+ + H_2AsO_4^- = \underline{S}\text{-}H_2AsO_4 + H_2O; K_{S1}$; (6)
$\underline{S}OH_2^+ + HAsO_4^{2-} = \underline{S}\text{-}HAsO_4^- + H_2O; K_{S2}$; (7)
$\underline{S}OH_2^+ + AsO_4^{3-} = \underline{S}\text{-}AsO_4^{2-} + H_2O; K_{S3}$; (8)

Where K_{S1}, K_{S2} and K_{S3} are adsorption constants of the respective three negatively charged arsenic species. Assuming that the adsorption is in the linear range of the Langmuir isotherm, the concentration of adsorbed As(V) species can be calculated using the following equations:

$$[\underline{S} - H_2AsO_4] = K_{S1}\alpha_{S+}S_T\alpha_1[As(V)]_D \quad (9)$$

$$[\underline{S} - HAsO_4^{\ -}] = K_{S2}\alpha_{S+}S_T\alpha_2[As(V)]_D \quad (10)$$

$$[\underline{S} - AsO_4^{\ 2-}] = K_{S3}\alpha_{S+}S_T\alpha_3[As(V)]_D \quad (11)$$

Therefore, the adsorption ratio of arsenic can be expressed as:

$$R = \frac{[As(V)]_{ads}}{[As(V)]_D + [As(V)]_{ads}} = \frac{\alpha_{S+} S_T (K_{S1}\alpha_1 + K_{S2}\alpha_2 + K_{S3}\alpha_3)}{1 + \alpha_{S+} S_T (K_{S1}\alpha_1 + K_{S2}\alpha_2 + K_{S3}\alpha_3)} \tag{12}$$

where $[As(V)]_{ads}$ is total concentration of adsorbed As(V) species.

MATERIALS AND METHODS

Fly Ash Samples

Three ash samples were used in this study. Samples AN/Col #1 and AN/Col #2 were respectively collected from Unit #1 (with SNCR) and Unit #2 (conventional) of a facility burning eastern bituminous coal. Their loss on ignition (LOI) were, respectively, 12.7% and 6.7%. Sample AN/NRT #2, with LOI of 9.8%, was collected from the Unit #2 of the same facility when it was burning a different higher calcium eastern bituminous coal. All these samples were collected from the cold side electrostatic precipitator (ESP).

Raw ash samples were used for basic leaching experiment. All samples were dried at 105 °C for at least 24 hours in an oven before the experiments. Washed ashes were used for surface characterization and arsenic partitioning experiment. The purpose of washing was to remove soluble materials to get a relatively clean surface for the experiments. For the arsenic partitioning experiment, a 0.2 M NaOH solution was used to perform ash washing to maximize the arsenic removal. For other experiments, ashes were washed with DI water. All washing was performed at the solid/liquid ratio of 1:5, and was repeated for 5 times. Aeration was used to agitate the ash – water mixture, and each washing lasted 20 hours. Washed ash was dried in an oven at 105 ^{0}C for at least 24 hours before use.

Batch Equilibrium Titration

A batch equilibrium titration method including mathematical models developed by Wang, et al.[18, 19] was employed in this study to determine the surface site density and acidity constant of the fly ash.

As(V) Partitioning Experiment

Batch method was employed for arsenic partitioning studies.[18] The solid/liquid ratio was 1/10. Ionic strength was adjusted with 0.01M using stock $NaNO_3$ solution. For this study, samples were divided into 4 groups, with 1, 2, 5 and 10 ppm As(V) addition, respectively. To make sure the adsorption is in the linear range, the total arsenic concentration should be less than 10 percent of the surface site concentration. The equilibrium time used in this study was 24 hours. After shaking, all samples were settled overnight, the supernatant was then collected for arsenic analysis. The final pH was measured using the rest of the mixture in the bottle.

Basic Leaching Experiment

Arsenic leaching from raw ash under various pH conditions was investigated using batch methods.[18] Ionic strength was not adjusted in this experiment. At least 10 pH values in the range between 2 - 12 were selected for leaching. Solid/liquid ratio of 1:10 was used in the experiment. Arsenic in the supernatants was analyzed after 24 hrs of shaking. The final pH in each bottle was also measured.

Surface Analysis

The XPS analysis was carried out using Kratos Axis 165 X-Ray Photoelectrons spectrometer. Mg Kα radiation (1253.6 eV) was employed to provide the x-ray beam. By measuring the photon electron energy in a high-resolution analyzer, information regarding the concentration and oxidation states of the surface elements can be determined.

Analytical Method

A graphite furnace atomic absorption spectrometer (AAnalyst 600, Perkin-Elmer Corp., Norwalk, Connecticut, USA) was used to determine arsenic concentrations in the solution. An Orion PerpHecT Triode pH electrode (model 9207BN) and a pH meter (perpHecT LoR model 370) were used for pH measurement.

Data Analysis

The non-linear regression program Kaleidagraph^{TM} was used to conduct curve fitting for the determination of the surface acid characteristics and arsenic adsorption constants, based on the respective models we developed.

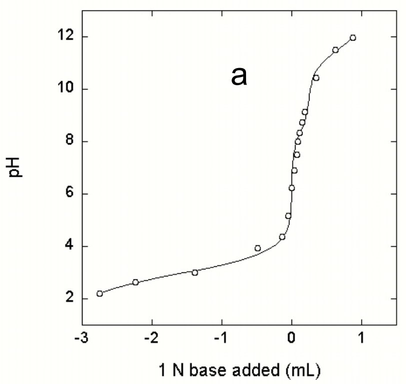
RESULTS AND DISCUSSION

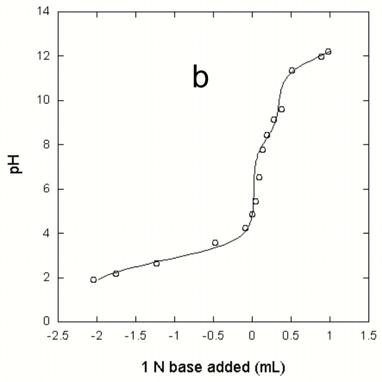
Surface Acidity

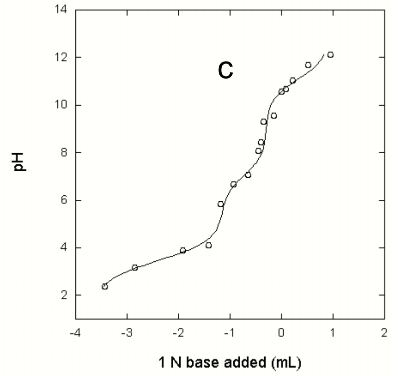
The surface characteristics of three washed ash samples AN/Col #1, AN/Col #2 and AN/NRT #2 were investigated. AN/Col #1 and AN/NRT #2 were washed with DI water only. The AN/Col#2 was washed with both DI water and 0.2M NaOH solution. Figure 1 shows the titration and curve fitting results for all samples. Results indicated that all samples have three types of acid sites on their surface. Table 1 shows the site density and the acidity constant of each site. Since the protonated form of the site α is positively charged, it may be the most responsible site for adsorption of arsenic anions.

Table 1. Surface site density and acidity constant of washed ash samples AN/Col #1, AN/Col #2, and AN/NRT #2.

Sample	Washing Agent	Site	α	β	γ
AN/Col #1	DI water	Site density (10^{-5}mol/g)	32 ± 1	2.5 ± 0.8	8.6± 2.7
		Acidity constant (pK_H)	3.0 ± 0.1	8.4 ± 0.5	11.6 ± 0.4
AN/Col #2	DI water	Site density (10^{-5}mol/g)	23 ± 1	3.2 ± 0.1	11± 4
		Acidity constant (pK_H)	2.8 ± 0.1	8.3 ± 0.5	12.0 ± 0.4
AN/Col#2*	0.2M NaOH	Site density (10^{-5}mol/g)	25± 2	8.5± 1.3	11± 1
		Acidity constant (pK_H)	3.5 ± 0.1	7.0 ± 0.3	11.1 ± 0.1
AN/NRT #2	DI water	Site density (10^{-5}mol/g)	47 ± 2	2.5 ± 1.2	16 ± 20
		Acidity constant (pK_H)	3.4 ± 0.1	8.8 ± 1.1	12.1 ± 0.9







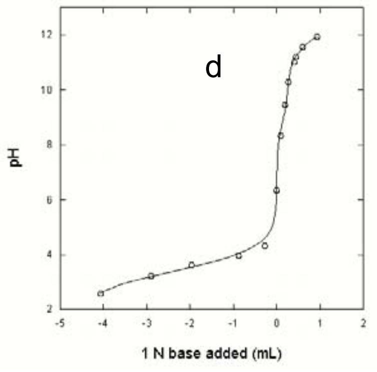


Figure 1 Titration and curve fitting results for washed ashes: (a) AN/Col #1; (b) AN/Col #2 (DI water washed); (c) AN/Col #2 (0.2M NaOH washed); and (d) AN/NRT #2. Ionic strength = 0.01 M ($NaNO_3$), temperature = 20 – 25 ^{0}C; equilibration time = 24 hours.

Surface Analysis with XPS

To obtain ash surface composition information and oxidation states of arsenic, the raw ash and washed ash of AN/Col #2 were scanned with XPS. Table 2 shows the relative amounts of each element detected on ash surface. It can be seen that C, O, Al, and Si are major elements on surface, while the amounts of Ca, As and Se are much lower. Quantitative change of these elements before and after washing is also observed. The increase of oxygen may be due to the surface contamination by oxygen in air. The decrease of carbon could be caused by the removal of carbon content during the washing process. For Se and Si, their concentrations on surface increased after washing, which suggests that these elements tend to be under the top layer of the ash surface. The amount of As and Al decreased, suggesting that these elements may be desorbed or dissolved in water during washing. It may also indicate that arsenic tends to be concentrated on the ash surface.

Table 2. Surface composition of ash AN/Col #2 based on XPS analysis.

Element		C	O	Al	Ca	Si	As	Se
Relative Amount (%)	AN/Col #2 Unwashed	7.88	60.8	16.2	0.016	15.1	0.0062	0.019
	AN/Col #2 Washed	3.43	66.4	10.8	0.016	19.3	0.0042	0.033

Effect of pH on Arsenic Leaching

Effect of pH on arsenic leaching from raw ash AN/Col #1 and AN/Col #2 was investigated using batch leaching methods. Figure 2 shows the soluble arsenic concentration as a function of pH. Figure 2 shows that more arsenic can be released from ash AN/Col #1 than from AN/Col #2. Results also indicate that arsenic can be released when pH is less than 3 or greater than 7, while in the pH range between 3 and 7, very little arsenic is released. This can be explained with arsenate speciation analysis.

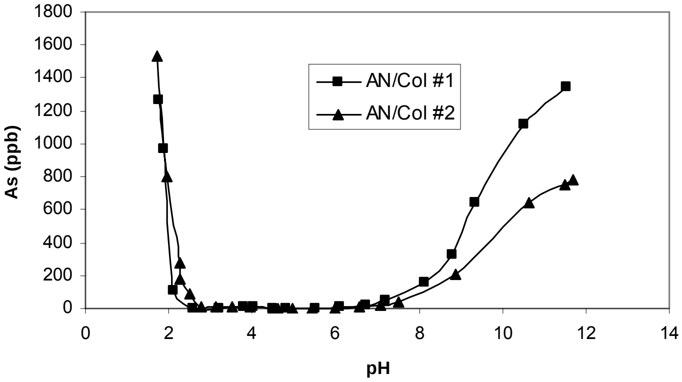


Figure 2. Basic leaching results for As from ash AN/Col #1 and AN/Col #2. Experimental conditions: S/L = 1:10; temperature = 20 – 25 ^{0}℃; equilibration time = 24 hours.

Figure 3 shows the As(V) speciation diagram. When pH is very low (less than 2), the major arsenic species is the H_3AsO_4, which does not have charge. It appears that the neutral arsenic molecules are not easily adsorbed by ash surface. When pH is increased above 2, the total concentration of anionic arsenic species ($H_2AsO_4^-$ and $HAsO_4^{2-}$) is also increased. These anions can be strongly adsorbed by positively charged ash surface sites. When pH is further increased above 7, both the ash surface and arsenic are negatively charged, which results in the arsenic release.

Coal ash AN/NRT #2 was also investigated using batch leaching approach. This coal ash had a higher calcium content than the other two coal ashes. Figure 4 shows the leaching results under two S/L ratios. Results indicate that the leachate arsenic concentration for this ash is significantly greater than the other two ash samples. The leaching behavior of arsenic is similar to the other two ashes when pH is less than 9. However, the soluble arsenic concentration deceases with the increase of pH when pH is greater than 9, and increases again with the increase of pH when pH is greater than 11. This behavior may be caused by the precipitation of arsenate compounds. When pH increases, more arsenic is in the free arsenate ion form, which will form precipitates with many cations including calcium. Therefore, the total arsenic concentration decreases with the increase of pH when pH is greater than 9. If we further increase the pH above 11, free cation concentration will be decreased due to the formation of metal-hydroxides. Therefore, some precipitated arsenic can be dissolved due to the decrease of free cation concentration.

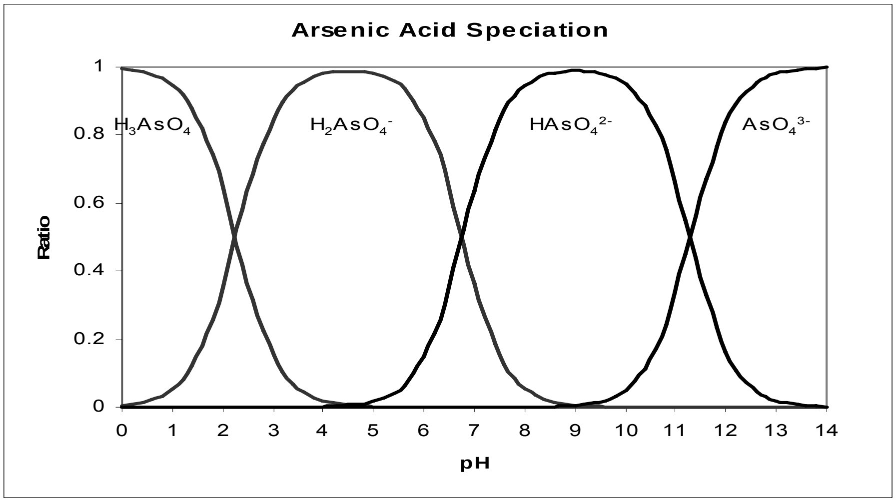


Figure 3. Speciation of arsenic acid.

Figure 4 also shows that, in alkaline pH range, the soluble arsenic concentration is high when the S/L ratio is low. This suggests that, under the low S/L conditions, the total cation concentration is low. Therefore, more arsenic is in soluble form under the saturation condition.

Leist reported that the calcium concentration in the leachate was mirrored in the arsenic concentration, suggestive of As-Ca precipitation.[20] To verify whether As-Ca correlation exists in our system, calcium concentrations in supernatants were measured. The results are also shown in Figure 4. Based on K_{sp} of $Ca_3(AsO_4)_2$ and dissolved calcium concentrations, the saturation concentrations of AsO_4^{3-} and total dissolved arsenic were calculated. However, our calculation results are about 10 times greater than experimental data, which indicates that some other factors may also present in the system affecting arsenic release. This will be investigated in our future studies.

Results also show that when pH is less than 9, the soluble concentrations of arsenic under two ash S/L ratios are overlap. This could be caused by joint effects of adsorption and precipitation. It is speculated that due to the arsenic speciation, there is less chance of precipitation under low pH. The details of this “overlap” phenomenon will be investigated in future.

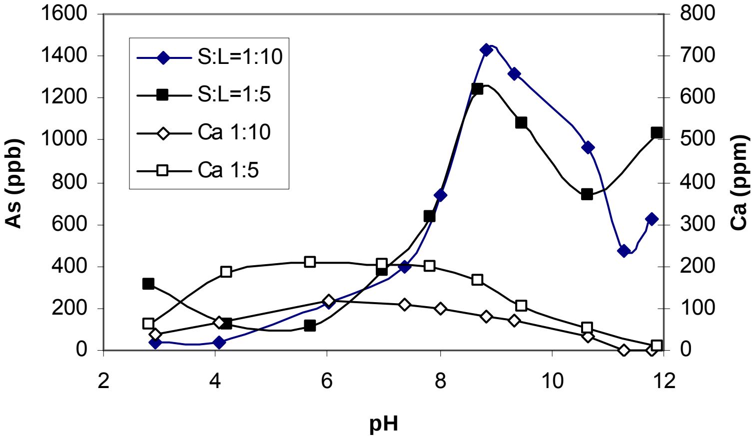


Figure 4. Basic leaching results for As & Ca from ash AN/NRT #2. Experimental conditions: S/L = 1:10; temperature = 20 – 25 ^{0}C; equilibration time = 24 hours.

As (V) Interactions with Washed Ash

In order to determine the significance of adsorption on arsenic leaching, an arsenic partitioning experiment was conducted using washed ash. In this experiment, the NaOH washed ash AN/Col #2 was used for arsenic partitioning studies. Different initial As(V) additions were used: 0, 1, 2, 5 and 10 ppm. Figure 6 shows the arsenic partitioning results. Results indicate that pH has the similar effect on soluble As (V) concentrations for systems containing washed ash and raw ash. The 0 ppm addition data indicate that the washed ash still contained some leachable arsenic. Results also show that, in a broad pH range, the soluble arsenic concentration is proportional to the arsenic addition, which indicates that the adsorption plays a major role on arsenic partitioning. However, when pH is greater than 9, the soluble arsenic concentration for the 10 ppm arsenic addition scenario decreases with the increase of pH. This could be caused by the arsenic precipitation with the cations but this explanation needs to be further verified. Compared with the basic leaching results in Figure 3, the higher percentage of As(V) is in soluble phase for the washed ash. This could be caused by the removal of other cations during the washing process.

Modeling for As(V) Partitioning

Equation 12 was used to model As(V) partitioning results. Previously determined parameters including the surface site density and acidity constant were applied to the model. For this study, only site α was considered, which is most possible to be the arsenic adsorption site. Since a certain amount of arsenic can be released from the ash with 0 ppm addition, a background concentration was estimated to calculate the total arsenic concentration in the system after arsenic addition. The arsenic uptake ratio R can be expressed as $[1 - M_d/(M_{add}+M_b)]$, where M_d, M_{add} and M_b are the dissolved, added and background arsenic concentrations, respectively. Considering that precipitation may occur at very high pH, only the data with pH condition of lower than 9 was used for curve fitting.

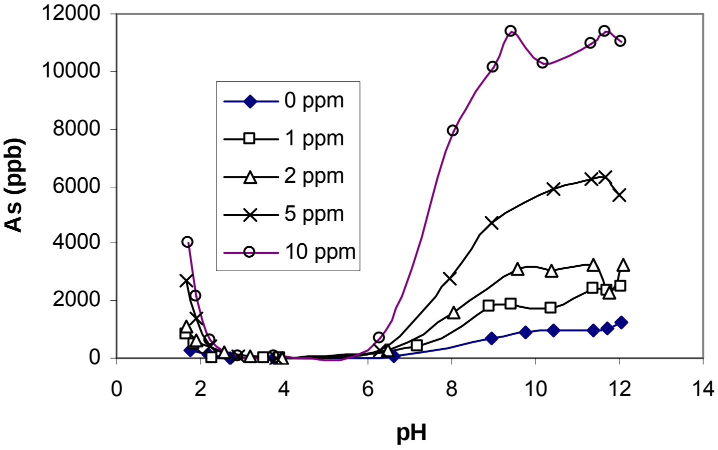


Figure 5. As(V) partitioning results for 0.2 M NaOH washed ash AN/Col #2. Experimental conditions: S/L = 1:10; ionic strength = 0.01M $NaNO_3$; temperature = 20 – 25 ^{0}C; equilibration time = 24 hours.

Based on the soluble arsenic concentrations in Figure 5, the amount of arsenic addition, and the estimated background arsenic concentration, the arsenic partitioning can be calculated. Figure 6 shows the arsenic partitioning (R) as a function of pH (points). It shows that, regardless of the amount of arsenic addition, the percentage of arsenic on the ash surface is constant for a given pH. It indicates that all experiments were conducted within the linear range of the Langmuir isotherm.

Kaleidagraph^{TM} was used to perform the curve fitting and determine the adsorption constants of two species $H_2AsO_4^-$ and $HAsO_4^{2-}$. Because the species AsO_4^{3-} is significant only under very high pH conditions when the surface sites are negatively charged, the chance of AsO_4^{3-} adsorption by positively charged surface sites is minimum. Therefore, the adsorption of AsO_4^{3-} was not considered in the model. The solid curve in Figure 6 is the model result. Table 3 shows the calculated adsorption constants, their standard errors, and the correlation factor for the curve fitting. The good agreement between experimental data and the theoretical model indicates that this model is successful and practical for simulating arsenic partitioning under different pH conditions.

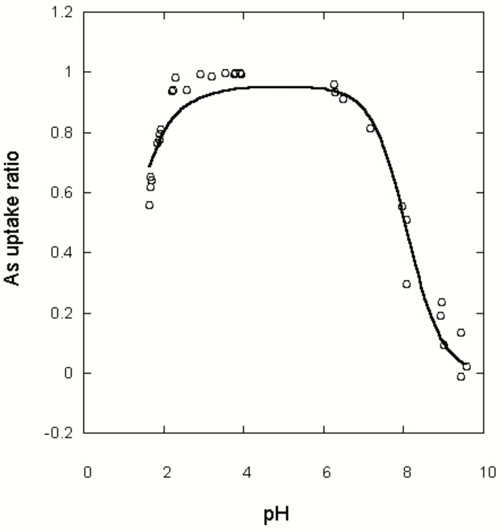


Figure 6. The adsorption results of As(V) onto washed ash AN/Col #2. Experimental conditions: metal concentrations = 1 - 10 mg/L; S/L = 1:10; ionic strength = 0.01M ($NaNO_3$); temperature = 20 – 25 ^{0}C; equilibration time = 24 hours.

Table 3 Adsorption constants between As(V) and ash AN/Col #2

Species	$\log K_s$	Standard Error	R^2
$H_2AsO_4^-$	2.64	0.06	0.95
$HAsO_4^{2-}$	6.20	0.06	

CONCLUSIONS

Results indicate that there are three acid sites on ash surfaces, among which the first acid site is most likely responsible for adsorption of arsenic. The model developed in this study based on arsenic speciation analysis can be used to quantify the As (V) partitioning. The adsorption constants ($\log K_S$) for $H_2AsO_4^-$ and $HAsO_4^{2-}$ are determined to be 2.6 and 6.2, respectively. Results also indicate that adsorption and precipitation may concurrently exist to control arsenic leaching.

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Experimental Analysis of Nutrient Uptake in Streams

Basic Information

Title:	Experimental Analysis of Nutrient Uptake in Streams
Project Number:	2004MO35B
Start Date:	3/1/2004
End Date:	2/28/2005
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Congressional District:	8th
Research Category:	Water Quality
Focus Category:	Nutrients, Water Quality, Nitrate Contamination
Descriptors:	
Principal Investigators:	Dev Niyogi

Publication

Missouri Water Resources Research Center Grant Program
Progress Report
May 2005

Title: Experimental Analysis of Nutrient Uptake in Streams
Name: Dr. Dev K. Niyogi
University of Missouri-Rolla
Status: In-progress (project end-date was extended for one year)
Amount funded: $18,985
Amount spent: appr. $13,100
Number of students supported: 3
1 Ph.D. graduate student, Cem Selman
3 undergraduate students, Cindy Buschmann, John Campbell, Jessica Wilson

Project objectives

Excess nutrients, primarily nitrogen and phosporus, in natural ecosystems represent one of the greatest environmental problems of our time (Vitousek et al. 1997). The addition of nutrients, from a variety of anthropogenic sources, can have profound effects on terrestrial, freshwater, estuarine, and marine ecosystems. Aquatic ecosystems, including lakes and estuaries, are of special concern given the effects of eutrophication from excess nutrients on the resources and services that these systems provide to humanity (Carpenter et al. 1998). From declines in lake clarity to the imperilment of estuarine fisheries, many aquatic ecosystems have suffered from excess nutrients.

The delivery of nutrients, often derived from agricultural lands, to lakes and estuaries is mediated by streams (Hall 2003). Streams have often been viewed as simple pipe-like conduits that passively transport pollutants, but that view is changing. As nutrients are transported in streams, they may be taken up by stream algae (and higher plants) and microbes (bacteria and fungi), thereby dampening the flux of nutrients to downstream systems. Several recent studies using large-scale models have suggested that small streams can be particularly effective at retaining nutrients from agricultural landscapes en route to fragile open water systems (Alexander et al. 2000; Seitzinger et al. 2002). The exact mechanisms of nutrient retention, however, are not well understood. Understanding what controls nutrient uptake in streams is critical to predicting and managing the flux of excess nutrients to fragile systems. In this project, I am using a combination of experimental and observational approaches to increase our ability to predict the uptake of nutrients in streams.

The central goal of the research is to examine the biotic controls on nutrient uptake in streams. My research team and I are using experimental streams to measure uptake under varying ecological conditions. In addition, we are measuring uptake in natural streams and comparing actual rates to rates predicted from experimental studies. Our specific goals for the project include:

1) Determine effects of biological demand from algae and microbes on leaf litter on nutrient uptake in experimental channels.

2) Extend the mechanistic understanding of nutrient uptake gained from experimental channels to the prediction and validation of uptake in whole streams.

Results to date

Experimental channels

My students and I have conducted several trials using experimental channels to measure uptake rates of nitrogen and phosphorus. The tests are being used to develop predictive models of the influence of algal biomass and leaf litter on nutrient uptake rates. For example, increasing amounts of algal biomass from Mill Creek, an Ozark stream, are related to higher uptake rates of both soluble reactive phosphorus (SRP) (Fig. 1) and nitrate-nitrogen (NO_3^--N) (Fig. 2).

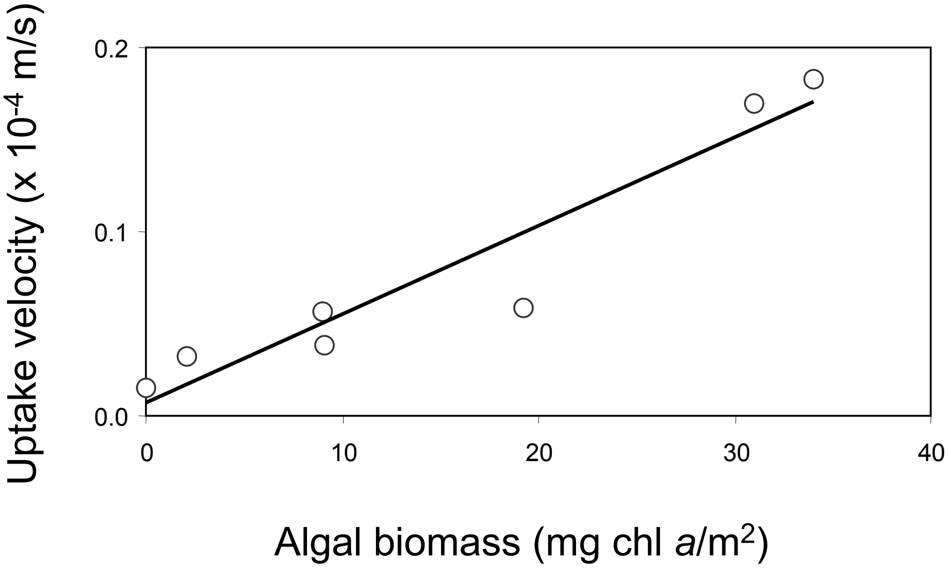

Figure 1. Uptake velocity of soluble reactive phosphorus (SRP) versus algal biomass (measured as chlorophyll *a*) in experimental channels. Experiments were conducted under full sun in late summer; water and algae were collected from Mill Creek in Mark Twain National Forest. $R^2 = 0.91$ for regression line ($P < 0.01$).

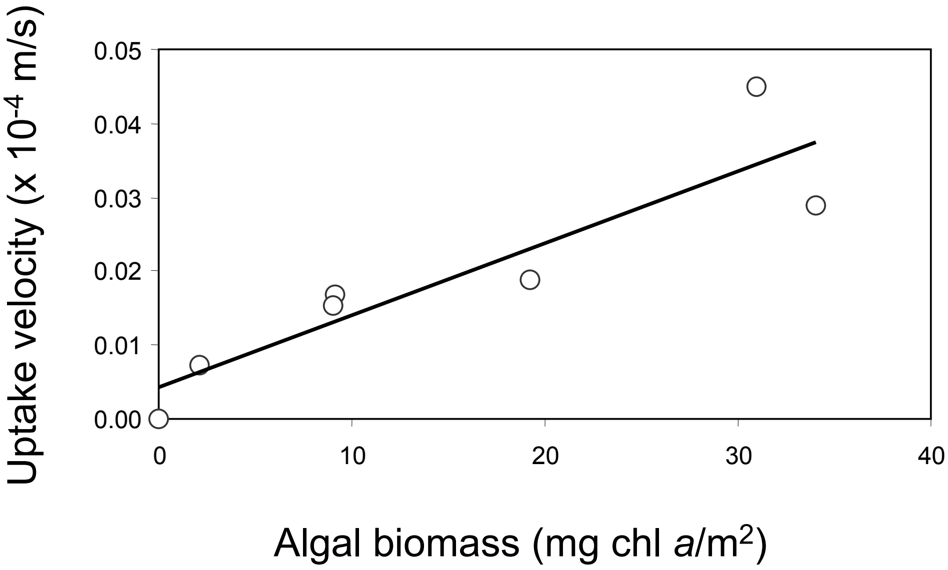

Figure 2. Uptake velocity of nitrate-nitrogen (NO_3^-) versus algal biomass (measured as chlorophyll *a*) in experimental channels. Experiments were conducted as described in Figure 1. $R^2 = 0.81$ for regression line ($P < 0.01$).

Additional experiments were carried out in autumn and winter with varying amounts of decomposing leaf litter in experimental channels. As expected, the amount of leaf litter in experimental channels was closely related to uptake rates of SRP (Fig. 3).

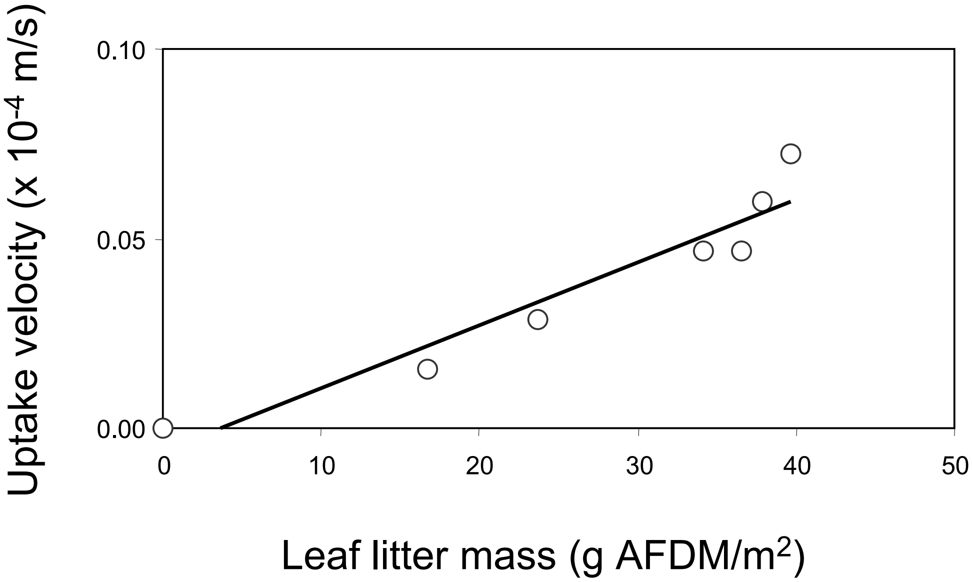

Figure 3. Uptake velocity of soluble reactive phosphorus (SRP) versus leaf litter mass (measured as ash-free dry mass, AFDM) in experimental channels. Experiments were conducted in the lab; water and leaf litter were collected from Mill Creek in Mark Twain National Forest. $R^2 = 0.91$ for regression line ($P < 0.01$).

Natural streams

As part of our research, my students and I have conducted monthly sampling of several nearby streams. Downstream changes in nutrient concentrations, although influenced by several factors, can reflect uptake of nutrients by stream biota. For example, nutrient concentrations decline along Mill Creek from its source at a spring to its confluence with the Little Piney River (Fig. 4). This section of Mill Creek is a losing stream without any tributaries, so the decline in nitrate is probably related to uptake by

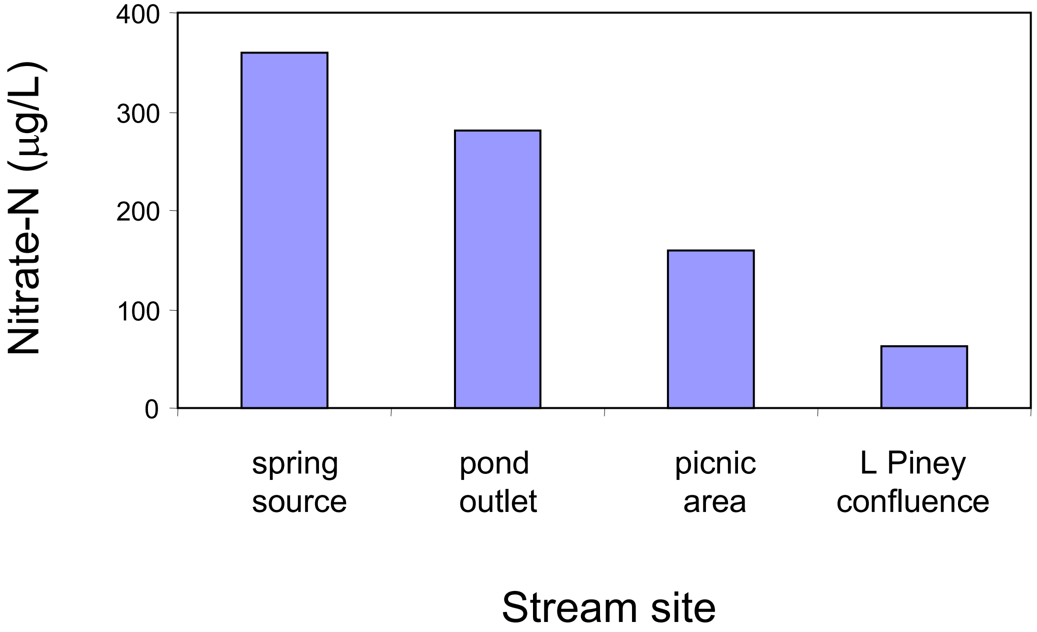

Figure 4. Concentrations of nitrate-N at several sites along Mill Creek in Mark Twain National Forest on April 5, 2005. Water emanates from a spring (first site) and then enters a pond (second site). The third site is at a USFS picnic area about 5 km downstream from the source, and the confluence with the Little Piney River is an additional 5 km from the picnic area.

algae and microbes in the stream. Measurements using the experimental channels at this site (Fig. 1) support this idea. It is remarkable that most of the nitrate present in the source water at the spring is attenuated by the biota in the stream.

My research team has also directly measured uptake rates in natural streams. Currently, we have collected data from several small streams, including one located in a new preserve purchased by the Audubon Society. Uptake rates of SRP and NO_3^- vary across the seasons (Fig. 5), with the highest rates thus far seen in late summer. Several factors can influence these rates, including hydrology, temperature, and stream biota. Stream temperature was highest during the measurement during late summer, and high algal biomass was also present then. During the winter measurement (March 2005), rates were still somewhat high (compared to other studies), probably because of the large

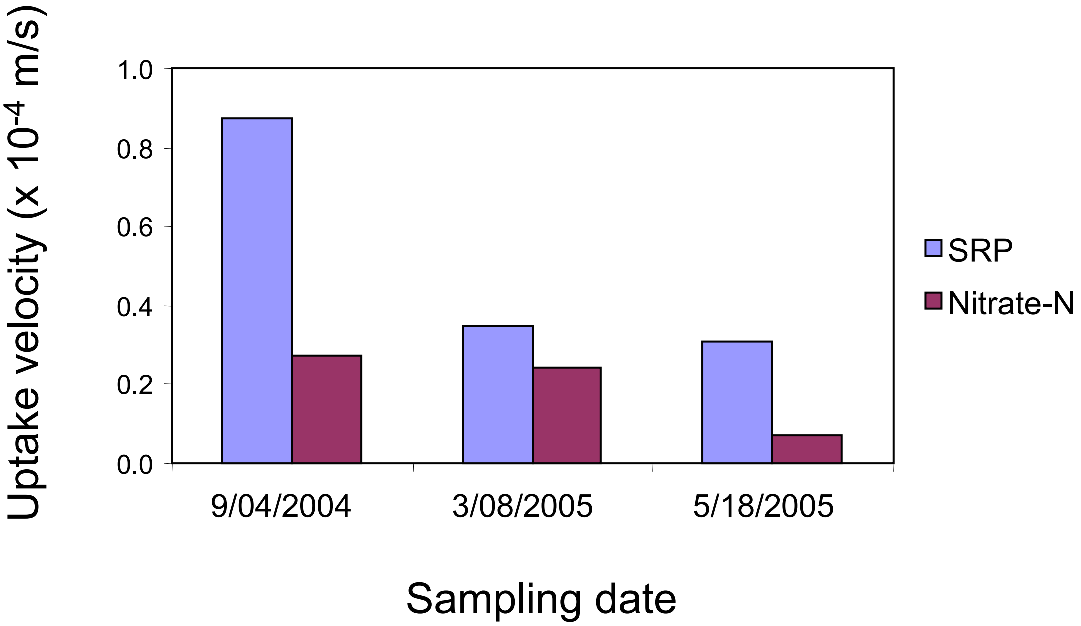

Figure 5. Uptake velocities of soluble reactive phosphorus (SRP) and nitrate-N in a small stream flowing through the Audubon Society nature preserve in Rolla. The site is a small (2nd-order) stream with a baseflow discharge of about 5 L/s during the measurements.

amounts of leaf litter present in the stream. Future experiments will help elucidate the main controls on uptake rates in this and other streams during different times of the year.

Plans for the coming year

My graduate student and I are currently running additional trials with the experimental channels to predict the effects of algal biomass on uptake rates. These measurements will add to the data shown in Figure 1, and allow testing of other factors that affect algal uptake, such as temperature and light. Some of these new experiments will be conducted in the new greenhouse at UMR (on the roof of the new Civil Engineering building). Similar experiments will be conducted during autumn and winter with the focus on the role of leaf litter on nutrient uptake.

We are also planning to expand our sampling of natural streams to include additional sites in the Ozarks. These measurements will be conducted over the summer, and again in the autumn/winter when leaf litter inputs are highest. Additional assays will be conducted to measure activity of primary producers (mainly algae) and leaf litter microbes in the streams, as these biota are thought to primarily responsible for nutrient uptake. The final part of the project will be the development and refinement of predictive models to compare the experimental results with measurements along natural streams.

Student involvment

Up to this point, 4 students have been directly involved with the research project. Cem Selman is a graduate student at UMR pursuing a Ph.D. in the Department of Environmental Engineering. Three undergraduates (Cindy Buschmann, John Campbell, Jessica Wilson) from the Department of Biological Sciences have also helped out with both field and lab analyses. Additional undergraduate students will help out during the coming year. All students have gained experience in field stream sampling, including measuring stream discharge, collecting water and biological samples, and conducting nutrient uptake measurements. In the lab, students have gained experience in running nutrient tests using spectrophotometric and chromatographic assays, measuring algal biomass (as chlorophyll *a*) and leaf litter amounts, following lab safety and waste guidelines, and analyzing data using spreadsheet and statistical software. At least two of the undergraduate students are now considering careers in conservation or water quality given their training and experience with this project.

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Geographic Information Systems for Tracking Vessels on the Inland Waterways

Basic Information

Title:	Geographic Information Systems for Tracking Vessels on the Inland Waterways
Project Number:	2004MO59B
Start Date:	5/1/2004
End Date:	4/30/2005
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Focus Category:	Methods, Solute Transport, None
Descriptors:	GIS Tracking, Inland Waterway Transport, Tracking Systems
Principal Investigators:	Ray Mundy, James Campbell, Ray Mundy

Publication

Geographic Information Systems for Tracking Vessels on the Inland Waterways
USGS award No. 04HQGR0145 REVISED
Status Report – May 25, 2005

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This note summarizes the status for the project “Geographic Information Systems for Tracking Vessels on the Inland Waterways” (USGS award No. 04HQGR0145 REVISED). The major activities of the project are:

- Survey geographic information systems (GIS) and automatic tracking applications for inland waterway transport on the Upper Mississippi River (UMR) system.
- Develop a prototype GIS to display dynamic vessel locations, lock locations and operating conditions, river features, and important shore elements, with relevant attribute data.
- Document appropriate technologies necessary to implement the tracking system.
- Conduct a peer review of the GIS system from both academic and practitioner viewpoints.

Each of these activities is addressed in the remainder of this document, preceded by a brief introduction.

Introduction

Inland waterways in the United States carry over 600 million tons of commerce per year. This accounts for about 300,000 million ton-miles or approximately 8% of the total freight traffic in the U.S. The Mississippi River system is the most important component of the inland waterway system, accounting for about 65% of the total domestic inland waterway tonnage. A system of 29 locks and dams has been constructed along the Upper Mississippi River (UMR) to facilitate the transportation of bulk commodities vital to the United States economy. Tows (tow boats pushing groups of barges) traveling up and down the UMR may experience congestion at the locks which creates unproductive waiting time while other vessels utilize the lock chamber.

Many transportation systems rely on vehicle or vessel tracking with geographic positioning systems to improve operations, environmental protection, safety, and security. Vessel tracking technologies allow real or near-real time tracking of watercraft at remote locations. Geographic information systems (GIS) provide a visual display of location-based data integrated with descriptive attribute information. Integrating vessel tracking with GIS can help improve transportation system operations by visually presenting vessel positions and movements on electronic maps that display infrastructure and other relevant features, along with associated static and dynamic descriptive information. Current technologies for finding real-time locations and for mobile communications allow data to be collected and displayed efficiently in real or near-real time. This enhanced visibility and knowledge can lead to better management of limited transportation resources and constrained infrastructures. This project investigates the feasibility of vessel tracking for better managing lockages, thereby improving traffic flow on the inland waterways, and develops a prototype GIS-based vessel tracking system for monitoring vessels on the UMR.

This project compliments a companion project underway at the Center for Transportation Studies (CTS) at the University of Missouri – St. Louis entitled "Appointment Systems for Inland Waterway Traffic Control". The Appointment Systems project investigates how an intelligent appointment or scheduling system that better manages tows and barges for passage through the locks on the UMR might reduce congestion at the locks. A GIS-based vessel tracking system could support more effective and more efficient lockages and river traffic management by providing relevant individuals (e.g., a river "traffic manager") with a single information source including dynamic display of vessel locations and attribute information. Collateral benefits could accrue to inland waterway shippers and carriers through decreased costs and increased reliability from more efficient lock operations. A vessel tracking system on the UMR could also provide benefits in other areas, including homeland security, by providing information on where individual barges are located within the waterway system, as well as to whom they belong, their contents and their precise position in regard to various structures within and along the waterway.

The Upper Mississippi River (UMR) is an integral part of a national inland water transportation network. The UMR river navigation system provides an important transportation link into and out of America's Midwest. The UMR navigation system extends approximately 663 miles north from the confluence of the Mississippi and Missouri Rivers (just north of St. Louis, Missouri) to just beyond Minneapolis, Minnesota. There are more than one hundred terminals along the UMR that ship and receive commodities. Agricultural products are the primary commodities transported on the UMR; other common bulk commodities include chemical products, coal, cement, and petroleum products.

Safe and reliable navigation on the UMR from St. Louis to Minneapolis is created by a series of 29 lock and dam facilities that are designed to produce a minimum channel depth of nine feet for the entire length of the navigable system. Figure 1 presents a map of the UMR portion of the inland navigation system. The dams on the UMR create a sequence of connected pools that maintain the depth necessary for navigation of commercial tows, as well as other vessels. Lock chambers at each dam permit traffic to traverse up and down the river system. Figure 2 presents a schematic view of the UMR pool system.

Traffic congestion arises on the UMR at the locks when demand for lockages exceeds the throughput capacity. This may be due to heavy levels of traffic or to a decrease in capacity at the lock (for example, due to lock maintenance or closure). Unusual events such as lock malfunctions, tow pilot errors, and adverse vessel or lock operating conditions also contribute to delays at these locks. The time for a lockage depends on a range of factors including the structural design of the lock itself, the size and characteristics of the tow, the equipment on the barges and at the lock, the experience of the crew, flow conditions, weather, and the previous lockage. Also, significant use of the locks by non-commercial vessels, such as privately owned recreation craft, can contribute to congestion and lockage delays in the UMR system.

The original locks on the UMR were constructed in the 1930's with main chambers 600 feet in length and 110 feet in width. These locks were originally designed at 600 feet long to accommodate the largest commercial tows at that time. Since then towboats on the UMR have become significantly larger to take advantage of the strong economies of scale in river transportation. Large tows on the UMR now measure almost 1200 feet in length and are often comprised of 15 barges (each approximately 200 feet long) arrayed in five rows of three barges each, pushed by a single towboat. Movement of a tow longer than 600 feet through a 600 foot long lock chamber requires two passes or "cuts". To accomplish this passage, the tow enters into the chamber, decouples from a set of barges (less than 600 feet long), then backs out of the chamber. The chamber is then raised or lowered as desired and the barges in the chamber are then moved out of the chamber (e.g., using winches at the lock) and tied along a wall just outside the chamber. The chamber is then returned to the original level to take the remaining barges and towboat. These enter the chamber and are raised or lowered as a unit. Then the tow must be re-coupled by joining the two segments, before proceeding on its way. These "double lockages" require a relatively lengthy processing time: the mean lockage time for a two-cut tow is two to three times larger than the mean lockage time for a single cut tow on the locks of interest on the UMR.

Three locks on the UMR have been extended or replaced to now measure 1200 feet in length (locks 19, 26, and 27) and these locks experience relatively little congestion since their length precludes double lockages. The lower (southernmost) five 600 foot long locks of the UMR navigation system, Locks 20, 21, 22, 24 and 25 (there is no Lock 23) are the most heavily utilized 600 foot long locks, and are among the most congested of all locks in the inland navigation system. These locks have been selected as the study site for the companion project "Appointment Systems for Inland Waterway Traffic Control". These five locks experience periodic traffic congestion and strong seasonal variation in demands for service. They also tend to operate as a system in that they share a large amount of common interrelated commercial tow traffic. The prototype GIS-based vessel tracking system is developed for the portion of the UMR covering these five locks.

Congestion at the locks produces waiting times for the tows that arrive while the lock chamber is occupied. For the five locks in the study area, the U.S. Army Corps of Engineers OMNI lock data for 2000 through 2003 indicates that the average number of lockages per lock per year was 3,509 and vessels waited an average of 2.4 hours per lockage before beginning processing at a lock. Of these lockages, 84% were for commercial tows and the average wait per commercial tow was 2.8 hours per lockage. (The greater mean waiting time for commercial tows - 2.8 hours vs. 2.4 hours for all vessels - reflects the priority given to non-commercial recreation craft.) There was also relatively large variability in the distribution of the waiting times throughout the entire four-year period.

To familiarize ourselves with the operating environment we have made site visits to all five Lock and Dam facilities in the study region (Lock & Dam 20, 21, 22, 24 and 25). We have also visited the Volpe National Transportation Center in Cambridge, Massachusetts to learn of their experiences with vessel tracking and GIS/GPS. We have also met with barge industry representatives, U.S. Coast Guard personnel, GIS managers with the Corps, and inland waterway researchers to collect relevant information for our study.

GIS and Vessel Tracking Applications

Vessel and vehicle tracking technologies are well developed for a wide variety of transportation applications, in both the public and private sector. For example, air traffic control systems have long been used to manage air transportation, primarily for reasons of safety (though security concerns have become prominent more recently). Public transit and public works agencies often track vehicles to improve operations. Private sector firms in the rail and motor carrier industry also track vehicles – and have developed extensive information and decision support systems based on dynamic real and near-real time locational data. Vessel tracking systems have also been implemented in a variety of applications worldwide for both maritime (deep-sea) and inland water transportation.

Vessel tracking systems require determining the location of the vessel and communicating that information (along with other relevant information) to a central location capable of receiving and managing the locational information. Vessel tracking applications generally have one of the following primary motivations: safety and security, compliance, and operational improvements/traffic management. However, there is often some overlap between these categories, and technologies implemented for one purpose (e.g., safety) may have applications in other areas (e.g., traffic management).

The larger barge companies operating on the UMR have implemented real or near-real time tracking for their own fleets of towboats on the UMR and other inland waterways. This information can be used for a variety of strategic and operational purposes within the firm. The U.S. Coast Guard has recently instituted tracking barges carrying of hazardous cargos on a portion of the UMR. However, the U.S. Army Corps of Engineers is not currently tracking tows on the UMR (or elsewhere), and neither the individual operators nor the Coast Guard share their data with the Corps. The closest the Corps comes to vessel tracking is in creating a database of the lockages for each lock, in which a variety of information is recorded for every commercial tow that passes through a lock. In the pools between the locks, the Corps is generally unaware of the exact location of the tow, though they may estimate its position based on the elapsed time from the last lockage and any communications with tow itself.

We are currently preparing a report to document the use of GIS and vessel tracking in applications from around the world relevant to the inland waterways. This report will include the following:

- Automatic Identification Systems (AIS) and its use on the St. Lawrence Seaway and in vessel traffic services (VTS) areas managed by the U.S. Coast Guard,
- The Inland Rivers Vessel Movement Center (IRVMC) in St. Louis that tracks transportation of certain dangerous cargoes (CDCs) on the UMR,

- The Vessel Identification and Positioning System (VIPS) system developed by the Volpe National Transportation Center and implemented in a variety of locations for safety, security and environmental compliance,
- Vessel Monitoring Systems (VMS) required by the National Marine Fisheries Service (NMFS) for compliance purposes,
- Commercial barge tracking systems in use on the UMR, such as BOATRACS,
- The SMARTLOCK project using differential GPS at the Port of Pittsburgh,
- The Communications Tracking and Navigation (CTAN) system at the Panama Canal,
- The development of the comprehensive river information system (RIS) concept in the European Union, and
- Relevant geographic information systems application for the inland waterways.

Prototype Vessel Tracking GIS

We have developed a prototype geographic information system (GIS) to display dynamic vessel locations, lock locations and operating conditions, river features, and important shore elements, with relevant attribute data. This is built using the ArcGIS 9 geographic information system with the Tracking Analyst extension for managing the dynamic tow locations (both are software products of ESRI, Inc.). Creation of the electronic base maps of the study area required collecting and cleaning a variety of spatial data sets for the river and shore features, as well as the lock and dam infrastructure, and developing the associated attribute information. To demonstrate the vessel tracking capabilities we created input files for dynamic display of tow locations for a set of sample voyages along the UMR derived from actual tows trips as represented in the OMNI database.

The prototype vessel tracking GIS provides sample displays and vessel tracking to demonstrate the type of functionality possible. Static map views demonstrate the capabilities to display geographic (map) and attribute (tabular) data that would be of use to a traffic manager responsible for lockages in the study area. Dynamic views are used to show tows moving on the UMR through the study region. Figure 3 is a screen capture from the prototype vessel tracking GIS display with 12 tows in the study area between Lock and Dam 20 (near the top) and Lock and Dam 25 (near the bottom). The small numbers along the river from 210 to 350 are the river miles as measured upstream from the mouth of the Ohio River. Figure 4 shows the prototype vessel tracking GIS display of Lock and Dam 24. This figure shows one tow in the lock chamber, three tows in queue (nosed into the shore) upstream of lock (between river miles 274 and 275) and one tow in queue downstream of the lock (between river miles 272 and 273). The five oval icons above and to the right of the lock provide relevant attribute (tabular) data for the upstream and downstream pools, Pool 24 and Pool 25 respectively, (P24 or P25), the lock (L) and the tows and recreational vessels in the lock queue (QT and QR, respectively). Figure 5 shows the same view with the accompanying attribute information for the queue of commercial tows (from the QT icon) at lock 24. The information to display with the prototype GIS depends on the needs of the “traffic manager” and the traffic management alternative, as identified in the companion project “Appointment Systems for Inland Waterway Traffic Control”.

Technologies to implement vessel tracking on the UMR

Tows on the UMR can be tracked in real or near-real time with a variety of different methods and technologies. Most large tow operators track their tows with commercial or proprietary systems. Popular satellite-based systems, such as BOATRACS (an extension of the OMNITRACS system for vehicle tracking on land), provide tow locations, and other information, automatically at regular intervals (e.g., hourly) and every time a message is sent. The U.S. Coast Guard tracks tows with hazardous cargoes by requiring the tow operators to report their position and some associated information at various locations along the river and when specified activities occur. This information may be provided electronically from the tow operator's traffic management center, or by the individual tow pilot using email, fax or phone.

The key components of a vessel tracking system for lockage (or traffic) management are: (1) finding the tow's geographic position, (2) communicating the tow position to a shore station, and (3) integrating the information for managing lockages. The geographic position of a tow can be readily and economically determined by equipment onboard the tow using standard GPS technologies or via triangulation with satellites or shore-based antenna. The tow position could also be determined by remote sensing technologies such as radar. However, remote sensing technologies require additional communications to identify the vessel and link to relevant data. Communication of tow locations from the tow to shore stations relies on standard communication channels and technologies via satellite or radio (VHF) (e.g., AIS). These transmissions may be secure or non-secure (as with AIS). Integrating tow locations into a lockage management decision support system requires collection of the relevant tow and lock data in real (or near-real) time, verification of the data, integration of data from numerous tows and other inputs, including the lock, for input to the lock management algorithm, and creation of the outputs (e.g., suggested lockage sequences or lockage appointment times).

We are currently preparing a report to document the technologies to implement vessel tracking on the UMR. This will focus on relevant methods for (1) acquiring dynamic location and attribute data of vessels, and (2) communicating the real-time information to the lock management system. The report will include the following:

- Vessel location technologies including GPS and DGPS (differential GPS),
- Other satellite systems for geographic positioning,
- Discussion of extending AIS to the UMR as a data source for managing lockages,
- Commercial vessel tracking systems, especially those that have been applied on the UMR,
- Communication options from ship-to-shore and on to the "traffic manager",
- Identification of key issues in position reporting and communications,
- Identification of key data elements specific to the tow and the voyage needed for managing lockages, and
- Discussion of key organizational issues, including responsibility and authority, associated with vessel tracking on the UMR.

Remaining Activities

The activities remaining for completion of the project include:

- Peer review of the prototype vessel tracking GIS from both academic and practitioner viewpoints,
- Visit to the St. Lawrence Seaway traffic control center (May 26, 2005),
- Refinement of the prototype GIS-based vessel tracking systems,
- Documentation of the development and the system requirements of the prototype vessel tracking GIS,
- Documentation of possible extensions of the prototype, and
- Finalizing all reports.

We are scheduling a conference with representatives of the Army Corps of Engineers, the Coast Guard, and the barge industry on June 15, 2005, to present preliminary results and obtain their feedback. We anticipate completion of the project in July 2005.

Figure 1. Map of the Upper Mississippi River (UMR) Navigation System
Source: U.S. Army Corps of Engineers

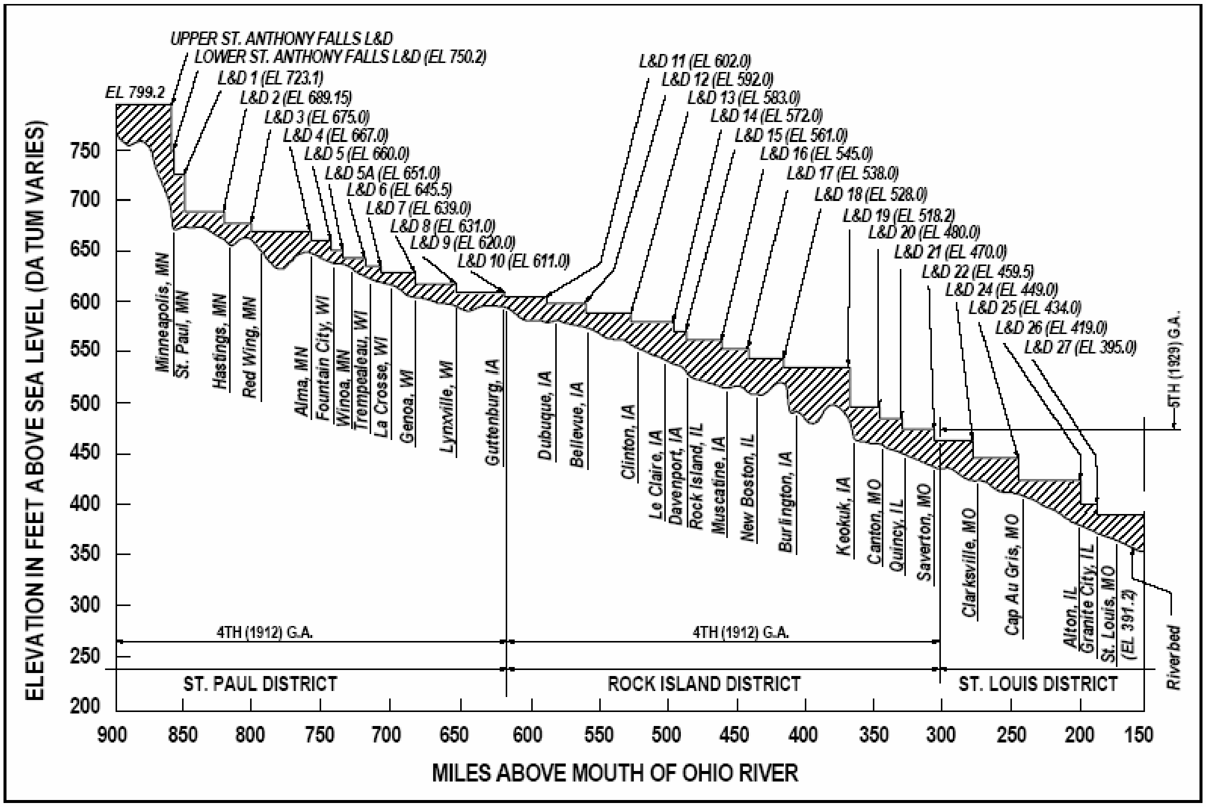


Figure 2. Schematic View of the Upper Mississippi River Pool System
Source: U.S. Army Corps of Engineers

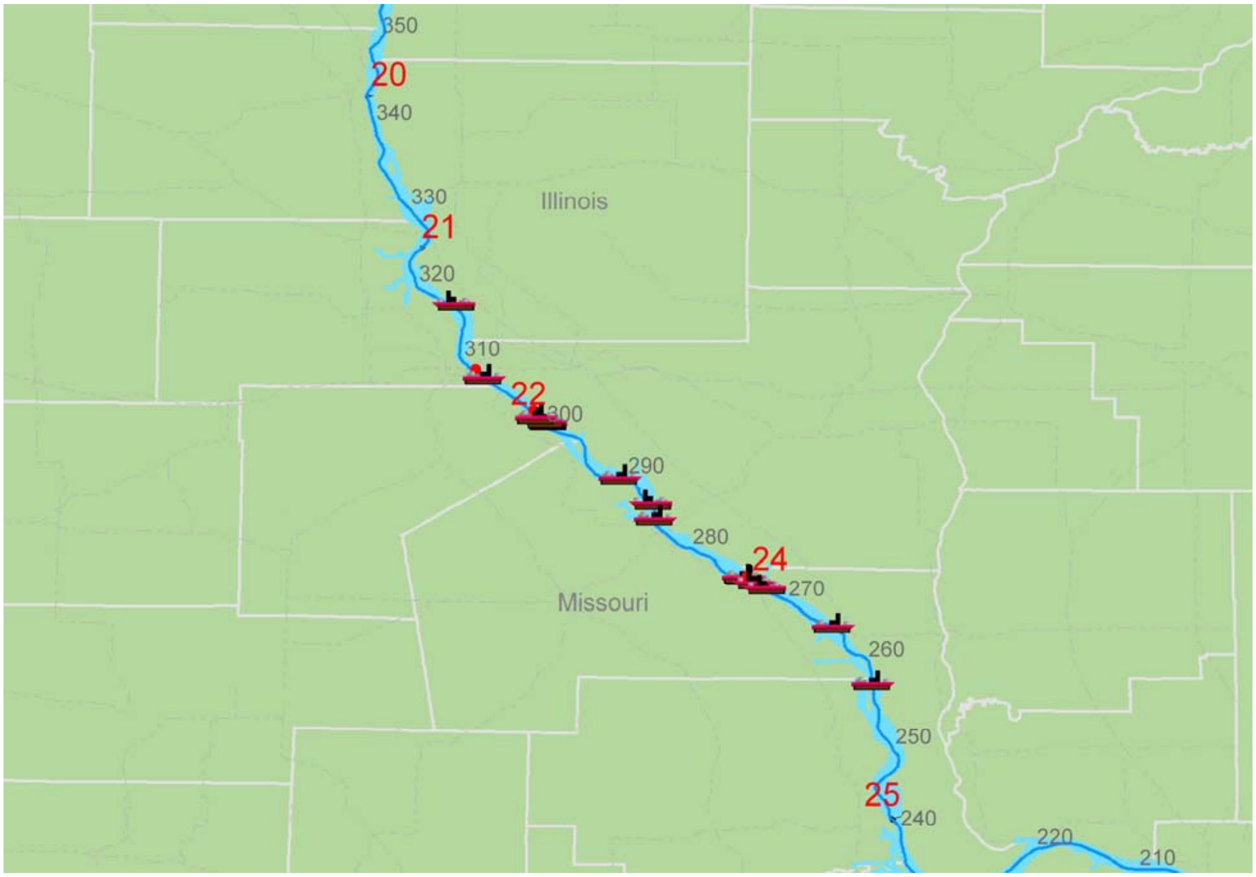


Figure 3. Prototype Vessel Tracking GIS Screenshot of the Study Area

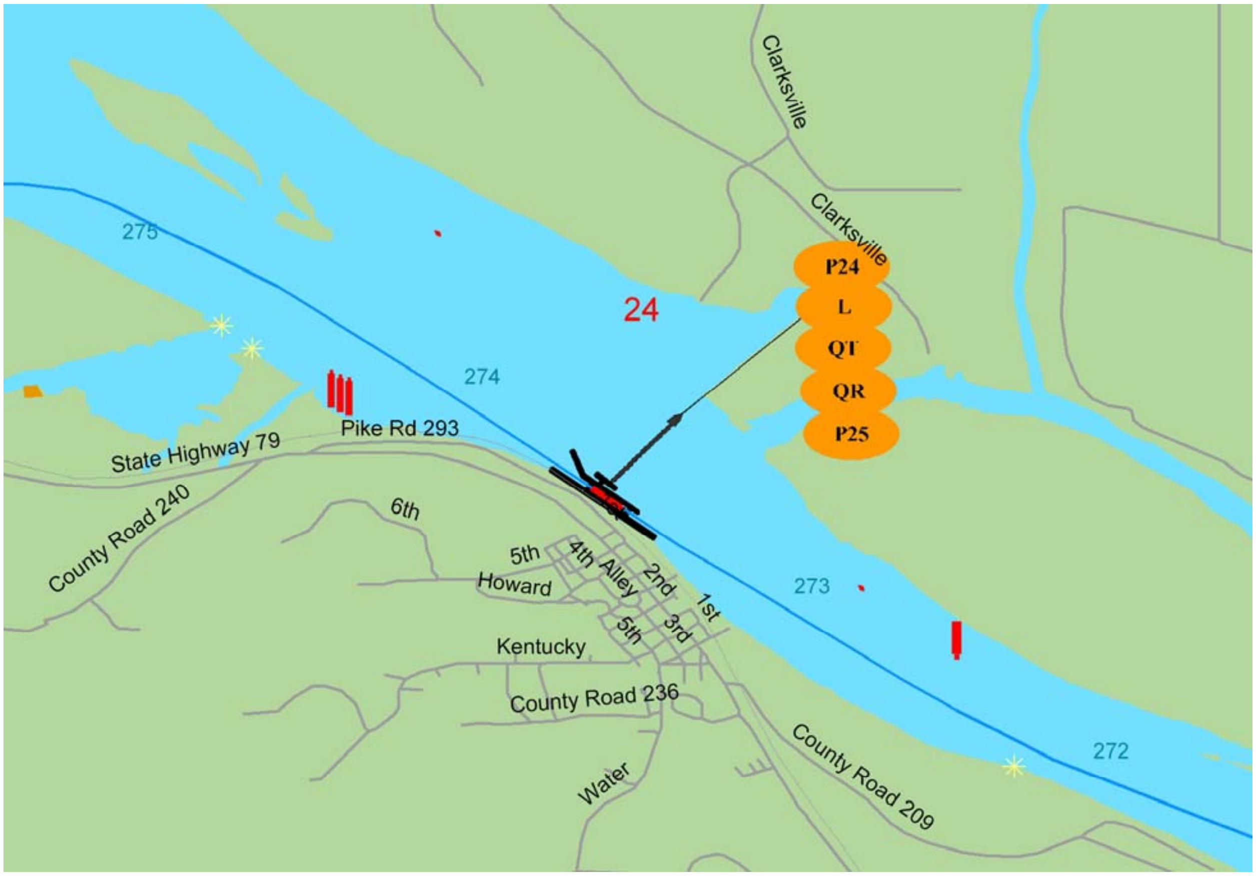
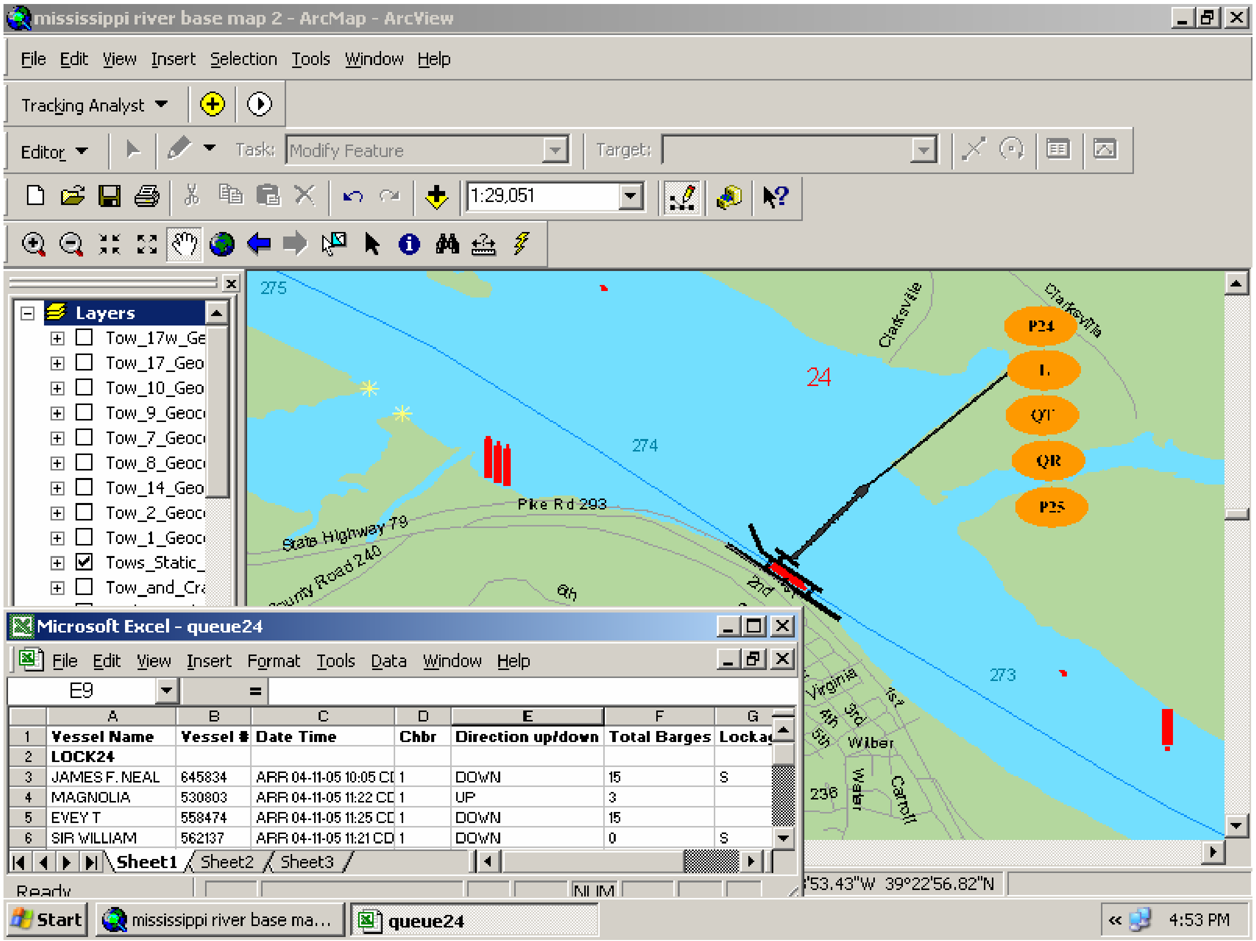


Figure 4. Prototype Vessel Tracking GIS Screenshot of Lock and Dam 24



	A	B	C	D	E	F	G
1	**Vessel Name**	**Vessel #**	**Date Time**	**Chbr**	**Direction up/down**	**Total Barges**	**Locka**
2	**LOCK24**						
3	JAMES F. NEAL	645834	ARR 04-11-05 10:05 C	1	DOWN	15	S
4	MAGNOLIA	530803	ARR 04-11-05 11:22 CD	1	UP	3	
5	EVEY T	558474	ARR 04-11-05 11:25 CD	1	DOWN	15	
6	SIR WILLIAM	562137	ARR 04-11-05 11:21 CD	1	DOWN	0	S

Figure 5. Prototype Vessel Tracking GIS Screenshot of Lock and Dan 24 with Lock Queue Data

Information Transfer Program

Student Support

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

Notable Awards and Achievements

The additional funding received for this research:

1. EPRI (project ID #060672) - $12,000 (initial match);

2. EPRI (project ID #007513) - $27,124;

3. EPRI has committed to provide an additional $24,932 to help us to set up the arsenic speciation capacity. We are processing the contract now. It should be in place in 2 3 weeks. This will allow us to have the most advanced HPLC-ICP-MS system to perform arsenic speciation research. There are only very few universities (2 3) in US have this capability.

Therefore, we have successfully attracted $64,056 in cash from EPRI so far for this research. We are expecting more funding from EPRI for related studies.

Publications from Prior Projects