Louisiana Water Resources Research Institute

Annual Technical Report FY 2004

Submitted By

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To:

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Water Resources Discipline
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Introduction

This report presents a description of the activities of the Louisiana Water Resources Research Institute for the period of March 1, 2004 to February 28, 2005 under the direction of Dr. John Pardue. The Louisiana Water Resources Research Institute (LWRRI) is unique among academic research institutions in the state because it is federally mandated to perform a statewide function of promoting research, education and services in water resources. The federal mandate recognizes the ubiquitous involvement of water in environmental and societal issues, and the need for a focal point for coordination.

As a member of the National Institutes of Water Resources, LWRRI is one of a network of 54 institutes nationwide initially authorized by Congress in 1964 and has been re-authorized through the Water Resources Research Act of 1984, as amended in 1996 by P.L. 104-147. Under the Act, the institutes are to:

"1) plan, conduct, or otherwise arrange for competent research that fosters, (A) the entry of new research scientists into water resources fields, (B) the training and education of future water scientists, engineers, and technicians, (C) the preliminary exploration of new ideas that address water problems or expand understanding of water and water-related phenomena, and (D) the dissemination of research results to water managers and the public.

2) cooperate closely with other colleges and universities in the State that have demonstrated capabilities for research, information dissemination and graduate training in order to develop a statewide program designed to resolve State and regional water and related land problems. Each institute shall also cooperate closely with other institutes and organizations in the region to increase the effectiveness of the institutes and for the purpose of promoting regional coordination."

The National Water Resources Institutes program establishes a broad mandate to pursue a comprehensive approach to water resource issues that are related to state and regional needs. Louisiana is the water state; no other state has so much of its cultural and economic life involved with water resource issues. The oil and gas industry, the chemical industry, port activities, tourism and fisheries are all dependent upon the existence of a deltaic landscape containing major rivers, extensive wetlands, numerous large shallow water bays, and large thick sequences of river sediments all adjacent to the Gulf of Mexico. Finally, many of the problems facing the state are derived from changes taking place in or affecting this delta landscape, including coastal erosion, landloss, sea level rise and climate change, hurricane flooding, run-off and riverine flooding, degradation of water quality and hypoxia.

The Institute is administratively housed in the College of Engineering and maintains working relationships with several research and teaching units at Louisiana State University. Recent cooperative research projects have been conducted with Center for Advanced Microstructures and Devices, the Louisiana State University Agricultural Center and the EPAs Hazardous Substance Research Center- South & Southwest.

Research Program

The primary goal of the Institute is to help prepare water professionals and policy makers in the State of Louisiana to meet present and future needs for reliable information concerning national, regional, and state water resources issues. The specific objectives of the Institute are to fund the development of critical water resources technology, to foster the training of students to be water resources scientists and engineers capable of solving present and future water resources problems, to disseminate research results and findings to the general public, and to provide technical assistance to governmental and industrial personnel and the citizens of Louisiana.

The priority research areas for the Institute in FY 2004 focus on a selected research theme. Because of the small nature of the projects, it was apparent that a greater impact is possible if a thematic area is chosen to focus several complimentary research groups on a single issue. Several themes were considered. At the State level, greater emphasis was being placed on pollutant transport issues. In particular these issues focused on characterizing particulates for heavy metals in aquatic systems using non-invasive spectroscopy and tomography. Projects selected were from a range of faculty with different academic backgrounds including agricultural engineers, environmental engineers and water resources. Supporting research in this priority area has increased the visibility of the Institute within the State. Two of the projects are in there second year of support.

The research projects are designated as Projects LA-17B, LA-18B, LA-19B, and LA-21B, as listed below.

Project 2003/04LA17B Willson, Use of Synchrotron Microtomography an X-Ray Fluorescence to Better Understand Contaminant Diffusion in Reactive Barrier Systems (2nd year)

Project 2003/04LA18B Roy, Metal Speciation in Particulates in the Mississippi River in Louisiana (2nd year)

Project 2003LA19B Paudel, Economic Assessments of Best Management Practices and Environmental Policy Options for Attaining the Total Maximum Daily Load (TMDL) Goal in Louisianas Major Milkshed (No Cost Extension)

Project 2004LA21B Singh Quantifying Hydrologic Impacts of Spatio-Temporal Variability of Stream Water Quality in Coastal Louisiana

These projects include 2 new projects in the areas of characterizing particulates for heavy metals in aquatic systems using non-invasive spectroscopy and tomography. These projects include two projects which focus on water quality issues (2003/04LA18B & 2004LA21B) and one project that focuses on a contaminated sediments and solute transport (2003/04LA17B). One of the no cost extension projects (2003LA19) has direct impact on non-point source pollution and mitigation problems associated with the TMDL regulatory issues. The three physical studies have also supported the Institutes long-standing commitment to computer modeling of water resources processes.

Use of Synchrotron Microtomography and X-Ray Fluorescence to Better Understand Contaminant Diffusion in Reactive Barrier Systems

Basic Information

Title:	Use of Synchrotron Microtomography and X-Ray Fluorescence to Better Understand Contaminant Diffusion in Reactive Barrier Systems
Project Number:	2003LA17B
Start Date:	3/1/2003
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	6
Research Category:	Ground-water Flow and Transport
Focus Category:	Sediments, Solute Transport, None
Descriptors:	Reactive Flow and Transport, Contaminated Sediments
Principal Investigators:	Clinton S. Willson

Publication

1. Hartono, S. and C.S. Willson, 2004, Improvements in Groundwater Systems Analysis Through the Spatial and Temporal Estimation of Irrigation Pumping, submitted ASCE Journal of Water Resources Planning and Management.
2. Rahman, A., C.D. White, D. Carlson, and C.S. Willson, 2004, Improvements in Groundwater Flow Modeling Through the Integration of Resistivity Logs and Hydraulic Conductivity and the Use of Variogram Uncertainty. submitted Mathematical Geology.
3. Crannell, B.S., T.T. Eighmy, C.S. Willson, D.D. Reible, and M. Yin, 2004. Pilot-Scale Reactive Barrier Technologies for Containment of Metal-Contaminated Sediments and Dredged Materials. A Final Report Submitted to: The NOAA/UNH Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET), November 2004.
4. Yin, M., C.S. Willson, and D.D. Reible, 2004, Investigation of Heavy Metal Migration from Contaminated Sediment to Capping material using XRF, presented at the 2004 AICHE Annual Meeting, November 7-12, 2004, Austin, TX.

Problem and Research Objectives

Sediment contamination can occur from the deposition of pollutants from the water column, deposition of contaminated particles, or through the seepage of contaminated groundwater. Unless removed or "controlled", contaminated sediments act as a continual source of pollutants to surface water bodies. This contamination may impact aquatic species and potentially render the water bodies unusable for recreation and/or drinking water supply.

Reactive barriers are capping materials that actively precipitate contaminants as they diffuse from contaminated sediment, rather than passively slowing the migration. The effectiveness of a reactive barrier depends on the ability to precipitate heavy metals from the pore solution onto the surface of the insoluble mineral by adsorption and surface precipitation. Continuous diffusion and subsequent precipitation within the reactive barrier also fills in the pore spaces around the materials, reducing permeability, and further inhibiting diffusion. The objective of this project is to continue the work where we are utilizing synchrotron X-rays to: (1) non-destructively quantify the diffusion of metals using X-ray fluorescence; and (2) quantify changes in the pore morphology of the reactive barrier using X-ray microtomography. Data and information obtained from these complementary experiments will help us better understand the pore-scale processes and phenomena impacting the transport of contaminant through reactive barrier systems. This work is also integrated with other research using X-ray absorption spectroscopy to look at metal speciation. The end result of this study will be better models and/or criteria for the design of reactive caps.

Methodology

X-ray Fluorescence (XRF): Basic XRF has become a well-established multi-element technique, capable of yielding accurate quantitative information on the elemental composition of a variety of materials. The technique is well-suited for studying environmental science problems because it is non-destructive, relatively rapid, and solids can be analyzed with little or no sample preparation. Apart from light elements, all elements with atomic numbers greater than 11 can be detected. The method is sensitive down to microgram-per-gram level and the results are precise and accurate if matrix effects can be corrected.

Synchrotron X-ray Microtomography (SXM): Synchrotron X-ray Microtomography has been developed over the past decade as a technique to non-destructively image the interiors of materials. Tomography deals with reconstruction of an object from its projections. Spatial resolutions on the order of ~ one to ten microns are possible because of the highly collimated and extremely bright X-rays produced by a synchrotron. These highly-parallel X-rays permit spatial resolution that is only limited by the optical components used to image them. Furthermore, the ability to tune to a monochromatic X-ray energy allows elemental discrimination.

In the spring of 2005, a multilayer monochromator was installed on the tomography beamline at CAMD. This monochromator will allow for high-resolution imaging of the sediment/reactive barrier cores.

Principal Findings and Significance

White-light and monochromatic XRF experiments have been performed at the LSU Center for Advanced Microstructures and Devices (CAMD) synchrotron facility. To date, these scans have been on cores obtained from a pilot-scale experiment currently being conducted at the University of New Hampshire. A final report to CICEET has been prepared (Crannell et al., 2004), one conference presentation has been made (Yin et al., 2004) and a manuscript is currently being prepared.

Metal sorption isotherm data is required to support the diffusion studies. Over the past year, a series of isotherm experiments at neutral pH values have been performed on sand, Anacostia sediment and two types of apatite for Cr(3), Cr(6), Zn, Cd, and Cu. These experiments were performed at neutral pH values. In addition, screening level diffusion tests were conducted to provide estimate of diffusion rates and concentrations.

Finally, based on the XRF data, we have been able to successfully fit a two-phase diffusion model and determine effective diffusivity values for a number of metals and sediment/barrier systems.

Metal Speciation in Particulates in the Mississippi River in Louisiana

Basic Information

Title:	Metal Speciation in Particulates in the Mississippi River in Louisiana
Project Number:	2003LA18B
Start Date:	3/1/2003
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	6
Research Category:	Water Quality
Focus Category:	Hydrogeochemistry, Toxic Substances, Water Quality
Descriptors:	speciation, remediation, toxic elements
Principal Investigators:	Amitava Roy

Publication

1. Ma, Jia, A. Roy, J. Sansalone, J. Pardue, 2005, Partitioning and Particulate-bound Distribution of Phosphorus in Rainfall-Runoff , J. Bennett Johnston Sr., Center for Advanced Microstructures and Devices, Baton Rouge, Louisiana, Annual Users Meeting, April 8th , 2005

Problem and Research Objectives

Phosphorus in stormwater

As a limiting nutrient for eutrophication in fresh waters, elevated concentrations of phosphorus have been identified in many types of non-point rainfall-runoff discharges from urban areas (EPA, 1993). Having many adverse consequences, eutrophication imposes a high environmental, ecological and health cost on many sectors of economy. For example, it is estimated that the costs of freshwater eutrophication in England and Wales are as high as US \$1.05-1.60 $x10^8$/year (Pretty et al., 2003). Phosphorus nominally partitions in urban rainfall-runoff between dissolved and particulate-bound phases (Filippelli, 2002). Results from partitioning analysis between the dissolved and particulate-bound fractions in rainfall-runoff on an event basis indicate that phosphorus can be predominately particulate-bound in urban pavement sheet flow for residence times less than an hour (source areas) at runoff pH levels between 6 and 8 and rainfall pH levels less than 6. In addition to a simple partitioning concept between dissolved and particulate phases, varying species of phosphorus adsorb and distribute across the whole particulate size gradation of particulates in rainfall-runoff. Ranging from less than 1 μm to greater than 9500 μm (Sansalone et al., 1998), particulate and solid matter in rainfall-runoff can be operationally classified as gross solids (> 4750 μm), sediment (> 75 μm), settleable (75 ~ 25 μm) and suspended (< 25 μm) based on the Imhoff settling test convention.

In natural waters and rainfall-runoff, the transport and eventual fate of phosphorus is controlled by reactions with solid surfaces. Characterized by large surface area to solid volume ratios, natural mineral oxides and oxide-coated media can serve as reservoirs for phosphorus with the amphoteric surface. In the presence of water, oxide surfaces such as Al, Ca and Fe are covered with surface hydroxyl groups, protons and coordinated water molecules. This leads to the idea that engineered amphoteric oxide coated surfaces on rainfall-runoff filter media can have large surface areas for adsorption and precipitation processes in a chosen pH range. The phosphorus removal by the oxide surfaces is through the mechanism of adsorption, precipitation, absorption and surface complexation.

Although the effectiveness of oxide coated media in phosphorus removal has been proven on a macroscopic scale in bench scale studies, the types of reactions of phosphate with the oxide coated media are not known. Initially, it was assumed that phosphate reacts with Ca^{2+}, Al^{3+} to form solid calcium or aluminum phosphate (Moore and Miller, 1994), which is insoluble in the pH range typical of urban rainfall-runoff. Although this assumption has been recognized as oversimplified, little, if any, information about the mechanisms of P fixation on oxide coated media is available, mainly due to the lack of methods sufficiently sensitive to determine the species, or form of P, in the heterogeneous materials.

In this study aluminum oxide coated cementitious media was used for phosphate removal from storm water runoff. The aluminum oxide coating was applied by treating the granules of concrete (about 2 mm diameter) with aluminum nitrate. For one batch of concrete granules, the coating was applied once and for another batch it was applied twice. Column studies were conducted where columns packed with these granules were used to remove phosphate from simulated stormwater at concentrations of 100, 50, 25

and 10 mg/L. A control study with cementitious granules without the aluminum nitrate coating, was also performed.

Phytoremediation

Phytoremediation, the technique of using plants to treat contaminated soils and waters, is being more routinely applied now since its first suggestion in the early eighties (Chaney, 1983). Several army ammunition sites and EPA superfund sites have been treated by phytoremediation. A survey by Baker and others (Baker et al., 2000) showed that 440 plants have been identified which can be used for phytoremediation. A database created by Environment Canada, called PHYTOREM, has more that 770 plants. However, a plant suitable for phytoremediation in one location may not work in others Introduction of alien plant species in a new environment can also wreak havoc on the local ecology. It is thus important that local plants be tested for phytoremediation.

Chromium contamination is present in more than half of all EPA superfund sites (Wright, 1991). One of the problems associated with chromium contamination is that chromium in the +VI oxidation state can readily dissolve in water and spread the contamination widely. Watercress has shown the ability to uptake thallium and arsenic (LaCoste et al., 2001; Robinson et al., 2003). Watercress, as the name suggest, grows best near a stream or other body of water. This makes watercress perfect for extracting metals out of a poisoned stream or river.

Methodology

Phosphorus in Stormwater

X-ray absorption near edge structure (XANES) was used to determine the phosphorus speciation in a suite of samples of urban rainfall-runoff particulates and oxide coated adsorptive media. The rainfall-runoff particles were divided into three groups in size: 25 μm, 75 μm and 850 μm. Replicate samples were analyzed from each group. Spent adsorptive cementitious media were also analyzed in three groups, according to the procedures they were prepared: uncoated, coated with aluminum nitrate once, and coated with aluminum nitrate twice. These media, used in column studies to treat initial phosphate concentrations of 100, 50, 25 and 10 mg/L, were analyzed in replicate.

Phytoremediation

Watercress was grown from seeds obtained from a commercial source for a three-week period. After the initial growing period the watercress ranged in height of 3.5 cm to 4.5 cm. The watercress was extracted from the soil, and washed with double deionized water to remove any remaining soil from the roots. After removal from the soil, the watercress was placed in a water culture system for one week. The plants were suspended directly in the water, and held in place by the cover of the tank. This setup eliminated the need for a support medium that could have affected the absorption of Cr. Once the watercress was in the hydroponic system, it was transported to a greenhouse on the Louisiana State University campus. The temperature of the greenhouse was $18.3 \pm 2.8^{o}C$. The relativity

humidity within the greenhouse varied depending on the weather. Four tanks were filled with 1.5 liters of distilled water, and all the setups were given the proper amount of hydroponic fertilizer to maintain the watercress. (Three quarters of a gram of Na_2CrO_4 were added to two of the tanks, to have a final chromium concentration of 500 part per million (ppm)). During the week, the watercress contaminated with Cr^{+VI} showed no signs of growth. In fact, several of the contaminated watercress died. After a week, the watercress was extracted and rinsed with double deionized water to remove any Na_2CrO_4 residue from the stems. Following the rinsing, the watercress was left to dry for a week. The dried watercress was then separated into three sections: stems, leaves, and roots.

X-ray absorption spectroscopy

The X-ray absorption spectra were collected at the J. Bennett Johnston Sr., Center for Advanced Microstructures and Devices (CAMD), Baton Rouge, Louisiana, Double Crystal Monochromator beamline. The synchrotron ring operated at 1.3 GeV. The current in the ring typically varied between 200 to 100 mA. The concentrated specimens were analyzed in transmission and those with low concentrations were analyzed in fluorescence by a 13-element high purity germanium detector.

The XANES spectra for phosphorus were collected in the fluorescence mode in a helium path to minimize X-ray absorption. Helium was flowed through the chamber at a pressure adequate enough to displace all the air in the chamber. Indium Antimonide (InSb) crystals were used in the double crystal monochromator. The sample powder was sprinkled on Kapton™ tape and spread thinly with a spatula. The tape was then gently tapped to remove any loose particles. The data collection parameters were: from 2050 eV to 2140 eV at 2.0 eV steps, from 2140 eV to 2180 eV at 0.3 eV steps, and from 2180 eV to 2450 eV at 2.0 eV steps; the integration time in each range was 5, 17, and 5 seconds, respectively. The integration time was varied in inverse proportion to the number of counts. The measurement time for each spectrum was typically two hours.

For chromium, Ge 220 crystals were used in the monochromator. The dried watercress samples were placed on Kapton tape for XAS analysis. Analysis was performed in air, with air also in the ionization chamber(s). The XANES spectra were collected from 200 eV below the edge with 3 Ev steps, from 20 eV from the edge to 40 eV above the edge with 0.3 eV steps, and up to 300 eV above the edge with 2 eV steps. The counting time at each step was determined in inverse proportion to the number of counts in that region.

The spectra were normalized with WinXAS (Ressler, 1998). A linear baseline was subtracted through the region without any pre-edge peaks. The normalization line was drawn about 60 eV above the white line through a several hundred eV region.

Principal Findings and Significance

Manganese oxide media

The XAS work related to manganese oxide cementitious media, discussed in last year's report, has been completed. Manuscripts are being prepared from that work for publication.

Figure 1 shows the XANES spectra of some common phosphate minerals. The white line A (due to the transition of the excited electron between 1s and sp^3 hybrid and oxygen 2p orbitals (Franke and Hormes, 1995)) appears to be stronger for the iron phosphate (strengite) than the other phosphates. The intensity of this line reported in the literature is somewhat lower (Hesterberg et al., 1999). The white line is wider in the minerals other than strengite. There is a distinct shoulder (B) on the high energy side of the white line for the calcium phosphates (Franke and Hormes, 1995). The calcium phosphates also have a minor oscillation B, and another stronger oscillation, D. The oscillation C is also absent in the iron phosphate.

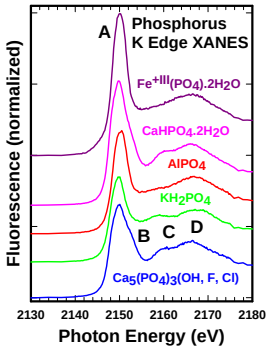

Figure 1
Phosphorus K edge XANES spectra of some standard phosphate minerals.

Figure 2 shows the phosphorus K edge spectrum in the different fractions of the particulates from storm water. The spectra are noisy because of the very low concentration of phosphorus in the particulates. The 25 µm fraction has a slightly higher peak height. This is possibly due to the difficulty in normalization through the noisy post-edge data range. Otherwise, all the size fractions appear identical. Adsorption of phosphate on ferrihydrite $Fe^{+III}_2O_3 \cdot 0.5(H_2O)$, goethite $Fe^{+III}O(OH)$ and boehmite AlO(OH) have been studied by Hesterberg and others (Hesterberg et al., 1999; Khare et al., 2004). They observed a statistical difference in the height of the white line of phosphate adsorbed on these minerals, the one for ferrihydrite being stronger than that for boehmite. According to Hesterberg et al. (Hesterberg et al., 1999) phosphate adsorbed onto goethite could be distinguished from the iron phosphate strengite by the lower intensity of the white line, the peak about 3 eV below the white line, the rising edge before the white line, and the stronger oscillation (peak D in Figure 1) at around 15 eV from the white line. A comparison of the spectra of the particulates with those reported in the literature would suggest that the phosphate in the particulates are present as adsorbed species on some iron oxide phases.

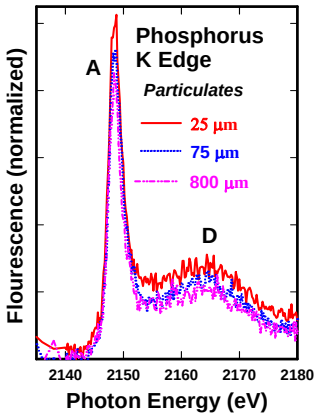

Figure 2

Phosphorus K edge XANES of the particulates collected from stormwater near Baton Rouge

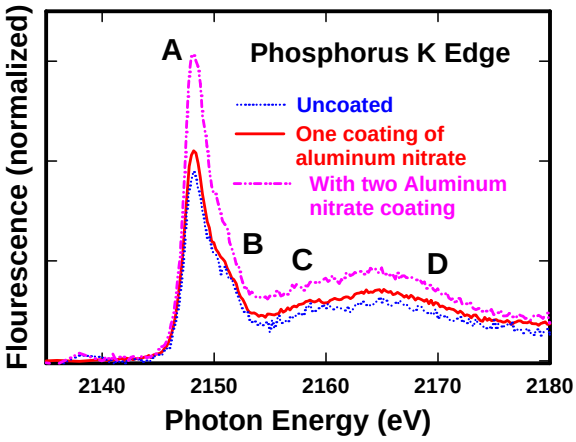

Figure 3

Phosphorus K edge XANES of concrete, with and without aluminum nitrate coating, used for removal of phosphate from stormwater.

Figure 3 shows the spectra of phosphate from the concrete, with and without aluminum nitrate coating, used from phosphate removal from storm water. The spectra of concrete without the coating and just one coating appear very similar. The intensity of the white line (ca. 2150 eV) is somewhat low. There is a bulge on the higher energy side of the white line (peak B from Figure 1) and a minor oscillation is also present around 2160 eV (peak D in Figure 1). A comparison of these spectra with the standards (Figure 1) indicates that these spectra are similar to the calcium phosphates. There is a pronounced difference when two coatings of aluminum nitrate are applied on the concrete. The bulge on the higher energy side of the white line is still visible but the intensity of the white line

is much stronger. It is inferred that in addition to being present as calcium phosphate, some of the phosphate ions are also adsorbed onto the concrete surface.

Because of the low concentration of phosphorus in these specimens, the data collection process is long. The low atomic number of phosphorus also makes measurements difficult as absorption of phosphorus X-rays is high in any tape used to hold the material. It is possible to arrive at quantitative estimates of different phosphate species with least squares fitting of the spectra.

Only preliminary data have been collected so far from the phosphate samples and more is planned. The inferences from X-ray absorption spectroscopy need to be corroborated with the chemistry, phase composition, and microstructure of the particulates and the oxide-coated cementitious media.

Phytoremediation

Cr^{+VI} has a distinctive pre edge peak at 5993 eV (Figure 4). This pre-edge peak is only present in Cr compounds that are in +VI oxidation state. When the watercress stems and leaves are compared to the Na_2CrO_4 standard, it is apparent that there is no $Cr+^{VI}$ in the watercress. Not only the pre-edge peak at 5993 eV is absent, the edge has shifted to higher energy. The edge jump for both stems and leaves correspond to that of the +III oxidation state.

The chromium concentrations in different parts of the plant (stems, leaves, and roots) were analyzed by flame atomic absorption spectrometry in replicate (Figure 5).

The two samples of stems had a Cr concentration of 8930ppm, and 11390ppm. The leaves had a lower concentration than the stems with concentration of 5365ppm, and 10120ppm. Final the two root samples had concentrations of 9480ppm, and 8120ppm. The elevated concentration of Cr in the stems, leaves, and roots shows watercress ability to hyperaccumulate Cr from a hydroponic system.

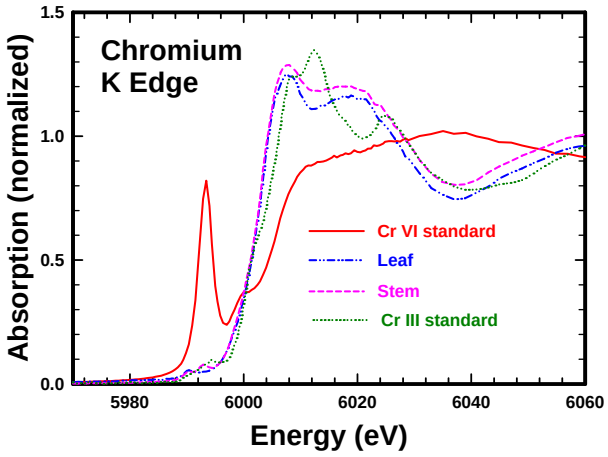

Figure 4

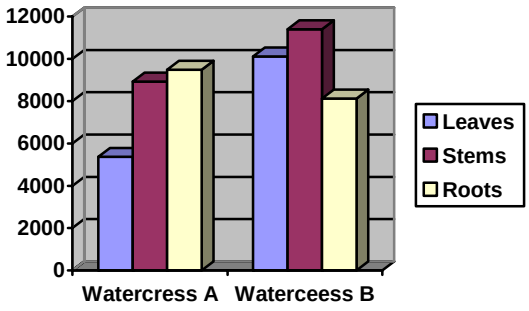

Figure 5

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Quantifying Hydrologic Impacts on Spatio-Temporal Variability of Stream Water Quality in Coastal Louisiana

Basic Information

Title:	Quantifying Hydrologic Impacts on Spatio-Temporal Variability of Stream Water Quality in Coastal Louisiana
Project Number:	2004LA21B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	6
Research Category:	Water Quality
Focus Category:	Non Point Pollution, Solute Transport, Surface Water
Descriptors:	Hydrologic Impacts; Hypoxia; Pollution; Streamflow; Space-Time Variability; Water Quality
Principal Investigators:	Vijay P. Singh, Y. Jun Xu

Publication

1. 1. Singh, V.P., Flow Routing in Open Channels: Some Recent Advances. Proceedings, River Flow 2004, held June 23-25, 2004, in Naples, Italy, 2004.
2. 2. Singh, V.P., Applications of Fluid Mechanics in Hydrology and Environmental Engineering. Recent Advances in Fluid Mechanics, Proceedings of the 4th International Conference on Fluid Mechanics, held July 20-23, 2004, in Dalian, China, edited by F. Zhuang and J.C. Li, pp. 29-40, 2004.
3. 3. Singh, V.P. and L. Zhang, Stochastic Dependence Modeling in Environmental Hydrology. Proceedings, International Conference on Hydraulic Engineering: Research and Practice, October 26-28, 2004, Indian Institute of Technology, Roorkee, India, pp. 46-59.
4. 4. Singh, V.P. and Zhang, L., Multivariate Stochastic Hydrologic Analysis. Proceedings, International Workshop on Watershed Management in Dry Areas: Challenges and Opportunities, January 4-6, 2005, Djerba, Tunisia, 2005.

Problem and Research Objectives

Louisiana is naturally blessed with an abundance of aquatic systems, including bayous, rivers, lakes, and aquifers, which provide Louisiana's citizens with fishing, hunting, boating, and recreational opportunities and contribute to the state's wealth and economic growth in agriculture and fisheries. While the state has more surface water available for its current use (84%) than any other state in the U.S., rapid urbanization and intensive agricultural and forest practices have increased the potential for reduction in the quality of the state's surface waters. Studies on hypoxia in the northern Gulf of Mexico have shown that an average midsummer hypoxic zone of 8,000-9,000 km^2 during 1985-1992 increased to 16,000-20,700 km^2 during 1993-2001 on the Louisiana/Texas continental shelf (Rabalais & Turner, 2001). This 3-fold increase of hypoxic zone over a relatively short period of time has been attributed to the increase of river-borne nutrients that can exacerbate coastal water eutrophication, favor harmful algal blooms, aggravate oxygen depletion, and alter marine food webs (e.g., Rabalais et al., 2002). The northern Gulf of Mexico is found to be the second largest zone of coastal hypoxia in the world (Rabalasis et al., 2002). This oxygen-depleted phenomenon is attributed to nutrient enrichment in the waters of the northern Gulf of Mexico, and it is especially profound from spring through late summer. Agriculture is considered as a major source of nutrient enrichment from the Mississippi river basin (Burkart and James, 1999; Ferber, 2001; Howarth, 2001; Winstanley, 2001; Snyder, 2001). Atmospheric deposition of nitrogen is seen as another significant source to nitrogen limited estuaries and coastal waters (Paerl et al., 2002).

In January 2001, an action plan with the major goal of reducing nitrogen discharge through Best Management Practices from the inland water into the Gulf was cleared by the state, tribal, and federal agencies and delivered to Congress (US EPA, 2001). The action plan recognizes a 30% nitrogen load reduction that is required to ensure a reduction of 5-year running average of the Gulf hypoxia zone to less than 5,000 km^2 by 2015. While this action plan called for an implementation of BMPs based on voluntary, incentive-based subbasin strategies, several key questions that will influence the success of this plan remained unanswered:

- How effective are the current BMP guidelines in protecting stream water quality from agricultural and forest activities?
- How feasibly and accurately can we provide estimates for subbasin nitrogen discharge based on the current water quality monitoring networks, especially for the areas on the lower coastal plains that have a very flat topography?
- To what extent do hydrological and hydrometeorological conditions, such as rainfall and temperature, affect the variability of coastal inland stream water quality?

These questions were addressed in this project.

A recent study by Thomson et al. (2002) reported that rainfall deficits accumulated since 1998 in Louisiana have culminated in a twofold increase in the mean annual salinity in the Lake Pontchartrain estuary. Using monthly measurements selected from 25 subbasins in Louisiana over a period of 1978–2001, Xu (2003) showed that the nutrient loads, total suspended solids, and dissolved oxygen concentrations all varied widely in the monitored streams and across seasons. However, monthly routine monitoring seems to work well for characterizing base flow

conditions, but may not be appropriate to characterize rapidly changing conditions in response to storm events. An understanding of hydrologic influences on water quality indicators at the watershed scale is apparently needed, and such an understanding is especially critical for the coastal regions of Louisiana where storm weather occurs throughout the year.

This proposed project assessed the relationship of stream water quality changes with hydrological and hydrometeorological conditions in Louisiana's six major basins close to the Gulf of Mexico. The project utilized existing long-term water quality data, hydrometeorological data, and stream discharge data maintained by Louisiana Department of Environmental Quality, Southern Regional Climate Center, US Geological Survey, and US Army Corps of Engineers. Information on land use activities and timber harvesting from the watersheds was also gathered to investigate the magnitude of hydrological influences on water quality under various land use activities. Specifically, the project had the following objectives:

1. To investigate the space-time variability of water quality indicators in the major stream/rivers on Louisiana's lower coastal plain;

2. To determine the interrelationships between water quality variability and hydrometeorological regime, such as storm weather conditions, rainfall intensity, and temperature fluctuation;

3. To identify the linkage between water quality variability and hydrological regime, such as base flow, peak flow, and groundwater recharge; and

4. To assess the impacts of land use activities on water quality of the coastal streams, wetlands, and estuaries in Louisiana under various hydrologic conditions.

Methodology

This project utilized existing long-term datasets collected from six coastal basins in Louisiana. Despite a large number of studies conducted on water quality in Louisiana's shore of the Gulf of Mexico during the past 2 to 3 decades, little knowledge has been actually gained about the impacts of hydrological and hydrometeorological variability on the dynamics of water quality indicators, even though it is inarguable about the ultimate role of hydrology on water quality. Many studies have been conducted, and many are being conducted on various aspects ranging from restoration of bottomland forests to microbiology of the coastal estuaries, inland streams and bayous; There exists a large amount of data that has not yet been fully analyzed, whereas USGS and LDEQ continue collecting water quality and streamflow data in Real-Time across the state's rivers and bayous.

To achieve its objectives described above, this project accomplished the following tasks:

1. Gathered existing water quality, stream discharge, and climatic data from all monitoring stations within the Atchafalaya, Barataria, Calcasieu, Mermentau, Terrebonne, and Vermillion-Teche river basins;

2. Identified spatial and temporal characteristics in water quality and hydrological and hydrometeorological conditions in the drainage basins;

3. Assessed the variability of annual nutrient loads and sediment runoff in relation to the variability of hydrological and hydrometeorological conditions; and

4. Utilized GIS and geostatistical techniques to determine land use impacts on water quality changes under hydrometeorological conditions across the landscapes.

Thus, the project involved the development of statistical analyses of hydrometeorologic, hydrologic and water quality data. Specifically, these included (1) analysis of variance, (2) identification of probability distributions, (3) determination of trends, and (4) development of prediction models relating hydrologic and hydrometeorologic conditions to space-time variability of stream water quality under a variety of land use changes. These models determined critical areas of water quality deterioration and the causes-land use and anthropogenic, and industrial. This information will be pivotal to defining BMPs.

Principal Findings and Significance

This research provided critical insights into the interrelationships between hydrological conditions, land use and the water quality of inland streams, wetlands, and coastal estuaries in Louisiana. The knowledge gained from this research contributes to developing site-specific TMDLs and applicable water quality standards, facilitating the assessment of the BMP effectiveness in protecting water quality in Louisiana's coastal watersheds, and helping improve the water quality monitoring strategies, all of which contribute to supporting the state's economic wealth and health of its citizens. Furthermore, the project and its results will be introduced in several Hydrology and Water Quality courses at LSU, immediately benefiting both graduate and undergraduate students in learning how science applications solve real world problems.

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Information Transfer Program

One of the Institute's objectives is to make research results available to the general public and to interested researchers and institutions through publications and other information transfer activities. Although the information transfer component of the budget of Section 104 funds is relatively small (10%), LWRRI attempts to meet this goal in many ways which include actively participating in conferences and workshops, distributing summaries and other Institute information to the public and governmental agencies, maintaining internet access and web sites, and maintaining a library of water research materials. The Institute requests that its investigators participate in reporting and information transfer activities such as publications in professional journals, workshops, and seminars.

The Institute's information transfer program is a subset of its administration program. Assisting with LWRRI's information transfer activities are two undergraduate student workers, a program coordinator (part-time LWRRI support), one research associate (half-time LWRRI support), and the associate director, Dr. John J. Sansalone. Two research associates are also available to assist in information transfer activities of the Institute. The Director, Dr. John Pardue, attends the annual National Institutes of Water Resources meetings in Washington, D.C., to discuss Institute and Program activities.

Further assisting in information transfer, the Engineering Incubation Research Center (EIRC) has given LWRRI access to image processing, GIS, and computing systems. This access provides the Institute with the necessary tools to transfer information in visual graphic format, utilize Internet resources, and develop state-of-the-art presentations. Because of the Institute's expanding development, more emphasis is being placed on updating the public and other organizations about activities and objectives using electronic media and presentation tools.

The Institutes staff continues to maintain emphasis on acquainting Louisianas research community with the research-funding opportunities through the U.S. Geological Survey Section 104 research program. 104 G program announcements, Mississippi SE-TAC RFPs, and Section 104 RFPs were widely distributed (113+ email addresses and 127 regular mail addresses, totaling 240) to Louisiana colleges and universities and to research organizations throughout the state. In addition, public announcements were made at professional and faculty meetings to encourage wide participation in the program. We send out notifications of meeting and events for the American Water Resources Association, The Capital Area Ground Water Conservation Committee, and the Louisiana Rural Water Association.

In addition, our organization is contacted regularly with various questions for the public and/or private sector concerning water issues; we try to connect these people with the proper experts within our organization and the broader academic community. We have built a comprehensive web portal LAWATER.com in conjunction with the LWRRI web site to help facilitate this effort. **LAWATER** is a new portal website developed by LWRRI designed to bring together the diverse web resources dealing with water resources in Louisiana for use by water professionals, researchers, students and other stakeholders. In addition, LAWater is directly linked with LWRRIs digital water library project which is providing electronic copies of all of the published Bulletins from the Institute, dating back to 1966.

LA Water is divided into 4 general areas, each addressing a specific area of interest for Louisianas water resources. These are: Water Quality Water Quantity/Supply Flooding/Hazards Coastal Restoration, with a focus on freshwater diversions One focus of LAWater is centralizing the real-time resources available on the web. These include USGS stream gauge data for discharge, DEQs statewide ambient water quality

data, LSUs WAVCIS system and other resources. In addition, LAWater provides lead stories on each page, directing you to timely information or articles impacting Louisianas water resources. We want LAWater to be a service to the public and water professionals across the state. Web site: http://www.lwrri.lsu.edu LAWATER: http://www.lawater.lsu.edu

Under the direction of our director, the Institute has developed a new branding symbol for all of the information transfer activities and publications and is reconstituting the newsletter. Our annual report is housed at the Louisiana State Archives, Hill Memorial Library at LSU, and is available online at the Institutes web site.

In response to the focused RFP for the 2004-2005 solicitations, we received 3 new proposals and funded 1 of those after advisory board review. In addition; two of the projects from the previous fiscal year submitted phase II of there projects and were funded after advisory review. The theme, selected in consultation with faculty and advisory board members, is focused on characterizing particulates for heavy metals in aquatic systems using non-invasive spectroscopy and tomography. In addition, a continuing interest in total maximum daily load (TMDL) calculations in Louisiana water bodies is being maintained.

NIWR-USGS Student Internship Program

The Louisiana Water Resources Research Institute did not have any students in the formal NIWR-USGS Intern Program during this reporting period. The Institute maintains both formal and informal relationships with the Baton Rouge office through part time employment of students not in the intern program, and the USGS District Chief serves on the Institute Advisory Board. During this reporting period we have undergone a series of discussions with the state USGS office on rapidly expanding our participation in the student intern program. At the time of this report, those discussions have not been finalized.

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	2	0	0	3	5
Masters	2	0	0	3	5
Ph.D.	4	0	0	1	5
Post-Doc.	2	0	0	2	4
Total	10	0	0	9	19

Notable Awards and Achievements

The Director, Dr. John Pardue, was named co-Director of the Hazardous Substance Research Center-South & Southwest in 2004. This will allow the continued sharing of staff and resources between the Center and Water Institute. Dr. Pardues funded grants are a result of his work in the water resources area: 1. Development of treatment wetland technology for VOC-contaminated groundwater John H. Pardue, William Moe and Fred Rainey, Louisiana State University, CICEET-NOAA, $250K, 2002-2004. 2. Phytoremediation of wetlands and CDFs, J. Pardue and W.M. Moe. Hazardous Substance Research Center-South & Southwest, 2001-2004. $210,000. 3. Assessment & Remediation of public health impacts due to Hurricanes and major flooding events Louisiana Millennium Health Excellence Fund; 2001-2006. I. Van Heerden, PI; Pardue and Reible, water modeling group, $120,000 and 4. A water quality decision model for the identification of priority sites for the implementation of best management practices to maintain dissolved oxygen levels In the Ouachita River Basin LA DEQ, Emy Roider, V Singh, D. Adrian, J. Pardue, 2001-2004, $381,000.

The Associate Director, Dr. John J. Sansalone was awarded the Wesley Horner Environmental Engineering Award-American Society of Civil Engineers, 2004. Dr. Sansalones follow-on funding is a result of his past projects with LWRRI prior to his Associate Directorship. His funded grants related to follow-on funding are: 1. Sansalone, J.J., (Principal Investigator), Settling Properties of Coastal Sediments, January 2004 December 2004, Soil Testing Engineers, $9800. 2. Sansalone, J.J. (Principal Investigator), Griffin, D.M., Cartledge, F.K, and Tittlebaum, M.E., Transport, Treatment and Toxicity of Urban Rainfall-runoff, June 2004 June 2005, LTRC, $20,000. and 3. Sansalone, J.J. (Principal Investigator), Griffin, D.M., Cartledge, F.K, and Tittlebaum, M.E., Transport, Treatment and Toxicity of Urban Rainfall-runoff, June 2003 June 2005, LTRC, $349,905.

Publications from Prior Projects

1. 2004LA-ADMIN ("Program Administration Project") - Articles in Refereed Scientific Journals - Dean, C., J.J. Sansalone, F.J. Cartledge, and J.H. Pardue. 2005. Influence of hydrology on storm water metal element speciation at the upper end of an urban watershed. J. Environ. Engr. ASCE

131:632-642.

2. 2004LA-ADMIN ("Program Administration Project") - Articles in Refereed Scientific Journals - Jackson, W.A., L. Martino, S, Hirsh, J. Wrobel and J.H. Pardue. 2005. Application of a dialysis sampler to monitor phytoremediation processes. Environmental Monitoring & Assessment. In Press.
3. 2004LA-ADMIN ("Program Administration Project") - Articles in Refereed Scientific Journals - Kassenga, G., J.H. Pardue, W.A. Moe, and K. Bowman. 2004. Hydrogen thresholds as indicators of dehalorespiration in constructed treatment wetlands. Environ. Sci. Technol. 38 (4): 1024-1030.
4. 2004LA-ADMIN ("Program Administration Project") - Articles in Refereed Scientific Journals - Tan, K., W. A. Jackson, T.A. Anderson, and J.H. Pardue. 2004. Fate of perchlorate-contaminated water in upflow wetlands. Water Research 38:4173-4185.
5. 2004LA-ADMIN ("Program Administration Project") - Articles in Refereed Scientific Journals - Jeon, Mi-An, W.A. Jackson, T. Anderson and J.H. Pardue. 2004. Perchlorate remediation by electrokinetic extraction and electrokinetic injection of substrates. J. of Bioremediation. 8:65-78.
6. 2004LA-ADMIN ("Program Administration Project") - Conference Proceedings - Hydrogen thresholds as indicators of halorespiration in constructed treatment wetlands. J.H. Pardue, G. Kassenga, W. Moe and K. Bowman. Remediation of Chlorinated and Recalcitrant compounds, 4th International Conference, Monterey, CA, May 24-27, 2004.
7. 2004LA-ADMIN ("Program Administration Project") - Conference Proceedings - 2) Bioaugmentation of engineered peat mixtures for enhanced bioremediation of chlorinated solvents. M.M. Lorah, E.J. Jones, M.A. Voytek and J.H. Pardue. Remediation of Chlorinated and Recalcitrant compounds, 4th International Conference, Monterey, CA, May 24-27, 2004.
8. 2003LA19B ("Economic Assessments of Best Management Practices and Environmental Policy Options for Attaining the Total Maximum Daily Load (TMDL) Goal in Louisianas Major Milkshed") - Articles in Refereed Scientific Journals - Wayne M. Gauthier, Krishna Paudel, John Westra, and Larry Hall. Influence of Cost Share and EQIP Incentive Payments on Adoptions of Best Management Practices by Louisiana Dairy Farmers. Forthcoming Journal of Agricultural and Applied Economics
9. 2003LA19B ("Economic Assessments of Best Management Practices and Environmental Policy Options for Attaining the Total Maximum Daily Load (TMDL) Goal in Louisianas Major Milkshed") - Articles in Refereed Scientific Journals - Wayne M. Gauthier, Krishna Paudel, John Westra, and Larry Hall Factors affecting the adoption of pollution reducing best management practices among dairy producers in Louisiana. Manuscript in process to be submitted in Waste management
10. 2003LA19B ("Economic Assessments of Best Management Practices and Environmental Policy Options for Attaining the Total Maximum Daily Load (TMDL) Goal in Louisianas Major Milkshed") - Articles in Refereed Scientific Journals - Larry Hall, Krishna Paudel, Wayne Gauthier, and John Westra. Integrating Survey Information and GIS Modeling Approach to Develop an Optimal Decision Making Tool for Controlling Water Pollution in the Louisiana Dairy Production Region. Manuscript in preparation to be submitted in Journal of Environmental Management