Water Resources Center
Annual Technical Report
FY 2008
Introduction

Pursuant to the Water Resources Research Act of 1964, the Water Resources Center (WRC) is the federally-authorized and state-designated Water Resources Research Institute (WRRI) for the State of Ohio. The WRC was originally established in 1959 as part of the Engineering Experiment Station, College of Engineering, OSU, and conducted an extensive program of research on water and wastewater treatment processes. The Center continues to be administered through the College of Engineering and has maintained a tradition of placing special emphasis on encouraging and supporting research in the area of physical, chemical, and biological treatment processes for water and wastewater. The mission of WRC is to promote innovative, water-related research in the State of Ohio through research grant competitions, coordination of interdisciplinary research proposals, and educational outreach activities.
Research Program Introduction

None.
Nanoscale Modification and Functionalization of Carbon Electrodes for the Detection of Harmful Organic Chemicals in Water such as Phenol and Domoic Acid

Basic Information

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<th><strong>Title:</strong></th>
<th>Nanoscale Modification and Functionalization of Carbon Electrodes for the Detection of Harmful Organic Chemicals in Water such as Phenol and Domoic Acid</th>
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<td>Water Quality, Water Supply, Toxic Substances</td>
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Publication

4. Yongjun Chen, Suzanne Lunsford, and Dionysios D. Dionysiou, Mesoporous ZrO2 film modified carbon electrode for the detection of Dopamine (in preparation)
8. Chen Yongjun, Suzanne Lunsford, and Dionysios D. Dionysiou, Mesoporous ZrO2 film modified carbon electrode for the detection of Dopamine (in preparation)
9. Lunsford Suzanne; Amber Yeary, PhuongKhanh Quoc Nguyen, and Rachel Kingdom,7/08, Electrochemical Detection of Phenol Utilizing a Synthesized Sonogel-Carbon Zirconium Oxide
(ZrO2), www.aslib.org, entry 10051.

14. STATEMENT OF REGIONAL OR STATE WATER PROBLEM: The Presence of Harmful Organic Chemicals (Toxins) in Ohio Water Resources

Lake Erie and the Ohio River are regional treasures from an ecological, economic, and social perspective. They provide drinking water to millions of Canadian and U.S. citizens, alluding to their significance as freshwater resources to humans [1]. Recent advances in environmental health are revealing that human generated or naturally occurring harmful organic chemicals in sources of water supply pose a great health threat to human and aquatic life [2]. Due to their well-known carcinogenic and lethal properties, the presence of human-produced toxic chemicals such as phenol and its derivatives are a critical threat to human health and aquatic life in water resources of the state [3]. Phenol is characterized as a high-priority Persistent Bioaccumulative and Toxic (PBT) chemical that does not break down readily in the environment and may accumulate in human or ecological food chains through consumption or uptake in the water supply. In addition, contamination of Lake Erie with biological toxins produced by cyanobacteria has attracted great attention of authorities in the Great Lakes [4]. A recent report reveals that cylindrospermopsin has been also found in Lake Erie [5]. Biological toxins, including microcystin, cylindrospermopsin and domoic acid, affect the number and diversity of wild animals, and bioaccumlulate in the bodies of animals and fish, and finally in humans through the food chain. For example, cyanotoxins have a wide range of health effects starting from mild including skin irritations, to more severe such as liver failure, irreversible damage of the nerves and even death. Domoic acid is also a naturally occurring biological toxin that creates a problem with loss of memory to people who eat shellfish consuming domoic acid-contaminated waters [6]. Domoic acid and metabolites released into water bodies can be sensitive indicators of environmental contamination. Many contamination events with these harmful compounds have occurred in Ohio drinking water resources and they might be a great threat to humans due to the absence of effective water treatment technologies to remove such toxins [2, 3-5,7].

Our motivation for this proposal integrating research in chemistry, biology, materials science, and chemical and environmental engineering stems from (i) The need for innovative and effective in-situ sensing methods - In parallel with the effective treatment of water contaminants, there is an urgent need to develop more innovative and effective in-situ measurement methods to detect such target toxins of interest in water, and thus assess their environmental fate and distribution in water bodies and ecosystems; and (ii) The experience on synthesis of nanoscale functional materials - The experience gained in the PI’s research group during the last several years in the field of nanoscience and nanotechnology as an approach to control the properties of materials at the nano-level and their design into functional materials with improved structural properties and functionalities for bio and environmental applications is believed to make it possible to synthesize new and innovative sensors to detect such toxins in water [8-12].

From the point of view of biological, ecological, and environmental importance of such toxic contaminant in water resources, it is a challenge to monitor them promptly. Therefore, the development of a simple and fast alternative in-situ method for sensing such organic toxins in water resources is of great importance and prerequisite. In this proposal, we investigate the synthesis, characterization, evaluation, and environmental applications of nanostructured electrodes to detect toxic chemicals in water such as phenol and domoic acid.

15. STATEMENT OF RESULTS AND BENEFITS: We expect that nanoscale electrodes will be successful for the quantitative and qualitative detection of the target water toxins, and
will possess mechanical stability, physical rigidity, and enhanced catalytic properties. This will be an innovative study and of interest to the scientific community for several reasons; it will: i) be focused on the fabrication of sensors for quick and easy detection of toxic chemicals, an important issue in the field of water quality, ii) introduce novel nanotechnological procedures combining sonocatalysis, surfactant self-assembly templating strategies, functionalization of materials surface with chemical markers, and fabrication of environmental sensors with improved functionalities and selectivity, and iii) provide the basis for other electrochemical sensors for a variety of other environmental, biochemical, and medical applications.

**Scientific Merit**: It is expected that specific scientific information and data will be generated through this study to (i) provide a better understanding on the interactions of selected toxins in water resources with the surface of modified and functionalized electrode for better selectivities and sensitivities and (ii) assess environmental fate and distribution of water toxins as an approach to develop monitoring technologies towards harmful organic molecules of interest.

**Broader Impacts**: We propose a variety of activities to enhance education on harmful organic chemicals in water resources, including phenolic compounds and biological toxins. These include (i) broad dissemination of results in journals, proceedings, conference presentations, (ii) enhancement of public awareness on toxins in water resources, and (iii) strengthening of national and international collaborations. The proposal has also strong societal impacts. First, it addresses a serious and emerging environmental problem, the presence of highly toxic chemicals, even naturally occurring biological toxins in natural water. Second, the technologies introduced in this research can be critical in the development of efficient technologies for sensing certain molecules of interest in ecosystem around the world. This will have a tremendous implication for protecting human health and aquatic life.

If this research project demonstrates successful progress, the results from this study will be used to prepare future proposals for major funding from the National Institutes of Health and National Science Foundation.

16. **NATURE, SCOPE, AND OBJECTIVES OF THE PROJECT; TIMELINE:**

**Nature and Scope**: Assessing and monitoring the degradation, distribution, and environmental fate of harmful toxins in water resources are important areas of research, given the increased demand for available water resources and increasing reports of toxin contamination events in freshwater drinking resources and estuaries, and other coastal habitats. In order to achieve effective assessment and monitoring of the toxins, the preliminary requirement is to detect them quickly in subseconds with a more efficient, innovative, and in-situ method.

High performance liquid chromatography (HPLC) was proven to be a sensitive method for the determination of many organic molecules including phenolic compounds and biological toxins [13,14]. However, it is a complicated and time-consuming process and requires a huge HPLC instrument, and thus is not proper to assess and monitor contaminants in-situ. Recently, electrochemical detection of target compounds of interest using smart sensors has attracted the attention of analytical chemists due to its simplicity, rapidness and high sensitivity [15]. The application of sol-gel chemistry in fabricating carbon-based electrodes has attracted great attention in developing new type of sensors [16,17]. Furthermore, the deliberate chemical modification of the electrode surface with suitable chemicals results in the control of the rates and selectivities of the relevant electrochemical reactions at the solid/liquid interface [14,18-21].

However, considering the challenges in successfully analyzing clinical and environmental samples in the presence of common interferents in water, the properties of the electrode should be significantly improved before it can become competitive for full-scale applications in...
developing such sensors to detect toxic chemicals in water. One of the major challenges involves the application of a biosensor for selective determination of target compound in water in the presence of many other compounds with similar structures that may cause interference problems. **Approaches, Rationale, and Previous Results:** Determination of phenol and domoic acid by their direct electrochemical oxidation is complicated due to the presence of possible interferences in water, which are also oxidized at the bare electrode. Other commonly coexisting organic and inorganic chemicals are also known to affect analytical detection of the toxins. Electrochemical selectivity is important to resolve these signals. Therefore, many other methods including selective determination of one of the species have been attempted by introducing self-assembled monolayer, Langmuir-Blodgett film, and single-walled carbon nanotube to bare electrode surface [22-25]. However, the sensitivity and selectivity are still not enough [25]. In this study, we propose to fabricate sonogel-carbon electrodes modified with highly active nanostructured TiO$_2$ with tailor-designed porous structure for facilitating adsorption of the target toxins of interest, and further functionalized with chitosan-tyrosinase composite film for enhancing the selectivity and sensitivity of the electrode towards phenol and domoic acid.

The synthesis of nanostructured TiO$_2$ is of great interest because of its attractive optical, electrical, chemical and catalytic properties [11,12]. More recently, the PI’s group has developed novel surfactant template-based sol-gel strategies to synthesize nanostructured TiO$_2$ [8-10]. Surfactants added in the sol can self-assemble into micelles, which can incorporate the titanium alkoxide around the micellar corona, forming surfactant organic core/TiO$_2$ inorganic shell composites. After heat treatment to remove the surfactant templates, the final TiO$_2$ has continuous phase porous inorganic network and tunable pore size similar to the micellar size. Using such a nanotechnological approach, we can fabricate TiO$_2$ material with tailordesigned porous structure, which can enhance adsorption of target molecules at the TiO$_2$ surface. As shown in Fig. 1 demonstrating previous experiments conducted by the PI’s group, the chemical modification of a carbon electrode with highly active nanostructured TiO$_2$ with around 5 nm porous inorganic network can facilitate the electrochemical detection of catechol (1,2-dihydroxybenzene), one of the neurotransmitters in the presence of ascorbic acid, a common interferent. This nanostructured TiO$_2$ exhibits interesting electrocatalytic properties for the redox of catechol. Catechol adsorbed onto TiO$_2$ rapidly reaches the electrode surface, then is oxidized, involving two electrons ($\text{e}^-$) and two protons ($\text{H}^+$). As a result, the surface of TiO$_2$ is believed to act as a redox mediator for the electron transfer between the carbon electrode and catechol [26,27]. This result implies that the TiO$_2$-modified electrode can be applicable to detect phenolic compounds since their structures with hydroxyl group are very similar to that of catechol.

![Fig. 1. Left: cyclic voltammograms of catechol and ascorbic acid using a carbon electrode (CE) and TiO$_2$-modified carbon electrode (TiO$_2$-CE). Right: facilitation of electron transfer.](image-url)
Currently, there is a great interest in designing functional membranes for analytical and biosensing applications because of their unique sensitive and selective properties [28]. The use of enzyme electrode is a definitely sensitive method for the detection of substrate. Tyrosinase catalyst can facilitate the oxidation of the phenolic compounds with hydroxyl groups to the corresponding o-quinones which can be further electrochemically reduced to phenolic substances, depending on the potential applied [29]. It has been reported that tyrosinase-based electrodes are still poor in sensitivity and selectivity [30]. In this study, the tyrosinase-based electrode is further functionalized by introducing chitosan as a selective film. Chitosan is a biologically important, chemically unique, biocompatible, and environmentally friendly polysaccharide. Due to the reactive amino and hydroxyl groups in chitosan, it has good membrane-forming ability, high water permeability, good adhesion, high mechanical strength and susceptibility to chemical modifications [31]. Chitosan researched so far was just used as a film forming agent. Recently, chitosan has been reported to be used to immobilize biomaterials for sensor applications to detect dihydroxyphenylacetic acid (DOPAC) [32]. DOPAC has the carboxylic acid functional group, which domoic acid possesses, and thus the chitosan-tyrosinase carbon electrode may be an alternative sensor for determination of phenol and domoic acid.

**Overall Goal:** In this proposal, we investigate novel ideas to synthesize and evaluate nanostructured electrodes to detect phenol and domoic acid. By introducing highly active nanostructured TiO₂ with tailor-designed properties for facilitating adsorption of the target compound of interest to carbon electrode and further functionalizing the electrode with chitosan-tyrosinase composite film for enhancing the selectivity and sensitivity of the electrode towards the phenol and domoic acid, the nanostructured TiO₂ chitosan-tyrosinase modified carbon electrode is able to easily monitor the toxins in-situ using electrochemical instrumentation. We attempt to meet the profitable features of electrode for the qualification and quantification of target water contaminants. Such features include selectivity, sensitivity, mechanical stability, physical rigidity, surface renewability, and catalytic properties.

**Objectives**
(i) Fabrication and optimization of nanostructured TiO₂-modified carbon electrode with tailor-designed structural properties for facilitating adsorption of phenol and domoic acid onto the TiO₂ and charge transfer between carbon electrode and the toxins.
(ii) Functionalization of TiO₂-modified carbon electrode with tyrosinase-chitosan composite film for enhancing the selectivity and sensitivity of the electrode towards phenol and domoic acid.
(iii) Electrochemical determination of phenol and domoic acid using the TiO₂ chitosan-tyrosinase SGC electrode.

**Timeline of Activities:** In order to ensure a successful outcome for the research plan, the key tasks to be accomplished and anticipated time schedule are described in the following table. During the final stage, a final report will be prepared and the results of the study will be disseminated through workshops, conferences, or meeting events. We anticipate that important findings and results will be summarized and submitted to peer-reviewed journals for publication.

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### 17. METHODS, PROCEDURES, AND FACILITIES

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<th>Task I. Fabrication of Nanostructured TiO₂-Modified Carbon Electrode</th>
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<td>For the fabrication of sonogel-carbon (SGC) electrode, 1.5 ml of methyltrimethoxysilane (MTMOS) is added into 0.3 ml of 0.2 M HCl solution. This mixture is insonicated in an ultrasonicator for 15 sec. Then, 3 g of graphite carbon powder is added into the MTMOS solution and mixed thoroughly for 10 min, where the total volume of the reactants is significantly reduced up to 20%, condensing the SGC. A 0.25 mm copper wire is installed inside 0.69 mm I.D. capillary glass tube (Sutter Instrument) used as the bodies of the SGC electrode. Only 1 cm out of 5 cm glass tube is filled with the SGC, and dried at 40 °C for 24 h. Finally, the tip of the SGC electrode is polished with a fine sand paper, followed by wiped with a soft tissue. Adherence between copper wire and SGC is tested in terms of tensile strength. The SGC electrode is coated with TiO₂ sol containing self-assembled surfactant as a pore directing agent. In order to control the structural properties of TiO₂ at the nano-level, the approach introduced in this study involves the use of an environmentally friendly surfactant for the precise orchestration of the titanium precursor in the sol formulation and the synthesis of the final TiO₂ material with tailor-designed porosity [9-11]. <strong>Polyoxyethylene sorbitan monooleate (Tween 80)</strong> surfactant is selected as a pore directing agent in TiO₂ sol. A suitable amount of Tween 80 is homogeneously dissolved in isopropanol (iPrOH). Acetic acid is added into the solution for the esterification reaction with iPrOH to generate water. When adding titanium tetraisopropoxide (TTIP) as TiO₂ precursor into the solution, hydrolysis and condensation reactions occur through in-taking of water molecules released from the esterification reaction. The molar ratio of the ingredients is optimized for the target-specific porous structure of TiO₂. The tip of SGC electrode is dipped into the TiO₂ sol and taken out. After coating, the SGC/TiO₂ electrode is dried at room temperature for 1 h and calcined in a multisegment programmable furnace (Paragon HT-22-D) to remove the surfactant templates and obtain a desirable crystal phase of TiO₂ (i.e., anatase, the most photoactive TiO₂ phase). The temperature is increased at a ramp rate of 3 °C/min to 400-550 °C, maintained at this temperature for 20 min, and cooled down naturally. Due to the difficulty to directly characterize the properties of TiO₂ materials on the SGC electrode, easy-to-remove TiO₂ coating is also prepared on borosilicate glass (Micro slide). For comparison, control SGC electrode without TiO₂ also follows the same heat treatment procedure. In this phase, we study the effect of type and concentration of surfactant on the controllability of the porous structure of TiO₂ inorganic network for the efficient adsorption of the target toxins.</td>
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<th>Task II. Functionalization with Tyrosinase-Chitosan Composite Biofilm</th>
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<td>In real environmental conditions, the “nonspecific adsorption” of coexisting organic and inorganic chemicals (interferents, natural organic matter (NOM), charged suspended solids, microorganisms, other than target compounds of interest in the drinking water resources) at the nanostructured TiO₂ surface constitutes a significant challenge [33,34]. In addition, competitive adsorption of other chemicals at the TiO₂ surface might inhibit the adsorption of target toxins, which can decrease the rates of their redox reaction (“electrode fouling”). In order to minimize</td>
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the nonspecific adsorption and electrode fouling and thus avoid complicated prior separation of other co-existing chemicals from target compounds, the TiO$_2$ surface is further modified with functional groups, which can prevent adsorption of interferent chemicals or facilitate adsorption of target toxins. As discussed in the section of Approaches and Rationale, the TiO$_2$-SGC or bare SGC electrodes are further functionalized with chitosan-tyrosinase composite film for enhancing the selectivity and sensitivity of the electrode towards the phenol and domoic acid [32]. A chitosan solution is prepared by chitosan powder in HCl solution, and then the solution is adjusted to pH 6. A chitosan-tyrosinase composite is prepared by mixing chitosan solution and tyrosinase solution (1:1 by volume). The composite solution is evenly cast onto the electrode surface. The modified electrode is further dried for the formation of the biofilm.

Task III. Functionalization with other Polymers and Introduction of Conducting Polymers: The other functional groups would include poly(ethylene glycol), which can be grafted in a mono-layer by their favorable silane interactions with oxides substrate [35]. The biocompatible polymer chains in the mono-layer on solid surfaces is proven to prevent protein adsorption since they provide entropic repulsive force between the surfaces and proteins. In addition, surface hydroxyl groups in TiO$_2$ introduced in the electrode have a great affinity with 1-hydroxy moiety of phenol and thus are believed to facilitate the formation of a chemical bonding between Ti in TiO$_2$ and O in the moiety, as suggested in Fig. 1. For further chemical modification of the electrode surface to improve the role of TiO$_2$ as charge transfer layer, we introduce conducting polymers such as poly(3-methylthiophene) and poly(2,2'-bithiophene) [15,36].

Task IV. Characterization of Electrodes: The TiO$_2$ chitosan-tyrosinase SGC electrodes are characterized using familiar methods. In order to determine the crystallographic structure of the materials, especially TiO$_2$, X-ray diffraction (XRD) analysis using a Kristalloflex D500 diffractometer (Siemens) with Cu K$_\alpha$ ($\lambda = 1.5406$ Å) radiation is employed. A porosimetry analyzer (Tristar 3000, Micromeritics) is used to determine structural characteristics of the materials including Brunauer, Emmett, and Teller (BET) specific surface area, porosity, and pore size distribution in the mesoporous range, using nitrogen adsorption and desorption isotherms. The structure of the materials at the nano-level is visualized using a JEM-2010F (JEOL) high resolution-transmission electron microscope (HR-TEM) with a field emission gun at 200 KV and further computerized using atomic force microscopy (AFM). An environmental scanning electron microscope (ESEM, Philips XL 30 ESEM-FEG) is used to investigate the electrode surface at the micro-level. An elemental composition analysis of the materials is performed using an energy dispersive X-ray spectroscopy (EDX, Oxford Isis) connected to the HR-TEM and ESEM and X-ray photoelectron spectroscopy (XPS, oxidation states). The other characterization includes zeta potential analysis (zeta potential), UV-vis spectroscopy, and contact angle analysis.

Task V. Electrochemical Detection of Toxins: Electrochemical measurements of target toxins in water (phenol and domoic acid) will be carried out with an Electrochemical Workstation (Epsilon, Bioanalytical Systems) in the presence of common interferents such as NOM, charged suspended solids, and microorganisms, based on cyclic voltammetry (CV) employing three electrodes: Pt auxiliary electrode, Ag/AgCl reference electrode, and TiO$_2$ chitosan-tyrosinase SGC working electrode, as demonstrated in Fig. 2. The scan rate of CV will be 100 mV s$^{-1}$. In addition to CV, other electrochemical analytic methods including linear sweep voltammetry, square wave voltammetry, differential pulse voltammetry and amperometry will be attempted. In this phase, we will investigate the effects of co-existing chemicals, including the above interferents as well as other organics and inorganics species that may affect the selectivity of the electrode for the target contaminants. The role of other conditions such as pH, ionic strength, and
temperature on the detection of toxins will also be studied. The chemical bondings between the TiO$_2$ chitosan-tyrosinase electrode and toxins during the experiment will be monitored using Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR). Finally, it is necessary to establish the calibration curve between concentration of toxins and oxidation and reduction peaks in CV at various environments.

**Task VI. Assessing and Monitoring of Environmental Fate and Distribution of Toxins:**

Once optimized, we will test the hybrid electrodes, which will be integrated in a flow-through cell, for the detection of phenol and domoic acid or other harmful organic contaminants in real conditions where water is contaminated with the chemicals. When a small flow cell with working volume of less than 2 cm$^3$ is constructed, continuous phase and long term monitoring of environmental fate and distribution of the toxins is possible in various spots of water resources.

**Task VII. Detection Mechanisms and Route:**

In order to investigate a possible mechanism and route for the enhanced detection of the water contaminants using TiO$_2$ chitosan-tyrosinase SGC electrodes, compared to bare carbon electrode, the roles of TiO$_2$ coating and chitosan-tyrosinase film will be elucidated with respect to: i) how toxins are adsorbed onto the surface of the nanostructured TiO$_2$, ii) how the adsorbed toxins are bonded and reacted with TiO$_2$ and/or chitosan-tyrosinase film, iii) how the TiO$_2$ exhibits electrocatalytic activity for the redox of toxins as a function of redox potential, iv) how the electrons in water toxins are transferred to SGC electrode via the Chitosan Tyrosinase-TiO$_2$ semiconductor layer, v) how tyrosinase acts as a biological enzyme to oxidize or reduce phenol and domoic acid, vi) how chitosan acts as a barrier to enhance the sensitivity and selectivity of the electrode towards phenol and domoic acid. In this phase, we will trace possible chemical bondings/covalent bonding and reactions occurring during the detection using Fourier transform infrared spectroscopy, Raman spectroscopy, nuclear magnetic resonance, and X-ray photoelectron spectroscopy. Especially, electrochemical impedance spectroscopy is a valuable technique to determine the important characteristics of electrochemically active TiO$_2$-modified electrode surface. Analysis of the impedance data assists in explaining the electron hopping and conductance properties of the modified surfaces developed to create redox reactions that will be utilized to detect common water and environmental toxins of interest. By understanding selective binding of specific functional groups in toxins with the surface of the electrode, it is feasible to develop better strategies to synthesize smart sensors for the detection of organic contaminants in water.

**Facilities:**

In order to perform the experiments, existing laboratory-facilities are used: 

(i) Dr. Dionysiou’s Laboratories, University of Cincinnati. Dr. Dionysiou and his students have exclusive use of 2000 ft$^2$ of contiguous research space and 600 ft$^2$ of contiguous office space.

(1) Rhodes Hall 705, Nanomaterials Characterization Lab: Nanomaterials preparation tools and kits, Micromeritics gas adsorption/desorption porosimetry analyzers, Micromeritics chemisorption analyzer, Membrane stir-cell devices, Fume hood.


(4) Engineering Research Center 781, Water Treatment Lab: HP UV-Vis spectrophotometer, Agilent high performance liquid chromatography, Shimadzu total organic carbon analyzer, Dionex ion chromatography, Photocatalytic reactors, Fume hood.

(5) Engineering Research Center 709, Student Office: 6 desks and desktop personal computers.
(6) Engineering Research Center 772, Student Office: 3 desks and desktop personal computers.
(7) Engineering Research Center 780, Dionysiou’s Office.
(ii) Other facilities at the University of Cincinnati. (University-wide access; available to project)
(1) Zanitsch Center for Interdisciplinary Environmental Research: The 15,000 ft² Zanitsch center is equipped with autoclaves, temperature control room, and various environmental analytical instruments including HPLC, GC, IC, TOC, and MS. It has one officer to maintain records, place orders, and receive shipments and two laboratory technicians for instrument maintenance, routine analyses, and fabrication of lab-devices and equipment.
(2) Materials Characterization Center: Advanced Materials Characterization Center has the ability to analyze and quantify materials at the nano and micro-level, using scanning electron microscopy, atomic force microscopy, time-of-flight EELS, transmission electron microscopy, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, X-ray diffractometer, and wide angle and small angle X-ray spectrometers.
(3) Institute of Nanoscale Science and Technology: The Institute brings together three centers of excellence, the Center for Nanoscale Materials Science, the Center for BioMEMS and Nanobiosystems, and the Center for Nanophotonics, composed of faculty from the Colleges of Engineering, Arts and Sciences, and Medicine. In order to achieve the development of a world class infrastructure for nanoscience-related research, to support advanced collaborative research on nanoscale materials and devices, and to advance high technology economic development within Ohio, the members in the institute, including the PI, are sharing any intellectual information and scientific knowledge as well as any physical equipment and instruments on nanoscale science and technology.
(iii) Dr. Lunsford’s Laboratories, Wright State University. 
(1) Oelman 110, Analytical Chemistry Instruments Lab: Bruker NMR Spectrometer, HP 6890 GC/MS, Millipore HPLC system, Perkin Elmer FT-IR, Dionex ion chromatograph, Perkin-Elmer atomic absorption spectrometer, HP UV-VIS spectrometers, Viscotek GPC system, Perkin Elmer differential scanning calorimeter and thermogravimetric analyzer.
(2) Oelman 320, Electrochemistry Lab: Epsilon electrochemical workstation, Various Pt and Ag/AgCl electrodes.
(3) Oelman 250, Lunsford’s office.
18. RELATED RESEARCH: As described earlier, this multidisciplinary research on the synthesis, characterization, evaluation, and environmental applications of nanostructured electrodes will unify experimentally and theoretically derived concepts related to intelligent engineering systems with applications across a wide variety of fields. The experience gained in Dr. Dionysiou’s research group during the last several years in the field of nanoscience and nanotechnology as an approach to control the properties of materials at the nano-level and their design into functional materials (i.e., tailor-made hierarchical membranes and films) with improved structural properties and functionalities for bio and environmental applications is believed to make it possible to synthesize new and innovative sensors to detect toxins in water.

Dr. Dionysiou and Dr. Lunsford together have produced preliminary data on fabrication of nanostructured TiO₂-modified carbon electrode to detect catechol, one of neurotransmitters, which are associated with mental and behavioral disorders such as schizophrenia, attention deficient disorder, Alzheimer’s disease, Parkinson’s disease, and cocaine addiction. In this project, we are expanding the application of the electrode to determination of harmful organic chemicals and toxins in water. One interesting aspect of this expansion is that the chemical structure of phenolic compounds with hydroxyl group is very similar to that of catechol.
Furthermore, chitosan-tyrosinase modified electrode is reported to be effective for the determination of DOPAC with carboxylic acid functional group which domoic acid possesses. These results imply that the TiO$_2$ chitosan-tyrosinase electrode, which we attempt to develop in this project, might be highly applicable to detect phenolic compounds and domoic acid.

Although several research studies so far have reported electrochemical detection of other compounds using newly developed sensors, such sensors have some common problems, including nonselective detection (poor selectivity), poor sensitivity and reproducibility, and electrode fouling. In order to minimize the problems and maximize the profitable features of electrodes, this study will combine more than two innovative strategies, including nanostructured catalytic TiO$_2$ coatings, biological enzyme tyrosinase, selective biomembrane chitosan, protein-fouling-resistant PEG monolayer and conducting polymer poly(3-methylthiophene). In order to achieve the proposed objectives, two investigators - Dr. Dionysiou with expertise in nanoscale science, environmental chemistry, and environmental remediation, and Dr. Lunsford with expertise in analytical chemistry and sensing - will collaborate in the project, which integrates aspects from the fields of chemistry, biology, chemical engineering, materials science, and environmental engineering. We believe that by understanding selective binding of specific functional groups in toxins with the surface of the electrode, it is feasible to develop better strategies to synthesize smart sensors for the detection of organic contaminants in water.

19. TRAINING POTENTIAL: We will encourage a Ph.D. student to learn educational themes of this proposal, including (i) fundamental nanoscale phenomena and processes in active nanostructured electrodes (multidisciplinary field combining environmental engineering, chemical engineering, chemistry, nanotechnology) and (ii) environmental fate and distribution of toxic contaminants in drinking water resources. Finally, the student will have the opportunity to perform innovative research, publish in respected refereed journals, present results at national and international conferences of multidisciplinary nature, augment her/his educational skills by attending courses in various colleges (Engineering, Medicine, Arts and Sciences), and develop inter- and multidisciplinary collaborations. Emphasis will be given to recruit a student from underrepresented groups in engineering (i.e., female and/or minority student).

In addition to the specific educational objectives described above, our overall educational objective of this proposal is to guide a Ph.D. student to pursue a dissertation of quality equal to that of the best students of top academic institutions nationally and internationally. We are extremely confident about i) a successful completion of the proposed research on the synthesis, characterization, evaluation, and environmental application of nanoscale electrode for the detection of harmful chemicals in water resources, ii) a multidisciplinary training of the student involved in this project through research and education, and iii) a high intellectual outcome of this work and its positive effect in the broader areas of science and engineering. Whenever appropriate, the Ph.D. student will interact with faculty members and students and take courses in other colleges/departments (Chemistry, Medicine, and other Engineering Departments).

During the duration of this project, we will also integrate knowledge acquired from this project in certain dual (unit operation process laboratory) and graduate level courses (advanced oxidation nanotechnologies) as case studies integrating environmental nanotechnology with sensing applications. These will help the students learn fundamental nanoscale phenomena and processes, aspects of the synthesis of advanced functional nanostructured electrodes and interesting sensing and environmental applications of nanotechnology. We also emphasize the multidisciplinary nature of this study covering ecology, chemistry, materials science, and chemical and environmental engineering.
REFERENCES

20. INVESTIGATOR’S QUALIFICATIONS

DIONYSIOS (DION) D. DIONYSIOU, Ph.D., Principal Investigator

Associate Professor, Water Quality Program, Department of Civil and Environmental Engineering (CEE), University of Cincinnati (UC)
765 Baldwin Hall, PO Box 210071
Cincinnati, OH 45221-0071, USA
Tel.: 513-556-0724, Fax: 513-556-2599, Email: Dionysios.d.Dionysiou@uc.edu

Education:
• Ph.D. Environmental Engineering, University of Cincinnati, Cincinnati, Ohio (2001) (Ph.D. Research Advisor: Makram T. Suidan, CEE, UC)
• M.S. Chemical Engineering, Tufts University, Medford, Massachusetts (1995)
• B.S./M.S. Chemical Engineering, National Technical University of Athens, Greece (1991)

Employment:
• 09/2005- Associate Professor (Tenured), Civil and Environmental Engineering, UC.
• 09/2000-08/2005 Assistant Professor, Civil and Environmental Engineering, UC.

Representative Recent Awards/Honors/Recognition:
• 2006 College of Engineering Research Award for Young Faculty, University of Cincinnati.
• National Science Foundation CAREER Award, 2005
• DuPont Young Professor Award, 2005
• 2003-2004 Distinguished Junior Faculty Research Award, University of Cincinnati, 2004.
• AWWA’s First Place 2002 Academic Achievement Award for Best Dissertation.

Research and Teaching Areas:
Environmental Nanotechnology; Advanced Oxidation Technologies; Drinking Water Treatment and Purification; Photocatalytic Destruction of Organic Contaminants in Water; Preparation of TiO₂ Photocatalysts, Ceramic Coatings and Inorganic Membranes; Colloids and Surfactants; Ionic Liquids in Environmental Applications.

Professional Society Affiliations (Member):
American Association for the Advancement of Science (AAAS); American Chemical Society (ACS); American Institute of Chemical Engineers (AIChE); American Society of Engineering Education (ASEE), American Water Works Association (AWWA); Association of Environmental Engineering & Science Professors (AEESP); Federal Water Quality Association (FWQA), International Ultraviolet Association (IUVA); Materials Research Society (MRS); Sigma Xi, The Scientific Research Society; Water Environment Federation (WEF).

Reviewer
Peer-Reviewed Journals: More than 40 journals in the area of Environmental Science and Engineering, Chemical Engineering, Materials Science, and Nanoscience and Nanotechnology.
Peer-Reviewed Conference Proceedings: International Conferences on TiO₂ Photocatalysis (since 2001); International Conferences on Advanced Oxidation Technologies (since 2001)

Funding Agencies—Proposals: National Science Foundation (NSF), Department of Agriculture (DOA), Environmental protection Agency (EPA), National Aeronautics and Space Administration (NASA), American Chemical Society (ACS).

Professional Service:
- Associate Editor, Journal of Environmental Engineering (ASCE).
- Associate Editor, Water Environment Research (WEF).
- Member of Editorial Board, Applied Catalysis B: Environmental (Elsevier)
- Member of Editorial Board, Environmental Progress (AIChE)
- Member of the Education and Awards Committees of the Association of Environmental Engineering and Science Professors (AEESP); Member of Water Environment Federation Groundwater Committee; Member of AWWA Organics Control Contaminant Committee.

Publications/Presentations:
107 Refereed Journal (51) and Conference Proceedings (56) Publications; 3 Book Chapter Publications; 7 Journal Manuscripts submitted to journals; 4 Journal Manuscripts in Preparation (with my students); more than 170 Conference Presentations and Invited Lectures.

Research Papers (Peer Reviewing) List of Five Relevant Publications:

Research Collaborators in the Past 48 Months:
- Suzanne Lunsford, Wright State University.
- Amid P. Khodadoust, Civil and Materials Engineering, University of Illinois at Chicago.
- Erick Bandala, Water Quality and Treatment, the Mexican Institute of Water Technology.
- Gregory V. Lowry, Carnegie Mellon University.
- Rajender Varma, Michael Gonzalez, Tom Speth, Armah de la Cruz, Souhail Al-Abed, USEPA, Cincinnati.
- Paul L. Bishop, George A. Sorial, and Daniel B. Oerther, CEE Department, University of Cincinnati.
SUZANNE LUNSFORD, Ph.D., Co-Principal Investigator

Associate Professor, Analytical Chemistry Program, Department of Chemistry, Wright State University (WSU)
245 Oelman Hall, PO Box 350001
Dayton, OH 45435-0001, USA
Tel.: 937-775-2480, Fax: 937-775-2717, Email: Suzanne.lunsford@wright.edu

Education:
• Ph.D. Analytical/Inorganic Chemistry, University of Cincinnati, 1995
• B.S. Chemistry, Xavier University, 1990

Employment:
• Associate Professor, 2006-present, Department of Chemistry, WSU, Dayton, OH
• Assistant Professor, 2001–2006, Department of Chemistry, WSU, Dayton, OH
• Instructor, 1997-2000, Department of Chemistry, WSU, Dayton, OH
• Post-Doctoral Associate, 1995-2000, University of Cincinnati, Cincinnati, OH

Representative Recent Awards/Honors/Recognition:
College Teacher of the Year Award at Wright State University, 2005–2006

Research and Teaching Areas:
Research and the development of modified conducting and nanoparticle (sol-gel methods) working sensor electrodes to detect common biological molecules in the biomedical field and environment (water quality) utilizing electroanalytical techniques. The sensor development research overlaps well with development of materials to teach instrumental chemistry, and graduate level inorganic chemistry at Wright State University.

Professional Society Affiliations:
• American Chemical Society (ACS)
• National Science Teachers Association (NSTA)
• Electrochemical Society (ECS)

Publications/Presentations:
12 conference proceedings, 14 conference presentations and invited lecturer, 19 publications and one book chapter in the Ohio Board of Regents, “SUSTAIN”.

Five Closely Related Publications:
2. Lunsford, S.K., Slattery, W., An Interactive Environmental Science Course for Pre-Education Science Students; Phase I: Fieldwork/Field Trips; Phase II: Data Evaluation/Laboratory Experience; and Phase III: Internet Course and Web Conferences. J. Chem Ed., 83 (2006) 233.

Research Collaborators in the Past 48 Months:
- Dionysios D. Dionysiou, University of Cincinnati, Department of Civil and Environmental Engineering
- Justyna Widera, Adelphi University, Department of Chemistry
- Vinnie Vsubrama, Ohio State University, Department of Chemistry
- Kumar Nedunuri, Central State University, Chemical Engineering
Evaluating Colloid Release from Natural and Model Porous Media

Basic Information

| Title: Evaluating Colloid Release from Natural and Model Porous Media |
|---|---|
| Project Number: 2007OH54B |
| Start Date: 10/1/2007 |
| End Date: 9/30/2008 |
| Funding Source: 104B |
| Congressional District: 15 |
| Research Category: Water Quality |
| Focus Category: Solute Transport, Groundwater, Hydrogeochemistry |
| Descriptors: None |
| Principal Investigators: John Lenhart |

Publication
Evaluating Colloid Release from Natural and Model Porous Media

Statement of Critical Regional or State Water Problem
The behavior of colloid-sized particles (nominally 1 nm to 1 μm in diameter) is of significant importance in natural and engineered systems. In natural systems, colloids comprised of singular and aggregated mineral, biological and organic components are ubiquitous in surface and subsurface waters. Due to their propensity to sorb otherwise sparingly soluble contaminants or in the case of biocolloids, inherent risk, their presence in water poses a potential health risk (McDowell-Boyer et al. 1986; McCarthy and Zachara 1989; Ryan and Elimelech 1996). Colloidal interactions are also important in water and wastewater treatment, chromatographic separation, oil production, extractive metallurgy, lubrication, coating and cleaning (Osipow 1962; Yao et al. 1971; Hiemenz 1986). Consequently, the physical and chemical processes that govern colloid interactions with surfaces have been extensively studied, and significant progress toward identifying processes responsible for colloid deposition has been made (e.g., Elimelech and O'Melia 1990; Song and Elimelech 1993; Lenhart and Saiers 2002; Lenhart and Saiers 2003; Tufenkji and Elimelech 2005). However, considerable uncertainty remains about the mechanisms that govern colloid interactions under unfavorable conditions, characterized by systems with like-charged surfaces, particularly with regard to mechanisms responsible for reversible deposition and colloid release in porous media (Kretzschmar et al. 1999). Knowledge of the fundamental processes that control the deposition, release and subsequent transport of colloidal particles and associated contaminants is crucial to maintaining the quality of ground water that the nearly five million residents of the Ohio (OhioEPA 2000) rely on for their daily needs.

Statement of Results and Benefits
Although the interfacial behavior of colloidal particles has been the subject of intensive research for several decades, much remains to be learned. In particular, discrepancies are frequently observed between experimental results and theoretical predictions in systems with like-charged surfaces. Reversible deposition of colloids within a secondary minimum is one of several mechanisms that could be potentially responsible. Despite this fact, however, little data exists to examine the role of fundamental system properties on reversible deposition. Furthermore, there is no rigorously tested or generally accepted approach to include reversible deposition within the often-applied framework of colloid filtration theory. Fundamental information on the mechanisms that control colloid behavior is required to accurately estimate colloid mobility in ground water and to protect public health.

Nature, Scope, and Objectives of the Research
Research Nature and Scope
Colloid stability in porous media can be estimated by calculating the total interaction energy ($\phi_{net}$) using the theory developed by Derjaguin and Landau (1941) and Verwey and Overbeek (1948). This is known as the DLVO theory, and it allows for the estimation of $\phi_{net}$ as a function of the distance separating two charged surfaces by summing Coulombic and van der Waals interactions. The magnitude and sign of these interactions depends on the composition of the two surfaces, and for Coulombic interactions, the chemical composition of the pore water (Israelachvili and McGuiggan 1988). For like-charged surfaces at low ionic strengths, repulsive electrostatic interactions generally prevail and the interaction energy profile takes on a distinctive
shape characterized by a deep primary minimum ($\phi_{\text{min}1}$) at low separation distances isolated from the shallow secondary minimum ($\phi_{\text{min}2}$) at larger distances by the presence of a repulsive energy barrier ($\phi_{\text{max}}$) (e.g., see Ryan and Elimelech 1996). These conditions are commonly termed “unfavorable” for colloid deposition, and if the energy of $\phi_{\text{max}}$ is sufficient, it not only hinders deposition it also hinders colloid release in $\phi_{\text{min}1}$. At high ionic strengths, however, the magnitude and range of the repulsive coulombic forces are reduced below that of the attractive van der Waals forces, and the net surface interaction between colloid and pore wall surfaces is attractive at all separation distances (Ryan and Elimelech 1996). A similar interaction profile results when the surfaces have opposite charge. These conditions are termed “favorable” for colloid deposition because the repulsive energy barrier is minimized or entirely absent, and colloids rapidly deposit or flocculate (Ruckenstein and Prieve 1976; Ryan and Elimelech 1996).

Under steady-state conditions colloid deposition is generally considered irreversible, for it typically requires a significant disturbance in the system to generate a measurable release of colloids. Such disturbances can be either hydrodynamic or chemical; however, in the case of water-saturated systems with steady and low porewater velocity hydrodynamic shear is not considered to be an important source of mobile colloids (Khilar and Fogler 1984; Ronen et al. 1992). Consequently, in water-saturated systems colloid release is primarily due to perturbations in the pore water chemistry. For example, modifying the porewater chemistry to produce like-charged surfaces in systems initially characterized by oppositely-charged surfaces, results in colloid release (Kallay et al. 1987; Ryan and Gschwend 1994; Seaman et al. 1995; Swartz and Gschwend 1998). Alternatively, in systems with like-charged surfaces release readily occurs upon diluting the porewater ionic strength (McDowell-Boyer 1992; Nocito-Gobel and Tobiason 1996; Roy and Dzombak 1996). In either situation, upon release the colloid pulse exhibits a sharp elution front (Nocito-Gobel and Tobiason 1996; Roy and Dzombak 1996), occurs concurrent to the advective front of the chemical transient (Nocito-Gobel and Tobiason 1996), and frequently exhibits tailing (Grolimund et al. 1996; Nocito-Gobel and Tobiason 1996; Roy and Dzombak 1996; Grolimund et al. 2001). Approaches to describe release using a single desorption rate constant based on theory (Dahneke 1975) have generally been of limited success (Grolimund and Borkovec 2001; Lenhart and Saiers 2003).

The bulk of the research on colloid mobilization centers on systems that employ initially constant or unknown immobile-phase colloid concentrations in laboratory-synthesized or natural porous media (e.g., Ryan and Gschwend 1994; Grolimund et al. 2001). Studies that vary the initial deposited colloid concentration, or conditions under which deposition occur, however, demonstrate that the extent and magnitude of colloid release is sensitive to the colloid deposition environment (Kallay et al. 1987; Lenhart and Saiers 2003; Hahn and O'Melia 2004). For example, increasing the ionic strength during deposition, or employing multivalent cations in the electrolyte, not only promotes colloid retention it also hinders colloid release (Kuo and Mattijevic 1979; Hahn 1995; Lenhart and Saiers 2003). Presumably this is due to the colloids depositing within the primary minimum, which as the energy barrier prohibiting deposition in the primary minimum decreases, becomes easier to access. Under these conditions DLVO theory predicts the deposited colloids will be tightly held within $\phi_{\text{min}1}$ and thus are typically considered to be unavailable for release. However, in many systems with like-charged surfaces this often proves to be incorrect, as deposition is readily reversed upon modifying the porewater chemistry (e.g., (Roy and Dzombak 1996; Lenhart and Saiers 2003; Tufenkji and Elimelech 2004). Possible explanations for these discrepancies between theory and observation as well as similar ones that
occur during deposition under unfavorable conditions, include surface roughness, charge heterogeneity, and the influence of the secondary minimum (Kallay et al. 1987; Elimelech and O'Melia 1990; Song et al. 1994; Litton and Olson 1996; Lenhart and Saiers 2003; Tufenkji and Elimelech 2004).

Evidence is mounting that these processes, as well as other so-called non-DLVO interactions (e.g., Grasso et al. 2002), markedly alter colloid behavior; particularly in systems comprised of like-charged surfaces (McDowell-Boyer 1992; Litton and Olson 1996; Hahn and O'Melia 2004; Li et al. 2004; Tufenkji and Elimelech 2004; Li and Johnson 2005). Furthermore, the influence of some non-DLVO interactions (e.g., steric repulsion) tend to be over very small distances (typically a few nanometers) and, according Hahn and O'Melia (Hahn and O'Melia 2004) their presence could potentially mask $\phi_{\text{min1}}$ in many natural and engineered systems. In such systems $\phi_{\text{min2}}$ becomes the locus of deposition if $\phi_{\text{min2}}$ exceeds the kinetic energy of the colloids (0.5 kT). As $\phi_{\text{min2}}$ can easily be greater than ten kT in depth, it seems reasonable to view colloid retention within the secondary minimum as an important mechanism for influencing colloid stability and transport in many natural and engineered systems (Hahn and O'Melia 2004; Tufenkji and Elimelech 2005).

Research Objective
The objective of the proposed research is to evaluate the extent and kinetics of colloid release in water-saturated porous media under conditions selected to promote unfavorable DLVO interactions. The work will couple laboratory-scale experimental work with mathematical models to test existing theory and approaches to model colloid transport. I expect to derive results that can be used to (1) evaluate the importance of the secondary minimum in reversible colloid deposition in systems with like-charged surfaces, (2) test the influence of system conditions (e.g., porous media, porewater velocity, porewater composition and colloid size) on reversible deposition, and (3) test the rigor of existing approaches that account for non-DLVO deposition (e.g., Tufenkji and Elimelech 2004) and examine their application to describe colloid release. Such information is needed to accurately predict colloid mobility and appropriately evaluate filtration technologies for their removal from source waters. Two overarching questions drive the proposed research. They are:

- To what extent does reversible deposition depend upon the presence of the secondary minimum?
- How do system conditions (e.g., grain size, solute composition) influence reversible deposition?

In order to address these questions I propose to link experimental work and numerical work with the fundamental principles that govern colloid filtration.

Timeline of Research Activities
To address the questions listed above it is expected that the proposed research will require a period of one year. The first first half-year will be devoted to evaluating whether reversible deposition depends upon the existence (at least theoretically) of a secondary energy minimum. The second question will be answered during the remaining period of the project by elucidating how the system conditions control colloid deposition and subsequent release.
**Methods, Procedures and Facilities**

*Methods and Procedures*

The deposition and mobilization of colloids will be evaluated in a series of bench-scale column experiments. Each experiment will consist of two stages, a deposition stage and a mobilization stage. During the deposition stage, a solution comprised of the colloids, suspended in a solution containing simple electrolytes (e.g., 0.03 M NaCl or 0.01 M CaCl₂ at pH 8), will be introduced into the column as a pulse. The concentration of the electrolyte and the valence of the cation in the influent suspension will be varied between experiments and a suite of experimental conditions will be tested in order to prepare columns that have different retained colloid profiles. Colloids deposited in the column during the first stage will be mobilized through a single, or through successive step-changes in the porewater electrolyte in the second stage. At the conclusion of each experiment, and for some experiments at the conclusion of the deposition stage the porous media will be extruded from the column and the profile of retained colloids will be measured.

*Preparation and Characterization of Experimental Materials.* Soda-glass beads and/or quartz sand will be used as the porous medium in all experiments. At least two fractions will be isolated for use with nylon sieves. As received, the media may be coated with metal oxides (Fe, Al and Ti) and trace quantities of organics. These impurities will be removed because they may influence surface charge characteristics of and thus may promote colloid deposition (Litton and Olson 1993). To remove the surface coatings a procedure developed by Kohler et al. (1996) will be followed. After sieving, the media will be rinsed several times in deionized water to remove native colloid-sized particles. The media will be transferred to ceramic dishes and combusted at 800 °C for four hours to remove organics. Metal-oxide coatings will be dissolved by boiling in 50% concentrated HNO₃ for two hours. The acid will be decanted and the solids will be repeatedly rinsed with deionized water until the pH of the rinse-water stabilizes at a near-neutral value. Amorphous silica and any remaining colloids will be removed by agitating the media in 0.002 N NaOH for two hours. The acid will be decanted and the solids will be rinsed thoroughly with deionized water before the final treatment, a rinse in 0.001 M HNO₃ for 12 to 14 hours to remove any remaining cations. Following the final acid wash, the media will be thoroughly rinsed a final time with deionized water until the pH approaches 7, and then dried at 110 °C.

The zeta potential of the porous media will be estimated from electrophoretic mobility measurements of native colloids according to the procedure of Johnson (1999). This procedure involves isolating colloid-sized particles from media immersed in electrolyte solution and subjected to ultrasound in an ultrasonic bath for specified period of time (e.g., 30 minutes). Aliquots of the solution containing the suspended colloids will be removed after the ultrasound treatment and filtered through a 0.45 μm PTFE filter. The electrophoretic mobility of the colloidal media will be determined at 25 °C using a ZetaPlus Analyzer (Brookhaven Instruments Corp). The tables of Ottewill and Shaw (1972) will be used to convert electrophoretic mobility measurements to zeta potential. The surface morphology and sphericity of the clean media will be evaluated using scanning electron microscopy.

Surfactant-free fluorescent spherical latex particles (Interfacial Dynamics Corporation) will be used in all experiments as the colloidal phase. These colloids are commercially available with a variety of surface groups in multiples sizes. Carboxyl-modified surfaces are commonly used (e.g., Litton and Olson 1996), and the sizes chosen will depend upon whether deposition within
the primary or secondary minima is to be accentuated. For example, Tufenkji and Elimelech (2005) evaluated the transport of 63, 320 and 3000 nm latex particles through 328 μm soda glass beads as a function of pH and ionic strength. Their results suggest that deposition within the primary minimum is highly unlikely for the 3000 nm particles, but possible for the same particles within secondary minimum. For the 63 nm particles, however, it is expected that the lesser magnitude of $\phi_{\text{max}}$ and corresponding minimal $\phi_{\text{min2}}$ suggests conditions might favor deposition within $\phi_{\text{min1}}$. Based on this interpretation, I suspect that compared to the 63 nm particles that the 3000 nm particles would be more amenable to release.

The manufacturer-reported diameter will be confirmed by dynamic light scattering using the ZetaPlus Analyzer. Latex colloid suspensions will be prepared by adding aliquots of a concentrated stock to the electrolyte solution to achieve the target colloid concentration. The average zeta-potential of the colloids in the different electrolyte solutions will be determined using the ZetaPlus analyzer and the tables of Ottewill and Shaw (1972) or the Smoluchowski equation (Hunter 1981).

**Column Design.** Experiments on the transport of the latex microspheres follow the methods outlined by Lenhart and Saiers (2003). Glass chromatography columns with an internal diameter of 4.8 cm or 2.4 cm and PTFE end fittings will be used to contain the porous media. Depending upon the desired flowrate a digital peristaltic pump or liquid chromatography pump will be used to control the flow of colloid and electrolyte solutions. The pump will be positioned at the base of the vertically oriented columns and the flow will be directed downward. Each experiment will use a fresh column prepared by wet-packing methods (Lenhart and Saiers 2003). The column will be packed to a predetermined height, and vibration will be used during packing to minimize air entrapment and the formation of layers. The porosity and pore-volume of each packed column will be measured using standard methods based upon media volume and solution displacement.

**Column Experiment Methodology - Stage 1: Colloid Deposition.** Each packed column will be pre-equilibrated with the electrolyte solution by pumping approximately 10 – 20 pore volumes of colloid-free electrolyte solution through the column prior to commencing the experiment. Colloid concentrations will be monitored in the column effluent during this period to verify that native colloid mobilization is negligible. The equilibration period will cease when the effluent pH matches that of the influent solution. Following column pre-equilibration, a suspension of latex colloids in electrolyte solution will be introduced to the top of the column. The colloid-containing solution will be pumped into the column for a specific period of time (e.g., 2.5 pore volumes), whereupon the colloid-free electrolyte solution will be redirected into the column. Effluent colloid concentrations will be monitored in effluent samples collected with a fraction collector (Foxy II, Isco Instruments) based upon fluorescence intensity (Shimadzu fluorescence spectrometer) or UV/Vis absorption (Shimadzu double-beam UV/Vis spectrophotometer), depending upon the particle size. Experiments will be conducted for different packing heights, electrolyte concentrations, porewater velocity and colloid concentration.

**Column Experiment Methodology - Stage 2: Colloid Mobilization.** Colloid mobilization will be induced at the conclusion of the deposition stage, when the effluent colloid concentrations return to baseline levels, by perturbing the composition of the electrolyte solutions to increase repulsive double-layer interactions between the colloid and media surfaces (e.g., by diluting electrolyte concentration (Lenhart and Saiers 2003)). Successive perturbations will be examined, depending upon the initial conditions, as well as the magnitude of the change in the electrolyte composition.
The concentration of the electrolyte in the effluent will be monitored in the effluent using a conductivity probe or specific ion electrode.

**Measuring Retained-Colloid Profile.** At the conclusion of each experiment the columns will be drained, disassembled, and the column packing will be extruded in order to measure the profile of retained colloids. A procedure developed by Bolster et al. (1999) will be followed. Upon extrusion, the porous media will be separated into sections approximately 1-cm in depth. These sections will be transferred into centrifuge tubes and appropriate volumes of approximately 1 mM NaOH will be added to the tubes. The samples will be equilibrated end-over-end for several hours to effect colloid release and then vigorously shaken using a vortex mixer to disperse the colloids throughout the solution. Aliquots of the supernatant will be removed, filtered (if necessary) and analyzed by fluorescent emission or UV/vis absorption. The solids will then be rinsed several times, oven-dried and weighed.

**Mathematical Modeling.** I am interested in evaluating the processes responsible for colloid transport in water-saturated media with like-charged surfaces and will utilize DLVO theory to estimate the interaction potential in the system and a transport model to evaluate colloid transport.

**Interaction potential.** The basic framework used in estimating the net or total potential energy between suspended colloidal particles or between colloidal particles and collector surfaces follows DLVO theory by summing van der Waals forces ($\phi_{VDW}$) and electrostatic double layer forces ($\phi_{EDL}$) (Derjaguin and Landau 1941; Verwey and Overbeek 1948). Hogg et al. (1966) derived expressions for electrostatic double layer interactions ($\phi_{EDL}$) between two surfaces separated by a solution containing dissolved ions using a linearized approximation of the Poisson-Boltzmann equation. Although Hogg et al. (1966) stipulate the approximation is appropriate for surface potential less than 60 mV, Russel et al. (1989) state that it remains valid up to electrolyte concentrations of 1 M and surface potentials of 200 mV. Equations are available for both sphere-plate and sphere-sphere interactions, and the expression for two non-identical spheres is given by (Hogg et al. 1966). Van der Waals forces, resulting from the interaction of dipoles, can be estimated assuming pair-wise additivity of the interatomic potentials (Hamaker 1937). At separation distances between the two surfaces greater than a few nanometers, the original Hamaker approach must be modified to account for a reduction in $\phi_{VDW}$ due to phase-shift between dipoles. To estimate the retarded $\phi_{VDW}$ I plan to use the expression of Gregory (1981). This equation was originally intended for separation distances less than 0.2$\tau_C$ (Gregory 1981), but its accuracy can be verified for greater separation distances by comparison to the more rigorous expression for retarded $\phi_{VDW}$ from Czarnecki (1979). The total interaction energy is determined by summing the expressions for electrostatic and van der Waals interactions.

**Model for Colloid Transport in Saturated Porous Media in Steady-State Conditions.** The model presented by Lenhart and Saiers (2003) will be used to evaluate colloid transport. This model ties colloid release to a critical solute concentration where the barrier to colloid release vanishes. It couples equations to account for the transport of solute and colloids with a mass balance equation to account for the deposition and subsequent release of colloids. To account for distributed release of colloids as a function of solute concentration the model assumes surface irregularities in terms of potential or shape induce heterogeneities in the interaction energies between deposited colloids and the mineral grains. This heterogeneity is accounted for by
dividing the immobile-phase colloid population into a series of compartments, where each compartment releases colloids at a characteristic critical solute concentration. The model can describe (1) the transport and deposition of colloids, (2) the consequent profile of the deposited colloids, (3) solute transport, (4) colloid release coupled to porewater solute concentrations, and (5) colloid release across a range in porewater solute compositions.

Facilities
The experimental program will be conducted in the OSU Environmental Engineering Laboratories. The program maintains three well-equipped wet-labs with 5 large fume hoods and 2 walk-in 50ft² constant temperature rooms. State-of-the-art analytical equipment for use in the proposed research includes: Shimadzu fluorescence spectrometer, Shimadzu double-beam UV/Vis spectrophotometer and a Brookhaven Instruments ZetaPlus Electrophoretic Light Scattering instrument. Laboratory equipment also includes: Millipore Milli-Q water purification system, laboratory and portable pH and conductivity meters, Mettler-Toledo digital balances, orbital and end-over-end shaker tables, high-flow peristaltic and positive-displacement pumps, glass columns and associated fittings, low flow peristaltic and Teflon double-diaphragm pumps, muffle and evaporative ovens, constant-temperature recycling water baths and multiple personal computers with associated hardware.

Related Research
Although the research examining colloid deposition under conditions both favorable and unfavorable for deposition is extensive, the research examining reversible colloid deposition or colloid release is comparatively small. In nearly every instance the researchers follow conventional colloid filtration theory and emphasize the role of the primary minimum. Attempts to reconcile discrepancies between theoretical predictions and experimental results typically require the inclusion of one or several non-DLVO processes to account for short-range repulsive interactions (Ruckenstein and Prieve 1976; McDowell-Boyer 1992; Ryan and Elimelech 1996; Bergendahl and Grasso 1999). Although this improves model fits, the extra parameters are often poorly constrained and thus are merely fitting terms. Such phenomenological approaches are system-specific and although they may provide insight into the behavior of certain systems they are not readily transferable to other systems. Alternative modeling approaches have recently been proposed to include secondary minimum deposition within the framework of colloid filtration (e.g., Hahn and O’Melia 2004; Tufenkji and Elimelech 2004; Tufenkji and Elimelech 2005), but their ability to quantify the impact of the secondary minimum or other mechanisms on the extent or rate of colloid release remains to be rigorously examined.

References

**Training Potential**
This research will be used to support and train one M.S. level graduate student in environmental engineering for two years.

**Information Transfer (IT) Plan**
The subject of colloidal transport in porous media is of concern to the general public, however, the fundamental nature of the proposed research limits the target audience to researchers in academic and government facilities. My intention is to prepare at least one manuscript from the results of the proposed research and submit it to a quality, peer-reviewed journal (e.g., *Environmental Science and Technology*). Furthermore, I plan to present the research at regional and national conferences organized by professional societies such as The American Chemical Society.

**Investigator’s Qualifications**
Dr. John J. Lenhart is an Assistant Professor in Environmental Engineering at The Ohio State University and he will provide research oversight. As shown in the attached resume Dr. Lenhart has extensive research experience on different aspects of colloid behavior and has published several peer-reviewed papers on the subject. Dr. Lenhart holds a B.S. in Engineering (1989), and a M.S. (1993) and a Ph.D. (1997) in Environmental Science and Engineering from the Colorado School of Mines.
JOHN J. LENHART
Department of Civil & Envir. Engrg. & Geodetic Science
Ohio State University
470 Hitchcock Hall
Columbus, Ohio 43210
Tel: (614) 688-8157
Fax: (614) 292-3780
E-mail: lenhart.49@osu.edu
Website: http://www-ceg.eng.ohio-state.edu/~lenhart/

PROFESSIONAL PREPARATION

Colorado School of Mines, Golden, Colorado
Ph.D., Environmental Science and Engineering
Dec. 1997

Colorado School of Mines, Golden, Colorado
Master of Science, Environmental Science and Engineering
Dec. 1993

Colorado School of Mines, Golden, Colorado
Bachelor of Science, Engineering, mechanical emphasis
May 1989

APPOINTMENTS

The Ohio State University - Columbus, OH
Mar. 2003 - present
Assistant Professor, Department of Civil and Environmental Engineering and Geodetic Science
- Research interests: Environmental chemistry, adsorption phenomena, contaminant fate and transport, colloidal filtration.
- Teaching duties: Analysis of Natural and Polluted Waters; Adsorption of Pollutants in Environmental Systems; Introduction to Environmental Engineering; Env. Eng. Capstone Design.

Yale University – New Haven, CT
May. 2000 - Feb. 2003
Postdoctoral Associate, School of Forestry and Environmental Studies
- Investigated the transport of inorganic colloids and organic macromolecules in variably saturated porous geomedia under steady-state and transient conditions.

United States Geological Survey – Menlo Park, CA
June 1998 – April 2000
National Research Council Postdoctoral Fellow, National Research Program
- Examined the molecular-level structure of metal ions adsorbed to mineral surfaces in the presence of organic acids using combined wet chemical and spectroscopic techniques.

Colorado School of Mines – Golden, CO
Research Professor and Graduate Research Assistant, Division of Env. Science & Engineering
- Research: Metal-NOM interactions, surface complexation modeling, uranium geochemistry.
- Instructor: Short course in Physical and Environmental Chemistry
- Teaching Assistant: Aquatic Chemistry, Water and Wastewater Treatment, and Environmental Pollution: Sources, Characteristics, Analysis, and Fate.

Martin Marietta – Lakewood, CO
June 1989 - July 1991
Materials and Processes Engineer, Astronautics Group

HONORS
- Co-recipient, OSU College of Engrg. Lumley Award for Interdisciplinary Research, 2005
- National Research Council Postdoctoral Fellow, 1998
- Co-recipient, ACS Outstanding Student Paper Award, 1997
PROFESSIONAL SERVICE


• **Proposal Reviewer:** National Science Foundation (Hydrology), U.S. Department of Energy (Environmental Management Science Program and Environmental Remediation Science Program), National Institutes of Health (National Institute of Environmental Health Science Superfund Basic Research Program), Ohio Water Resources Center.

SELECTED PUBLICATIONS


Competitive Learning to Develop a Biomarker Forecasting Tool for Classifying Recreational Water Quality

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Publication

Competitive Learning to Develop a Biomarker Forecasting Tool for Classifying Recreational Water Quality

Dominic Boccelli

University of Cincinnatti

Problem and Research Objectives

Recreational users of surface waters can be at risk when there are elevated pathogens in the water. In urban areas, such as Cincinnati, non-point source contamination can occur through increased runoff (due to impervious surface area) and direct discharge of storm water, or combined storm water and sewage, into local surface waters. Indicators such as E. coli and fecal coliforms are used as water quality surrogates due to their relative ease of measurement. Unfortunately, complete analysis and data reporting requires, at a minimum, 24 hours, thus limiting the utility of observed data to provide information to the population on water quality aspects in a timely fashion. However, the ability to predict microbial outbreaks in recreational waters would provide engineers, managers, regulators, and public health officials an important tool in disseminating pertinent public safety information in a timely fashion. Data-driven modeling approaches, such as linear regression or artificial neural networks, seek to capture the important forcing factors associated with microbial concentrations within a simple modeling framework. These data-driven models are then used to predict the microbial concentrations, which are then classified with respect to water quality standards. However, these approaches may still suffer from high rates of false-positives and false-negatives regarding classification.

The objective of the proposed study is to develop a Recreation Management Program tool capable of providing water quality classifications to the public regarding the safety of recreational waters. Previous research efforts have focused on quantifying microbial concentrations, prior to classification, using multivariate linear regression or artificial neural networks (used as a “black box” model). The proposed tool utilizes a type of neural network based on self-organizing maps entitled Learning Vector Quantization (LVQ). Rather than estimate the microbial concentration, the tool to be developed will predict the water quality classification directly, thus potentially eliminating the impact of errors in estimating the microbial concentrations. The LVQ approach will be compared to the more “typical” data-driven approaches such as linear regression and neural networks for microbial concentrations with emphasis on comparing the true and false classification rates.

Methodology

The approach for this study has utilized hydrologic and water quality data collected by the Charles River Watershed Association (CWRA) to develop a tool capable of providing a water quality indexing system for recreational water at the Larz Anderson bridge sampling location. CWRA has collected E. coli samples as well as flow and precipitation
data for approximately two recreational seasons (May through October) at multiple locations in the watershed that will be used in model development.

Previous research studies developed models that estimate the microbial indicator concentration first, which is then transformed into a classification. However, these approaches result in measurable false-positive and false-negative rates. Since classification of the water quality is of most importance, the neural network based approach of LVQ is proposed to use the available data to develop a tool that, given the appropriate hydrologic and meteorologic data, will directly produce a classification. This approach removes the reliance on adequate prediction of microbial concentrations.

To adequately compare the performance of the LVQ algorithm to other approaches, equivalent versions of linear regression and artificial neural network (ANN) models based on previous studies will be developed to represent the same data set. For simplicity, the explanatory variables used in the LVQ algorithm will be the same used to develop the linear regression model for the CWRA data (Eleria and Vogel, 2005). However, the dependent variables in the comparative models will be the actual E. coli concentrations with classifications performed after estimation. Comparisons between the different modeling approaches will be made based on the classification characteristics (i.e., true/false positive/negative rates) of each algorithmic approach.

Principal Findings and Significance

The linear regression, ANN, and LVQ modeling approaches have been developed to represent the Larz Anderson bridge monitoring data using E. coli concentrations as the dependent variable, and the antecedent rainfall during the previous 24- and 168-hours and lag-1 E. coli concentration data used as the independent variables. These independent variables were selected based on previous work performed by Eleria and Vogel (2005). The resulting model classifications were evaluated with respect to the ability of three modeling approaches to satisfy a primary and secondary contact recreation standard (200 and 1000 colony forming units/100 mL of sample).

While there are differences in the classifications from each algorithm, each individual algorithm showed little difference when comparing performance associated with the boating and swimming standards. In fact, all three algorithms performed well with respect to the true negative rates (>92% in all cases; equivalent false positive rates <8%) regardless of the standard.

With respect to the linear regression and ANN approaches, the ANN algorithm performed slightly better than the linear regression. The ANN model produced a true positive rate about 10 percentage points higher than the linear regression model (true positive rates for the linear regression were 45%/50% and for the ANN were 52%/62% for the swimming/boating standards, respectively; false negative rates are equivalent to 100-true positive rate). The LVQ algorithm, however, showed significant improvements for representing the true positive rates (82%/87% for the swimming/boating standards, respectively).
These results suggest that the LVQ approach for direct classification is capable of eliminating the uncertainty associated with classifications based on "concentration prediction first, classification second" approaches. This preliminary data analysis is very encouraging and additional studies associated with varying the independent variables may further improve the results.
Bioremediation of heavy metals using the genetically engineered bacterium Caulobacter crescentus

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Publication

1. Problem and Research Objectives

Every year, around 2.4 million tons of metal wastes from industrial sources and 2 million tons from agriculture are generated in the US (http://es.epa.gov/ncer/publications/meetings/8-18-04/ppt/wilfred_chen_aug_20.ppt). Pollution caused by heavy metals poses a great danger to humans and the environment which has led to stringent regulations over the allowable limits of heavy metals in drinking water. Heavy metals such as Pb\(^{2+}\), Hg\(^{2+}\), and Cd\(^{2+}\) are currently ranked second, third, and seventh, respectively, on the EPA’s priority list of metals that are of major environmental concern. Because heavy metals bioaccumulate in the food chain, exposure to them even at low levels is harmful and may eventually cause adverse health problems, such as nerve damage and cancer. A recent study has also suggested links between heavy metals (particularly cadmium) and some autoimmune diseases, such as multiple sclerosis and scleraderma. Because of their extreme toxicity, there are growing needs for safe and effective ways to remediate metals released to the environment.

Lake Erie provides drinking water for about eleven million people (http://www.epa.gov/glnpo/lakeerie/), including several million Ohio residents living within its watershed. However, four Ohio coastal areas have been designated in the Great Lakes Water Quality Agreement as Areas of Concern, at least in part due to elevated levels of heavy metals, which contributes to impaired beneficial use of these areas, including “restrictions on drinking water consumption, or taste and odor” (http://www.epa.gov/greatlakes/aoc/).

Although contaminant levels in the Great Lakes are declining in general in recent years, health concerns from environmental heavy metal exposures in the Lake Erie basin remain (http://www.great-lakes.net/humanhealth/drink/index.html). As a result, reducing the loading of persistent bioaccumulative toxics (such as heavy metals) to Lake Erie remains a priority on Ohio’s Lake Erie Action List. Although more stringent regulations will help to reduce the loading of heavy metals to the Lake, what has been released previously can only be retrieved by remediation. According to the Ohio Coastal Management Program, “It is the policy of the State of Ohio to coordinate the development and implementation of Remedial Action Plans for Ohio’s four Lake Erie Basin Areas of Concern as identified in the International Joint Commission’s reports on Great Lakes water quality”.

The objectives of this study included the following:
**Surface-expression of heavy metal-binding peptides on Caulobacter**

Heavy metal-binding peptides were fused to the surface layer protein RsaA of *Caulobacter* by gene manipulation techniques. Due to the intrinsic ability of *Caulobacter* to process RsaA to the cell exterior, metal-binding peptides tagged to RsaA are pre-coded to be transported to the cell surface, ready to directly interact with the external environment.

**Bioaccumulation of heavy metal ions by engineered Caulobacter cells**

Engineered *Caulobacter* strains were evaluated for their ability to sequester dissolved cadmium ions. Bacterial cells were cultivated and harvested according to standard procedures. Drinking water spiked with Cd$^{2+}$ metal ions as well as environmental samples from Lake Erie were tested with the engineered *Caulobacter* strains (Fig 1).

![Fig. 1. Scheme showing sequestration of heavy metals using surface expressed foreign peptides (not to scale).](image)

(a), wild type *Caulobacter* strains adsorb low levels of heavy metal ions through non-specific ionic attractions. (b), engineered *Caulobacter* strains retrieve heavy metals by both non-specific binding and specific affinity between hexa-histidine peptides and heavy metal ions.

**2. Methodology**

**2.1. Construction of genetically engineered Caulobacter crescentus with surface-expressed heavy metal-binding peptides.**

A DNA fragment encoding a heavy metal-binding peptide, hexa-histidine 6H or synthetic phytochelatin ECn, flanked by *Bg*I and *Pst*I sites were obtained by polymerase chain reaction (PCR) and were introduced to the corresponding sites inside of the *rsaA* gene sequence (Fig 2). The p4ArsaAGSCC vector was digested with *Bg*II and *Pst*I and mixed with the PCR fragment pre-digested also with the same enzymes. The two fragments were joined by DNA ligase, generating a recombinant plasmid which carries the synthetic sequence “sandwiched” in *rsaA* gene. Finally, the recombinant plasmids, coding for the S-layer (RsaA) fusion proteins, were introduced to a *Caulobacter* host strain and selected by a solid agar medium.
2.2. Bioaccumulation of heavy metal ions using engineered *Caulobacter* cells

Stationary phase *Caulobacter* cell cultures grown in PYE were diluted with the same medium to cell densities ranging from 0.1 OD\textsubscript{600nm} to 1.0 OD\textsubscript{600nm}. Various amounts of 1000 ppm CdCl\textsubscript{2} were added to the cell cultures. The mixtures were incubated at 30°C at 250 rpm for 15-120 min followed by centrifugation at 3300 g at 4°C. The cadmium content in the supernatant was measured with an iCAP 6500 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (Thermo Electron Corporation) or an Analyst 100 Atomic Absorption Spectrometer (AAS) (Perkin Elmer Corporation) at a wavelength of 228.8 nm and was compared with the input concentration of cadmium. Cell dry weight (CDW) was determined by filtering cell cultures through 0.22 μm GV Durapore membrane filter cups (Fisher Scientific) and drying overnight at 77°C. One liter of cell culture at 1.0 OD\textsubscript{600nm} provided 300 mg of CDW.

3. Principal Findings

3.1 Expression of RsaA-6His protein in *Caulobacter* JS4022.

S-layer proteins were extracted from recombinant *Caulobacter* strains JS4022/p4ArsA(723Δ)GSCC\textsubscript{Δ} and JS4022/p723-6H using a low-pH method. The Rsaa\textsuperscript{-} strain JS4022 was used as the negative control. As based on SDS-PAGE analysis, a strong band of ~110 kDa

![Fig. 2. Construction of the recombinant plasmid expressing RsaA-ECn (not to scale).](image)

![Fig. 3. Scheme showing sequestration of heavy metals using surface expressed foreign peptides (not to scale). (a), wild type Caulobacter strains adsorb low levels of heavy metal ions through non-specific ionic attractions. (b), engineered Caulobacter strains retrieve heavy metals by both non-specific binding and specific affinity between hexa-histidine peptides and heavy metal ions.](image)
was detected in both recombinant strains but was missing from the host strain JS4022 (Fig. 3a). The size of the bands correlates well with the deduced 108 kDa molecular weight of the two proteins. The correct insertion of the 6His fragment was confirmed by Western blotting (Fig. 3b) with a positive band corresponding to the size of RsaA proteins detected from the JS4022/p723-6H strain only. These results demonstrate that RsaA-6His was successfully expressed in strain JS4022, and its expression level was as high as RsaA(723).

Fig. 4. Physiological characteristics of JS4022/p723-6H. The growth rates of recombinant and control strains are compared in (a), as indicated by the optical density of cell cultures at 600 nm. The sensitivities of the strains to 0.1% (w/v) SDS and 2 mM EDTA are summarized in (b) and (c), respectively. Percentages of absorbance at 600 nm prior to addition of the test agent are presented. Data in (b) and (c) represent results from three independent experiments.
Physiological studies of the recombinant strain JS4022/p723-6H.

The expression of RsaA-6His S-layer proteins did not inhibit the growth of host cells as the growth rate of JS4022/p723-6H was comparable to that of the control strains JS4022 and JS4022/p4ArsA(723Δ)GSCCΔ (Fig. 4a). To evaluate its suitability to serve as a whole-cell adsorbent, the sensitivities of JS4022/p723-6H to detergents and chelators were monitored. Exposure to 0.1% (w/v) SDS resulted in widespread cell lysis with a 65-75% decrease in culture turbidity (one-way ANOVA; \( P < 0.0005 \)) within 25 min of exposure (Fig. 4b). Initially each strain was affected to a similar degree by SDS exposure; however, following 100 min, control strain JS4022 proved most susceptible with >90% decrease in culture turbidity (one-way ANOVA; \( P < 0.001 \)), likely due to the lack of a S-layer, which provides modest protection to the integrity of cell envelopes. Strains JS4022/p723-6H and JS4022/p4ArsA(723Δ)GSCCΔ offered similar, albeit limited, resistance to SDS treatment (Tukey HSD Test).

Exposure to 2 mM EDTA also resulted in cell lysis although the effect was less severe than that of SDS with a 20-35% decrease in culture turbidity (one-way ANOVA; \( P < 0.05 \)) within 25 min of exposure (Fig. 4c). Similar to SDS exposure, there was no difference in the degree to which each strain was affected by EDTA through 75 min incubation. Following 100 min exposure, control strain JS4022/p4ArsA(723Δ)GSCCΔ proved most resistant to the chelator EDTA showing only 53% decrease in culture turbidity compared to 75-80% declines for JS4022 and JS4022/p723-6H (one-way ANOVA; \( P < 0.01 \)). An increase of divalent ions in the growth medium provided the cells extended protection against EDTA. When grown in PYE medium containing 0.3% CaCl\(_2\)·2H\(_2\)O, only 35% of the JS4022/p723-6H cells experienced lysis after 100 min of exposure to EDTA whereas for JS4022/p4ArsA(723Δ)GSCCΔ, only about 10% of the cells were subject to lysis (data not shown).

Optimization of contact time for removal of cadmium.

Recombinant strain JS4022/p723-6H was tested for its metal-binding dynamics in solution. Within 15 min, JS4022/p723-6H removed 94.3% of cadmium from the aqueous phase, whereas, the control strain JS4022/p4ArsA(723Δ)GSCCΔ removed only 13.2% (Fig. 5). Extending the incubation time to 120 min increased the cadmium removal only marginally to 97.7% and 18.7% by JS4022/p723-6H and JS4022/p4ArsA(723Δ)GSCCΔ, respectively. These results suggest that the time required by JS4022/p723-6H to sequester heavy metals can be as short as 15 min. For the convenience of handling multiple samples, we chose to adopt the contact time of 30 min for further studies.

Effect of the amount of biomass on sequestration of cadmium.

When cell density was as low as 0.03 g L\(^{-1}\) (CDW), non-specific binding of Cd(II) was dominant in JS4022/p723-6H; it removed just 3% more cadmium than did the control strain (Fig. 6). As the cell density was increased, so did the specific binding of metal ions delivered by RsaA-6His. As cell density was increased from 0.03 g L\(^{-1}\) to 0.21 g L\(^{-1}\), the Cd(II) removed by JS4022/p723-6H improved step-wise from 15.2% to 99.9%. In contrast, the non-specific binding of cadmium by the control strain fluctuated at lower levels, ranging from 11.4% to 18.4%. Further increases in cell density to 0.30 g L\(^{-1}\) had little effect on binding of Cd(II) by
JS4022/p723-6H but increased the non-specific binding of JS4022/p4ArA(723Δ)GCCΔ to 37%.

![Graph](image.png)

**Fig. 5.** The percentages of cadmium removed by JS4022/p723-6H (indicated as RsaA-6His, square) and JS4022/p4ArA(723Δ)GCCΔ (indicated as RsaA(723), diamond) as a function of time. Total input of Cd(II) was 1 ppm.

![Graph](image.png)

**Fig. 6.** The percentages of cadmium removed by recombinant strains at various cell densities. Solid bars, JS4022/p723-6H, shown as RsaA-6His. Crossed bars, JS4022/p4ArA(723Δ)GCCΔ, shown as RsaA(723). Total input of Cd(II) was 1 ppm.

**Removal of cadmium at different initial concentrations.**

We next tested the metal removing capacity of JS4022/p723-6H at different concentrations of cadmium: 1, 5, 10, and 15 ppm. Cell density of 0.30 g L⁻¹ (CDW) was used for this test with the rationale that more biomass would be needed to adsorb higher levels of Cd(II). At each concentration tested, strain JS4022/p723-6H was more efficient at removing cadmium compared to control strain JS4022/p4ArA(723Δ)GCCΔ (one-tailed t-test) (Fig. 7). The largest difference in Cd removal efficiency was evident at 1 ppm Cd where JS4022/p723-6H removed 2.7 mg of Cd(II) per gram CDW, which was 154% higher than the control strain JS4022/p4ArA(723Δ)GCCΔ achieved (1.1 mg g⁻¹) (one-tailed t-test; P < 0.0001). As total Cd
concentration increased, the Cd removal efficiency between strains became less distinct. At 15 ppm Cd, strain JS4022/p723-6H removed 16.0 mg g⁻¹ (or 37% of the added) of the metal compared to 11.6 mg g⁻¹ (or 27% of the added) for the control strain (one-tailed t-test; P < 0.05). Whereas adsorption with more concentrated Cd(II) was not tested, the total accumulated metal by each gram of biomass was expected to be higher if more cadmium was added. Similarly, improvement of removal efficiency could be anticipated with an increase of biomass.

4. Significance

In this study, we successfully inserted hexa-histidine peptides in a permissive site of RsaA, the S-layer protein of *Caulobacter crescentus* (Fig. 2 and 3). The expression of RsaA-6His fusion proteins sustains normal growth of host cells and offers similar level of protection to the host from the deleterious effects of detergents and chelators as RsaA does (Fig. 4). The constructed recombinant strain JS4022/p723-6H was useful as a whole cell adsorbent to sequester Cd(II) from aqueous solutions. When challenged with 1 ppm Cd(II), strain JS4022/p723-6H demonstrated remarkable specific affinity to the heavy metal, especially at sub-ppm levels, where 94.3 ~ 99.9% of the Cd(II) could be removed from the growth medium depending on experimental conditions. Control strain JS4022/p4ArsA(723Δ)GSCCΔ, shown as RsaA(723), sequestered only 11.4% ~ 37.0% of the added Cd(II) (Fig. 5 and 6). The required contact time can be as short as 15 min. The highest binding capacity achieved by JS4022/p723-6H in this study was found to be 16 mg g⁻¹ CDW (Fig. 7), which is also comparable to the findings from other studies.

In conclusion, the construct strain JS4022/p723-6H offers a robust bioremediation agent that is most useful in applications where low levels of heavy metals contaminate a system such as natural water bodies, sediments, and industrial wastewater or sewage sludge that are in need of a secondary remediation process. Although we only tested Cd(II) in this study, the constructed strain is expected to be effective in removing other divalent heavy metal ions as well, such as nickel, lead, copper, and zinc. To improve the binding capacity or narrow the specificity of the *Caulobacter* recombinant strains, one can incorporate to RsaA other types of heavy metal-
binding peptides, for example, metallothionines, phytochelatins, or desired sequences screened from peptide libraries. This work demonstrates the effectiveness of employing a recombinant Caulobacter strain as free cells in the remediation of the heavy metal cadmium and lays the foundation for the construction of bioremediation reactors of high efficiency and low cost.

5. Publications

Observations of River Topography and Flow Around Bridges

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Publication
Observations of River Topography and Flow Around Bridges

Thomas C. Lippmann

*Center for Coastal and Ocean Mapping, University of New Hampshire, Durham, NH 03824*

Formerly of

*Dept. of Civil and Environmental Engineering & Geodetic Science, and the Byrd Polar Research Center, The Ohio State University, Columbus, OH 43210*

**Rationale**

This investigation was motivated by the amount of river, estuarine, and coastal infrastructure that is susceptible to extreme wave and flooding events. The high velocities and resulting shear stresses associated with high flow velocities are capable of scouring or depositing large quantities of sediment around hydraulic structures. Preventing the failure of these structures and sedimentation in inlets alone costs federal and state agencies billions of dollars annually. In addition to being costly, the manual monitoring of bridge scour - as mandated by the Federal Highway Administration - can be inefficient in states such as Ohio where the flood events that initiate the scour process occur sporadically. According to the National Scour Evaluation Database, there are 23,326 bridges over waterways in the state of Ohio, of which 5,273 are considered scour susceptible and 191 are considered 'scour critical'.

Previous methods for identifying bridge scour have relied on the manual (diver-based) sampling of local water depths that are generally limited to periods of low water flow. As the dynamic scour and deposition of sediments around structures is highest during periods of high flow, traditional sampling methods have limited our ability to predict quantitatively scour or deposition levels and to evaluate sediment transport models. This research is aimed at developing and testing new methods to observe riverbed topographic evolution around piles and under bridges where the structures themselves interfere with GPS based positioning. Simultaneous measurements of the velocity profiles can be used in conjunction with the observed bathymetry to make inferences about bridge scour and the effect of bridge piles on local riverbed topography.

Related to problems generated by sediment scour are issues of sediment deposition in navigational channels. On the Maumee River, OH, alone, the Army Corp of Engineers spends millions of dollars annually to dredge an average of 850,000 cubic yards of sediment. With the elimination of open lake disposal of dredged sediments, an inter-agency collaboration of government and private citizens has been formed to identify possible methods for reducing the amount of deposition by reducing the soil erosion along river bank’s. Clearly, development of new observational capabilities and a subsequent increase in observations of riverbed topography and flow around structures will improve our ability to utilize available resources in the most efficient manner.
Objectives

The objectives of this research were to

1. observe the variability of riverbed topography in and around bridge support piers on the Great Miami River near Hamilton and the Ohio River near Cincinnati.

2. develop methods to conduct detailed topographic and hydrographic surveys in and around bridges where the structure limits GPS positioning.

3. infer the affects of bridge structure on topographic variability and scour, and relate these to observed flow characteristics.

Methodology

The first survey site for this project was located in Butler County, Ohio near the Columbia Bridge over the Great Miami River at Hamilton, Ohio (Figure 1). The Hamilton, OH, field site has been identified by USGS collaborators (D. Straub and S. Jackson, USGS, Worthington, OH) to have previously experienced up to 1 m variability in local morphologic variability and was the subject of a previous multi-year monitoring project. The bridge is four lanes wide constructed with four monolithic concrete bridge piers. River and bank surveys were completed 2005, 2006, 2007, and again in 2008 as part of this ongoing research program. An example survey is shown in Figure 2.

Figure 1. Photo of the Columbia Bridge over the Great Miami River at Hamilton, OH.
The surveys were conducted with the Coastal Bathymetry Survey System (CBASS), a Yamaha GP1200 Waverunner (personal watercraft) equipped with a differential GPS receiver, dual-transducer 192 KHz sonic altimeter, and custom onboard navigation system (Figure 3). As part of previous research efforts, the system has been utilized extensively in coastal marine and fresh water environments where waves and currents are present (and sometimes energetic). The system has accuracies of about +/- 7-10 cm in both the horizontal and vertical coordinates of the measured bathymetry. The bank survey was conducted by walking with a backpack-mounted differential GPS receiver and antenna. The bathymetric survey spans about 1.2 km along the river, and was done over 2.5 hours with about 60 cross-river transects spaced every 20 m.

Figure 2. (left panel) Bathymetric survey of the Great Miami River in Hamilton, OH, conducted using the CBASS survey system (Figure 3). The depths are shown in meters as color contours relative to the approximate mean water level at the bridge (located at about y=200 m in the figure). The horizontal coordinates are in meters relative to our GPS base position. The survey tracks are shown as dashed black lines in the figures. The riverbanks exceeding 6-8 meters above water level were surveyed with differential GPS manually (e.g., walking) but are omitted from the plot so that the river topography can be seen more clearly. (right panel) Interpolated river bathymetry including sonar data under the bridge using preliminary dead reckoning technique. Also shown are the locations of the bridge piles.
GPS-based bathymetry surveying near bridge structures and piles (indicated in Figure 2 for the Columbia Bridge at Hamilton) is difficult due to line of sight blockage of the GPS satellite constellation near the bridge. In past surveys this has resulted in sparse bathymetry data near the piles and under the bridge because of positional uncertainties, and thus details of the scour and topographic irregularities were not observed. Sonar data are collected for these areas; however, the lack of positional data precluded the use of the depth measurements.

Ideally multibeam or interferometric swath bathymeters would be used to measure the sub-bridge bathymetry in and around the piles. However, these systems are extremely expensive to purchase, rent, or operate, and thus are not readily available for repeated surveys over time by a wide range of interested entities (including governmental, research, engineering, and management entities). What is needed is a simpler, more cost-effective way to obtain estimates of the river topography near bridge structures where the GPS satellite are blocked. As part of this work, we will test an age-old method for estimating vessel positions based on simple inertial and geometrical ideas.

The navigational method known as dead-reckoning was developed over 500 hundred years ago by sailors and is still used today in combination with other navigational aids such as GPS and inertial systems. This method requires an initial known position and assumed trajectory. A simple form of dead-reckoning utilizes a measured velocity vector, then integrates the horizontal $x$ and $y$ components over a finite time scale to find the corresponding spatial position.

In this case, the initial and final positions are determined from the last known fixed GPS position before the signal dropout under the bridge and the first fixed position on the
other side of the bridge, respectively. Velocity is maintained (and assumed) constant by the survey vehicle operator until a fixed position is acquired again. The vehicle is kept on a constant heading using visual landmarks by the operator to minimize spatial deviations from the assumed trajectory. A schematic of the geometry used in dead reckoning is shown in Figure 4. The distance and heading between the last two known points, \((x_0, y_0)\) and \((x_1, y_1)\) respectively, can be easily calculated. The times of these two points are taken from the GPS record, and the times along this line are calculated based on the desired number of points and sampling frequency. The sonar record is then interpolated to these times and depths are extracted for the specified times. Figure 5 show a detailed map of the survey tracks near and under the bridge during a preliminary field test of the technique.

![Figure 4. Illustration showing two known points along with the heading and distance between them. The speed of the survey vessel is assumed to be held at a constant velocity between known positions.](image)

This pseudo dead reckoning technique is a viable method based on a preliminary field test conducted in the spring of 2007. Figure 6 show the interpolated elevation data under the pier (shown as a time series of observed depths). However, in this preliminary test no ground truth were available. As part of the present research, extensive tests over known river topography (obtained with the CBASS) in regions away from any structure will be conducted in order to quantify the accuracies of the dead reckoning techniques. Once verified, the technique was applied to regions close to and under bridges where GPS drop-outs occur.

This technique, with our current equipment, is limited to areas that the water surface can be assumed flat because there is no way to determine fluctuations in water surface elevation (\textit{i.e.}, surface waves). The incorporation of an inertial system may allow this technique to be effective in the presence of waves. In most instances, it can be assumed that surface wave fluctuations are small, and associated errors will have only a minimal effect on the bottom topography.
Figure 5. Close up plot of the survey tracks. Red tracks indicate walking survey, the black tracks indicate CBASS survey, and the cyan tracks indicate interpolated positions based on the dead-reckoning technique.

Figure 6. Sonar data from CBASS. The black points are the data from the known GPS positions and the red points are the data extracted from the sonar record based on the interpolated spatial and temporal points.
In addition to riverbed topographic observation, vertical profiles of river flow velocity were obtained with a Sontek Rivercat Acoustic Doppler Current Profiler (ADCP) integrated into the CBASS survey system. The sensor can remotely sample three-components of velocity at about 20 cm range bins at a 0.2 Hz sampling rate. The observations were used to map the general flow field over the region surveyed around the piles and under the bridge. Flow measurement will allow inferences of the effect the bridge structure has on the local riverbed topography.

The second field site is located on the Ohio River near Cincinnati. This site is significantly different than the first with significantly larger flows spanning a deeper and wider river basin. Bathymetric observations made at this site were similar to Hamilton, except that the deeper depths of the Ohio River precluded the use of the Sontek ADCP which needs to track the bottom in order to remove vessel motion from the current measurements but could not follow the bottom over a significant range. No other ADCP was available for use in this study, and thus current measurements are limited to the Hamilton site.

Results

A bathymetric survey was conducted along a 3 km stretch of the Ohio River near Cincinnati over a 2 day period on 01 and 10 July 2008 (Figures 7 and 8). This region of the Ohio River is characterized by an approximately 300-400 m wide basin with water depths at the time of the survey ranging a few meters near the banks to 17 m in some parts of the channel. There are also 5 bridges that cross the river in the survey area, and a small creak that flows northward into the Ohio River in about the middle of the domain. The CBASS survey tracks are shown on the bathymetry in Figure 7, and the location of the bridges in Figure 8. The bottom topography is highly variable over the region, with shoals, holes, sandbars, and other detritus scattered along the banks. At the time of the survey, significant water hazards in the form of logs and tree limbs were observed through out the region (but did not negatively impact the surveys).

The effect of the bridge pilings on the topography is qualitatively evident in the survey (Figure 8). Below bridges 1, 2, and 3 there are significant holes and scour channels that extend several hundred meters downstream of the piles and increasing the depth by up to 5 m or more. Across-river transects showing the river basin profile 100 m both upstream and downstream of each bridge are shown in Figure 9. The location of the transects is also indicated in Figure 8. There is significant variability in the bottom profile up and down stream of bridge piles 1-3. In contrast, an interestingly, the profiles above and below bridges 4-5 show relatively minor variability in the vicinity of the bridges. It is possible the gentler slope of the river bed (shown in along-river profile in Figure 10) in this region limits the scour effects near those piles. As well, this region is upstream of the inflow tributary to the south. Although not measured herein, it was qualitatively observed how the river flow increased noticeably downstream of the river confluence.

In order to test the dead reckoning methods described earlier, repeated cross-river profiles were used to simulate conditions where navigation was lost periodically and under varying vessel speeds and river flow conditions. A total of 51 cross-river transects were
arbitrarily selected through the 3 km river section. In each case an estimate of the mean vessel speed and direction was determined by points near the riverbanks along various transect lines. These estimates were then used to estimate the position of the vessel through time assuming a constant speed and direction. The estimated times and positions of the vessel were used with the raw sonar data to estimate water depths across the channel. An example (typical) comparison is shown in Figure 11 for the vertical and horizontal uncertainties. Overall, we observed a mean root-mean-square (RMS) error of 7.9 cm in water depths, and 9.1 m in spatial location. The mean vertical bias observed was -5.2 cm, most likely owing to the unknown behavior (motion and heave) of the vessel while underway. The higher spatial offsets are primarily a result of the river flows tending to carry the vessel downstream. Although pilot corrections were made, and an onboard navigation system available, it was still difficult to transit in a straight line. This offset did not seem to result in higher uncertainties in water depth estimates, a result of the (in general) relatively gently sloping bottom except near the bridge scour regions.

A summary of the RMS errors is shown Figure 12. The RMS vertical errors are plotted as a function of RMS horizontal errors. As expected, the RMS vertical uncertainty goes up as the horizontal positioning gets worse. The correlation squared is 0.68. These results show that even for positional errors of order 25 m or so, the RMS vertical errors are still less than 15 cm (and half that on average). This order of error is close to the accuracies of the CBASS (with estimated errors of order 7-10 cm in the vertical based on sonar and GPS errors).

Over the past 4 years we have surveyed the Great Miami River near the Columbia Bridge in Hamilton, OH. Figure 13 shows the survey from 29 November 2005 and the survey from 10 July 2008. Each plot shows the same color scale and the contour intervals are 0.25 m. The location of the bridge pilings are indicated on the plots. Only the bathymetry below the water line is shown (that is, now GPS walking survey data are included in the figures; and it should be noted that the river banks were not observed to migrate during the 4 year period). It should be noted that where possible the dead reckoning techniques – verified with the Ohio River data – were used to fill in the bathymetry in and around Columbia Bridge as the nearly continuous bathymetry map shows in Figures 13 and 14.

Clearly there are changes that have occurred over this period, including shifting sand bars, holes, and the depth and location of scour pits. The data from each survey were smoothed onto a similar spatial grid and subtracted to quantitatively evaluate the riverbed changes that occurred (Figure 14). Evident is the appearance of a migrating sand bar oblique to the river bank to the north of the bridge. This feature is (likely) due, in part, to multi-year construction of the upstream tressel in Hamilton. Also evident are substantial reworking of the river bed to the south of the bridge, but in a less coherent manner appearing somewhat random in evolution. What is striking is that the largest changes occur right under the bridge where the scour has eroded the river bed by nearly a meter in places, a 25% change in water depth in some locations. Without the dead-reckoning techniques, it is not likely this change would have been observed.

Our final goal, was to make spatial maps of the depth-averaged flow field in and around the bridge piers to demonstrate how the flow measurements could be coupled with
bathymetry observations to examine in more detail the sediment transport impact by fluid-
bed-structure interactions (such as scour processes). The Sontek Rivercat ADCP was
deployed on the CBASS simultaneously while conducting a survey of the Great Miami
River. In order for ship-board ADCP measurements to be made, the motion of the vessel
must be removed. This was done with the Rivercat by tracking the apparent motion of the
assumed stationary bottom as the vessel passes by. A comparison of the bottom finding
algorithms from the Rivercat bottom tracking and the CBASS are shown in Figure 15. The
accurate bottom tracking allowed the Rivercat to be closely synced to the CBASS GPS and
sonic data streams. Shown in Figure 16 are the estimated vessel speeds and directions from
the Rivercat bottom tracking and independently from the CBASS differential GPS. Although
there is reasonable agreement between these data streams, the differences resulted in
significant uncertainty in the velocity estimate. As such velocity profiles were averaged over
40 m along-river by 10 m across-river regions.

The depth, time, and spatially averaged mean flow pattern observed on 10 July 2008 is
shown in Figure 17. The flow vectors indicate a downstream flow of about 1 m/s over most
of the domain, with a slight increase towards the center of the channel and a general trend of
the flow following contours of the sand bars and channels. In general the general flow
pattern was captured; but a close relationship to the observed bathymetry or changes over
time were not found.

Significance and Additional Benefits

This research has shown that coincident observations of mean flow patterns and
riverbed bathymetry can be obtained simultaneously. We have also shown that simple and
relatively inexpensive dead-reckoning navigational techniques can be used to estimate river
bathymetry accurately (within about 15 cm uncertainty) around bridges and other structures
where GPS navigation is temporarily lost. The coupled observation of detailed flow and
riverbed evolution around bridge structures will improve our understanding of the scour
process. Engineers and river managers can make use of the developed observational
techniques to further their observational programs, and to make predictions of riverbed
evolution to improve structural design, streamline mitigation procedures, and reduce
response times to predicted high flow events by focusing resources to projected high scour
regions. The observations may also be used to select locations for future sampling sites, and
to identify those sites where scour is expected to be problematic for future structural
integrity. Our field methods represent new ways to monitor and evaluate bridge scour, and
together these results will highlight potential areas of concern.

This project provided funds for two senior level Honors undergraduate students who
assisted in the collection of the data, developing experience in field methodology for survey
related projects, and assisted in the analysis of the observations. The students were trained in
the use of GPS and sonar equipment used in state-of-the-art survey systems, and gained
experience conducting surveys on natural rivers around bridges and structures. The students
learned about sediment transport around bridges, and the influence of flow-structure
interaction on the surrounding topography. A research engineer (Gabe Smith) lead the field
work and data processing, and thus gained valuable experience and training in leading students in field experiments.

Figure 7. Bathymetric survey of the Ohio River at Cincinnati, OH, conducted over 2 days (01 & 10 July 2008) and showing the CBASS track lines.
Figure 8. Bathymetric survey of the Ohio River at Cincinnati, OH, showing the location of 5 bridges and the location of cross-river and along-river transects shown in Figure D. The color scale is depth in m relative to the approximate mean water level near bridge number 4.
Figure 9. Across-river profiles 100 m upstream and 100 m downstream of each bridge location. The across-river coordinate is arbitrary distance along the transect (in meters).

Figure 10. Along-river transect at about the mid stream location. Also shown are the location of the bridge piers.
Figure 11. Comparison of dead-reckoned across-river profiles compared to CBASS measurements. The vertical comparison is on the left, and the horizontal positioning error is on the right.

Figure 12. Scatter plot of the RMS vertical errors along 51 transects as a function of RMS horizontal errors. The correlation squared is 0.68, and mean vertical bias is -5.2 cm.
Figure 13. Bathymetry observed along the Great Miami River near Hamilton Ohio on 29 November 2005 and again on 10 July 2008. The location of the bridge piles supporting the Columbia Bridge are indicated with the black dots. The coordinate system is UTM Northing and Easting in km. The color scale indicates the water depth relative to the water level at the bridge. Contour intervals are 0.25 m.
Figure 14. Difference in bathymetry between the 29 November 2005 and 10 July 2008 surveys. Clearly evident is the large wedge of accreted sand to the north of the bridge and the substantial scour around the bridge piles over the 31 month period between surveys. South of the pier also experience substantial rearrangement of sediments but what appears to be a generally random pattern.
Figure 15. Comparison of the Sontek Rivercat ADCP’s bottom tracking depth estimate compared with CBASS. The temporal agreement is due to shifting the time series into alignment, necessary to synchronize the two data streams so that the bathymetric map can be populated with velocity estimates.
Figure 16. Time series comparison of the vessel (CBASS) speed (upper panel) and direction (lower panel) between the Sontek Rivercat bottom tracking algorithm and the CBASS differential GPS estimates. Although reasonable agreement is apparent, the differences contribute to substantial uncertainties in the velocity estimates.
Figure 17. Observed depth-averaged flow field on 10 July 2008 with the Sontek Rivercat mounted on the CBASS. The flow vectors are overlayed onto the bathymetry measured on that day. General flow patterns can be grossly related to the variation in bathymetry, primarily in directional changes as the flow follows contours of the bottom.
Information Transfer Program Introduction

The Ohio Water Resources Center (WRC), at Ohio State University, conducted a number of activities to transfer water related information to a wide range of state, federal, county, and municipal agencies, to the private sector, academic community, students, and to private citizens throughout Ohio. Specific activities included, - preparation of information for the web site of the Ohio Water Resources Center and maintenance of the web site - administration of a Special Water and Wastewater Treatment Grants Competition funded through the Ohio Water Development Authority - administration of the 104(B) In-State Competition and the 104(G) National Competitive Grants Program - encouraged investigators of projects funded through the Ohio WRC to develop publications in peer-reviewed journals and other outlets - continued administrative support for the Water Management Association of Ohio (WMAO) and associated WMAO meetings, conferences, and division activities - support for Ohio Water Education Program, especially Project WET (Water Education for Teachers) - participation of both directors in the Future Engineers Summer Camp (FESC) which focuses on introducing 8th grade girls to careers in various areas of engineering, including water resources and environmental engineering - responding to questions from the public regarding water resources issues in the state of Ohio - assisted organizing Ohio American Water Works Association (AWWA) South East district section meeting at Ohio State University to facilitate transfer of research results to the water treatment profession. - advised the newly started WEF/AWWA student chapter at Ohio State University
USGS Summer Intern Program

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Notable Awards and Achievements

Yongjun Chen in project 2007OH49B: Graduate Student Award for Excellence in Graduate Studies in Environmental Science, Division of Environmental Chemistry, American Chemical Society, 2007. The student received this award for exceptional achievements in the field of environmental chemistry and water treatment. Typically this award is given to 10 to 15 students annually in the Nation.