

Louisiana Water Resources Research Institute

Annual Technical Report

FY 1999

Introduction

Research Program

The 1999 program of the Louisiana Water Resources Research Institute (LWRRI) addressed several priority water resources problem areas identified for Louisiana; management of surface water supplies, groundwater control and restoration, wastewater treatment alternatives, and treatment of point and nonpoint sources of pollution. Three research projects are currently being funded to address these priority issues: (1) Mercury Contamination in Louisiana Freshwater Lakes: The Effect of Anaerobic Condition on Methylation and Demethylation of Mercury, (2) Mitigation Of Urban Storm Water Discharges To City Park Lake Through Integrated Passive Adsorptive-Filtration, and (3) Photocatalytic/Adsolubilization Semiconducting Monolith Reactor for the Treatment of Dilute Wastewater. These projects focus expertise on issues that are important in Louisiana with its vast wetland areas, agricultural base, and threatened ecosystems. A synopsis on each of these projects follows. The Natural Systems Engineering Laboratory, a unit of the LWRRI, has grown to over \$1.7 million in funding in the last few years. Current projects include modeling hurricane effects on coastal Louisiana, flood management in other areas and coastal restoration. Other funds support this effort and are not reported here but are summarized in the Notable Achievements section.

Technical highlights of projects include:

Project 02- Inorganic mercury compounds can undergo methylation in sediments under proper anaerobic conditions with a resulting increase in solubility, mobility and bioaccumulation in the food chain in freshwater Louisiana lakes. Combination of substrate biogeochemical conditions will minimize methylmercury formation and maximize demethylation.

Project 03- A novel passive treatment system, a pavement effluent reactor (PER), synthesizes the treatment mechanisms of both dissolved heavy metal adsorption, and a particulate-bound heavy metal filtration system are being tested. To date, the project has developed a unique experimental site, which serves as the prototype field demonstration of economical multi-purpose urban storm water treatment, located and constructed along the east right of way of East Lakeshore Drive where I-10 crosses over City Park Lake in Baton Rouge.

Project 04 - Combination of photocatalysis and adsolubilization are used to overcome the problem of low conversions observed in conventional photocatalysis and the problem of short breakthrough times in adsolubilization to develop a comprehensive treatment technology for groundwater aquifers using surfactant solutions.

These projects reflect a continuing effort by LWRRI to develop engineered solutions to Louisiana and regional water issues. Joint activities between the Institute and other university organizations were continued. Significant efforts by the Director continue to enhance coordination of LWRRI research with other units at LSU,

the state, and region.

Basic Project Information

Basic Project Information	
Category	Data
Title	Mercury Contamination in Louisiana Freshwater Lakes: The Effect of Anaerobic Condition on Methylation and Demethylation of Mercury
Project Number	GR02673/C-02
Start Date	03/01/1999
End Date	08/31/2000
Research Category	Water Quality
Focus Category #1	Toxic Substances
Focus Category #2	Sediments
Focus Category #3	Non Point Pollution
Lead Institution	Louisiana State University

Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
William H. Patrick	Professor	Louisiana State University	01
Robert P. Gambrell	Professor	Louisiana State University	02
Ronald P. DeLaune	Professor	Louisiana State University	03
Istvan Devai	Assistant Professor	Louisiana State University	04
Aroon Jugsujinda	Post Doctoral Student	Louisiana State University	05

Problem and Research Objectives

Mercury contamination of lakes and streams has taken on new importance worldwide since it was discovered several decades ago that inorganic mercury compounds can undergo methylation in sediments under proper anaerobic conditions with a resulting increase in solubility, mobility and bioaccumulation in the food chain. Many waterbodies worldwide have elevated mercury levels in top predator fish that has prompted the issuance of advisories on fish consumption by various public health agencies. Lakes and waterbodies in the Southern U. S. including Louisiana have been impacted by mercury contamination. Recent finding of elevated mercury concentrations in fish and wildlife from fresh water lakes throughout much of the Southern United States including Louisiana has caused great concern for persons for whom fish are a significant part of their diet and for pregnant women and

nursing mothers. Levels up to 3 ppm have been found in largemouth bass in some lakes, which is considerably above the maximum permissible level (1 ppm) for edible fish tissue. Along with other southern states, the Louisiana Department of Health and the Department of Environmental Quality have issued mercury advisories for a number of lakes in the state with the result that the desirability of these lakes for fishing and fish consumption has decreased. This proposal describes a study of the conditions in freshwater lakes in Louisiana that govern the formation and removal of methylmercury, the form of mercury that bioaccumulates in the food chain of lakes.

Methodology

The approach we have taken in this research project is to carry out incubations that duplicate the range of substrate conditions that exist in the freshwater lakes and to determine the biogeochemical conditions in the lakes that control both methylation and demethylation of mercury. The overall objective is to determine the combination of substrate biogeochemical conditions that will minimize methylmercury formation and maximize demethylation.

Principal Findings and Significance

During the past year, we have set up state-of-the-art instrumentation for analyzing methyl mercury in water, sediment, and tissue samples. This instrumentation consists of a Perkin-Elmer Model 6890 gas chromatography equipped with an atomic fluorescence mercury-specific detector. The methyl mercury compound is separated from other sample components by selective extraction procedures and subsequently by gas chromatography. After separation on the gas chromatograph column, the methyl mercury is pyrolyzed at 800°C to convert the mercury to elemental mercury that then is sent to the atomic fluorescence detector. This instrumentation has a detection limit of approximately 0.2 parts per billion (0.2 micrograms per liter) for mercury as methyl mercury chloride in a calibration standard. During 1999, R. Gambrell completed a training course for the extraction and analysis of methyl mercury from environmental samples at Florida International University.

We have collected sediment samples from three lakes in Louisiana where we have data on selected sediment properties and total mercury content for use in this project. These lakes are Black Lake, Chicot Lake, and False River. Advisories pertaining to eating fish from Black Lake and Chicot Lake have been issued by the LA Department of Environmental Quality. Fish from False River collected in the LA DEQ monitoring program have less mercury in edible tissue and no advisories have been issued for this lake. Generally, the literature has shown that where fish contain elevated mercury, this mercury is present as the methylmercury species. Duplicate flasks of each sediment are being maintained under anaerobic and aerobic conditions simulating subsurface sediments (below approximately 0.5 cm) and surface sediment conditions, respectively. These sediments are being sampled periodically to look for sediment oxidation-reduction effects on the sediment levels of methyl mercury.

Thought there were procedural problems early in the extraction methods, these have been solved and we are now routinely extracting and analyzing samples for methyl mercury. Using standard methods for calculating instrument detection limits, the detection limit for methyl mercury chloride is 0.2 parts per billion with good reproducibility between subsamples extracted and analyzed independently.

We have set up laboratory microcosms where we can look at sediment pH and redox potential effects on the rate of methylation and demethylation of mercury in addition to other factors affecting these processes. Thus other experiments are being set up to examine how changes in sediment redox conditions affect methyl mercury formation and decomposition.

Descriptors

Water quality, fish advisories, food chain, health effects, and biogeochemistry.

Articles in Refereed Scientific Journals

Book Chapters

Dissertations

Water Resources Research Institute Reports

Conference Proceedings

Other Publications

Basic Project Information

Basic Project Information	
Category	Data
Title	Mitigation of Urban Storm Water Discharges to City Park Lake Through Integrated Passive Adsorptive-Filtration
Project Number	GR02673/C-03
Start Date	03/01/1999
End Date	08/31/2000
Research Category	Water Quality
Focus Category #1	Non Point Pollution
Focus Category #2	Treatment
Focus Category #3	Toxic Substances
Lead Institution	Louisiana State University

Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
John J. Sansalone	Assistant Professor	Louisiana State University	01
Frank K. Cartledge	Professor	Louisiana State University	02
Kelly A. Rusch	Associate Professor	Louisiana State University	03

Problem and Research Objectives

Storm water runoff from NPDES Phase II urban areas transports significant loads of heavy metals, a wide gradation of particulate matter, dissolved solids and organic compounds to receiving waters (Sansalone et al., 1998). Heavy metals are not degraded in the environment and constitute an important class of potentially acute and chronic toxic contaminants generated mainly through modern urban transportation activities and abrasion of infrastructure. In urban storm water levels of Zn, Cu, Cd, Pb, Cr and Ni are significantly above ambient background levels, and for many urban areas, Zn, Cu, and Cd often exceed USEPA and State EPA surface water discharge criteria on an event basis (Sansalone et al., 1997). Annual heavy metal, total suspended solids (TSS), chemical oxygen demand (COD) loadings and storm water flows from urban pavement equal or exceed annual loadings and flows from untreated domestic and industrial wastewater combined, for urban areas (Sansalone et al., 1998). With regard to storm water regulation and treatment, there are 32 NPDES Phase II urban areas and an additional 14 “incorporated places” that come under the proposed Phase II regulations in Louisiana. Both Phase II regulations and third-party lawsuits from organizations such as the National Resources Defense Council have helped spur a focus by municipalities, State DOTs and federal agencies such as FHWA on the treatment methodology for roadway stormwater.

Treatment of urban roadway storm water continues to pose unique challenges due to unsteady nature of processes including rainfall-runoff, mobilization and transport of heavy metal as well as other constituent loads. Additionally, kinetics of heavy metal partitioning as a function of pH, residence time and particulate matter characteristics can have a profound effect on the selection and effectiveness of treatment systems. Treatment systems for the clarification of runoff have included sedimentation (detention/retention) basins, constructed wetlands, vegetated filter strips and infiltration systems such as porous pavement and infiltration trenches. While many of these have varying degrees of viability, none are applicable for the many sections of elevated roadways in Louisiana. The State of Louisiana has more miles of elevated roadways than any other state in the USA. Storm water effluent from these roadways is currently discharged untreated into receiving waters and surficial soils. A novel passive treatment system, a pavement effluent reactor (PER), synthesizes the treatment mechanisms of both dissolved heavy metal adsorption and particulate-bound heavy metal filtration. The PER is a tubular packed-bed reactor designed to accept storm water runoff flows that currently discharge directly from elevated roadway scuppers and drainage boxes directly into receiving waters. The two-stage PER consists of a layer of pretreatment aggregate and a bed of oxide-coated media to promote sorption of dissolved heavy metals and filtration of particulate-bound heavy metals. The PER is mounted directly onto the outlet end of the drainage appurtenances, typically 150-mm to 200-mm diameter downspout or drainage pipes.

From preliminary research and experience in the field of nonpoint pollution treatment, the investigators have not identified any rigorous scientific attempts to integrate passive treatment into existing elevated roadway infrastructure and evaluate the effectiveness of such treatment. As a result the objectives of this proposed research are fourfold. The primary objective is to demonstrate the effectiveness of a PER on heavy metal mitigation for elevated roadway sections in Louisiana. One typical local example for the Southeastern region of Louisiana is the I-10 elevated roadway section over City Park Lake in urban Baton Rouge. Storm water effluent from this heavily travelled elevated roadway is discharged directly into City Park Lake has not been quantified but is considered a major source of heavy metal loading to City Park Lake (Malone et al. 1988). The westbound elevated roadway section and a portion of the storm water effluent from that section over the lake will serve as the experimental site. The second objective will also include an evaluation of the potential for clogging of the PER including the development of any required maintenance and backwashing procedures. The third objective is to investigate PER removal mechanisms as a function of storm water residence time/flow and heavy metal

partitioning. The final objective is to provide a database for PER performance as a treatment technology and evaluate PER economic benefits as a multi-purpose environmental infrastructure. Results and analysis will be fully documented in a final report and provided for peer-review through at least two manuscripts.

Methodology

Storm water runoff from urban areas transports significant loads of heavy metals, a wide gradation of particulate matter, dissolved solids, organic compounds and inorganic constituents. Heavy metals are not degraded in the environment and constitute an important class of contaminants generated through modern urban activities and infrastructure. In urban areas one major source of heavy metals are traffic activities. In urban runoff discharges levels of Zn, Cu, Cd, Pb, Cr and Ni are significantly above ambient background levels, and for many urban areas, Zn, Cu, and Cd often exceed USEPA and State EPA surface water discharge criteria on an event basis.

Treatment of storm water continues to pose unique challenges due to unsteady nature of processes including rainfall-runoff, mobilization and transport of heavy metal as well as other constituent loads. Additionally, kinetics of heavy metal partitioning as a function of pH, residence time and particulate matter characteristics can have a profound effect on the selection and effectiveness of treatment systems. Treatment systems for the clarification of runoff have included sedimentation (detention/retention) basins, constructed wetlands, vegetated filter strips and infiltration systems such as porous pavement and infiltration trenches. A novel passive treatment system, a pavement effluent reactor (PER), synthesizes the treatment mechanisms of both dissolved heavy metal adsorption and particulate-bound heavy metal filtration. The PER is a tubular packed-bed reactor designed to accept storm water runoff flows that currently discharge directly from elevated roadway scuppers and drainage boxes directly into receiving waters. The two-stage PER consists of a layer of aggregate and a bed of oxide-coated media to promote sorption of dissolved heavy metals and filtration of particulate-bound heavy metals. The PER is mounted directly onto the outlet end of the drainage appurtenances, typically 150-mm to 200-mm diameter downspout or drainage pipes.

Bench scale testing of various PER configurations and oxide-coated media has demonstrated proof-of-concept (Sansalone, 1998). Bench scale testing using actual storm water and tubular packed-bed configurations indicate that the design life of a PER can exceed 5-years at a 50 percent heavy metal breakthrough level. Therefore this research approach intends to build on this development and proposes to construct, monitor and analyze a prototype PER (tubular, Fe-sand packed-bed configuration) subject to urban loading and conditions. The proposed PER demonstration experiments will be configured as two separate reactors, one with experimental oxide-coated media and the second reactor used as control, containing uncoated media. The diameter of each reactor will be approximately 50-cm and 150-cm in length based on a drainage area to each reactor is approximately 200 m² of pavement. The pretreatment aggregate of the PER strains incoming particulate matter while providing a hydraulic surface-loading rate up to 100 L/m²-minute.

This project serves as a prototype field demonstration of economical multi-purpose urban storm water treatment. Construction, monitoring and sampling equipment procurement and installation will require 4 months. Data collection and analysis will continue for 18 months and the final report will be written during the final 2 months of the 24-month project. Each treatment system will be monitored. On-site climate monitoring will include rainfall, runoff, temperature, previous dry days, and traffic data will also be collected. Flow rates will be monitored and influent and effluent samples taken at regular intervals.

Influent and effluent characteristics will also be analyzed. These include heavy metals, pH, redox, conductivity, TSS and TDS. The objectives of this proposed research are fourfold. The primary objective is to demonstrate the effectiveness of a PER on heavy metal mitigation for elevated roadway sections in Louisiana. The 2nd objective will evaluate the maintenance and potential for clogging of the PER. The 3rd objective is to investigate PER removal mechanisms as a function of storm water residence time/flow and heavy metal partitioning. The final objective is to provide a database for PER performance as a new treatment technology and evaluate PER economic benefits as a multi-purpose environmental infrastructure.

Experimental site location

Baton Rouge is located in southeastern Louisiana and is the state capital. The Baton Rouge area has a population of 600,000. Mean annual rainfall is 1420-mm. The sites are located in East Baton Rouge Parish, designated a NPDES Phase II Urbanized Area. The experimental sites are located in the urban area of Baton Rouge and have traffic counts (ADT) exceeding 100,000. Louisiana Transportation Research Center (LTRC) provides experimental sites and access to each site. LTRC will provide in-kind services that include but not be limited to supplying PER materials, construction, guardrail, fencing, access to LTRC laboratories, assistance in material testing and validation procedures, installation of instrumentation and maintenance for the project duration.

Principal Findings and Significance

A unique experimental site has been located and constructed along the east right of way of East Lakeshore Drive where I-10 crosses over City Park Lake. The Louisiana Transportation Research Center (LTRC) has provided access, concrete infrastructure, SFBC mountings, plumbing, scupper and bridge downspout access, a chain-linked fenced and gated area at the site for PER installation, loading and testing. Louisiana Department of Transportation and Development has provided lighting, 220-V and 110-V power with GFIC receptacles for experimentation at the Baton Rouge site. LTRC is providing traffic counting data for each site so that the researchers can assess pollutant loadings as a function of vehicle count during either antecedent dry conditions or more critically during sampled runoff events. Measured average daily traffic (ADT) values at the site during three measured rainfall events to date range from 100,000 to 131,000 for the eastbound lanes that drain to the experimental facility.

Both oxide-coated (experimental) and control media has been synthesized. Laboratory testing has been carried out on these media for both physical and chemical characteristics that include density, surface area, surface charge and experimental measurement of surface complexation stoichiometry. Analyses that include x-ray diffraction, scanning electron micrographs (SEM) and microprobe analyses have been carried out for the media.

Media has been produced in sufficient quantities for prototype PERs at the experimental site. Three prototype PERs were constructed and first tested in the laboratory at a range of surface loading rates from 5 to 50 liters/ft²/minute. Testing included head loss measurements as a function of surface loading rate and pH and alkalinity changes across the PER as a function of surface loading rate. This testing represents baseline performance against which field behavior will be compared. Three full-scale

prototype PERs (two experimental and one control) have been constructed and plumbed at the field experimental site. The first full scale tests of these PERs were underway at the time this synopsis was completed.

To date, three rainfall runoff events have been fully characterized at the experimental site. Results of significance indicate that storm water influent to the PERs range from 500 to 1500 mg/L as total chemical oxygen demand (COD). Heavy metal values are in the process of analyses, with samples fractionated between dissolved and particulate bound fractions and preserved. Storm water pH values range from 6.4 to 7.5 and surprisingly, corresponding alkalinity values range from 180 mg/L down to 20 mg/L as CaCO₃. Turbidity values ranged from 1300 to 40 NTU.

Descriptors

Storm water, Adsorption, Filtration, Heavy Metals, Urban Drainage, Breakthrough

Articles in Refereed Scientific Journals

Book Chapters

Dissertations

Water Resources Research Institute Reports

Conference Proceedings

Other Publications

Basic Project Information

Basic Project Information	
Category	Data
Title	Photocatalytic/Adsorbubilization Semiconducting Monolith Reactor for the Treatment of Dilute Wastewater
Project Number	GR02673/C-04
Start Date	03/01/1999
End Date	08/31/2000
Research Category	Water Quality
Focus Category #1	Groundwater
Focus Category #2	Treatment
Focus Category #3	Water Quality

Principal Investigators

Principal Investigators			
Name	Title During Project Period	Affiliated Organization	Order
Kalliat T. Valsaraj	Professor	Louisiana State University	01
David W. Constant	Professor	Louisiana State University	02

Problem and Research Objectives

The treatment of dilute aqueous streams continues to be at the forefront of environmental and chemical process R&D efforts (NRC, 1988). This is mainly due to two reasons: (1) the relative abundance of the streams; they are found literally everywhere in the CPI, municipal treatment facilities, natural environment, etc. and (2) the exponentially growing number of environmental laws regulating pollution emission. The costs to treat the streams have followed an exponential growth as well. Moreover, in many cases, the type of treatment utilized (air stripping or activated carbon etc.) only changes the nature of the problem rather than solving it. Since we cannot affect the relative abundance of the streams without sacrificing the quality of life we have all been accustomed to, we must focus on reducing the costs of treatment. One way in which this can be done is to explore new ways in which developing technologies can be combined to overcome current limitations. In this work, we investigated a combination of photocatalysis and adsorbabilization to overcome the problem of low conversions observed in conventional photocatalysis and the problem of short breakthrough times in adsorbabilization. This proposal draws upon areas in photolytic physics, chemistry, hydrodynamics, and chemical engineering. The main goal of this research is to develop a comprehensive treatment technology for groundwater aquifers using surfactant solutions.

Methodology

Materials Used:

The anionic surfactant used, sodium dodecylsulfate (SDS) of 99% purity, was obtained from Aldrich Chemical Company, Milwaukee, MI. Phenanthrene (PHE) of 98% purity was obtained from Aldrich Chemical Company while 1,2-dichlorobenzene (DCB) of 98% purity was obtained from EM Science, Gibbstown, NJ. Powdered titania (P25) was purchased from Degussa Corporation, Ridgefield Park, NJ. It was produced from $TiCl_4$ in the gas phase and was >99.5% pure anatase with a BET surface area of 60 - 70 m^2/g . Degussa P-25 TiO_2 has been suggested to be the standard photo-catalyst for the elucidation of photocatalytic reactor performance.

A stock solution of SDS was prepared by dissolving 20 g in one liter of distilled, deionized water. A stock solution of 1M NaCl (Fisher Scientific Co., MO) was prepared for ionic strength adjustment. Solutions of desired DCB concentrations in distilled water were prepared by appropriate dilution of saturated solutions of DCB obtained by mixing excess pure DCB in distilled water. Solutions of desired PHE concentrations were prepared by appropriate dilutions of phenanthrene solutions in acetonitrile. pH measurements were made using a standard Corning combination pH/ion electrode.

Adsorption of SDS on Titania:

Batch experiments were performed in glass bottles of total volume 125 mL supplied by Fisher Scientific Company, MO. To each bottle 1 g of alumina, 3 mL of 1M NaCl solution and a prescribed amount of SDS solution were added. A constant ionic strength was maintained in the experiments, since adsorption of SDS on mineral oxides is dependent on the ionic strength of the aqueous medium. The final volume of each bottle was then made up to 50 mL by addition of distilled water. The pH of the solution was adjusted using either 1N sulfuric acid or 1N sodium hydroxide solution. The bottles were capped and equilibrated for 48 hours in an isothermal shaker (Gallenkamp Orbital Incubator equipped with a safety thermostat) maintained at 26°C. After equilibration the pH of each solution was recorded. The difference between the initial and final pH values were less than 0.2 pH units in all cases. The solutions were then centrifuged at 4500 rpm for 30 minutes and filtered through a 0.01 micron filter before analysis of SDS using the classical methylene blue assay method. The mass of SDS adsorbed was determined from mass balance. Experiments were repeated for various pH values ranging from 3 to 7.

Adsorption of DCB and PHE on SDS-coated Titania:

Batch experiments were conducted in a manner similar to that described above for SDS adsorption. The only difference was that the solution contained 1g of TiO₂ and 3 mL of 1M NaCl in the case of PHE and 7 mL of 1M NaCl in the case of DCB experiments. Prescribed amounts of SDS were added and the pH adjusted using either 1M sulfuric acid or 1M sodium hydroxide solution. The final total aqueous volume was 120 mL for experiments involving DCB and 50 mL for the experiments involving PHE. The bottles were capped and equilibrated for 48 hours at 26°C. The experiments were repeated for several pH values between 3 and 7.

After equilibration the supernatant solution was analyzed for both the hydrophobic compound (DCB or PHE) and SDS. SDS analysis was done using the methylene blue assay method. PHE was analyzed using a Hewlett-Packard liquid chromatograph (1090L) equipped with a UV diode array detector. DCB was analyzed using a Hewlett-Packard gas chromatograph (5890A).

The amounts of SDS, DCB and PHE adsorbed were determined from material balances.

Principal Findings and Significance

The adsorption isotherms for SDS on TiO₂ at four different pH values (3.2, 3.8, 4.8, 5.7 and 6.8) were obtained and reported (Yuan et al, 2000). As observed earlier for adsorption of SDS on alumina, the isotherms for SDS on TiO₂ also show the characteristic S-shape for anionic surfactants on metal oxides. As the pH of the aqueous solution increased, the mass of SDS adsorbed on titania decreased. The pH of the solution influences the surface charge of oxides; with increasing pH the surface charge becomes more negative. The pH at which point the surface has zero charge is called pH_{pzc} which is 6.8 for titania. This decrease in surface potential with increasing pH leads to unfavorable Coulombic interactions between the surfactant head group and the metal oxide surface. At low surfactant concentrations, Coulombic interactions are the primary forces responsible for adsorption, and adsorption is linear in surfactant concentration. At slightly higher surfactant concentrations, SDS molecules aggregate on the surface through van der Waals interactions between the hydrocarbon tails of the molecule. These surface aggregates are called *hemi-micelles* and have been the focus of previous discussions. The aqueous concentration at which hemi-micelles are formed on the surface is called the hemi-micellar concentration (HMC). The HMC value increased with increasing pH. At the pH of 3.2, at which the titania surface is positively charged, the HMC value was 22 mg/L compared to 165 mg/L at a

pH of 6.8 at which the titania surface is uncharged. As the SDS concentration in the aqueous phase increased further, bilayers of surfactant called admicelles are formed on the titania surface, and as mentioned earlier, these structures are characterized by a hydrophilic exterior and a hydrophobic interior. The adsorbed concentration increased only slightly at this stage and as the aqueous concentration increased further, a plateau in the isotherms was evident. At low pH values the transition to hemi-micelles is not clear, while at the higher pH values this is clearly evident and has been noted earlier for alumina as well. The plateau in the surface adsorption of SDS is due to the fact that at these concentrations the repulsive interactions between the head groups of the surfactant are unfavorable to further adsorption of SDS. Notice, however, that in all the cases the SDS concentrations at the plateau are still much smaller than the critical micellar concentration (2287 mg/L) of SDS. The maximum adsorbed concentration decreased from 110 mg/g at a pH of 3.2 to 57 mg/g at a pH of 6.8.

The adsorption isotherms for PHE on SDS-coated titania was also obtained (Yuan et al, 2000). SDS concentrations are in the range where hemi-micelles are formed. Two pH values are noted, viz., 4.5 and 5.6. In both cases, the isotherms are linear, i.e., the adsorbed concentrations of PHE increase linearly with adsorbed PHE concentration as is typical of the adsorption of hydrophobic compounds on solids from aqueous solutions. Similar trends were observed for PHE adsorption on Al_2O_3 , as reported previously (Jain et al, 1999). The slope of the adsorbed PHE concentration ($\mu\text{g/g}$ of titania) versus the equilibrium aqueous concentration ($\mu\text{g/L}$ of water) gives the linear partition constant, K_d (L/g) for phenanthrene.

The adsorption isotherms for DCB on SDS-coated titania at pH values of 3.4, and 6.2 were also obtained (Yuan et al, 2000). Similar data were obtained at other pH values as well (4.3 and 5.3). K_d values and correlation coefficients for linear isotherm fits were obtained. As in the case of PHE, the adsorption isotherms were linear and values of K_d increased with the increase in values of SDS adsorbed on titania.

For comparison, the DCB isotherm on titania without any added SDS gave a K_d value of 0.0019 L/g. The relative magnitude of K_d with and without SDS on titania exemplifies the enhancement in adsorption of DCB in the presence of the hemi-micelles of SDS. Although not shown, a similar treatment of the data for PHE on titania without SDS showed the magnitude of K_d to be 0.021 L/g. As in the case of alumina reported previously (Jain et al, 1999), the adsorption of both PHE and DCB on bare titania in the absence of any SDS hemi-micelles is expected to be negligible since nonionic organic compounds interact weakly and nonspecifically with metal oxides.

The values of K_d were plotted against the adsorbed SDS concentrations on titania. The partition constant is seen to vary linearly with SDS concentration for both PHE and DCB, indicating that in both cases the adsorption enhancement is definitely related to the presence of SDS hemi-micelles on titania. Thus for each chemical (DCB and PHE) all points collapse onto a single line, and the slope is independent of the pH, but dependent only on the adsorbed SDS concentration. The slope in the two cases gives the normalized sorption constant, K_h unique to the chemical and specific to the influence of SDS on the adsorption of the chemical to titania. The magnitude of the normalized partition constant is larger for PHE than DCB and is in accord with the higher hydrophobicity of PHE relative to DCB.

Data showed that $\log K_h$ for PHE and DCB on both SDS-coated TiO_2 and Al_2O_3 are of similar magnitude. However, the values differ with the type of surfactant used to modify the surface. This

indicates that the uptake is solely dependent on the type of surfactant and is independent of the underlying solid surface. In other words, the solid surface has only one characteristic function, i.e., to provide as large a surface area for adsorption of SDS as possible, so that the maximum amount of organic pollutant can be adsolubilized in the hemi-micelle formed by SDS on the surface. It is also clear that the values are only slightly smaller than the $\log K_{ow}$, the octanol water partition constant. The implication is that the hemi-micellar environment where adsorption occurs is similar in hydrophobicity to bulk octanol, which is known to be an ideal hydrophobic environment for all kinds of organic compounds.

Implications for Oxidation of Hydrophobic Organic Compounds in Dilute Wastewater:

The mechanism of oxidation of organic compounds on the TiO_2 surface starts with the creation of an electron-hole ($e^- + h^+$) pair and the subsequent migration of the carriers to the surface. The two opposing steps are recombination and electron transfer. Recombination of the electron-hole pair is undesirable and can occur either in the bulk or on the surface of the semiconductor. Electron transfer requires an electron acceptor (O_2) for the photoelectron and an electron donor (or hydrogen source) for the h^+ hole. Due to the short lifetimes of the charged pairs, only fast reactions with adsorbed species at the surface lead to efficient charge separation. It has been shown that surface modification of TiO_2 can lead to enhanced oxidation properties. Matthews showed that electron transfer is far more efficient if the species is preadsorbed on the surface. One interesting means of improving the quantum yield in direct photolysis (non-catalytic) is by the addition of surfactant to water. Orders of magnitude enhancement have been reported in some cases since surfactants act as hydrogen sources (electron donor). It is, therefore, appropriate to ask whether the adsolubilization of organic compounds in hemi-micelles on the surface can similarly improve the oxidation of compounds through a combination of surface modification and electron donor properties. A mechanism was proposed. The surfaces of TiO_2 have been shown to become more hydrophilic with continued UV illumination, and the presence of surfactants on the surface may counteract this effect as well. Experiments are underway in our laboratory to test the proposed mechanism and the special attributes of surfactant-modified TiO_2 particles for heterogeneous photo-catalysis in small scale reactors; these will be reported in a subsequent paper.

Descriptors

Groundwater Quality, Hazardous Waste, Adsorption and Exchange, Industrial Wastewater, Wastewater Treatment, Organic Compounds.

Articles in Refereed Scientific Journals

Book Chapters

Dissertations

Water Resources Research Institute Reports

Conference Proceedings

Other Publications

Information Transfer Program

The information transfer activities of the Institute were upgraded during Fiscal Year 1999. In addition to participation in conferences, contact was established with several federal, state and local agencies and several public presentations were made.

A major information transfer activity of the Institute for FY 1999 was involvement on planning committees and sessions in conferences. These activities included the 1999 Louisiana Office of Emergency Preparedness Hurricane Exercise, the Impact of Hurricane Camille Symposium, the National Council Congress, and New Orleans Urban Water Quality Council. The Institute is working closely with several Louisiana Departments, private companies, other Louisiana State University units, and the USGS Offices. One project underway enhanced the information transfer of the institute. A small project finished up in 1999 involves the Lake Pontchartrain Basin Foundation, through the LA Institute. This program built an informational database dealing with lake and coastal issues, which are complex and involve many stakeholders and agencies. The Institutes Web site was re-configured to include hypertext links to NIWR RFPS, USGS RFPS, and electronic submission of proposals.

The Natural Systems Engineering Laboratory (NSEL) has been in place for the last few years as a joint effort between Civil Engineering and the Institute to promote research in this important area for coastal zone management. Several grants for related work have been received by the Laboratory to model and aide in flood control along the LA Gulf Coast and recently on hurricane protection for New Orleans. Information on the NSEL has been transferred to the public and professional sectors through several recent newspaper articles in Baton Rouge and New Orleans, coverage on Channel 6 in New Orleans, Channel 9 in Baton Rouge, the Discovery Channel, Time Magazine, ABC in New York, presentations of results to the LA delegation in Washington, and a presentation to FEMA in Washington.

The Institute's staff has maintained emphasis on acquainting Louisiana's research community with the research funding opportunities through the U.S. Geological Survey Section 104 research program. Announcements for the 104 program were widely distributed (300+) to Louisiana college 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. Table 1 depicts this participation in response to the announcements.

Table 1. Louisiana's Participation in LWRRI Research Programs, Proposals Submitted

<u>Year</u>	<u>Section 104</u>	<u>Section 105</u>
2000	12 Proposals	3 Funded

Presentations by the Director have been given to a number of organizations to help acquaint these audiences with the activities of the Institute. The Director annually attends NIWR, UCOWR and other professional meetings to discuss Institute and Program activities.

USGS Internship Program

Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 RCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	8	N/A	N/A	N/A	8
Masters	4	N/A	N/A	N/A	4
Ph.D.	N/A	N/A	N/A	N/A	N/A
Post-Doc.	2	N/A	N/A	N/A	2
Total	14	N/A	N/A	N/A	14

Awards & Achievements

Ongoing projects provided partial support or full time training to a significant number of students (14). The Patrick et al. project is developing a reproducible method for extracting methylmercury from freshwater sediments at a minimum concentration of approximately 0.2 parts per billion. The Sansalone et al. experimental site is located in a very visible and public area. Therefore much publicity has been generated for LWRRRI at the research. For example, The Advocate featured a story on the research and sponsors, Louisiana Sea Grant's "Coast and Sea" periodical featured a story on the research, students and sponsors as did Louisiana's Department of Development and Transportation in their monthly periodical. Dr. Valsaraj and Constant's project received a recent award from the U.S. EPA through the Gulf Coast Hazardous Substance Research Center based at Lamar University, TX has been received to continue the study and develop the monolithic reactor for photoadsolubilization of aromatic compounds. This project is to begin in September 2000.

The Natural Systems Engineering Laboratory (NSEL) has continued developing the capability to study and understand the complexities of hybrid environmental systems involving large scale man-made alterations of natural systems. The focus is on flooding and environmental restoration. NSEL was established in 1994 to respond to the opportunities in the field of environmental restoration and remediation with a focus on the State of Louisiana. One example of NSEL focus is on wetland and coastal restoration. It is estimated that during the next decade, over 0.5 billion dollars will be spent in Louisiana on restoration projects and innovation is sought in the areas of data collection, computer simulation and environmental designs for cost effective solutions. Other areas of NSEL focus include flood control and mitigation of nonpoint sources of pollution. Emphasis is placed on improved in-situ data acquisition equipment, enhanced models of natural systems, and evaluation of the performance of engineered designs.

Dr. Vibhas Aravamuthan serves as the Associate Director of the Institute and manages the NSEL. Current projects and award amounts to the NSEL are listed below, as these are awards through the Institute but are not pass-through USGS or other agency funds.

PROJECT	SPONSOR	AWARD AMOUNT
Lake Pontchartrain Basin Foundation	LPBF	\$39,077
Board of Regents Coastal Modeling Grant	LABR	\$119,983
LUMCON 4114	LUMCON	\$6,500
Flood Forecasting for St. James Parish, Louisiana	St. James Parish Emergency Preparedness Office	\$9,500
Coastal Image Archive	LA Governor's Office of Coastal Activities	\$40,337
Hydrologic Model Task	U.S. Corps of Eng	\$102,995

The above awards are focused on coastal mapping, flood protection, and prediction of hurricane effects. The Institute has received significant exposure on these issues in recent months, with presentations to Public Television, Statewide newspapers, and congressional offices. We clearly see and anticipate further impact of these NSEL efforts on coastal management and life and property protection in severe weather events.

Follow-on Funding:

Dr. Sansalone et al., through the grant from LWRRI, generated another year of funding (\$ 25,000) by USEPA Office of Water for the research. The LWRRI funding was used as match to secure \$20,000 of funding from LTRC for site development. The LWRRI funding helped the PI secure \$104,000 of National Sea Grant funding that will continue for the next year. The LWRRI funding also helped permit Drs. Sansalone, Cartledge and Singh to submit a \$249,000 USGS proposal in response to a USGS RFP on non-point pollution. This site offers the very real potential to develop into a site for long-term experimentation from which a long-term database in both non-point pollution and effective treatment strategies can be generated.

Publications from Prior Projects

Articles in Refereed Scientific Journals

Citation	Supportin Project Nur
Gambrell, R.P., R.D. DeLaune, A. Jugsujinda, and W.H. Patrick, (In press, 2000) "Mercury Distribution in Sediment Profiles of Six Louisiana Lakes," <i>Journal of Environmental Science and Health</i> .	GR0267 C-02
Reyes, Enrique, Jay Martin, Mary White, Paul Kemp, John Day, and Vibhas Aravamuthan, (In press, 2000) "Landscape Modeling of Coastal Habitat Change in the Mississippi Delta." <i>Ecology</i> .	GOV OFFI
Yuan, Q.; P. M. Jain and K. T. Valsaraj, (In press, 2000) "Reusable Adsorbents For Dilute Solution Separation. 4. Adsorption Of 1,2-Dichlorobenzene And Phenanthrene On A Surfactant-Modified Semiconductor (Titania) Surface," <i>Separation and Purifications Technology</i> .	GR0267 C-04

Book Chapters

None

Dissertations

None

Water Resources Research Institute Reports

Citation	Supporting Project Number
Suhayda, J.N. (1999) LA Water Resources Research Institute Annual Program Report, Louisiana Water Resources Research Institute, Louisiana State University, Baton Rouge, LA, 18 pages.	GR0267-B-01

Conference Proceedings

Citation	Supporting Project Number
Cristina C. and J. Sansalone “Non-equilibrium partitioning and solid phase distributions of heavy metals in highway runoff – Implications for highway shoulder treatment” at Annual Meeting of Transportation Research Board in Washington D.C..	GR026 C-03
Hird J., Cristina C., Beecher, L. Sansalone, J. “Passive Treatment of Elevated Roadway Runoff over Coastal Waterways using Upflow Clarification Technology” at the 4eme conference internationale sur les nouvelles technologies en assainissement pluvial in Lyon, France.	GR026 C-03
Liu, D., Zheng, T. and Sansalone, J. “A Granulometry-Based Screening Methodology to Assess Selection of Urban Storm Water Particle Separation Processes” at the 4eme conference internationale sur les nouvelles technologies en assainissement pluvial in Lyon, France	GR026 C-03
Sansalone, J.J., Cartledge, F.K, and Tribouillard, T., (In press, 2000) “Equilibrium partitioning of heavy metals as a function of urban storm water sediment granulometry – Implications for eco-treatment”, International Association for Hydraulic Research Conference in Italy, Balkema Publishing.	GR026 C-03
Sansalone, J.J., Glenn, D.W., Cartledge, F.K. and Tittlebaum, M., (In press, 2000) “Adsorption mechanisms for in-situ eco-treatment of urban waters as influenced by non-equilibrium partitioning of heavy metals”, International Association for Hydraulic Research Conference in Italy, Balkema Publishing.	GR026 C-03

Other Publications

Citation	Support Projec Numb
Aravamuthan, V. and J.N. Suhayda, "Real Time Forecasting of Hurricane Winds and Flooding," Internet Conference on Hurricanes and Chemical Hazards, June 1 1999. (www.hurricane.lsu.edu/internetconf.htm)	LAOE
Aravamuthan, V. and J.N. Suhayda, (May 18, 1999) "Bay Response To Freshwater Diversion Based Upon Computer Modeling,"CWPPRA Salinity Workshop, Louisiana State University, Baton Rouge LA.	LUMC
Sansalone, J.J. and T. Glenn. "Temporal variations in heavy metal partitioning and loadings in urban roadway sheet flow – Implications for in-situ treatment design," 79th Annual meeting of the Transportation Research Board, Washington DC, January, 2000.	GR026 C-03
Sansalone, J.J. Programme for Stormwater Seminars, "Characterization of storm water heavy metals and solids – Implications for treatment," Department of Sanitary Engineering, Chalmers University, Goteburg, Sweden, October 1999.	GR026 C-03
Sansalone, J.J. Programme for Stormwater Seminars, "Control of urban storm water heavy metals and solids through adsorptive-filtration", Department of Sanitary Engineering, Chalmers University, Goteburg, Sweden, October 1999.	GR026 C-03
Sansalone, J.J. American Society of Environmental Sciences Conference, "Passive treatment of urban storm water in coastal areas using ecological infrastructure", Baton Rouge, LA, December 1999.	GR026 C-03
Suhayda, J.N., V. Aravamuthan, and M. Alawady, (February 2000) "Hydrologic Modeling of the Barrataria Terrebonne Estuary," Prepared for Barrataria/Terrebonne National Estuary Program, Dept. of Environmental Quality, DEQ Contract No. 24400-93-10.	DEQ
Thiagarajan, G. and V. Aravamuthan, "Comparative Study of Solution Times in FE Problems on Workstations and Parallel Computers," ETCE 2000 & OMAE 2000 Joint Conference, ASME International, New Orleans, LA, February 14-17, 2000.	ASM