Water Resources Center
Annual Technical Report
FY 2003

Introduction

Research Program

The Effect of Humic and Fulvic Acids on Arsenic Solubility in Drinking Water Supplies

Basic Information

Title:	The Effect of Humic and Fulvic Acids on Arsenic Solubility in Drinking Water Supplies
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Principal Investigators:	John Lenhart

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The Effect of Humic and Fulvic Acids on Arsenic Solubility in Drinking Water Supplies

Interim Report

Statement of Critical Regional or State Water Problem

Arsenic in ground water results primarily from natural geochemical interactions that occur between water and As-containing rocks and minerals (Welch et al., 2000; Smedley and Kinniburgh, 2002). Due to its known toxic effects on humans, arsenic in drinking water is a threat to public health and is regulated in the United States by the Safe Drinking Water Act. On January 22, 2001 the United States Environmental Protection Agency (USEPA) published a Final Rule in the Federal Register (40 CFR 141.62(b)(16)) establishing a new maximum contaminant level (MCL) for arsenic of 10 μg/L, down from 50 μg/L. This revision reflects an improved understanding of the toxic effects of arsenic on humans, and is expected to decrease annual deaths from cancer by at least 20 (USEPA, 2002). On February 22, 2002 the new arsenic drinking water limit became effective. Enforcement of the Rule begins on January 23, 2006 and is expected to increase annual treatment costs by approximately $181 million (USEPA, 2002).

Ground water is crucial to meeting the industrial and domestic needs of the residents of Ohio, with 79% of the community water systems, over 99% of the non-community water systems, and nearly 1 million rural homes utilizing ground water (OhioEPA, 2000). Arsenic concentrations in ground water above the MCL of 10 μg/L occur throughout Ohio, particularly in areas with sand and gravel aquifers (OhioEPA, 2000). In many instances treating As-containing ground water to meet regulatory needs and protect public health will require costly modifications to optimize existing treatment processes or the addition of point-of-use treatment techniques. The United States Environmental Protection Agency has issued guidance in selecting treatment methods for removing arsenic, and emerging technologies utilizing membranes (e.g., reverse osmosis), adsorptive processes (e.g., activated alumina), and precipitative processes (e.g., enhanced coagulation/filtration) show particular promise (Hering et al., 1997; Brandhuber and Amy, 2001). Common inorganic and organic ground water constituents reduce removal efficiency, and natural organic matter (NOM) decreases removal by 20 - 50 % (Hering et al., 1997; Brandhuber and Amy, 2001). Recent evidence suggests that NOM can complex arsenic to form stable solution complexes (Redman et al., 2002), and the increase in arsenic solubility resulting from the presence of such stable As-NOM complexes could be responsible for reduced removal efficiency. Details of these interactions are limited, however, and their importance is currently unknown. Knowledge of the fundamental processes that control As solubility, transport, and treatment, including interactions between arsenic and NOM, is crucial to maintaining the quality of ground water that approximately five million people in Ohio depend upon for their daily needs.

Nature and Scope of the Research

Arsenic (As) is a naturally occurring trace element in the earth's crust and is a common constituent in many igneous and sedimentary rocks. Arsenic is readily mobilized into solution through the combined effects of geochemical interactions and biological activity, and is normally present in surface and ground water at low concentrations (≤ 1 μg/L) (Welch et al., 2000; Smedley and Kinniburgh, 2002). Although high As concentrations are associated with anthropogenic sources, the majority of environmental As problems are the consequence of natural processes (Welch et al., 2000; Smedley and Kinniburgh, 2002). Arsenic toxicity to humans is well documented (NRC, 1999), and its presence at elevated concentrations in the public water supply is of great contemporary concern (Nickson et al., 1998; NRC, 1999; Welch et al., 2000; Berg et al., 2001; Smedley and Kinniburgh, 2002).

In natural water systems, arsenic predominately exists in the inorganic form as oxyanions of trivalent arsenite, As(III), or pentavalent arsenate, As(V). Oxidizing conditions favor the formation of arsenate species (H_3AsO_4, $H_2AsO_4^-$ and $HAsO_4^{2-}$), whereas reducing conditions favor arsenite species (H_3AsO_3 and $H_2AsO_3^-$). The species $H_2AsO_4^-$, $HAsO_4^{2-}$ and H_3AsO_3 prevail under environmental conditions, where the pH spans 4 to 9 (Baes and Mesmer, 1976). Although the redox state of a system is important, arsenic solubility and transport is dominated by adsorption reactions that occur at the surface of reactive iron and aluminum oxide minerals. Adsorption of arsenic oxyanions by mineral surfaces is favored at low pH, and adsorption decreases in magnitude with increasing pH in a manner consistent with other anions (Sigg and Stumm, 1981). In general, arsenate is adsorbed to a greater extent than arsenite, except at elevated pH (≥ 9) where the opposite occurs (Xu et al., 1988; Wilkie and Hering, 1996; Raven et al., 1998). Consequently, in most environmental systems arsenite is more mobile and bioavailable, hence more toxic than arsenate (NRC, 1999; Smedley and Kinniburgh, 2002).

Co-occurring anionic solutes alter the adsorption and thus the solubility of arsenic. Sulfate and phosphate directly compete with arsenic for surface sites on reactive metal oxides, particularly at low pH, and increase arsenic solubility (Xu et al., 1988; Manning and Goldberg, 1996; Wilkie and Hering, 1996); molybdate, however, has little net effect on As adsorption or mobility (Manning and Goldberg, 1996). Surface complexation models suggest that dissolved carbonate should interfere with arsenic adsorption on mineral surfaces at carbonate concentrations typically measured in ground and soil waters (Appelo et al., 2002). Experimental evidence in support of these calculations is still lacking because carbonate adsorption reactions are difficult to study (Wilkie and Hering, 1996).

The formation of solution complexes between arsenic oxyanions and other elements is limited (Cullen and Reimer, 1989), however, even such limited interactions still influence arsenic speciation (Lowenthal et al., 1977; Wilkie and Hering, 1996; Redman et al., 2002). For example, in artificial seawater arsenate forms ion pairs with magnesium and calcium (Lowenthal et al., 1977). These ion pairs result from charge screening that is induced by the high solution ionic strength and their presence increases the concentration of arsenic (Lowenthal et al., 1977). A similar process decreases arsenic solubility by enhancing As (V) adsorption at elevated pH (Wilkie and Hering, 1996) where the adsorption of calcium reduces unfavorable coulombic interactions that otherwise would limit the adsorption of arsenate oxyanions.

The adsorption of arsenate and arsenite to mineral surfaces is reduced in the presence of natural organic matter (NOM) (Xu et al., 1988; Xu et al., 1991; Bowell, 1994; Grafe et al., 2001; Grafe et al., 2002; Redman et al., 2002). NOM is ubiquitous in aquatic systems and consists of a heterogeneous mixture of polyfunctional molecules of varying size and reactivity. The ability of NOM to bind contaminants and mineral surfaces can markedly alter contaminant mobility and has resulted in extensive research (e.g., Davis, 1984; Pignatello and Xing, 1996; McCarthy et al., 1998; Lenhart and Honeyman, 1999). The effects of NOM on As adsorption differ depending upon the NOM source, as well as the charging characteristics and surface area of the adsorbent mineral (Xu et al., 1988; Xu et al., 1991; Bowell, 1994; Grafe et al., 2001; Grafe et al., 2002). Like sulfate and phosphate, the reduction in arsenic adsorption is presumed to result from competition between As and NOM for surface sites (Xu et al., 1988; Xu et al., 1991; Bowell, 1994; Grafe et al., 2001; Grafe et al., 2002). Redman et al. (2002), however, present evidence that supports the formation of stable As-NOM solution complexes, which could be the reason for the reduced As adsorption. The complexation of As by NOM depended upon the NOM source and increased with NOM-bound cationic metals, particularly Fe (Redman et al., 2002).

A comprehensive framework for understanding the extent and importance of arsenic complexation by NOM in natural waters awaits development. Scant evidence, other than that presented by Redman et al. (2002), exists examining the formation of solution complexes between NOM and As (Tanizaki et al., 1985; Thanabalasingam and Pickering, 1986). Thanabalasingam and Pickering (1986) find that the association of As(V) and As(III) with two commercial humic acids followed a Langmuir relationship, and that NOM binds arsenate more strongly than arsenite. Tanizaki et al. (1985) sampled river water in Japan and report that approx. 60% of the As was associated with colloidal matter that consisted primarily of organic carbon. These results provide little additional insight into the complexation of As by NOM, and many questions remain, including the role of coexisting cationic solutes, the impact of solution pH, and the dependence of As complexation on the physicochemical properties of NOM.

Research Objective

The objective of this research is to investigate the association of inorganic arsenic with different sources of NOM in the presence of metal cations (e.g., Ca^{2+}, Mg^{2+} and Al^{3+}). Arsenic is highly toxic and readily mobilized in significant concentrations by natural processes that occur in ground water. The EPA considers arsenic to be a priority pollutant and recently lowered the MCL to 10 μg/L from 50 μg/L. Preliminary results focused on examining interactions between As, metal cations, and NOM using capillary electrophoresis.

Materials and Methods

Stock solutions of arsenate (As(V)) and arsenite (As(III)) were prepared using sodium hydrogenarsenate heptahydrate, $Na_2HAsO_4 \cdot 7H_2O$, and sodium metaarsenite, Na_3AsO_3, respectively (both purchased from Aldrich). Water for all experiments was supplied from a Milli-Q water system (>18 MΩ × cm resistance, Millipore). Two samples of NOM were purchased from the International Humic Substances Society (Table 1); Suwannee River NOM (SRNOM) and Nordic Lake NOM (NLNOM). In this interim report we focus on results using SRNOM. The elemental composition of SRNOM (108 mg/L, pH 3.85) was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Varian) and graphite furnace atomic absorption spectrometry (GFAA; Varian) and confirmed the arsenic content in the sample was negligible (Table 2).

Table 1 - IHSS NOM Elemental Compositions and Stable Isotopic Ratios (%(w/w)).

Aquatic NOM	H_2O	Ash	C	H	O	N	S	P	^{13}C	^{15}N
Suwannee River	8.15	7.0	52.47	4.19	42.69	1.10	0.65	0.02	nd	Nd
Nordic Lake	nd	41.4	53.17	5.67	nd	1.10	Nd	nd	nd	Nd

Table 2 - Elemental Analysis of SRNOM (mg/g).

Al	As	Ba	Ca	Cu	Fe	K	Mg	Pb	S	Se	Si	Sr	Zn
0.85	nd*	<0.01	0.35	0.01	2.19	0.28	0.09	nd	2.90	nd	4.20	<0.01	1.44

* Limit of detection by GFAA for As is 0.9 μg/L

An HP^{3D} capillary electrophoresis (CE) system (Agilent Technologies, Inc.) with direct UV detection and normal electroosmotic flow (EOF) was used as the CE device to separate arsenate and arsenite. A fused-silica capillary of 50 μm i.d. × 48.5 cm was used in all experiments. The effective length of the capillary to the detector is 40 cm and the capillary temperature was maintained at 20˚C. The separation voltage was set to +15 kV, although a range in values between +10 kV and + 25 kV was investigated. Hydrodynamic injection at a pressure of 50 mbar was used for sample introduction and and on-capillary UV diode-array was used for detection at a wavelength of 192 nm. (The minimum wavelength is 191 nm for the Agilent, diode-array with a deuterium lamp). The total injection time was 5 s or 10 s. To ensure uniform capillary surface conditions, the capillary was washed with a 0.1 M NaOH solution for 10 min at the beginning of each workday. Prior to each injection, the fused-silica capillary was flushed with 1 M NaOH for 1 min, Milli-Q water for 1 min and electrolyte buffer for 2 min.

Results

CE studies with Arsenite and Arsenate: The absorption of ultraviolet light by inorganic arsenic species increases as the wavelength is decreased below 250 nm and appears strongest near 190 nm. Sun et al. 2002 applied CE at a wavelength of 192 nm to measure arsenate and arsenite solutions down to approximately 1 to 6 mg/L. Under similar experimental conditions we measured arsenite at 5.2 min., but seemed unable to detect arsenate (Figure 1). Investigating further using a UV-VIS spectrophotometer (Shimadzu Co., Kyoto, Japan), we scanned arsenite and arsenate samples from a wavelength of 190 to 300 nm. For a 20 mg/L arsenite sample at pH 6.58 the maximum absorbance at a wavelength of 192.8 nm was 0.73; however, at the same wavelength the maximum absorbance of a 200 mg/L arsenate sample at a similar pH of 6.84 was only 0.12. Although this suggests that the low absorptivity of arsenate (0.6 L cm^{-1} g^{-1}) compared with arsenite (36.5 L cm^{-1} g^{-1}) might be responsible for our inability to detect arsenate additional work is necessary to confirm the actual cause. In the remainder of this report we focus on results obtained with arsenite.

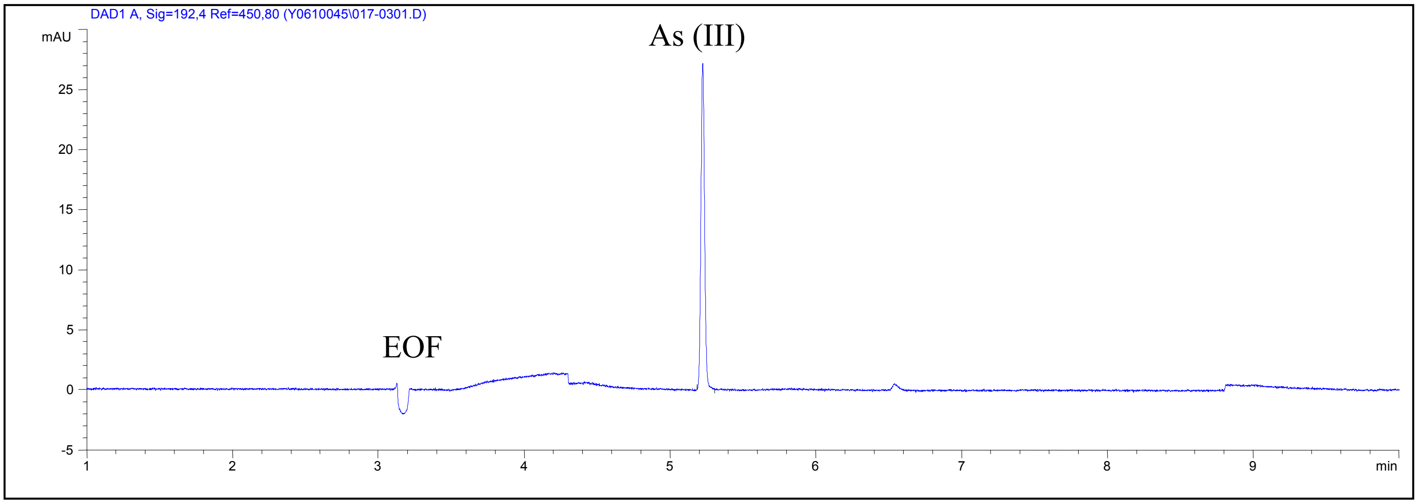

Figure 1. Electropherogram of arsenite (44.11 mg/L) in the borate buffer (20 mM, pH 10).

The ability of CE to separate analyte species is dependent upon a proper buffer selection. We tested four common buffer solutions; carbonate (20 mM, pH 10), borate (20 mM, pH 10), phosphate (20 mM, pH 5, 7, 9, 10, and 11), and acetate (20 mM, pH 7.3). Optimum separation of arsenite occurs at elevated pH where both borate and carbonate are the most effective buffers, but due to its lower UV background borate is a better choice than carbonate.

Studies examining the pH effect on arsenic and NOM complexation will be performed at different pH values and in preparation we investigated the influence of buffer pH on arsenite detection using phosphate buffers at pH 5, 7, 9, 10, and 11. At pH values of 5 and 7, the arsenite peak was very close to the EOF peak, indicating it will be difficult to accurately analyze the peak area. The pH of the electrolyte has a significant influence on the migration time of analytes and potentially the separation efficiency as well. Furthermore, it is possible that the electrophoretic mobility of arsenic is a weighed average of individual arsenic species. Careful attention to the ability of the buffer to impact migration times and separation efficiencies will be an important consideration for future experiments.

Evaluation of two-component interactions. Preliminary results examining interactions between arsenite and SRNOM were collected by mixing 5-mL aliquots of arsenite and SRNOM solutions in polyethylene tubes. The initial arsenite and SRNOM concentrations were 44 mg/L and 57.27 mg/L, respectively. The pH value was not recorded. Tubes were rotated in the dark for 24 hours at room temperature (25 °C). Blanks run in parallel ensured that adsorption of arsenite to the surface of the polyethylene tubes was negligible. After equilibration, the mixture of arsenite and SRNOM solution was analyzed using CE. The detection wavelength was fixed at 192 nm although the maximum absorbance of SRNOM was measured at 195.5 nm.

The peak in the electropherogram associated with As(III) exhibits a slight decrease (~ 3%) in the mixed arsenite-SRNOM sample (Figure 2a) compared with the peak in an NOM-free electropherogram at the same concentration (Figure 1). This we attribute to a decrease in the concentration of free arsenite anions due to the formation of a small amount of SRNOM-As(III) complexes. The arsenite peak in Figure 2a occurs simultaneously with an “NOM hump” in the arsenite-free SRNOM sample (Figure 3). Changes in the peaks associated with NOM also suggest the formation of As(III)-NOM complexes (Figure 2b). For example, the height of the NOM peak at 9 minutes, NOM C, decreases and splits in the presence of arsenite (Figure 2b) which occurs, according to Nordén and Dabek-Zlotorzynska (1996), when complexes are formed with NOM. Note that the sharp peaks in the SRNOM electropherogram (NOM A, NOM B, and NOM C) and the broad NOM hump occur as a result of the heterogeneity and polydispersity of NOM. NOM macromolecules span a range in size and functional group content, and thus exhibit nonuniform charge-to-mass ratios and electrophoretic mobilities. In general, during normal EOF molecules having more negative charge-to-mass ratios also have greater electrophoretic mobilities and longer migration times.

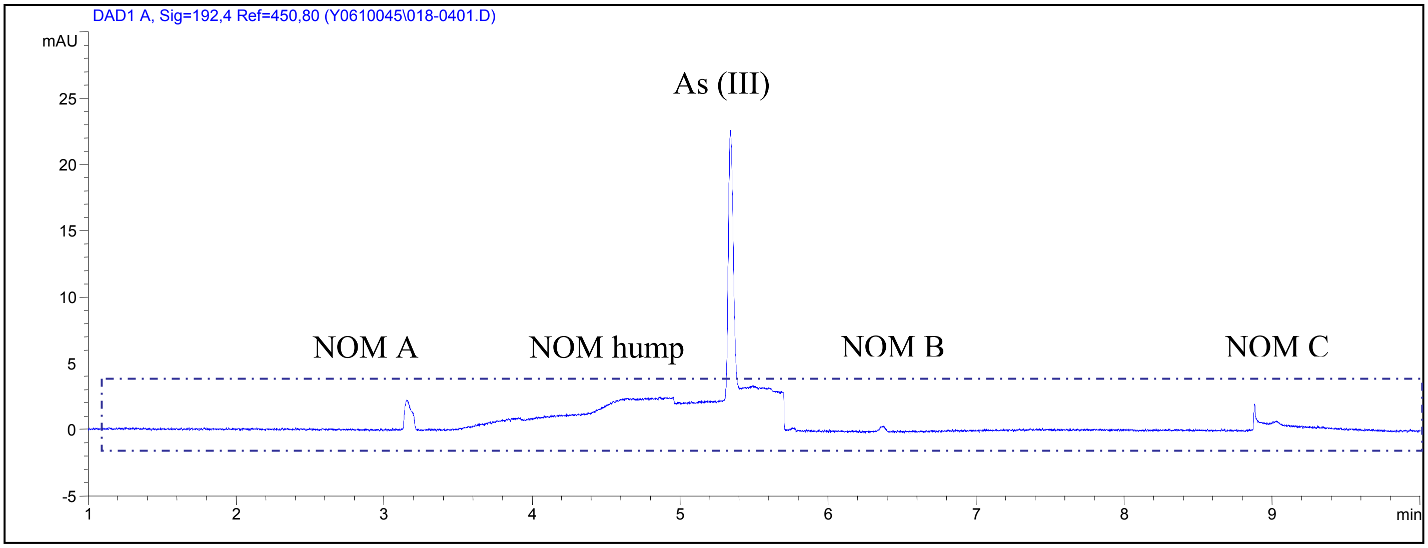

Figure 2a. Electropherogram of arsenite and SRNOM (20 mM borate, pH 10).

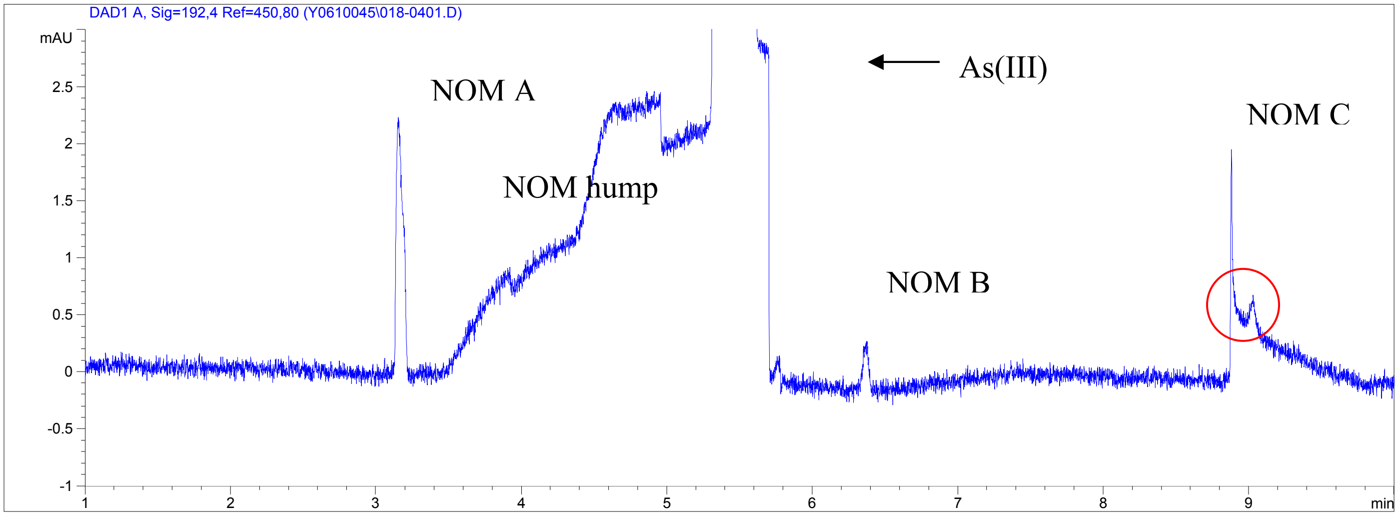

Figure 2b. Exaggeration of lower absorbance region in the electropherogram of arsenite and SR-NOM mixture in the borate buffer (Figure 2a).

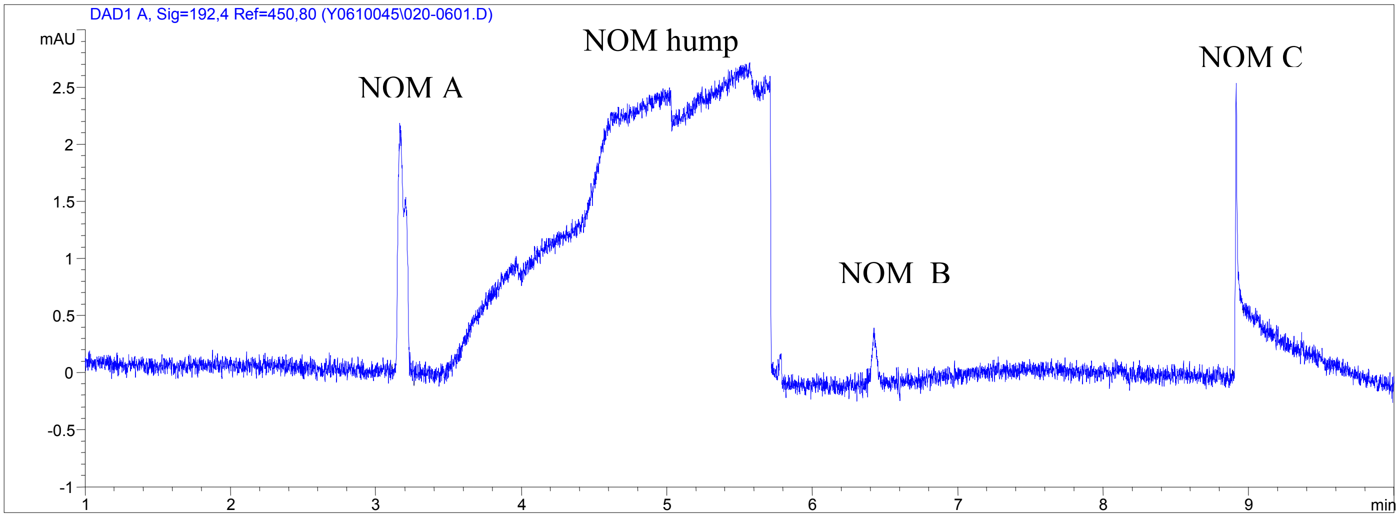

Figure 3. Electropherogram of SR-NOM (57.27 mg/L) in the borate buffer (20 mM, pH 10).

Future Research

Work continues with SRNOM, varying pH, and constituent ratios. The cationic impurities in SRNOM (see Table 2) will be removed for future measurements. Similar experiments are planned for NLNOM, which must also be cleansed of the large ash content (Table 1). Experiments to examine the acid-base characteristics and pH-dependence of As-NOM interactions will also be conducted.

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Methodology for Estimating Total Maximum Daily Load in Watersheds with Considerable Groundwater-Surface Water Interaction

Basic Information

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Focus Category:	, Models, Non Point Pollution
Descriptors:	
Principal Investigators:	Maged Hussein, Frank Schwartz

Publication

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Duration: 9/00-9/03

Title: Methodology for Estimating Total Maximum Daily Load in Watersheds With Considerable Ground-Water Surface-Water Interaction

Investigator:
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Congressional District: Ohio 15th

Focus Categories: MOD, NPS, and GW

Keywords: Water Quality Modeling, Ground-Water Surface-Water Interaction, Total Maximum Daily Loads, Geographic Information Systems

Problem and Research Objectives

The purpose of this study is to use advanced and rigorous modeling techniques to evaluate the impact of point and nonpoint pollution sources on groundwater and surface water quality in the Mad River Watershed in western central Ohio. Of specific interest is the considerable interaction between the surface and subsurface processes, and an exploration of how agricultural and other land use practices within the watershed effect this coupled system. A major deficiency in the current modeling methodology commonly implemented through BASINS is a lack of rigorous treatment of the groundwater domain. Soil properties and groundwater hydraulics are neglected in estimating surface water losses to the subsurface (HydroGeoLogic, 2001). None of the above-mentioned models account for transport in the shallow ground-water (Hussein & Schwartz, 2003).

By developing a combined GW/SW model for the Mad River watershed where all aspects of the hydrologic cycle are rigorously simulated in a fully coupled fashion, a better understanding of the watershed dynamics will be gained. This modeling will ultimately be applied to the Total Maximum Daily Load (TMDL) analysis required by section 303(d) of the Clean Water Act. The modeling code selected for his task is MODHMS.

Methodology

The numerical model currently being applied to the Mad River watershed is called MODHMS, which is a much-modified and extended version of the popular and well used Modular Three-Dimensional Finite-Difference Ground-Water Flow Model, or MODFLOW

(McDonald and Harbaugh, 1988). Improvements to the original MODFLOW code are numerous, but of specific interest to this research is the capability to simulate flow of water in both the subsurface as well as in the surface domain, including simulation of unsaturated zone flow, two-dimensional overland flow and one-dimensional channelized flow (figure 1). This allows for simulation of the complete hydrologic system using well established governing equations describing the physics of flow. The conjunction between surface water (SW) and groundwater (GW) flow is handled in a numerically robust and fully coupled manner so problems involving strong interactions between surface and groundwater regimes can be rigorously investigated (HydroGeoLogic, 2002).

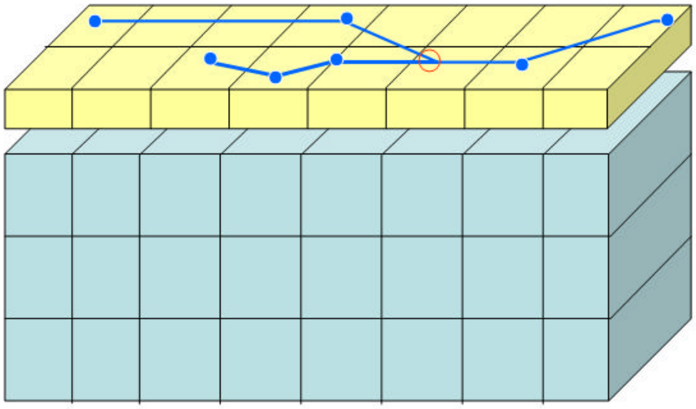

Figure 1. Conceptualization of MODHMS formulization consisting of 1D channelized flow, 2D overland flow, and 3D variably saturated groundwater flow

There have been many hydrologic models developed to aid in understanding rainfall, runoff, and flood events, as well as models to simulate subsurface flow. Traditionally, the equations describing the physics of the SW/GW domains have been solved separately, or only partially coupled via interaction terms. Such an approach may be restrictive or entail inappropriate assumptions about spatial variability, dimensionality, or chemical transport. The purpose of employing MODHMS is to provide a comprehensive, spatially distributed, multidimensional, and fully integrated hydrologic model capable of simulating overall hydrologic cycle behavior, including fate and transport of dissolved contaminants (HydroGeoLogic, 2002).

The Mad River watershed and the underlying Great Miami Buried Valley (GMBV) aquifer system provide a complex situation where there is strong interaction between SW/GW, making the use of a coupled model appropriate (Dumouchelle, 1993). MODHMS was selected for the modeling effort due to it's capacity to simulate both the physics of flow and and chemical transport in channelized flow, overland flow (runoff), and both saturated and unsaturated subsurface environments.

One drawback of distributed parameter models is the large amount of spatial data required for model input. In the case of MODHMS this input is facilitated by ViewHMS, a graphical pre- and post-processing tool. This tool allows for input file creation and parameter estimation and interpolation by interfacing with common database formats as well as GIS data. This combination takes full advantage of the wealth of spatial data available from numerous government and private agencies, including soil type, vegetation type, land use and land cover. ViewHMS can also be used for processing model results. Hydrographs can be created from stream observation nodes, and flow and concentration data can be exported for viewing and animation in 3-D visualization software.

The Mad River Sub Basin

The Mad River sub basin as delineated in by ArcView GIS utilities occupies 645 mi^2 of the eastern portion of the Upper Great Miami River Basin and includes the Mad River and eight major tributaries (Figure 2). It ranges in elevation from 457 m (1499 ft) above MSL in the northeastern corner of the sub basin to 235 m (784 ft) MSL in the vicinity of Dayton, Ohio Land use in the study area is greater than 75% agricultural and approximately 15% urbanized. The remaining 10% is comprised of forest land and water cover.

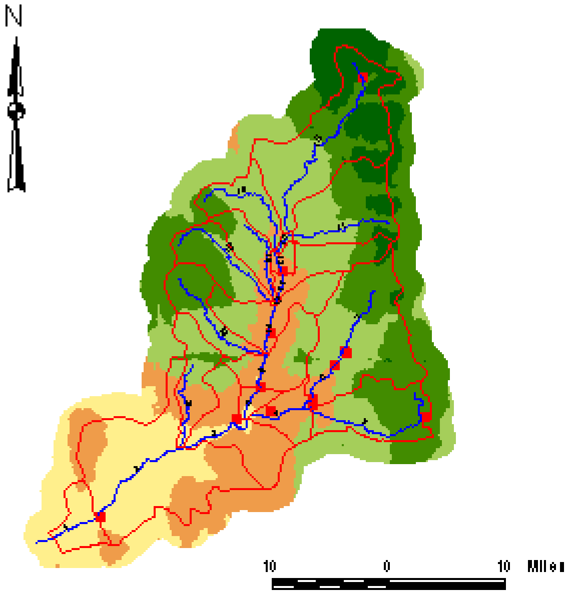

Figure 2. Sub Basins Within the Mad River Basin

A total of 20 individual watersheds ranging in size from approximately 0.01 to 106 mi^2 were delineated within the Mad River sub basin based on topographical information and/or the location of USGS stream gaging stations. Each watershed contains a segment of or tributary to the Mad River ranging in length from 0.4 to 21 miles. The active USGS gaging stations in the Mad River sub basin are located at Dayton (03270000), Springfield (03269500), St. Paris (03267900), and Urbana (03267000).

Principle Findings and Significance

A necessary precursor to model development is the creation of a thorough and organized GIS database containing data sets such as land use/land cover (LULC), soil types, land use, hydrography, digital line graphs (DLG), and digital elevation models (DEM). This was achieved through a collection of GIS layers from a variety of government sources, including state of Ohio agencies such as GIS Support Center, as well as the US EPA and USGS. Of particular importance was the acquisition of accurate topographic data. A collection of 42 1:24,000 scale DEMs were compiled, coordinate and elevation corrected, and tiled into a uniform DEM covering the Mad River Watershed (Figure 3). This DEM has a resolution of 50 meters per grid cell. In addition to the above coverages, the GIS also contains point data consisting of dams, stream gages, and chemical sampling locations.

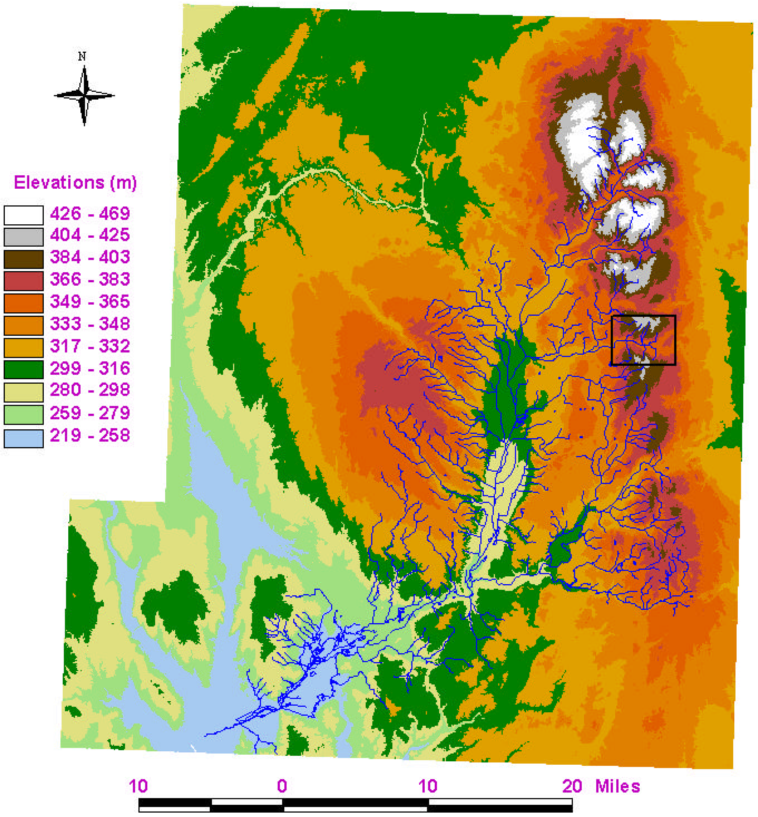

Figure 3. Digital Elevation Model for the Mad River Watershed. Kings Creek model domain shown by the black box.

The initial step in the creation of a complete model of the Mad River watershed was the generation of a smaller cutout model of the Kings Creek tributary (Figures 3, 4). This smaller model was created for the purpose of familiarizing ourselves with the processing tools, input structure and data available for modeling while reducing computer processing time required for a larger, more complex simulation of the entire watershed. The top surfaces of the model and the grid spacing are a direct product of the DEM. Preliminary results from the steady-state Kings Creek model can be seen in Figure 4. Groundwater head values from the steady state model were input into a transient model, where recharge was varied over the stress periods to simulate storm events. Post-processing of model results entails the generation of stream hydrographs from observation nodes.

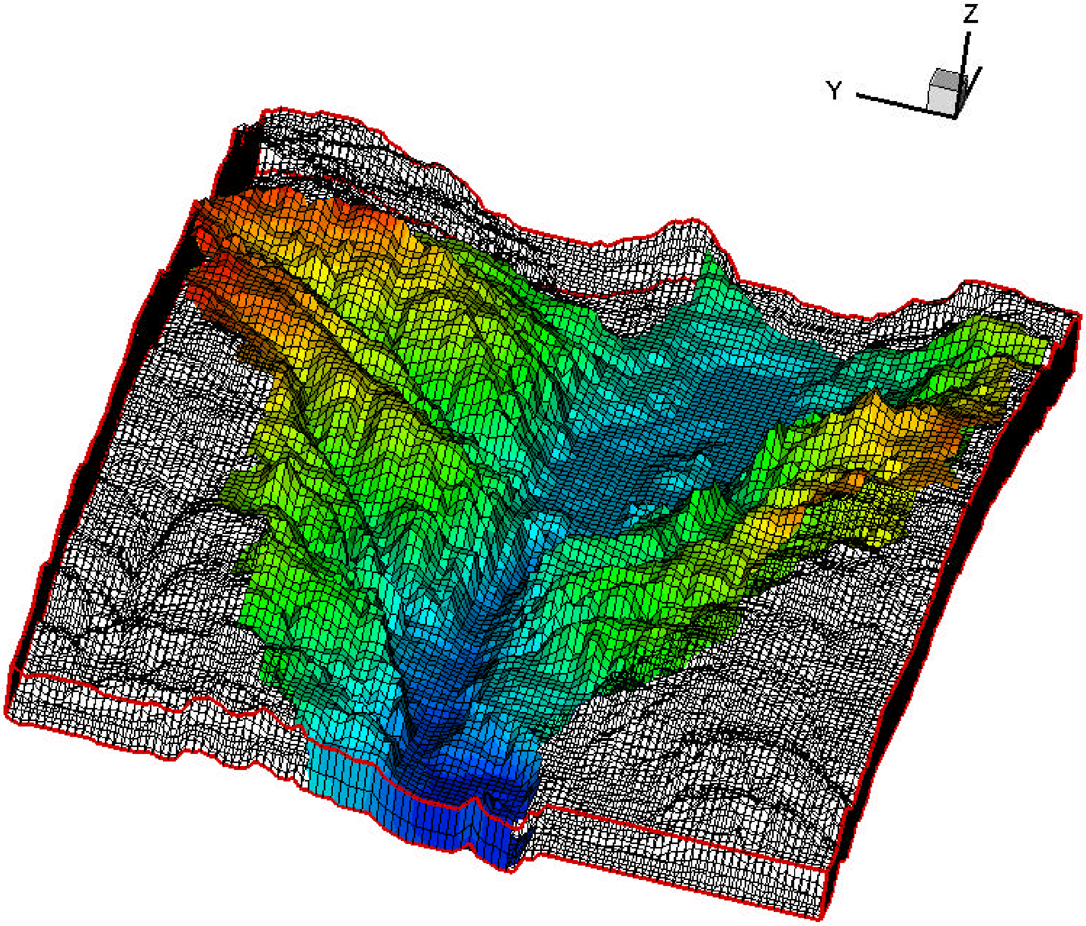

Figure 4. Groundwater head as simulated by the steady-state Kings Creek model. No-Flow cells are shown without a contour color.

The second phase of modeling continues with the gridding and assignment of surface characteristics and aquifer properties to the finite difference grid for the entire Mad River Watershed model. The current grid consists of 145 rows, 119 columns, and 3 layers. Grid cells are a uniform 500 meters by 500 meters. This grid spacing is used for initial modeling for the sake of simplicity and conservation of CPU resources, but will be further refined to better portray surface topography and aquifer variability where slopes or hydraulic gradient are steep.

The assignment of properties to the grid continues with the incorporation of geological parameters such as bedrock elevation, hydraulic conductivity, soil type, and storage. Overland flow and surface parameters, such as roughness coefficients and rill storage heights are being interpreted from proxy data including land use, vegetation type, and aerial photography. Channel inputs are being developed from EPA RF3 river reach files as well as parameters recorded on actual site visits, including channel geometry, bed material and roughness, vegetation type and height, and meander regularity. One of the more important parameters not easily measured but necessary for hydrologic modeling is evapotranspiration. The collection and analysis of this type of data is discussed in the following section.

Case-Based Reasoning Prediction of Evaporation and Evapotranspiration

Case-based reasoning (CBR) is a relatively recent problem solving technique that is attracting increasing attention by scientific researchers. Emerging from research in cognitive psychology as a model of human memory and remembering, it has been embraced by researchers of artificial intelligence applications as a methodology that avoids some of the knowledge acquisition and reasoning problems that occur with other methods for developing knowledge-based systems (Cunningham, 1999). The CBR approach is based on two tenets concerning the nature of the world. First, the world is regular, and similar problems have similar solutions. Second, types of problems tend to reoccur, and future problems are likely to be similar to current problems (Leake, 1996).

Reasoning is often modeled as a process that draws conclusions by chaining together generalized rules, starting from scratch (Leake, 1996). In CBR, the primary knowledge source is not generalized rules, but a memory of stored cases recording specific episodes. New solutions are generated not by chaining, but by retrieving the most relevant cases from memory and adapting them to fit new situations. Medical diagnoses and judiciary procedure have employed this rationale for millennia.

Accurate evaporation (E) and evapotranspiration (ET) data are essential for the hydrologic modeling of any watershed. With the development of more complex hydrologic models, especially the continuous moisture accounting models, algorithms for making reasonable estimates of E and ET losses for periods of 1 day or less, are needed (McCuen, 1998). Although not widely available, the U.S. Weather Service Class A pan and lysimeter are direct measurement-based techniques for estimating daily E and ET, respectively. Consequently, several empirical approaches are available that utilize various meteorological parameters to calculate actual and/or potential evaporation and evapotranspiration. Meteorological data are available from various meteorological stations within or close by the Mad River sub basin, but accurate, site-specific E and associated ET data are generally lacking.

The North Appalachian Experimental Watershed (NAEW), located in Coshocton, Ohio, approximately 100 miles east of the Mad River sub basin, was opened in the mid-1930's to address soil erosion problems. In 1954 the NAEW was transferred to the newly formed Agricultural Research Service which initiated studies of the movement of insecticides and plant nutrients in surface and subsurface waters in the 1960's. Today, in cooperation with The Ohio State University/Ohio Agricultural Research and Development Center, the NAEW maintains a focus on field-based environmental research of soil erosion, hydrology, and water quality concerns. The NAEW is one of only two hydrologic stations worldwide with over 60 years of continuous data collected from small watersheds and groundwater lysimeters. Daily meteorological data collection began in 1939 and changed to an hourly format in 1990. Daily weighing lysimeter evapotranspiration (ET) and Class A pan evaporation (EoPan) data have been recorded since 1945 and 1965, respectively.

The Coshocton dataset is ideally suited for development of a CBR approach to predict missing Class A pan evaporation and evapotranspiration data for the Mad River watershed for inclusion in the MODHMS model. Basic steps are as follows:

- Individual or combined Coshocton datasets have been compiled that will include up to 12 recorded or calculated daily meteorological parameters (Table 1). These datasets will be the CBR known cases. Each case has associated daily EoPan or ET or both values. Because EoPan and ET data are relevant only from April or May through October, this dataset will consist of approximately 20 years of record or 4000 individual daily cases.

- Similar daily meteorological datasets (sans EoPan and ET data) have been collected from National Climatic Data Center records and will be compiled for weather stations located within or close by the Mad River sub basin. These datasets will be the CBR unknown cases. An estimated 15 to 20 years of record will be required to accurately define yearly and seasonal E and ET values.

- A Case-Based Reasoning designed FORTRAN code will select the three closest matches between the meteorological parameters for the individual unknown case years and the known cases dataset via standard or *Z*-score statistical procedures. The associated EoPan and ET known case values for the three closest matches will be averaged to predict daily EoPan and/or ET value for each individual unknown case.

Preliminary CBR test runs using individual years from the Coshocton dataset as the unknown cases have yielded good results with estimated EoPan and ET within 5% of actual recorded values, depending on seasonal and yearly variability.

- Maximum Temperature (°F)
- Average Temperature (°F)
- Minimum Temperature (°F)
- Dew Point Temperature (°F)
- Wind (mpd)
- Radiation (Langleys)
- Precipitation (Inches)
- Soil Moisture (Inches)
- Relative Humidity (%)
- Date of Meteorological Data Collection
- Number of Days Since Last Precipitation
- Previous 10-Day Cumulative Precipitation (Inches)

Table 1. Recorded or Calculated Daily Meteorological Parameters

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Preventing the Initiation of Biofouling of Membrane Bioreactors in Wastewater Treatment

Basic Information

Title:	Preventing the Initiation of Biofouling of Membrane Bioreactors in Wastewater Treatment
Project Number:	2003OH18B
Start Date:	3/1/2002
End Date:	11/30/2003
Funding Source:	104B
Congressional District:	1st
Research Category:	Engineering
Focus Category:	Waste Water, Treatment, None
Descriptors:	Wastewater, Biological Treatment, Membranes, Bioreactors, Fouling
Principal Investigators:	Daniel Barton Oerther, Dionysios Dionysiou, George Sorial

Publication

1. Hyeok Choi, Kai Zhang, Dionysios D. Dionysiou, Daniel B. Oerther and George A. Sorial, Influence of cross-flow velocity on membrane performance during filtration of biological suspension, Journal of Membrane Science (in press).
2. Hyeok Choi, Kai Zhang, Dionysios D. Dionysiou, Daniel B. Oerther and George A. Sorial, Effect of permeate flux and tangential shear on membrane fouling for wastewater treatment, Separation and Purification Technology (in press).
3. Hyeok Choi, Kai Zhang, Dionysios D. Dionysiou, Daniel B. Oerther and George A. Sorial, Membrane filtration performance with activated sludge of continuous stirred-tank reactor and plug flow reactor for the treatment of paper mill wastewater: membrane fouling, Water Science and Technology (in review).
4. Kai Zhang, Hyeok Choi, Dionysios D. Dionysiou, George A. Sorial, and Daniel B. Oerther, The Influence of MBR Operating Conditions on Bacterial Community Structure and Relationship to Membrane Biofouling, Applied and Environmental Microbiology (in preparation).
5. Hyeok Choi, Kai Zhang, Dionysios D. Dionysiou, Daniel B. Oerther and George A. Sorial, Membrane filtration performance with activated sludge of continuous stirred-tank reactor and plug flow reactor for the treatment of paper mill wastewater: membrane fouling, in: Proceedings of the International Water Association Specialty Conference on Water Environment-Membrane

Technology, Seoul, Korea, June, 2004, p. 809-816.

6. Kai Zhang and Daniel B. Oerther, Examining the Initiation of Biofouling in Membrane Bioreactors for Wastewater Treatment, Research/Scholarship Forum, University of Cincinnati, March, 2004, p. 28.
7. Kai Zhang and Daniel B. Oerther, Examining the Initiation of Biofouling in Membrane Bioreactors for Wastewater Treatment, American Society for Microbiology, 104th General Meeting, New Orleans, LA, May 19-23, 2004, CD-ROM, ISBN 1-555-81-315-1.
8. Kai Zhang, Hyeok Choi, George A. Sorial, Dionysios D. Dionysiou and Daniel B. Oerther, Examining the initiation of biofouling in membrane bioreactors treating pulp and paper wastewater, in: Proceedings of the 77th Annual Conference of Water Environment Federation, New Orleans, October, 2004 (in press).

Completion Report

Project Title.

Preventing the Initiation of Biofouling of Membrane Bioreactors in Wastewater Treatment

Project Team.

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Summary.

Membrane bioreactors (MBR) can be expensive to operate because membrane fouling results in high operating pressures, excessive membrane cleaning, and increased product replacement costs. Although MBR systems are a useful technology to protect water quality, the high costs have limited wide-spread application.

The governing hypothesis of this project was that developing operating strategies to prevent the initiation of biofilm formation on membrane surfaces would reduce membrane fouling in MBR systems resulting in lower costs and wide-spread adoption of MBR technology.

To test this hypothesis, we investigated the connection between the physiochemical properties of membranes and the ecology of bacterial communities inhabiting MBR systems.

The specific interdisciplinary aims that were undertaken in this study included:

a) determining the physicochemical properties of membranes;
b) examining the impact of synthetic pulp and paper wastewater on the physiochemical properties of membranes;
c) examining the impact of bacterial populations on the physiochemical properties of membranes;
d) examining the impact of bioreactor operating conditions on the bacterial community structure in MBR systems; and
e) examining the relationship among bacterial community structure and the physiochemical properties of membranes.

The research team that executed this project included: a tenure-track faculty member with experience in physiochemical properties of membranes (Dionysiou); a tenure-track faculty member with experience in biological treatment of industrial wastewaters (Sorial); a tenure-track

faculty member with experience in molecular biology and conventional microbiological analysis of environmental samples (Oerther); and two graduate research students.

During approximately two years of research, major project accomplishments included:

1. developing a theoretical model describing membrane biofouling;
2. designing, fabricating, and operating a laboratory-scale membrane reactor system to quantify transmembrane flux;
3. comparing the results of the model with the results of the laboratory-scale membrane reactor system;
4. designing, fabricating, and operating four laboratory-scale membrane bioreactor systems using activated sludge to treat a synthetic pulp and paper mill wastewater; and
5. comparing the results of the laboratory-scale membrane reactor system with the laboratory-scale membrane bioreactor system and the model.

The most significant results of this study have been presented at international scientific gatherings and published in the archival peer-referred literature, including:

- Hyeok Choi, Kai Zhang, Dionysios D. Dionysiou, Daniel B. Oerther and George A. Sorial, Influence of cross-flow velocity on membrane performance during filtration of biological suspension, *Journal of Membrane Science* (in press).
- Hyeok Choi, Kai Zhang, Dionysios D. Dionysiou, Daniel B. Oerther and George A. Sorial, Effect of permeate flux and tangential shear on membrane fouling for wastewater treatment, *Separation and Purification Technology* (in press).
- Hyeok Choi, Kai Zhang, Dionysios D. Dionysiou, Daniel B. Oerther and George A. Sorial, Membrane filtration performance with activated sludge of continuous stirred-tank reactor and plug flow reactor for the treatment of paper mill wastewater: membrane fouling, *Water Science and Technology* (in review).
- Kai Zhang, Hyeok Choi, Dionysios D. Dionysiou, George A. Sorial, and Daniel B. Oerther, The Influence of MBR Operating Conditions on Bacterial Community Structure and Relationship to Membrane Biofouling, *Applied and Environmental Microbiology* (in preparation).
- Hyeok Choi, Kai Zhang, Dionysios D. Dionysiou, Daniel B. Oerther and George A. Sorial, Membrane filtration performance with activated sludge of continuous stirred-tank reactor and plug flow reactor for the treatment of paper mill wastewater: membrane fouling, in: Proceedings of the International Water Association Specialty Conference on Water Environment-Membrane Technology, Seoul, Korea, June, 2004, p. 809-816.
- Kai Zhang and Daniel B. Oerther, “Examining the Initiation of Biofouling in Membrane Bioreactors for Wastewater Treatment,” Research/Scholarship Forum, University of Cincinnati, March, 2004, p. 28.
- Kai Zhang and Daniel B. Oerther, “Examining the Initiation of Biofouling in Membrane Bioreactors for Wastewater Treatment,” American Society for Microbiology, 104th General Meeting, New Orleans, LA, May 19-23, 2004, CD-ROM, ISBN 1-555-81-315-1.
- Kai Zhang, Hyeok Choi, George A. Sorial, Dionysios D. Dionysiou and Daniel B. Oerther, Examining the initiation of biofouling in membrane bioreactors treating pulp and

paper wastewater, in: Proceedings of the 77th Annual Conference of Water Environment Federation, New Orleans, October, 2004 (in press).

In brief, we concluded from our study that permeate flux through ultrafiltration and microfiltration membranes increased linearly with increasing cross-flow velocity and a cross-flow velocity was more effective for reducing fouling for MF membrane than for UF membrane. A cross-flow velocity of around 3.0 m/s for MF membrane and 2.0 m/s for UF membrane was sufficient to prevent the formation of an easily removed reversible fouling layer. However, a higher cross-flow velocity was shown to be needed to reduce irreversible fouling. The magnitude of reversible and irreversible filtration resistances matched well the mass and thickness of their corresponding fouling layer. The density of the fouling layer was another important factor affecting filtration resistance and dissolved organic carbon rejection. Distinct fouling layers as well as pore blocking and narrowed pore sizes effected DOC rejection. When examining mixed liquor removed from the laboratory-scale MBR bioreactors, we observed that the propensity to foul increased in the order of well settled plug flow reactor < bulking continuously stirred tank reactor < well settled continuously stirred tank reactor < bulking plug flow reactor. For completely stirred tank reactors, sludge produced using a bag-filtration method for particle separation caused slightly more fouling than the sludge produced using gravity settling. In contrast, for the plug flow reactors, sludge produced using the bag-filtration method caused slightly less fouling than the sludge produced using gravity settling. The mean particle size of the sludge was approximately the same in all sludges but the sludges produced using the bag-filtration method had a narrow particle size distribution. Compared to a low cross-flow velocity of 0.1 m/sec, a high cross-flow velocity of 3.5 m/sec reduced MF membrane fouling significantly. The effect of cross-flow velocity on UF membrane fouling was much less important. As expected, each specific filtration resistance decreased with increasing cross-flow velocity. However, the contribution of concentration polarization to the total filtration resistance increased while that of reversible and irreversible fouling decreased with an increase in cross-flow velocity. The results on the magnitude of irreversible fouling resistance and the mass of the fouling layer were in agreement. A low cross-flow velocity caused a high filtration resistance due to the formation of reversible and irreversible fouling layers. However, this also resulted in high DOC rejection by these fouling layers. Enhanced DOC rejection was accomplished within 1-2 hours of filtration time, which corresponded to a pseudo-steady state of the permeate flux and the formation of the fouling layer. Molecular analysis of the bacterial community on the surface of membrane samples as compared to the planktonic bacterial community present in suspension showed that membrane biofouling is a selective process with significant accumulations of specific bacterial populations on the surfaces of the membranes. These results support our overall hypothesis suggesting that operating conditions for MBR bioreactors influence the composition of the bacterial community which in-turn impacts the degree of biofouling. Thus, we conclude that future work should focus upon identifying the optimum bioreactor configuration for selecting for a bacterial community demonstrating the least propensity for biofouling membrane surfaces.

Information Transfer Program

Program Administration Project

Basic Information

Title:	Program Administration Project
Project Number:	2003OH19B
Start Date:	3/1/2003
End Date:	2/28/2004
Funding Source:	104B
Congressional District:	15
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Earl Whitlatch

Publication

A series of tasks were continued, including; the administration of the Water Resources Center at The Ohio State University and activities to transfer and disseminate information and technology developed by researchers affiliated with the WRC to a wide range of state, federal, county, and municipal agencies; to the private sector, academic community, and to private citizens throughout Ohio. Specific tasks were: the administration of a Special Water and Wastewater Treatment Grants Competition; administration of the 104(B) In-State Competition and the National Competitive Grants Program; assemblage of a directory of college and university water resources research publications and capabilities in Ohio; preparation of information for a web site of the Ohio Water Resources Center, and continued administrative support for the Water Management Association of Ohio and the Ohio Water Education Program.

Student Support

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

Notable Awards and Achievements

Publications from Prior Projects