Water Resources Center
Annual Technical Report
FY 2005

Introduction

Research Program

The Scour and Deposition around River and Estuarine Bridges

Basic Information

Title:	The Scour and Deposition around River and Estuarine Bridges
Project Number:	2004OH13B
Start Date:	3/1/2004
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	15th
Research Category:	Not Applicable
Focus Category:	Geomorphological Processes, Floods, Sediments
Descriptors:	scour, deposition, rivers, esturaries, bridges
Principal Investigators:	Diane L Foster, Thomas C Lippmann

Publication

The Scour and Deposition around River and Estuarine Bridges
Final Report

Principal Investigators:
D. L. Foster and T. C Lippmann
Ohio State University

Abstract

This report gives the results of a two-year effort directed at increasing our understanding of sediment scour and deposition surrounding bridge piers exposed to wave and mean flows. A combined numerical and observation effort resulted in new techniques for more accurately resolving the flow and bed evolution surrounding submerged objects. Results from this study may 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 and modeling methods represent new ways to monitor and evaluate bridge scour, and together these model-data results will highlight potential areas of concern.

Introduction

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”.

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, an increase in our understanding of how sediment is scoured or deposited around structures will improve our ability to utilize available resources in the most efficient manner.

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.

The objectives of this research were to increase our ability to predict how variations in flow conditions affect the scour and/or deposition of sediment around bridge piers. We have approached this objective through a combination of pilot field observations, detailed laboratory observations, and three-dimensional numerical simulations. This synergistic effort will ultimately allow results derived from small-scale numerical model and laboratory studies to field applications.

Methodology

Model

In this work, we simulate the flow and sediment transport field surrounding submerged objects in both wave and current dominated flows with FLOW-3D (Flow Science, Inc., Santa Fe, NM), a robust three-dimensional, non-hydrostatic computational fluid dynamics (CFD) numerical model that solves the nonlinear Navier Stokes equations (*e.g.*, Chopakatla, *et al.*, 2006). FLOW-3D incorporates one of several closure schemes, including large eddy simulations (LES) and *k-e* models, to resolve fine scale turbulence and dissipation throughout the domain. FLOW-3D uses a fixed rectangular grid (Eulerian approach), and overcomes the problem of incorporating geometry in a structured gird by using the trademark Fractional Are Volume Obstacle Representation method (FAVOR; FLOW-3D manual, 2002). The primary strength of FLOW-3D is its ability to accurately resolve three-dimensional flows in great detail, while tracking complex fluid behavior at flow-structure and flow-sediment interfaces, allowing coupled fluid-sediment equations to be incorporated. The sediment transport module of FLOW-3D is based on the bulk conservation of mass with an advection/diffusion scheme coupled with the interface tracking capabilities of the Volume-of-Fluid (VOF; Hirt and Nichols, 1981) scheme for bed level tracking. This method differs significantly from traditional sediment transport models as the grid is not fitted or regenerated to match morphology changes.

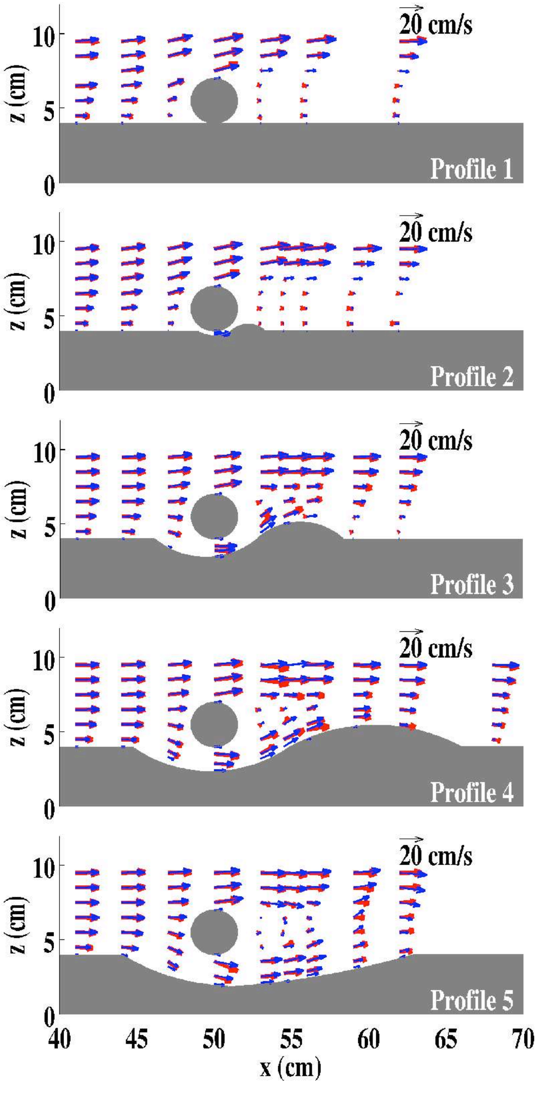


Figure 1. Observed (blue) and simulated (red) velocity profiles around a two-dimensional pipeline over 5 bed static-bed profiles. The model resolves the recirculating region present on planar and near-planar beds (profiles 1 and 2) and vortex shedding present on present on scoured beds (profiles 4 and 5).

Laboratory

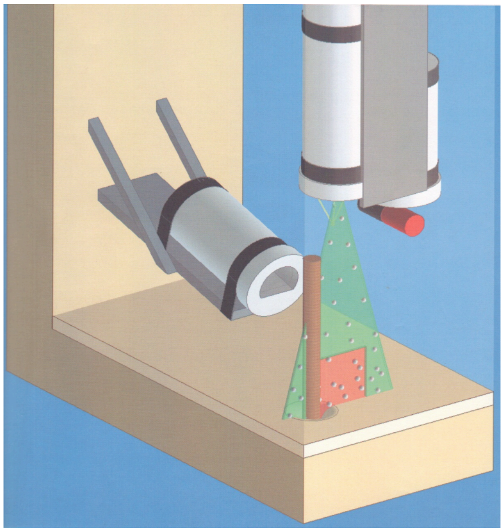


Figure 2. A sketch of the CROSSTEX laboratory deployment. The red highlight box shows the location of PIV observations of velocity and scour. The location of the two-axis sonar is identified with the red and black cylinder in the mid-water column.

Laboratory observations of the wave-induced flow field, suspended sediment, and morphologic response surrounding a vertical pile were obtained at the collaborative 2005 CROSSTEX prototype laboratory experiment held at the O. H. Hinsdale Research Lab in Corvallis, OR. The laboratory facility is 104 *m* long, 3.7 *m* wide, and 5 *m* deep, and capable of generating prototype scale random wave fields with greater than 1 *m* wave heights impinging on a sloping beach with a single, subtle sand bar approximately 40 *m* from the shoreline. In our experiments, the evolution of the flow field and seabed offshore of a vertical pile was observed under both random and monochromatic waves in the shoaling region (seaward of the breakpoint) in approximately 1.5 *m* water depth. A 6 *cm* diameter pile was hydraulically jetted vertically into the bed composed of a mixture of quartz sand with median grain size diameter of 0.19 *mm*. An underwater Particle Image Velocimetry (PIV) system consisting of a 1 mega-pixel digital camera focused on a two-dimensional laser sheet oriented along the tank in the direction of the shoreward propagating wave field was used to observe the two-dimensional (*x-z*) time dependent flow fields at 3 *Hz*. A two-axis variable-frequency acoustic backscatter sensor observed the sediment suspension at 1 *cm* range bins over the *x-z* plane, as well as the bed geometry over a 1 *m* range in the *x-y* plane. Figure 2 shows a sketch of the instrument deployment. Scour simulations were performed for offshore wave heights ranging from 20 to 40 *cm* with wave periods ranging from 4 to 6 *sec* for both regular and irregular waves.

Field

Figure 3. The waverunner survey system is capable of measuring water depths from approximately 0.4 m to 15 m.

The riverbed topography upstream, downstream, and right at one of the support piers of a bridge located on the Great Miami River (ODOT ID-BUT-128-0855) in Hamilton, OH, was observed under high flow using state-of-the-art acoustic survey instrumentation. The river bottom topography was measured with a bathymetric survey system consisting of a Yamaha GP1200 waverunner equipped with differential GPS receiver, dual-transducer sonic altimeter, and custom navigation software (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 +/- 5-7 *cm* in both the horizontal and vertical coordinates of the measured bathymetry.

The local deposition upstream of one of four bridge piers was measured with a rotating two-axis IMAGENEX profiling sonar attached to the upstream side of a bridge pier. The sonar resolved the two-dimensional centimeter-scale bathymetric variations over a 5-20 *m* radius. Figure 4 shows the IMAGENEX sonar system attached to the upstream side of the ellipsoidal pier for deployment on 30 November 2005.

Figure 4. Snapshot of an IMAGENEX deployment at the proposed Hamilton site (ODOT ID-BUT-128-0855). Figure courtesy of Dave Straub (USGS).

Results

Model

The CFD model (FLOW-3D) was evaluated for two-geometries, (1) a short, horizontally oriented cylinder placed on and near the bed and exposed to both steady and oscillatory flow similar to environments with both surface waves and mean flows, and (2) a vertical pile embedded into the bottom and exposed to steady flow similar to that found in unidirectional river flow.

In the first numerical study, the short-cylinder simulations were run in a small domain approximately 1 *m* horizontally and 15 *cm* vertically with dense, O(*cm*), grid cells. The simulations were repeated over differing seabed geometries that were fixed in time and space and thus not allowed to evolve (*i.e.*, no sediment transport was allowed). The mean flows averaged over about 1 *min* time period are compared with laboratory observations obtained by Testik, *et al.* (2005) over similarly sized cylinders and bed topographies that approximately matched the idealized geometries used in the simulations. Results show for the first time that the LES model is able to accurately reproduce the vortex shedding surrounding near bed structures (Smith and Foster, 2006). Results from this work were used in a recent follow-up study, in which the model was evaluated with field observations of submarine scour around a horizontally oriented cylinder placed in 15 *m* water depth on the continental shelf offshore of Martha's Vineyard in 2005. Results (non shown) indicate that FLOW-3D accurately predicts the scour and depositional regimes from an undisturbed flat bed (Hatton, *et al.*, 2006).

In the second numerical study, steady unidirectional flow surrounding a vertical pile of 56.3 *cm* diameter was simulated and compared qualitatively to laboratory observations. In this work, the three-dimensional flow field was computed over a domain with 11.5 *m* length (downstream direction), 5.9 *m* width (cross-stream direction), and 1.7 *m* height. The grid dimensions varied with coarser cell volumes (cubes with 9.0 *cm* sides) at the edges (far field relative to the pile) and finer cell volumes (cubes with 1.8 *cm* sides) near the pile to better resolve the flow near the pile while speeding up the simulation run time without loss in resolution of flow structure. The flow was initiated at the upstream (inflow) boundary with steady mean currents of 32.6 *cm/s.* A continuous outflow boundary condition at the downstream end of the domain was specified that minimized wave reflections. The bottom boundary condition allows no flow through the bottom, and contains small roughness elements needed for numerical stability. The surface boundary condition was specified as rigid lid (no temporal variations in the sea surface elevation). Figure 5 shows both downward and sideward looking predictions of the velocity field. In this case, the water depth was twice that of the pile diameter. Upstream of the pile, the simulations show a region of high stress induced by the presence of a horseshoe vortex, visual in the figure by the velocity magnitudes larger than the undisturbed flow. The presence of the horseshoe vortex suggests a region where sediment will be removed and the potential for a scour hole to develop on the upstream side of the pile. On the other hand, downstream of the pile the mean flow field shows lower velocities than the undisturbed flow suggesting a region where sediment would be deposited. Interestingly, the simulations predict the presence of vortex shedding downstream of the pile, which should decrease the depositional regimes.

Laboratory

The nature of the complex flow field modeled with FLOW-3D, characterized by an erosional regime on the upstream side of the pile and with potentially competing accretional and depositional regimes downstream of the pile, is qualitatively evaluated with laboratory observations obtained as part of the CROSSTEX experiment. The fluid forcing for the model was determined by the observed free stream flow during CROSSTEX, and thus shows the predicted bed changes that would arise from flow patterns initially over a featureless, flat bed with no scour hole or depositional wedge by the pile. Figure 6 shows two snapshots of the velocity field in the *x-z* plane over a 22 *cm* x 22 *cm* region just offshore (upstream) of the pile. The snapshots occur at the start and end of the 20 *min* experiment. At the beginning of the run, a stagnation point eddy was qualitatively observed at the sediment-pile interface (not shown in the figure). At the equilibrium bed state (which occurred at 26 *min* into the run), the bed has developed ripples and a 3 *cm* scour hole has developed around the upstream side of the pile. This bed change is qualitatively consistent with the predicted bed changes from the model simulations.

In ongoing research conducted by our graduate students, the modeled flow field will be quantitatively evaluated with the CROSSTEX observations in a similar manner as with the horizontal cylindrical experiments (Smith and Foster, 2005). Preliminary results (Figure 7) show that the scour depth*, S*, relative to the vertical pile diameter*, D*, is increases for increasing wave period (T) but is relatively insensitive to wave period or the narrowbandedness of the wave spectrum. The modeled sediment transport will also be evaluated with observations of suspended sediment and seabed elevations obtained by the two-axis variable frequency sonar co-located with the PIV system.

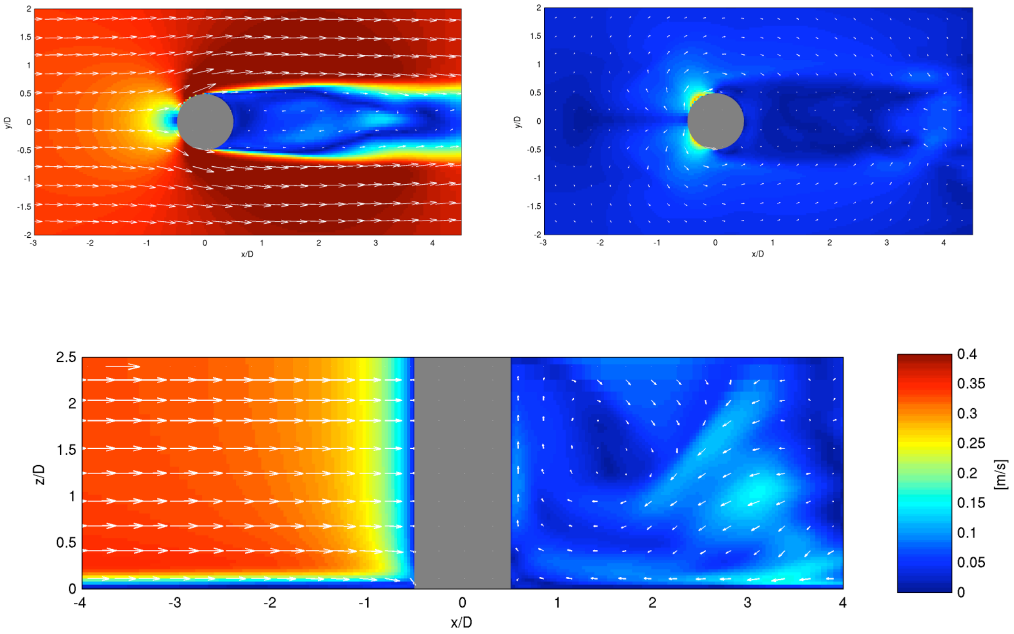


Figure 5. (top panels) Mean of the modeled flow around a vertical pile, viewed from above, and taken at a depth of (right panel) one pile diameter and (left panel) at the bed. (bottom panel) Mean of the modeled flow around a vertical cylinder, viewed from the side at the centerline of the pile. The pile diameter, *D,* is 53.6 *cm*. The along-tank (horizontal axis) and cross-tank (vertical axis) dimensions are scaled by the pipe diameter, D. Flow is traveling from left to right in the figure, with a mean velocity of 32.6 *cm*/*s*. The gray shaded area represents the pile, while the color map indicates the velocity magnitude (*cm*/s). Vectors indicate velocity and are scaled by the single vector appearing in the upper left-hand corner of the image representing a 40 *cm*/*s* velocity.

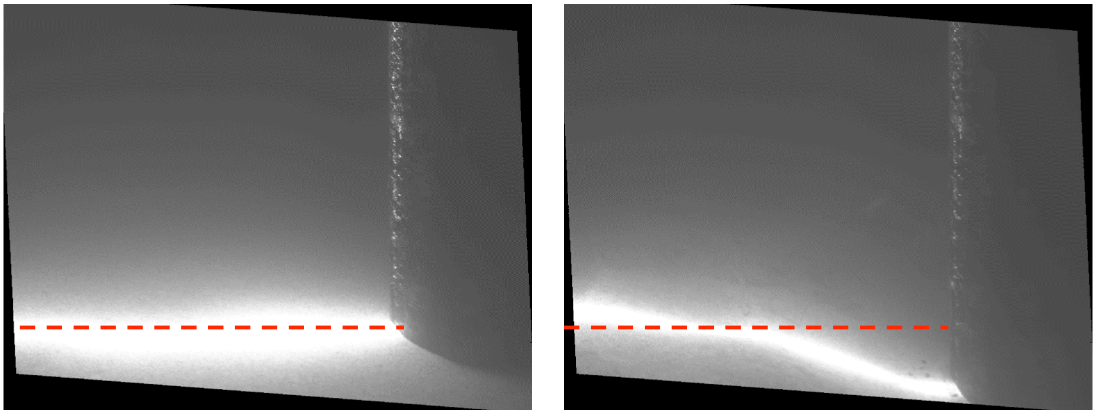


Figure 6. The (right panel) initial and (left panel) final bed profile offshore of a vertical pile as measured with the PIV system during the CROSSTEX experiment. The bed elevation is indicated with the bright light reflected from the bed. The pile is indicated as the dark gray area on the right of each image. The red dashed line indicates the position of the initial bed elevation.

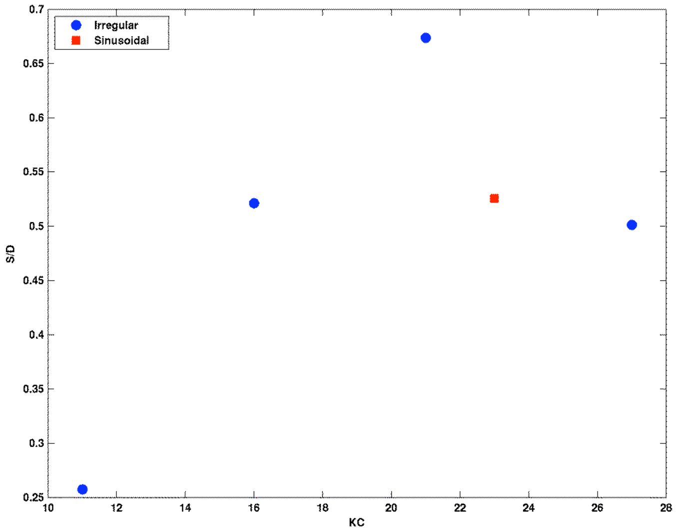


Figure 7. The final scour depth (non-dimensionalized by the pile diameter) versus the Keulagan-Carpenter number, where KC=UT/D.

Field

Figure 8 shows images of our waverunner survey of the Great Miami River at Hamilton obtained on 30 November 2005. Both figures show color contours of the bathymetry, with the left panel showing the survey tracks from the waverunner as well as a walking GPS survey of the river banks. The right figure shows the location of the pier piling edges (as circles) and the locations of cross-river transects where comparisons to a USGS 1999 survey can be done. The elevations of the river banks in the plots are omitted because the high elevation of the banks obscures the details of the subsurface river topography.

The horizontal (x, y) coordinates are in meters relative to our established GPS base position. North is toward the top of each figure. The vertical elevations (given by the color contours defined by the scale on the right-hand-side of the figures) is also in meters relative to the mean waterline elevation observed by the waverunner averaged over the whole survey length. The elevations were transformed in this manner so that the approximate water depths are given. The actual coordinates before transformation are in the ITRF00 reference frame. Note that the cross-river and along-river scales are not the same, with the cross-river scales exaggerated by a factor of 2 for visual clarity.

The survey spans about 1.2 *km* along the river, and was done over 2.5 *hrs* with about 60 cross-river transects spaced every 20 *m*. We were also able to get close to the river's edge owing to the relatively steep banks. The bridge where the Imagenex sonar was deployed (see Figure 4) is located about $y = 200$ *m* in the plot. There is a gap in the tracks where the bridge is located as we were only able to get within about 10 *m* or so of the bridge before the GPS satellites were blocked. The raw survey data were smoothed onto an evenly spaced grid and interpolated beneath the bridge; however, the accuracy of the water depths under the bridge is not known owing to potential largish changes right by the bridge pilings. Techniques are presently being developed that will allow for accurate surveys everywhere beneath the bridges (based on dead-reckoning navigation of along-river waverunner transects).

The river bed topography shows significant variability. For example, about 200 *m* downstream (south) of the bridge there are deep holes (up to 4.5 *m* depths) on the west side of the river, whereas on the east side there is a shallow bar that extends toward the middle as you move downstream. The cross-river gradient is about 1:20 at about $y = 0$ *m*. There also appears to be a shallow bar on the western bank toward the northern end of the survey (about 400 *m* upstream of the bridge) and a general deepening of the river toward the south (about 600 *m* downstream of the bridge).

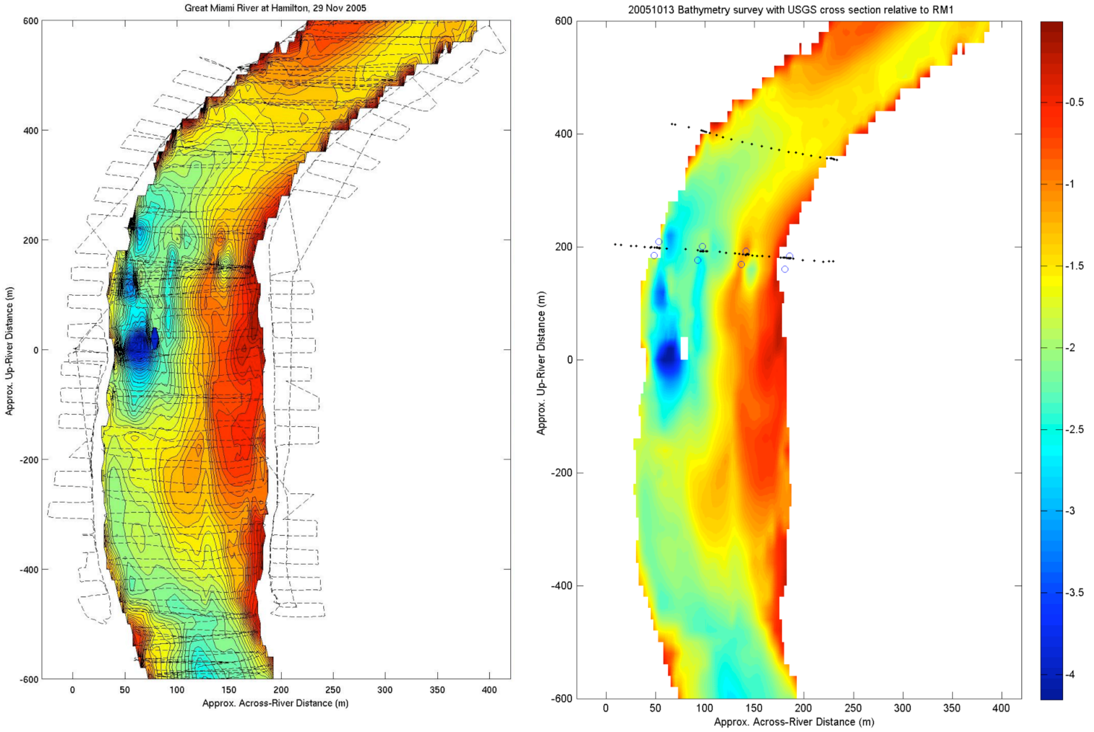


Figure 8. Bathymetric survey of the Great Miami River in Hamilton, OH, conducted on 29 Nov 2005. The depths are shown in meters as color contours relative to the approximate mean water level at the bridge (located at about $y = 200$ *m* in the figure). The horizontal coordinates are in meters relative to our GPS base position. The bridge pilings are shown as circles in the right-hand panel located an across-river distance of approximately $x = 130$ *m*. The survey tracks are shown as dashed black lines in the left panel. 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. The location of cross-river transects compared with USGS surveys (Figure 9) is shown in the right-hand panel.

It would be expected that highly variable flow over the inhomogeneous river topography would result in significant changes in the river morphology over time, with inter annual variability approaching meter scale in some instances. Limited survey data exists to compare with our surveys, particularly of the dense grid scales obtained with our state-of-the-art survey system. Still, in 1999, two cross-river transects were conducted by the USGS. A comparison between these data and our 2005 survey is shown in Figure 9. Owing to uncertainties in the USGS vertical origin, the USGS data is offset 14 *m* vertically in the figures. Although there is some cross-river depth variation observed between 1999 and 2005, the general characteristics of the profile are retained. The general agreement in location of the river banks at the edge of each survey indicates that the vertical offset applied to the USGS data is reasonable, and that changes to the river bed topography have not been substantial. As no surveys were done downstream of the bridge, no comparison to the downstream profiles can be made with the 2005 survey. Plans to resurvey this section of river periodically are under way and a part of ongoing research efforts.

The river bed geometry just upstream of one of the pier pilings was observed with the Imagenex sonar system for about a 2 *hr* period on 30 November 2005. Figure 10 shows sample acoustic slices taken over a 5 *m* radius across the river (left panel) and along the river (right panel). In 4 *m* of water, the images show 1.5-2 *m* of deposition upstream of the pier, with maximum deposition right at the piling. Interestingly, these steady river flow observations with no apparent surface wave energy are in contrast to that observed by the steady flow numerical simulations and laboratory wave flume observations obtained under strong surface wave action. These results suggest that deposition and scour around bridge piles in riverine flow may be significantly altered by the presence of large debris (e.g. trees limbs) hitting the stagnation point on the upstream side of the pier.

In future studies, the numerical model geometries matching the observed field observations will be initialized with observed mean surface flow fields obtained with *in situ* and remote sensing systems deployed concurrently at the field site. This work is part of ongoing research.

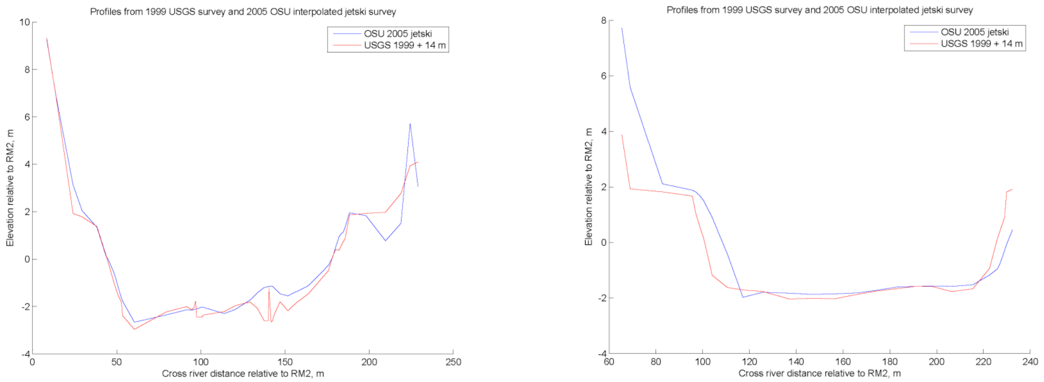


Figure 9. Comparison of 2005 across-river topography obtained by our GPS-based waverunner survey system with a 1999 survey conducted by the USGS. The locations of the transects are shown in Figure 7. Owing to uncertainties in the origin of the USGS survey, the coordinates for the USGS surveys were offset vertically 14 *m* to approximately match that of the waverunner surveys. After adjustment, little change in the river topography upstream of the bridge was observed in the 6 years between surveys. Note that no USGS surveys were done downstream of the bridge so no comparisons with our 2005 survey could be done.

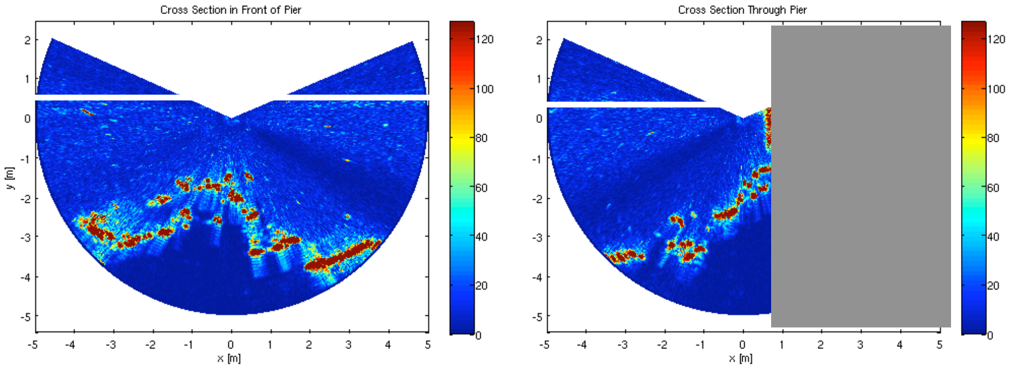


Figure 10. The 5 *m* radius cross sections of local bathymetry obtained in front of and perpendicular to the pier (left) and upstream of and in line with the pier (right). The colors indicate backscatter intensity with hot colors showing the high return of the bottom and the cool colors showing the low return of the water column. The white bands indicate approximate position of the water surface. The gray rectangle indicates the approximate location of the bridge pier. These images show a 2 *m* high deposition present upstream of the bridge pier that is consistent with the waverunner surveys.

Significance

Thus far, we have simulated the response of the fine scale flow field and local morphology around submerged objects in both two- and three-dimensional environments. In the two-dimensional mode, the flow around fixed, scoured bed profiles is simulated and compared favorably with laboratory observations (Smith and Foster, 2005). These results show that the CFD model (FLOW-3D) well captures the complexities of flow very near the bed and around objects placed close to or on the seabed. In addition to clear applications to pipelines and buried or unburied objects on the sea bed, this work sets the groundwork for looking at flows around vertical piles and bridge piers relevant to the present research. In the three-dimensional mode, the flow and scour of sediment beneath a cylindrical object lying on an initially flat bed is simulated and compared with laboratory observations that show excellent agreement in mean flow characteristics (Smith and Foster, 2006). This work demonstrates the capabilities of the numerical model to accurately resolve fine scale flows near obstacles (vertically or horizontally oriented) impinging on bottom topography with arbitrary form and with unconsolidated sedimentary material.

Numerical model results for combined wave-current flow about a vertical pile are in qualitative agreement with prototype laboratory observations, suggesting that the model is well reproducing the essential flow characteristics and sediment transport. In contrast, *in situ* acoustic observations of river topography at a bridge pier located on the Great Miami River (near Hamilton, OH), where wave motions are minimal and river flow is approximately unidirectional and steady, show a distinct region of deposition of sedimentary material just upstream of one of the pier pilings. This qualitative result suggests that deposition and scour around bridge piers in natural rivers can be significantly altered by the presence of large debris.

Ongoing research efforts will utilize *in situ* acoustic observations of the river bed topography evolution, and surface remote sensing techniques to measure the surface flow fields, to initialize and verify the numerical model (verified with laboratory observations) to predict bed changes under a variety of flow conditions.

References

Chopakatla, S. C., T. C. Lippmann, and J. E. Richardson, 2006, Field verification of a CFD model for wave transformation and breaking in the surf zone, *J. Waterw. Port Coast. Ocean Eng.*, sub judice.

FLOW-3D user's manual, 2002, *Flow Science, Inc*., Sante Fe, NM.

Hatton, K.A., D. L. Foster, P. A. Traykovski, P.A., and H. D. Smith, 2006, Scour and Burial of Submerged Mines in Wave Conditions, *IEEE-Journal of Ocean Engineering*, in press.

Hirt, C. W., and B. D. Nichols, 1981, Volume of fluid (VOF) method for the dynamics of free boundaries, *J. Comp. Phys.*, 39, 201-225.

Smith, H. D., and D. L. Foster, D.L., 2005, Modeling the Flow around a Cylinder above Scoured Bed, *ASCE Journal of Waterway, Port, Coastal and Ocean Engineering*, 131(1), 14-24.

Smith, H. D., and D. L. Foster, D.L., 2006, Three-dimensional flow around a bottom mounted short cylinder, *ASCE Journal of Hydraulic Engineering*, in press.

Testik, F. Y., Voropayev, S. I., and Fernando, H. J. S., 2005, Flow around a short horizontal bottom cylinder under steady and oscillatory flows. *Physics of Fluids*.

Publications resulting from this work

Hatton, K.A., D. L. Foster, P. A. Traykovski, P.A., and H. D. Smith, 2006, Scour and Burial of Submerged Mines in Wave Conditions, *IEEE-Journal of Ocean Engineering*, in press.

Smith, H. D., and D. L. Foster, D.L., 2005, Modeling the Flow around a Cylinder above Scoured Bed, *ASCE Journal of Waterway, Port, Coastal and Ocean Engineering*, 131(1), 14-24 (2005).

Abstracts of Work Presented at National and International Meetings

Hatton, K. A., and D. L. Foster, 2004, Scour and Burial of Submerged Mines in Wave Conditions, *Eos Trans. AGU*, 85(47), Ocean Sci. Meet. Suppl., Abstract OS21B-1222.

Foster, D. L., H. D. Smith, and K. H. Hatton, 2004, Modeling the 3-D Flow around a cylinder, *Mine Burial Workshop, Woods Hole Oceanographic Institution, MA*, 2004.

Transport and Fate of Iron Nanoparticles in Groundwater

Basic Information

Title:	Transport and Fate of Iron Nanoparticles in Groundwater
Project Number:	2005OH16B
Start Date:	7/7/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	6th
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, None, None
Descriptors:	iron nanoparticles, TNT, 2,4,6-trinitrotoluene, groundwater
Principal Investigators:	Guy Riefler, Lindsey Sebastian Bryson

Publication

TRANSPORT AND FATE OF IRON NANOPARTICLES IN GROUNDWATER

Guy Riefler and Sebastian Bryson
Department of Civil Engineering
Ohio University

Problem and Research Statement

Groundwater resources provide substantial quantities of drinking water statewide to both municipalities and personal land owners. In Ohio, many streams rely on groundwater baseflow to maintain yearlong sustained flows. Yet, many groundwaters have become contaminated from improper disposal of chemicals, most notably by petroleum products and chlorinated solvents. Extensive research efforts have focused on the remediation of contaminated groundwater, however success has been limited. Some chemicals particularly those resistant to biodegradation and that can be found in pure phase in the subsurface, are difficult to treat in any cost-effective manner. One efficient technology that has been utilized at numerous sites is the installation of permeable barriers constructed with iron filings. As contaminants are transported through the permeable barrier, the metallic iron serves as a strong reductant, reducing the targeted chemicals to less toxic or non-toxic products. This technology is extremely attractive because of its ability to detoxify a broad range of pollutants for an extended period of time. Also iron is inexpensive, non-toxic, and already common in the environment. Unfortunately, use of this technology is limited to sites with relatively shallow, confined contamination where construction costs for installing the barrier are minimized.

A promising new technology involves injecting nanoscale iron particles (i.e. 100 nm to 500 nm) directly into a contaminated aquifer. This techniques has many of the advantages of macroscale iron, with the added flexibility of being able to inject iron to the subsurface at multiple locations and at great depth. Nanoscale iron particles increase reaction rates from 500 to 1000 times that of conventional granular iron filing remediation systems (Wang and Zhang, 1997). Current costs of nanoscale iron particles are $50 per kilogram as opposed to a cost of about $200 per kilogram for iron filings (Glazier et al., 2003). In addition, once injected into the groundwater, nanoscale particles can move with the contaminant plume to treat pollutants away from the injection source. This technology has been documented in the literature at two trichloroethene contaminated sites. Glazier et al. (2003) provided the results of a study performed at an industrial/research facility located in Research Triangle Park, NC. In this study, 1,600 gallons of 1.9 g/L iron nanoparticles were injected into a TCE plume (average concentration of about 14 mg/L) over a period of two days. TCE was completely removed within 20 days near the injection well and within 50 days 7.5 m downgradient. Similarly, Elliott and Zhang (2001) reported a field demonstration performed at a manufacturing site in Trenton, NJ. For this study, nanoscale palladium-coated iron particles were gravity-fed into groundwater contaminated by TCE and other chlorinated aliphatic hydrocarbons. Approximately 1.7 kg of nanoparticles were introduced into the test area over a 2-day period. TCE reduction efficiencies of up to 96 percent were observed over a 4- week monitoring period.

This technology holds great promise for cleaning up contaminated groundwater throughout Ohio. Iron targets a broad range of chemicals and injection can occur over a wide range of site geologies, thus this technology is extremely versatile. Further, it is relatively inexpensive and utilizes non-toxic chemicals. Finally, creative application of this technology may allow for meeting varied site goals including: (1) treatment of dissolved chemicals away from the injection point as the iron nanoparticles transport with the groundwater, (2) targeted treatment of sources zones using direct push injection, (3) creation of stagnant treatment zones if the iron nanoparticles attach to the aquifer materials in significant quantities (Zhang, 2003). Clearly, an understanding of the transport and fate of the nanoparticles in the subsurface is critical information needed for successful implementation of this technology.

Many questions remain about the transport and fate of iron nanoparticles in groundwater. Little is currently known about the attachment rate of these particles to porous media under different chemical conditions and different delivery rates (Lecoaneet and Wiesner, 2004). Further, the persistence and total catalytic capability of these particles under different chemical conditions has not been quantified (Lien and Zhang, 2001). Only through a greater understanding of these mechanisms can this technology be effectively utilized and optimized. Further, greater knowledge of the transport and fate of iron nanoparticles may allow for more creative remediation approaches.

In this research project we assessed the transport and fate of iron nanoparticles through aquifer sediment, by (1) fabrication and characterization of iron nanoparticles, (2) assaying the rate of 2,4,6-trinitrotoluene (TNT) transformation under various conditions, and (3) measurement of the transport of iron nanoparticles in sand columns.

Methodology

Production of Nano-size Zero Valent Iron

Two chemicals, sodium borohydride ($NaBH_4$) and iron (III) chloride ($FeCl_3$) were used to make nano-size zero valent iron (NZVI) in a process called reductive precipitation. Solid $FeCl_3$ was stored in a dessicator to prevent oxidation. 10 mL of $NaBH_4$ (1.6 M) were added dropwise to 10 mL of $FeCl_3$ (1.0 M), and NZVI was formed immediately upon contact in a violent reaction (Li et al, 2003).

$$2FeCl_3 + 6NaBH_4 + 18H_20 \rightarrow 2Fe^0_{(s)} + 6B(OH)_3 + 21H_2 + 6NaCl$$

The mixture was stirred on a magnetic stir plate with a stir bar for 20 minutes to allow the reaction to come to completion, and to allow all gas formed to be released. The iron and supernatant were placed in 15-mL centrifuge vials and centrifuged for 10 minutes at 11,000 rcf. The supernatant was then decanted and discarded while the NZVI was rinsed with ultra pure water purged with N_2 for 10 minutes and centrifuged again. The NZVI was rinsed and centrifuged a total of three times. It was then place in a beaker and dried in an oven at 100˚C under nitrogen for several hours. The particles dried to the walls of the beaker and were scraped off. After the NZVI was removed from the sidewalls, it was stored in a microcosm bottle purged with N_2 and crimped shut with a Wheaton butyl septum cap (Millville, NJ).

Characterization of Nanoparticles

Photos of the nanoparticles were taken with a transmission electron microscope (TEM) and with an S240 scanning electron microscope (SEM), shown in Figures 1 and 2. Photographs from the TEM show individual particles. The magnification on photos (1-2) is 22,800 and 34,390 on photos (3-8). These particles were used in an experiment before photographing them, so they are somewhat, if not entirely oxidized.

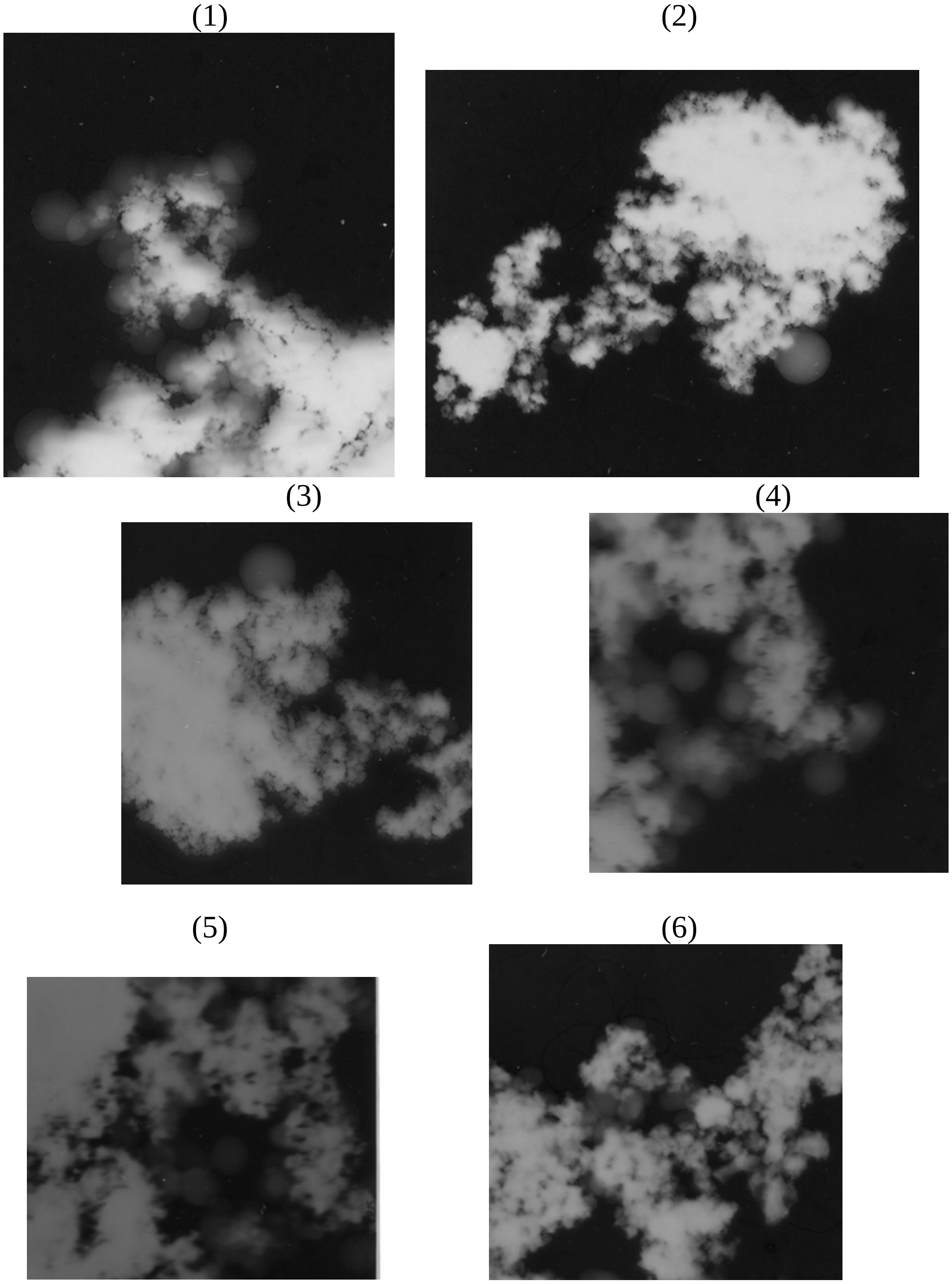


Figure 1: TEM Images of Regenerated NZVI. Photos: 1-2 10 nm = 2.28 mm; photos 3-6: 10 nm = 3.44 mm

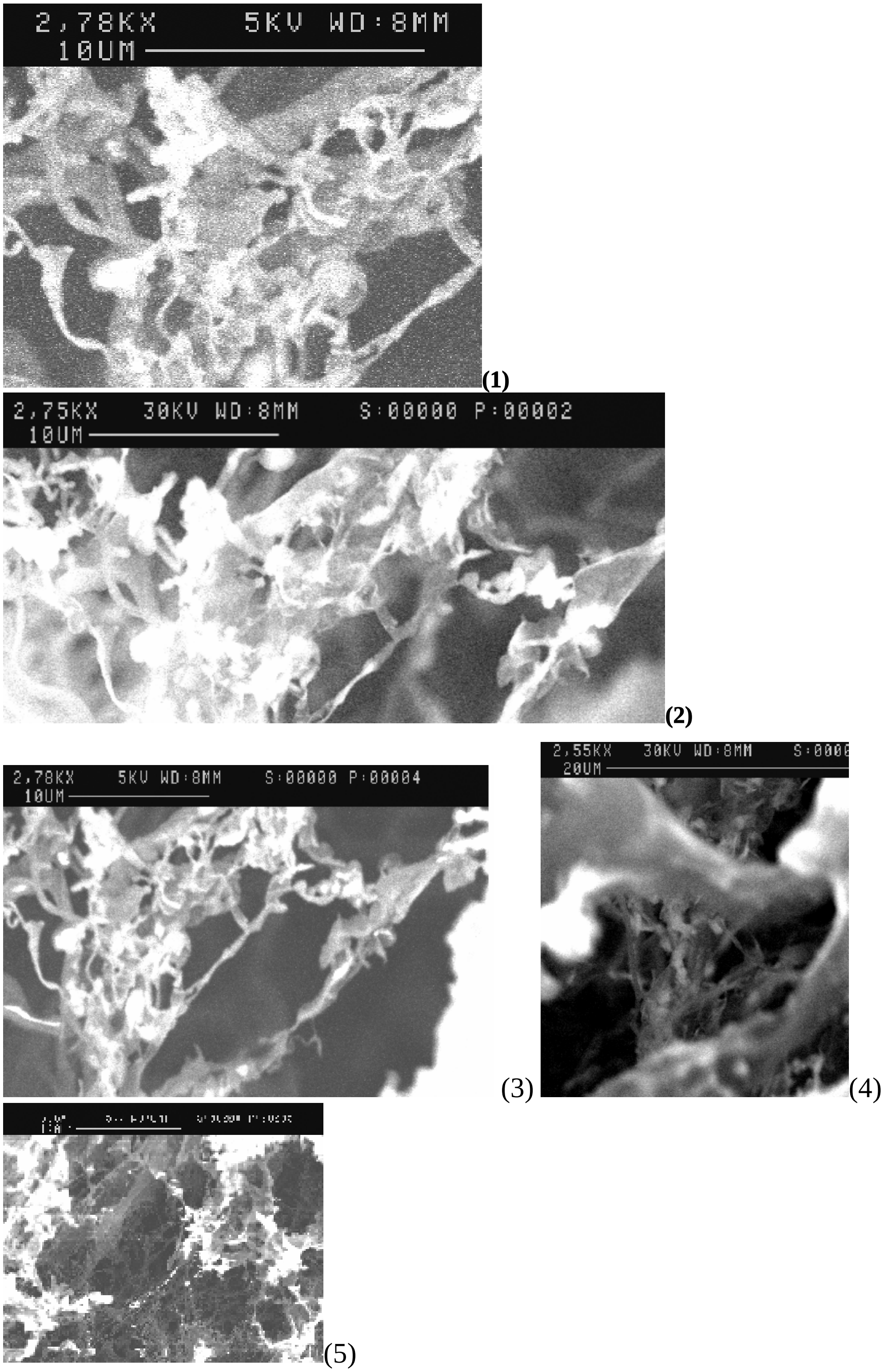


Figure 2: SEM Images of NZVI and 20 nm Silica Spheres

Thus, even though a portion of surface area is probably lost through particle agglomeration, tremendous surface area is retained because of the web-like structure. 20 nm silica spheres appear in white in the SEM photos for scale. These uniform microspheres were purchased from Bangs Laboratories (Fishers, IN).

HPLC Analysis

TNT analysis was done on a Hitachi high performance liquid chromatographer (HPLC), which consists of a Hitachi AS4000 Intelligent Sampler, an L-6200 Intelligent Pump, a D-6000 Interfaces, and an L4500 Diode Array Detector (Tokyo, Japan). A 35% methanol eluent was used in the column (Themo-Hypersil C-18 100mm × 4mm, 3µm particle size). The software used was Hitachi Model D7000 Chromatography Data Station. The monitoring wavelength was 254 nm and the chromatograms were integrated between wavelengths of 240-260 nm.

Preparation of HPLC Standards

In order to identify TNT and its breakdown products by the HPLC, standards of known concentration were prepared. High concentrations of TNT, 2-ADNT, 4-ADNT, 2,4-DANT, and 2,6-DANT were purchased from AccuStandard (New Haven, CT). Standards were prepared in 2-mL HPLC vials in concentrations of 10, 20, and 50 mg/L, diluted with 35% methanol. Each standard was prepared in its own HPLC vial for ease in determining spectra properties and peak times. Standards were refrigerated between uses.

Standards were run on the HPLC for 30 minutes with an eluent of 35% MeOH. A spectra library was developed in order to quickly and easily identify TNT and its degradation products. Each compound has its own spectrum and peak time, which allowed for identification in samples.

Concentrations of samples were determined using calibration curves found with the standards. The standards were of known concentration, and HPLC absorbance units were matched in Excel to these concentrations by plotting the concentration of each standard against the corresponding absorbance unit value. The points were fit to a linear model that was forced through zero. These calibration curves allowed for the determination of TNT and by-product concentrations during experimentation.

Preparation of TNT Stock Solution

A TNT stock solution of approximately 100 mg/L was prepared by combining 100 grams of TNT crystals with 1 L of ultra pure water. The TNT crystals purchased from Chem Service (West Chester, PA) were at most 30% water; pure TNT is not legally commercially available. Actual concentration of the stock solution was unknown until run on the HPLC. The solution was placed on a magnetic stirrer and allowed to mix continuously for several days at room temperature. TNT has a low solubility in water, so it was not used until completely dissolved. Once the TNT had fully dissolved, 100 mL was placed in a microcosm bottle and purged with N_2 for 10 minutes. The 100 mg/L deoxygenated stock solution was used for experiments with the NZVI. Due to its toxicity, the remaining volume of TNT stock solution was kept sealed and continuously stirred under a hood.

Kinetics Experiments

In order to determine removal rates, TNT and iron were combined and samples were taken at regular intervals. As reaction rates became better understood through trial and error, optimal time between sampling and total experiment time was determined. Reaction kinetics were easily monitored when 0.05 grams/L of NZVI was combined with 10 mL of TNT stock solution and tested every five minutes. The temperature for all experiments was 22ºC and the water was at pH 6.

First, 0.05 grams of NZVI was weighed and placed in a microcosm bottle, sealed, and purged with N_2. Then, 10 mL of TNT stock solution was added with a gas-tight syringe, and the bottle was placed on a shaker table at 150 rpm. The first sample was taken immediately after addition of the TNT and afterwards, every 5 minutes for 30 minutes. Sample volumes of 0.5 mL were extracted into a syringe filled with 0.5 mL of 35% methanol to stop the reaction between the NZVI and TNT. Samples were placed into 1.5 mL centrifuge vials and centrifuged for five minutes at 13,000 rpm to separate the nanoparticles from the liquid. Supernatant was then decanted into 2 mL HPLC vials and run on the HPLC. Controls consisting of 0.5 mL of TNT stock solution mixed with 0.5 mL of 35% methanol were run along with the samples.

Kinetics experiments were performed in triplicate. Once concentrations of all samples were determined, they were plotted in Excel. The resulting curve matched a first-order reaction type curve, and the kinetics were determined using a first-order reaction rate equation. The average of the three reaction rate constants was found and used as the final reaction rate constant.

Re-spiked NZVI

In order to determine the useful life of the iron, TNT stock solution was added repeatedly to the same mass of NZVI. Once again, 0.05 grams of NZVI was placed into a microcosm bottle and purged with N_2. 10 mL of TNT stock solution was added and the bottle was placed on a rotary shaker at 150 rpm. Samples were taken at 1 minute and 30 minutes. After 30 minutes, when all TNT had been reduced, an additional 10 mL of stock solution was added. This was sampled immediately and every 10 minutes thereafter for 70 minutes. The samples were then centrifuged and run on the HPLC. After 24 hours, a third 10 mL of stock solution was added and sampled at the same intervals. This procedure was repeated until no further TNT removal was observed.

Efficacy of Oxidized Particles

Groundwater is seldom completely anaerobic, so the efficacy of partially oxidized particles was determined in order to see how effectively partially oxidized particles remove TNT. Water samples with enough oxygen to cause 1%, 2%, 4%, 10%, 15%, and 20% oxidation of iron were added to NZVI. After samples were well mixed and oxidation reactions complete, TNT stock solution was added and samples were collected at 10-minute intervals for 1 hour. Samples were centrifuged and run on the HPLC.

Oxygen requirements for desired degrees of oxidation were determined based on the following equation.

$$4Fe + 3O2 \rightarrow 2Fe_2O_3$$

Oxygen was added to oxidize the selected percentage of total iron present as NZVI. The dissolved oxygen concentration of water in equilibrium with the atmosphere was measured and the amount of air-saturated water required to deliver the desired mass of O_2 determined. This water was then mixed with the anaerobic NZVI solution.

Column Study

A column study was performed to understand how NZVI is transported through the soil and how it interacts with the soil. TNT fate and transport was also studied, as well as the interaction between NZVI and TNT in the soil.

Water from an elevated 5-gallon bucket flowed by gravity upward through a glass column, 300 mm long with a 26 mm internal diameter (see Figure 3). Water was continuously pumped from a 3-gallon reservoir into the bucket at a rate faster than the column flow rate to maintain constant head in the 5-gallong bucket at a drain port.

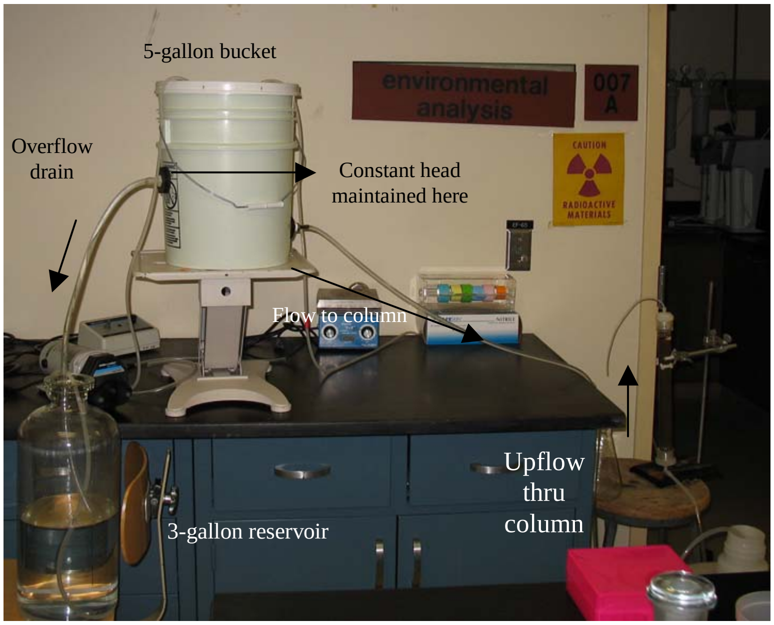


Figure 3: Column Setup

A conservative tracer analysis was performed first to determine the properties of the clean sand in the column. A chloride probe was used with a Denver Instruments Model 225 ph/ISE meter to determine the Cl^- concentration coming through the column. In order to introduce chloride into the column, a NaCl stock solution with 182 mg/L Cl^- was prepared and added to the bucket and the reservoir. The flow to the column was closed and the Cl^- solution circulated until the concentrations in the bucket and reservoir were equal. The flow to the column was then opened and column effluent samples were taken every two minutes for 90 minutes, or until the concentration stabilized. This was repeated three times and chloride tracer curves were obtained. Between each run, the column was flushed with ultra pure water for several hours to allow residual Cl^- to be removed.

To understand the properties of TNT in the column, a TNT solution was added and monitored. Flow to the column was closed and then 100 mg/L TNT was added to the reservoir and the bucket and left to equilibrate for several hours. Once the concentrations in the bucket and reservoir were equivalent, flow was opened to the column and samples were collected every 2 minutes for 90 minutes. Effluent samples were collected in 0.5 mL volumes and combined with 0.5 mL of 70% MeOH and then run on the HPLC.

In order to study the behavior of NZVI in soil, a 5 g/L slurry was injected into the base of the column through a silicone tube. Changes in iron concentration were monitored using absorption spectrophotometry.

A Perkin-Elmer AAnalyst 300 atomic absorption spectrophotometer (Norwalk, CT) was used to determine the concentration of iron in the column effluent. 25 mL standards were made from a Fisher Scientific iron reference standard (Fair Lawn, NJ) in concentrations of 5, 10, and 20 mg/L. An air-acetylene flame was used for analysis with a Perkin-Elmer Intensitron Hollow Cathode Lamp (Norwalk, CT). Calibration of the three standards resulted in a correlation coefficient (R^2) value of 0.999.

Samples were collected from the column effluent every two minutes for several hours. They were diluted 100× by taking 100 µL of effluent and adding it to 9.9 mL of ultrapure water. The samples were then run on the AA until the iron concentration stabilized.

Principal Findings

Reaction between TNT and NZVI

Combination of 10 mL 75 mg/L TNT and 0.05 g of NZVI under anaerobic conditions results in the complete removal of TNT from water in less than 30 minutes. The TNT stock solution had a pH of about 7 and all experiments were performed at room temperature, 22°C. The curve formed from data collected shows a pseudo first-order reaction. Pseudo first-order kinetics were determined from this curve. Figures 4 and 5 show the TNT removal curves and corresponding pseudo first-order fits. The equation used in first-order kinetics was:

$$\frac{dC_{TNT}}{dt} = -k_1 C_{TNT} \tag{1}$$

where k_1 = TNT degradation rate constant, t^{-1}

The assumption with this model is that the concentration of the TNT is the only factor controlling the reaction and that the NZVI is in excess. For the five replicates, k_1 values varied from -0.135 to –0.304 min^{-1} with an average value of -0.216 $^{+}/_{-}$ 0.074.

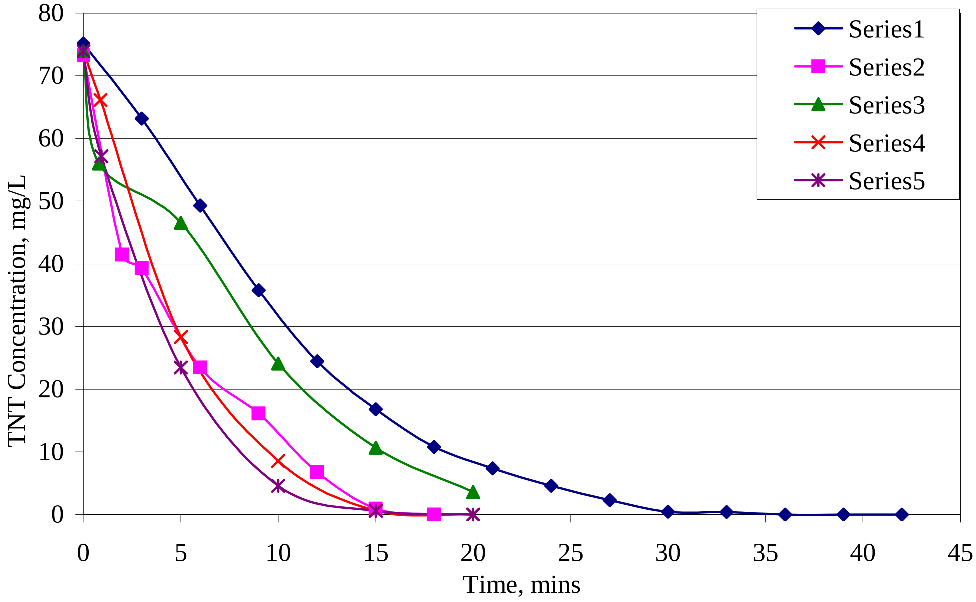


Figure 4: TNT Removal by NZVI

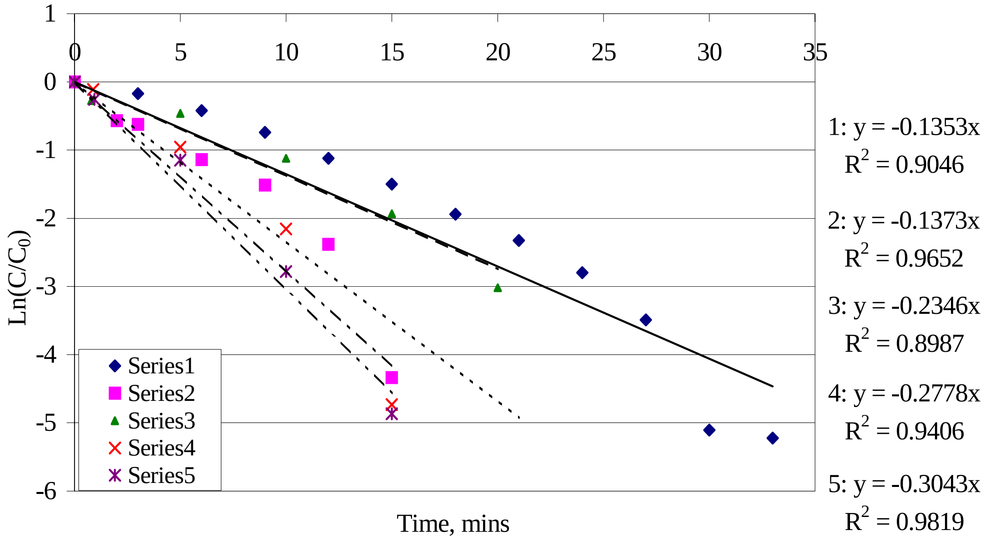


Figure 5: Pseudo First-order Kinetics of TNT Removal by NZVI

TNT degradation product formation was monitored along with TNT removal. Within 6 minutes of TNT exposure to NZVI, degradation is evident. Figure 6 shows the mass balance of TNT, 2-ADNT, 4-ADNT, 2,4-DANT, and 2,6-DANT for Series 1 on Figure 5. There is also a cumulative concentration curve shown. The mass balance is incomplete, and it is presumed that the missing mass is either in the form of TAT or azoxy dimers, both of which are highly unstable and therefore not monitored.

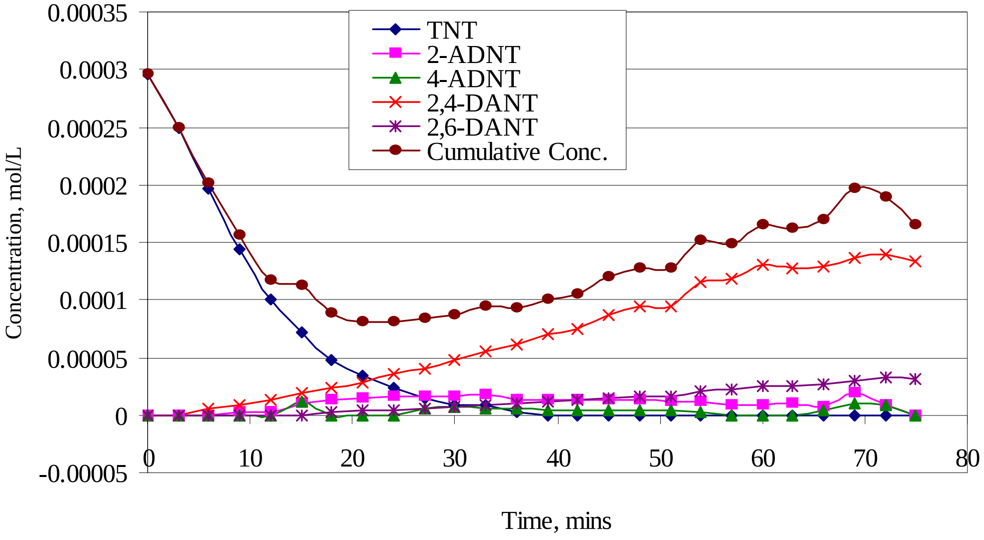


Figure 6: TNT and Degradation Products

Re-spiked NZVI

In order to determine the useful lifetime of TNT in in situ applications, a mass of NZVI was spiked repeatedly with TNT until transformation ceased. The data were then fit to both pseudo first-order and second-order reaction rate equations. Figure 7 shows the decrease in TNT removal rates as the NZVI becomes increasingly oxidized. Seven spikings of 10 mL of 80 mg TNT/L each were required to render 0.050 g NZVI ineffective. These data were analyzed using a model that assumes second-order kinetics with linked TNT reduction and NZVI oxidation:

Figure 8 shows the second-order model and the data from the re-spiked NZVI experiment. The solid lines represent the model while the points represent the actual experimental removal. The model was designed with the following equations.

$$\frac{dC_{TNT}}{dt} = -k_2 C_{TNT} C_{NZVI} \qquad (2)$$

$$\frac{dC_{NZVI}}{dt} = -k_3 \frac{dC_{TNT}}{dt} \qquad (3)$$

where k_2 = TNT degradation rate constant, t^{-1} and k_3 = Fe oxidation rate constant, t^{-1}.

The model and the data match reasonably well. As the iron is oxidized, its available surface area for oxidation decreases, decreasing the rate of TNT transformation. For this model, the value used for k_2 was determined independently from the pseudo first-order kinetics described earlier and was set equal to k_1. Only the value for k_3 was varied to fit the data. All of the curves were simultaneously fit to a single parameter set. That the model fits well suggests that the reaction behaves pseudo first-order initially and then second-order afterwards. That is, the NZVI is in excess for a period of time, but then as the degree of oxidation increases, the concentration of the NZVI that is not oxidized limits the rate of transformation.

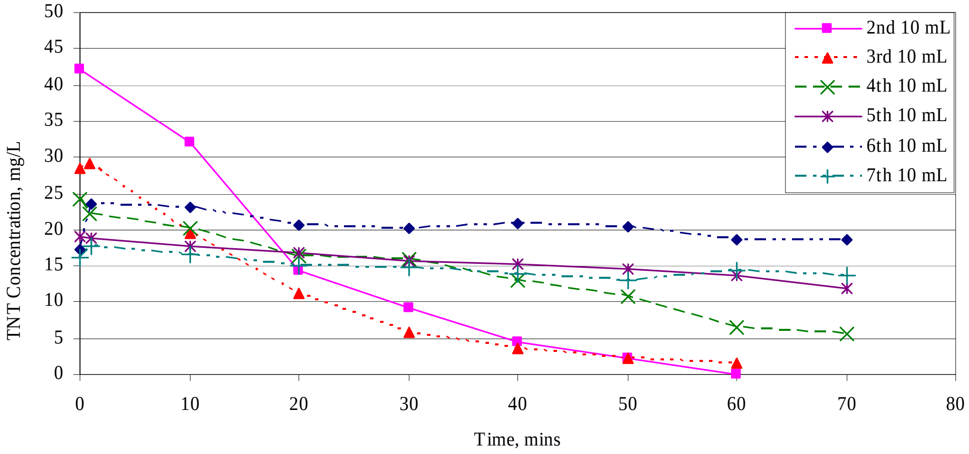


Figure 7: NZVI Spiked with TNT Multiple Times

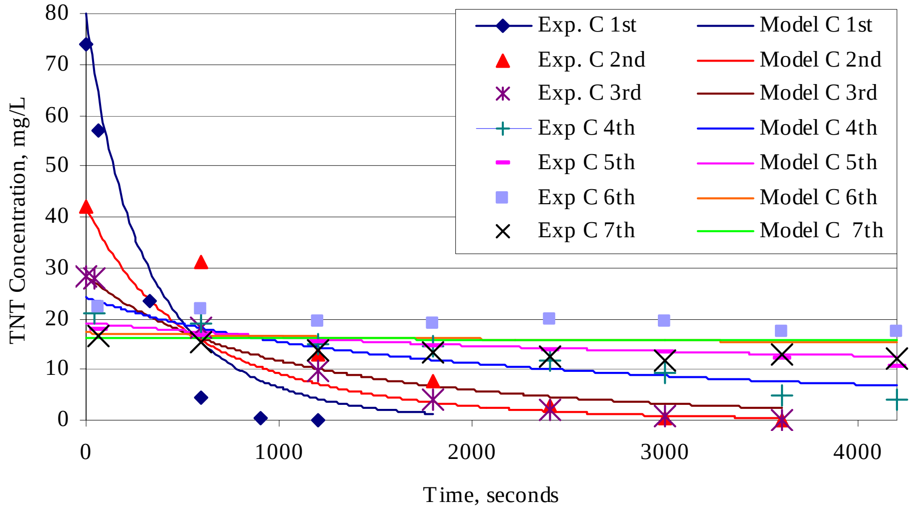


Figure 8: Second-order Kinetics Model

When both k_2 and k_3 are varied within the model, the sum square error (SSE) value changes only 7.4%, and the value for k_2 changes from -0.216 min^{-1} to -0.254 min^{-1}. The values for k_3 change only slightly also, from -0.348 min^{-1} to -0.348 min^{-1}.

Efficacy of Oxidized Particles

Figure 9 shows the effect of NZVI oxidation on TNT removal. Degrees of oxidation as low as 4% appear to have a significant effect on TNT transformation. Pseudo first-order fits to the kinetic assays are shown in Figure 10 and results are reported in Table 1. These compare with a fully reduced k_1 value of -0.216 min^{-1}. Even with only 1-2% oxidation, dramatic decreases in activity are observed. 4% and above behave similarly with near complete inactivation of NZVI. These results indicate NZVI is highly sensitive to oxidation. The minimum amount of oxygen to effectively inactivate 1 gram of NZVI is 26.9 mg O_2.

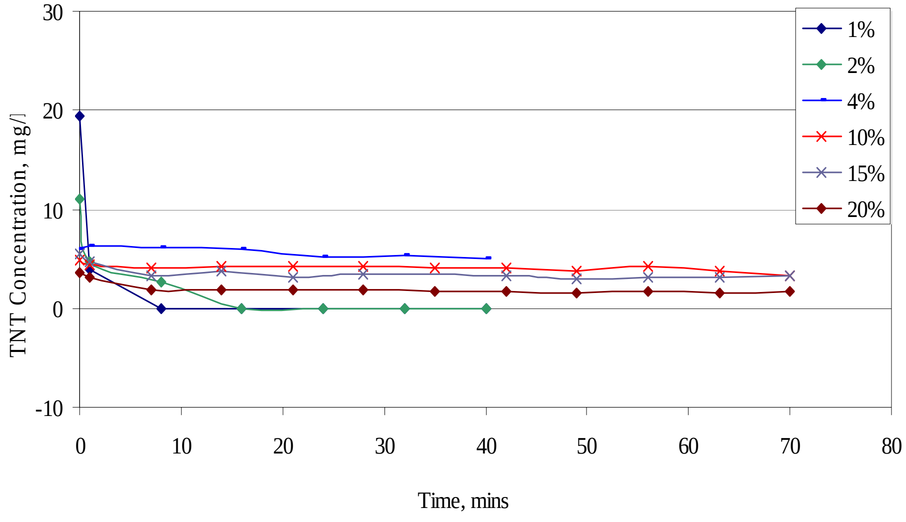


Figure 9: TNT Removal at Various ZNVI Oxidation Stages

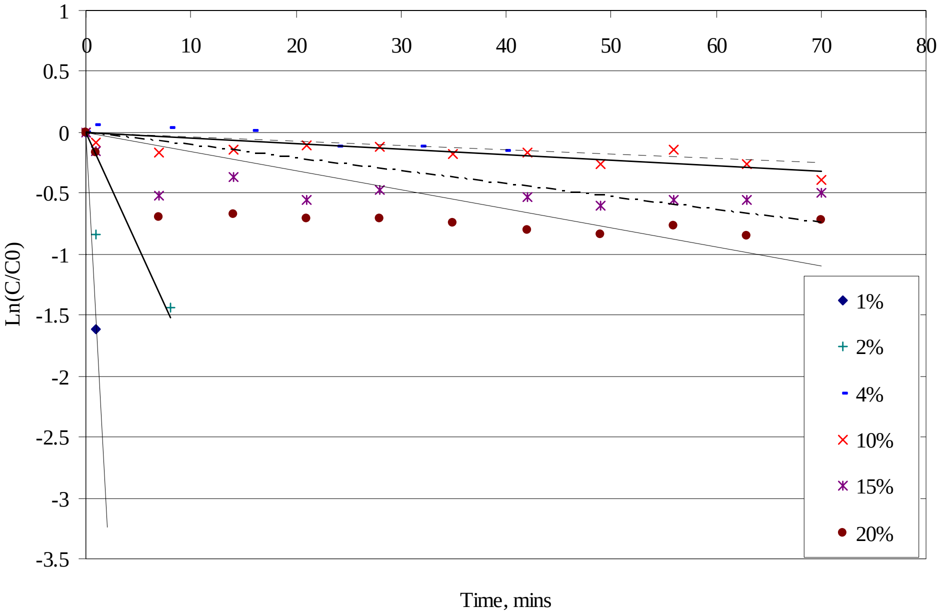


Figure 10: First-order Removal of Oxidized NZVI

Table 1: NZVI k Values

% Oxidation	k, min^{-1}	R^2
1	-1.6195	1
2	-0.1905	0.5985
4	-0.0036	0.7011
10	-0.0046	0.5329
15	-0.0106	0.3628
20	-0.0157	0.2733

Activities after oxygen oxidation were compared to activities after TNT oxidation. TNT reduction assays from repeated spikings were fit with a pseudo first-order model (Equation 1) and results are reported in Table 4. Also reported are values of iron concentration remaining at the beginning of each spiking as determined from the second order model (Equations 2 and 3). This model accounts for iron oxidation due to TNT reduction and is analogous to the iron oxidation from oxygen exposure.

Table 2: NZVI k Values

Spiking #	% NZVI, Available	$k_{1,}$ min^{-1}	R^2	% NZVI, Oxidized
1	100	-0.2203	1	0
2	54.09	-0.0556	0.9798	45.91
3	29.85	-0.0507	0.994	70.15
4	14.59	-0.0192	0.9436	85.41
5	4.560	-0.0061	0.9711	95.44
6	1.06	0.0028	-1.6692	98.94
7	0.223	-0.0029	0.7305	99.77

Column Study

The behavior of NZVI, TNT, and their interaction within soil has importance for in situ applications. Figure 11 shows three chloride breakthrough curves used to understand behavior of flow through the column. In these experiments, inflow to the column initially had zero chloride and at t = 0, chloride was added continuously to the influent. Source concentrations of chloride were between 29 and 39 mg/L. This figure shows a consistent 95% Cl^- breakthrough between 15 and 19 minutes and an average of $17^{+}/_{-}2$ minutes. This is important to understand because Cl- is conservative, that is, it will not react with soil and is thus not expected to adsorb. Should TNT or NZVI adsorb to soil, it will be evident if the breakthrough is greater than 17 minutes.

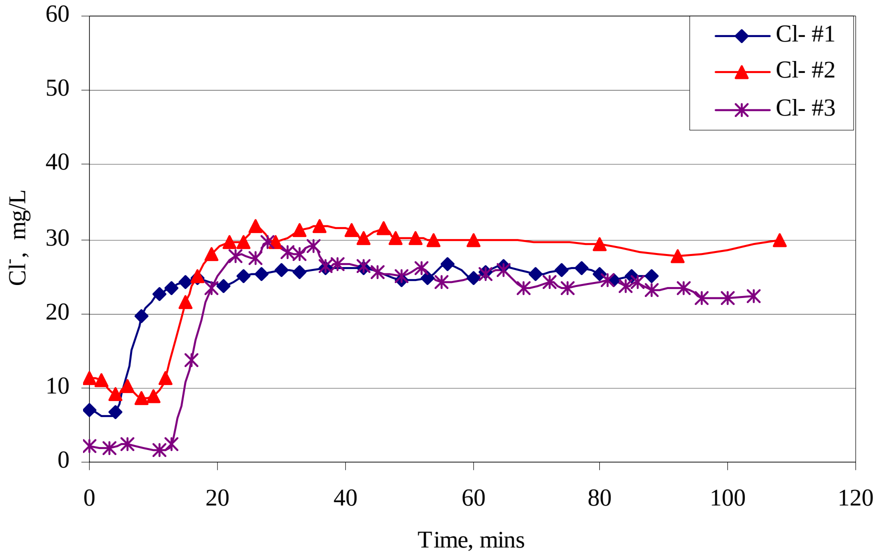


Figure 11: Chloride in Column

Figure 12 shows TNT breakthrough curves. In this experiment, inflow to the column initially had zero TNT and at t = 0, TNT was added continuously to the influent at concentrations between 7-9 mg/L. The time of TNT 95% breakthrough, 18 minutes, corresponds well to the time of Cl- breakthrough, suggesting that adsorption on to the soil medium is not a factor. However, it is evident from the difference between the source and effluent concentrations that not all TNT introduced actually flows through, since no metabolites were detected. This may indicate that the TNT does encounter some adsorption during its flow through the column.

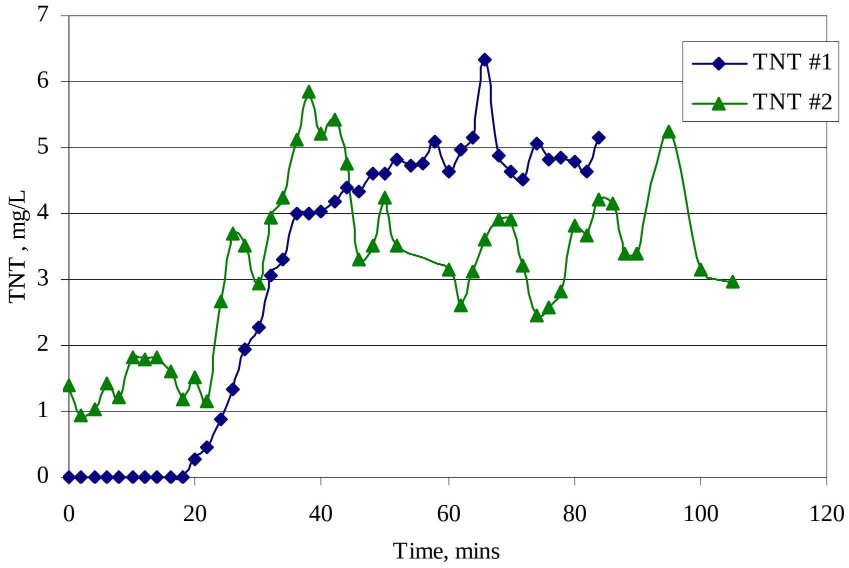


Figure 12: TNT in Column

This experiment involved adding 50 mg of NZVI to the column by spiking it at t = 0. Initial NZVI slurry was 5 g/L; 10 mL were added. Figure 13 suggests the same fate for NZVI as for TNT: breakthrough is around 20 minutes, but the concentration injected was several magnitudes greater than that in the effluent. The concentration of NZVI introduced into the column was approximately 5 g/L, while the maximum effluent concentration from the column was just below 160 mg/L. The actual concentration introduced is never reflected in the effluent concentration. This suggests significant adsorption of NZVI to the clean sand and poor transport through the column. The NZVI injected appears to act as a continuous source of low concentration NZVI far beyond the expected breakthrough time. The NZVI concentration did not approach 0 mg/L until more than 12 hours after injection.

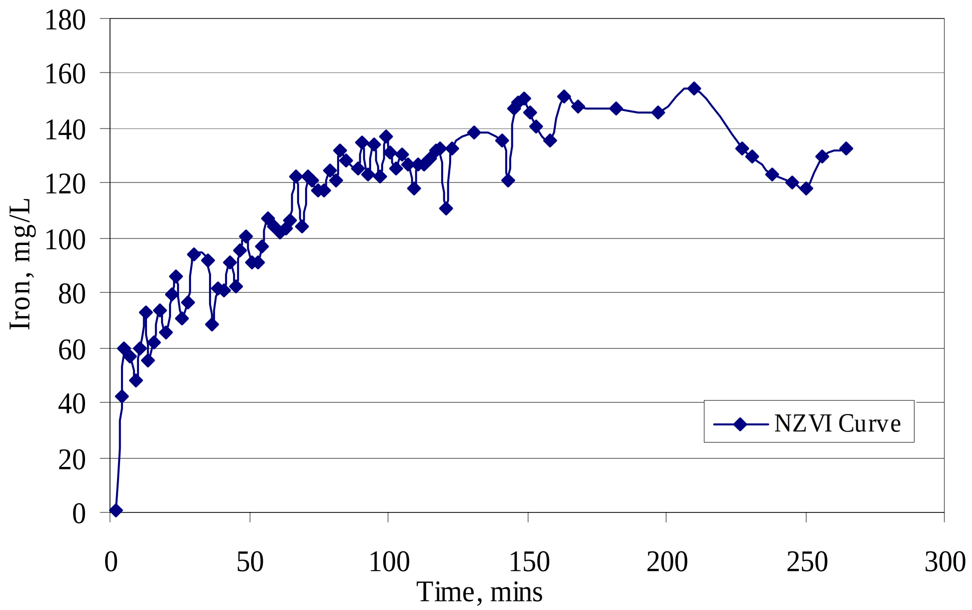


Figure 13: NZVI in Column

Significance

Use of NZVI for TNT remediation is a very promising technology. NZVI is affordable, easily made, and is appropriate for *in situ* applications. TNT is quickly transformed to its degradation products, 2,4-DANT and 2,6-DANT, which are less toxic and biodegradable, unlike the parent compound. This technology can help make contaminated areas safe for development and increase the volumes of clean water available. Further, it does not require disposal of degradation products or spent NZVI, making the overall process more attractive. Only 5 g of NZVI are needed to transform 1 L of 100 mg/L TNT.

There are some drawbacks, however. Once produced, NZVI agglomerates and must be kept agitated to prevent settling. Dried particles must be crushed to a fine powder before use. The particles are highly sensitive to oxidation and can be completely inactivated at 4% oxidation. The mass of O_2 required to oxidize 1 gram of NZVI is only 26.86 mg. Oxygen present in groundwater will likely have a detrimental impact on remediation efforts. It is therefore advisable to verify anoxic groundwater conditions if at all feasible before introduction of NZVI.

NZVI and TNT combined follow second-order kinetics. Reaction rate constants k_2 and k_3 were -0.216 min^{-1} and -0.348 min^{-1}, respectively. The required mass of NZVI for *in situ* applications is likely much higher than the value reported above, due to both oxidation rates of NZVI and high degrees of adsorption in soil. The recommended minimum mass of NZVI to transform 1 L 100 mg/L of TNT *in situ* is therefore 100 mg.

References

Bandstra, Joel Z., Rosemarie Miehr, Richard L. Johnson, and Paul G. Tratnyek. 2005. Reduction of 2,4,6-Trinitrotoluene by Iron Metal: Kinetic Controls on Product Distributions in Batch Experiments. *Environmental Science and Technology*, Volume 29, pp 230-238.

Choe, S., Lee, S., Chang, Y. Hwang, K., and Khim, J. 2001. Rapid reductive destruction of hazardous organic compounds by nanoscale Fe^0. *Chemosphere* 42:367-372.

Elliott, Daniel W. and Wei-Xian Zhang. 2001. Field Assessment of Nanoscale Bimetallic Particles for Groundwater Treatment. *Environmental Science and Technology*, Volume 35, pp 4922-4926.

Glazier, R., Venkatakrishnan, R., Gheorghiu, F., Wlata, L., Nash, R., and Zhang, W.. 2003. Nanotechnology takes root. *Civil Engineering* 73(5), 64-69.

Hundal, L.S., Singh, J., Bier, E.L., Shea, P.J., Comfort, S.D., and Powers, W.L. 1997. Removal of TNT an RDX from water and soil using iron metal. *Environmental Pollution*. 97(1-2):55-64.

Johnson, R. L., P.G. Tratnyek, R. Miehr, R.B. Thomas, and J.Z. Bandstra. 2005. *Ground Water Monitoring & Remediation*, Volumne 25 No. 1, pp 129-136.

Lecoanet, Helene F. and Mark R. Wiesner. 2004. Velocity Effects on Fullerene and Oxide Nanoparticle Deposition in Porous Media. *Environmental Science and Technology*, Volume 38, pp 4277-4382.

Li, Fang, Cumaraswamy Vipulanandan, Kishore K. Mohanty. 2003. Microemulsion and Solution Approaches to Nanoparticle Iron Production for Degradation of Trichloroethylene. *Colloids and Surfaces A: Physiochemical Engineering Aspects*, Volume 223, pp 103-112.

Lien, H. and Zhang, W. 2001. Nanoscale iron particles for complete reduction of chlorinated ethenes. *Colloids and Surfaces A* 191:97-105.

Moore, A.M., De Leon, C.H., Young, T.M. 2003. Rate and extent of aqueous perchlorate removal by iron surfaces. *Environmental Science and Technology* 37(14):3189-3198.

Rodgers, James D and Nigel J. Bunce. 2001. Review Paper: Treatment Methods for the Remediation of Nitroaromatic Explosives. *Water Resources*, Volume 35, No 9, pp 2101-2111.

Schrick, Bettina, Bianca W. Hydutsky, Jennifer L. Blough, and Thomas E. Mallouk. 2004. Delivery Vehicles for Zerovalent Metal Nanoparticles in Soil and Groundwater. *Chemistry of Materials*, Volume 16, pp 2187-2193.

US EPA. 1992. EPA Superfund Record of Decision: Bangor Ordnance Disposal (USNAVY) EPA ID: WA7170027265. OU 01. Bremerton, Washington, 12/10/2001. EPA/ROD/R10-92/037.

US DHHS. 1995. Toxicological Profile for 2,4,6-Trinitrotoluene. U.S. Department of Health and Human Services Agency for Toxic Substances and Disease Registry.

Wang, C. and Zhang, W. 1997. Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. *Environmental Science and Technology* 31:2154.

Zhang, Wei-Xian. 2003. Nanoscale Iron Particles for Environmental Remediation: An Overview. *Journal of Nanoparticle Research*, Volume 5, pp 323-332.

Manipulating residence time in agricultural headwater streams: impacts on nitrogen removal and aquatic communities

Basic Information

Title:	Manipulating residence time in agricultural headwater streams: impacts on nitrogen removal and aquatic communities
Project Number:	2005OH21B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	15
Research Category:	Water Quality
Focus Category:	Nitrate Contamination, Water Quality, Agriculture
Descriptors:	
Principal Investigators:	Virginie Bouchard

Publication

1. Herrman, K.S., Bouchard, V., Moore, R.H. Transport and removal of nitrates in agricultural headwater streams. Ohio Academy of Science 115th Annual Meeting, Dayton Ohio, April 21-23 2006. Oral presentation.
2. Herrman, K., Bouchard, V., Moore, R. Transport and removal of nitrate in agricultural headwater streams. USDA National Water Quality Meeting, San Antonio, Texas, February 5-9 2006. Poster.

Effects of Residence Time on Nitrogen Removal in Agricultural Headwater Streams

Virginie Bouchard and Kyle S. Herrman
School of Environment and Natural Resources
The Ohio State University

Problem and Research Objectives

The main objective of our study was to examine the effects of residence time on nitrogen removal via denitrification in headwater streams. We focused our attention in an agricultural watershed in Northeastern Ohio, severely impacted by nitrogen loading. Our study system, the Upper Sugar Creek Watershed, is indeed heavily impaired due to agricultural activity; land use in the watershed is roughly 90% agriculture (OEPA, 2002). Unfortunately, the majority of land within this watershed is privately owned. This made locating land owners that would allow us to artificially manipulate agricultural drainage – as originally planned – on their property difficult. Instead of manipulating the residence time within headwater streams, we located headwater streams that naturally have varying residence times. Within the Upper Sugar Creek Watershed we identified five headwater streams. Along each stream, we located one reach in agricultural/urban land use and one reach in forested land use. By selecting these specific reach types we expected to observe a wide range of residence times. At all our reaches, hydrology, water quality, sediment, and denitrification data were measured over 3 seasons (Summer and Fall, 2005 and Spring 2006) to determine if residence time significantly affects nitrogen removal.

Methodology

Each stream reach consisted of 50 meters of stream length and along each study reach there were no stream or tile inputs. Discharge was calculated using the 6/10 depth method and velocity was measured with a SonTek FlowTracker Handheld Acoustic Doppler Velocimeter. In order to measure residence time, we used slug injections of Rhodamine WT. Injections were made at the top of the each reach and the concentration of Rhodamine WT was measured at the bottom on each reach *in situ* with a YSI 6600 equipped with a Rhodamine probe. Using the time-concentration profiles collected in the field and equations from Fischer (1968), we measured the average time required for an aqueous contaminant to travel 50 meters (i.e., residence time).

Water samples were collected in the field and stored at 4°C. Once in the laboratory, water samples were analyzed for nitrate (NO_3^-) with a Lachat QuikChem 8500 after being filtered through a 0.45 µm membrane filter. The top 3 cm of sediments were collected at 4 random locations along each 50-meter reach. At each location, one sample was collected to determine the standing stock of ash free dry mass (AFDM) and one sample was collected to use for denitrification assays. All sediments were stored at 4°C until processed in the laboratory. Standing stock was calculated on an aerial basis by first measuring the surface area of sediment collected and then determining the AFDM. The AFDM of each sediment sample was assessed by taking the difference in mass of each sediment sample before and after combustion at 550°C. Denitrification rates were measured with the acetylene inhibition method on aggregate sediment slurries from each reach. Slurries yielded rates in units of mg N g AFDM^{-1} hr^{-1} and by multiplying these rates by the standing stock from each reach, denitrification rates were measured in units of mg N m^{-2} hr^{-1}.

To relate denitrification rates to an in-stream nitrogen removal metric we used the following equation from Alexander et al. (2000)

$$-k = \frac{U \cdot h}{C}$$

where –k is the loss rate of NO_3^- due to denitrification per unit time, U is the aerial denitrification rate, h is the water column height, and C is the concentration of NO_3^-. Sediment was also analyzed for total carbon on a CE Instruments NC 2100 Analyzer.

Principal Findings

Total carbon and standing stock were not significantly different ($p = 0.231$ and $p = 0.278$, respectively; Table 1) for agricultural/urban and forested reaches. In addition, NO_3^- concentrations from both reach types were not significantly different ($p = 0.823$; Table 1) and discharge from our reaches were not significantly different as well ($p = 0.782$; Table 1). Also, denitrification rates measured from the agricultural/urban reaches and the forested reaches were not significantly different ($p = 0.958$; Table 1). Because discharge can drastically affect residence time, we compared residence times by running an ANCOVA with discharge as the covariate. We found that the forested sites have a significantly higher residence time than the agricultural/urban sites ($p = 0.034$; Figure 1). Thus, the study sites included in our project did have significantly different residence times.

Table 1. Data obtained from the study sites over 3 field seasons (Summer and Fall, 2005 and Spring 2006). All values are the mean ± 1 standard deviation.

Reach Type	Discharge (m^3 sec^{-1})	NO_3^- (mg N L^{-1})	Total Carbon (%)	Standing Stock (g AFDM m^{-2})	Denitrification Rate (mg N m^{-2} hr^{-1})
	mean ± standard deviation				
Ag/Urban	0.02 ± 0.04	10.9 ± 10.8	3.3 ± 0.6	560 ± 234	4.4 ± 3.8
Forest	0.02 ± 0.03	11.6 ± 10.8	3.7 ± 1.0	638 ± 135	4.3 ± 4.1

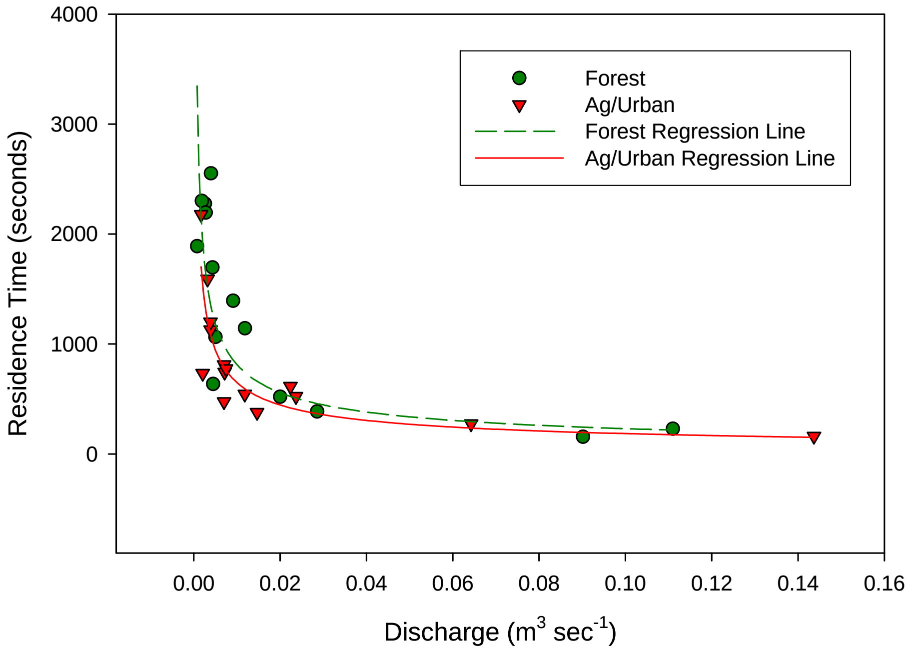


Figure 1. The 50-meter residence time (sec) and discharge (m^3 sec^{-1}) for each reach type. Forested reaches (circle) have a significantly higher residence time than agricultural/urban reaches (triangles) using discharge as a covariate ($p = 0.034$, ANCOVA).

Loss rates of NO_3^- were not significantly different between reach types in any of the 3 sampling seasons ($p = 0.458$, ANOVA; Figure 2). On the other hand, there were significant differences in NO_3^- loss rates between seasons ($p = 0.024$, ANOVA; Figure 2). This finding was expected as temperatures, rain events, and in-stream NO_3^- concentrations do vary seasonally. Residence time has little ability to explain nitrogen removal in these systems ($R^2 = 0.012$, $p = 0.569$; Figure 3). Nitrate concentration in the water column of our headwater reaches does explain a majority of the variation in the nitrogen removal data ($R^2 = 0.603$, $p < 0.001$; Figure 4). Further, the data suggest that our sites are saturated with NO_3^-, limiting the capability of these systems to process NO_3^- (Figure 4). This finding has been found in other agricultural systems as well (Bernot et al., 2006; Davis and Minshall, 1999).

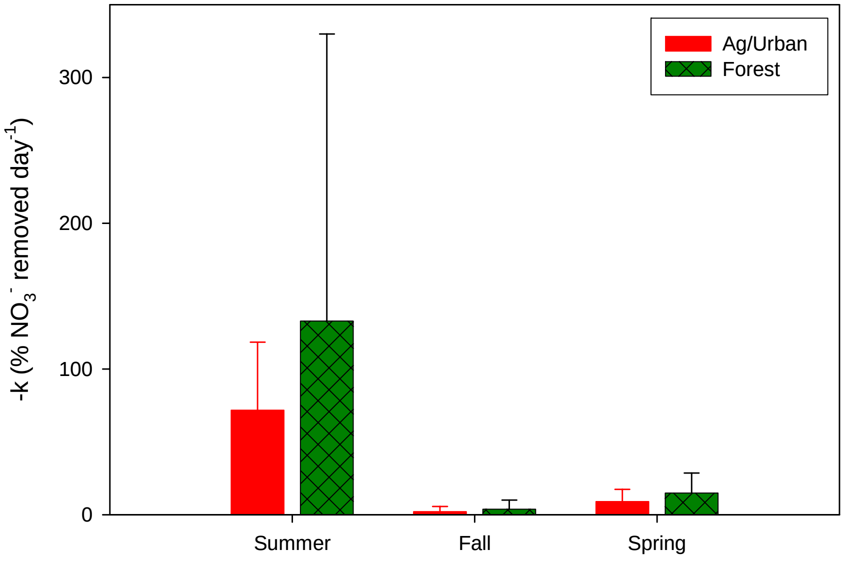


Figure 2. Nitrate loss rates (-k) for the agricultural/urban sites (solid bars) and the forested sites (hashed bars) for the Summer and Fall of 2005 and the Spring of 2006. There are no significant differences between reach types (p = 0.458) but there is a significant seasonal effect (p = 0.024). Error bars are standard deviations.

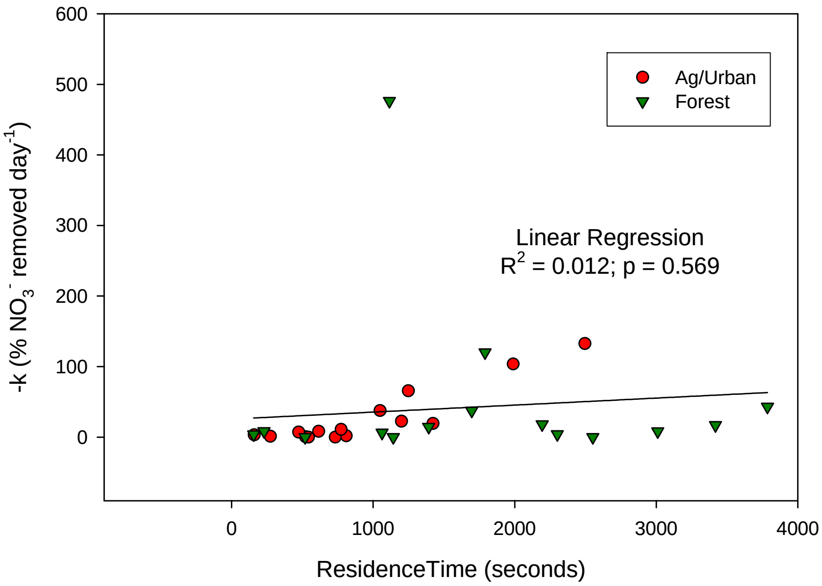


Figure 3. Nitrate loss rate (-k) and residence time (sec) for the agricultural/urban sites (circles) and the forested sites (triangles). The linear regression was run on all sites and was not significant (p = 0.569).

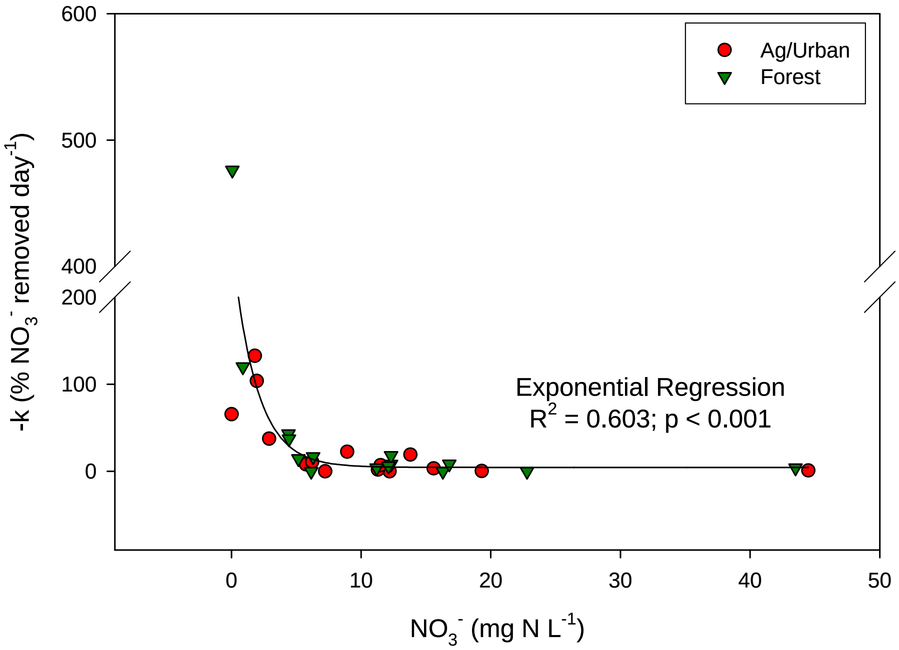


Figure 4. Nitrate loss rate (-k) and the water column NO_3^- concentration (mg N L^{-1}) for the agricultural/urban sites (circles) and the forested sites (triangles). The exponential regression was run on all sites and was significant ($p < 0.001$).

Significance

Our overall objective was to determine the effect of residence time on nitrogen removal via denitrification in agricultural headwater streams. We identified 2 stream reach types (agricultural/urban and forested) with significantly different residence times along 5 headwater streams in the Upper Sugar Creek Watershed. These 2 subsets did not, however, have significantly different nitrogen removal rates. A closer examination of the regression between the NO_3^- loss rate and residence time from the study sites determined that residence time has little ability to explain nitrogen removal. On the other hand, NO_3^- concentrations do explain a large amount of variability in the nitrogen removal data in our study. The data suggest that nitrogen removal is NO_3^- saturated and above concentrations of ~6 mg N L^{-1} these streams have no ability to remove NO_3^-. Although residence time may have some ability to control nitrogen removal in aquatic systems, our streams most likely do not represent a wide enough separation in residence times to show significant differences in nitrogen removal.

References

Alexander, R.B., Smith, R.A., and G.E. Schwarz. 2000. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. Nature 403:758-761.

Bernot, M.J., Tank, J.L., Royer, T.V., and M.B. David. 2006. Nutrient uptake in streams draining agricultural catchments of the Midwestern United States. Freshwater Biology 51:499-509.

Davis, J.C. and G.W. Minshall. 1999. Nitrogen and phosphorus uptake in two Idaho (USA) headwater wilderness streams. Oecologia 119:247-255.

Fischer, H.B. 1968. Dispersion predictions in natural streams. Journal of Sanitation Engineering Division, ASCE 94:927-944.

Ohio EPA. 2002. Total Maximum Daily Loads for the Sugar Creek Basin: Division of Surface Water, Columbus, OH.

USE OF PERSULFATE AND PEROXYMONOSULFATE OXIDANTS FOR THE DESTRUCTION OF GROUNDWATER CONTAMINANTS

Basic Information

Title:	USE OF PERSULFATE AND PEROXYMONOSULFATE OXIDANTS FOR THE DESTRUCTION OF GROUNDWATER CONTAMINANTS
Project Number:	2005OH26B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	01
Research Category:	Engineering
Focus Category:	Treatment, Groundwater, Methods
Descriptors:	Sulfate Radicals, Chlorophenols, PAHs, PCBs
Principal Investigators:	Dionysios Dionysiou

Publication

1. Rastogi Aditya and Dionysios D. Dionysiou*, Iron Mediated Activation of Peroxymonosulfate and Persulfate for Destruction of Chlorophenols. Paper in preparation.
2. Rastogi Aditya*, Souhail R. Al-Abed, and Dionysios D. Dionysiou, Treatment of PAHs and PCBs using sulfate radical based oxidation processes, Accepted for Poster Presentation of the General Papers, Division of Environmental Chemistry, 232nd American Chemical Society (ACS) National Meeting, September 10-14, 2006, San Francisco, California
3. Rastogi Aditya , Souhail Al-Abed, and Dionysios D. Dionysiou*, Destruction of PAHs and PCBs in Water Using Sulfate Radical-Based Catalytic Advanced Oxidation Processes, Accepted for Poster Presentation, 1st European Conference on Environmental Applications of Advanced Oxidation Processes (EAAOP), September 7-9, 2006, Chania, Greece.
4. Rastogi Aditya, Souhail Al-Abed, and Dionysios D. Dionysiou*, Iron-Peroxymonosulfate: A Novel Sulfate Radical Based Advanced Oxidation Technology for Degradation of PCBs. Submitted for Oral Presentation at The 12th International Conference on Advanced Oxidation Technologies for Treatment of Water Air and Soil, Sept. 25-28, 2006, Pittsburgh, Pennsylvania.

Program: **Ohio Water Resource Center; Ohio State University**
Project ID: **2005OH26B**
Title: **Use of Persulfate and Peroxymonosulfate Oxidants for the Destruction of Ground Water Contaminants**
PI: **Dionysios D. Dionysiou, PhD., Associate Professor, Department of Civil and Environmental Engineering, University of Cincinnati**

Summary of Research Accomplishments-Scientific Dissemination of Results

Peer-Reviewed Journal Publications (* denotes corresponding author)

1) Aditya Rastogi and Dionysios D. Dionysiou*, Iron Mediated Activation of Peroxymonosulfate and Persulfate for Destruction of Chlorophenols. Paper in preparation.

Presentations in State, National, and International Conferences (* denotes presenting author)

1) Aditya Rastogi*, Souhail R. Al-Abed, and Dionysios D. Dionysiou, Treatment of PAHs and PCBs using sulfate radical based oxidation processes, Accepted for Poster Presentation of the General Papers, Division of Environmental Chemistry, 232nd American Chemical Society (ACS) National Meeting, September 10-14, 2006, San Francisco, California

2) Aditya Rastogi, Souhail Al-Abed, and Dionysios D. Dionysiou*, Destruction of PAHs and PCBs in Water Using Sulfate Radical-Based Catalytic Advanced Oxidation Processes, Accepted for Poster Presentation, *1st European Conference on Environmental Applications of Advanced Oxidation Processes (EAAOP)*, September 7-9, 2006, Chania, Greece.

3) Aditya Rastogi, Souhail Al-Abed, and Dionysios D. Dionysiou*, Iron-Peroxymonosulfate: A Novel Sulfate Radical Based Advanced Oxidation Technology for Degradation of PCBs. Submitted for Oral Presentation at *The 12th International Conference on Advanced Oxidation Technologies for Treatment of Water Air and Soil*, Sept. 25-28, 2006, Pittsburgh, Pennsylvania.

Summary

This study investigates the fundamentals and applications of novel advanced oxidation technologies (AOTs) for ground water treatment. This new class of AOTs involves iron (Fe (II), Fe (III)) or hydrogen peroxide (H_2O_2) based activation of peroxymonosulfate (PMS) or persulfate (PS) to generate sulfate and hydroxyl radicals. These radicals are extremely reactive and readily attack organic contaminants present in groundwater.

Among the three AOTs evaluated during the study, Fe (II)-PMS system was found to be most effective in the removal of a model contaminant (4-chlorophenol) in short term studies lasting 4 hrs. The Fe (II)-PMS process was optimized with respect to Fe (II) and PMS molar concentrations. The performance of the proposed catalytic systems was also tested for long term degradation of 4-chlorophenol and was compared to other established AOTs like Fenton reagent. The Fe (II) – PS based catalytic system showed maximum TOC removal with significant residual oxidant at the end of 8 days. The stable nature of oxidant will give new direction to the development of the modern AOTs that can act for much longer time even after the application of oxidants.

AOTs using soluble iron as catalyst have been widely reported to suffer from the problem of iron precipitation. In the work presented here, approaches adopted to prevent iron precipitation included use of citric acid as a chelating agent for iron, phosphate buffer to maintain low pH and thiosulfate-oxidant redox couple to maintain iron in the soluble Fe (II) state in the solution. The use of citric acid showed improved process efficiencies and the optimum concentration of citric acid was determined in Fe (II)-PMS, Fe (II)-PS based catalytic systems. Systems employing thiosulfate-oxidant redox couple showed complete absence of precipitation but reduced contaminant removal efficiencies. The use of phosphate buffer led to a precipitate different from that observed in unbuffered systems and lower process efficiencies.

The catalytic systems were also tested for chlorophenols with increasing degree of chlorination and with other priority contaminants like PCBs and PAHs with widely different structures and properties.

Introduction

Organic contaminants in ground water pose serious threat to the ecosystem due to their toxic nature and harmful effect on human and animals. Examples of such chemicals include chlorinated aromatics, polycyclic aromatic hydrocarbons (PAHs), pesticides, herbicides, endocrine disrupting chemicals (EDCs), toxins, and warfare agents. Many of such organic pollutants are regulated by the USEPA, and their removal from the contaminated water is of high priority. Consequently, the need for efficient treatment of these contaminants is imperative. In particular, for groundwater treatment, such technologies must be efficient for the *in-situ* treatment of contaminants since pump-and-treat remedial strategies are usually very expensive. In addition, *in-situ* biological processes are not always applicable for many groundwater contaminants because of their high toxicity *[1-4]*.

Chemical oxidation is a treatment technology that has the potential to completely destroy harmful non-biodegradable and biocidal organic contaminants in water. The so-called Advanced Oxidation Technologies (AOTs) are among the most effective chemical oxidation processes and play a crucial role in water treatment. In AOTs, the reactions follow a specific oxidation pathway, which, in most of the cases, includes the formation of free hydroxyl radicals. The hydroxyl radicals are extremely reactive and readily attack organic molecules. The final products formed are carbon dioxide, water and, depending upon the precursor chemical composition, other ionic inorganic residues such as chloride. The process of the complete oxidation of the parent contaminants is called "mineralization" and is a feasible outcome at optimum conditions of most AOTs. Typical examples of AOTs include ozonation, UV/H_2O_2, sonolysis, the Fenton Reagent (Fe^{2+}/H_2O_2), Fenton-like reactions (Fe^{3+}/H_2O_2 with and without UV-light irradiation), electron beams and γ-irradiation and TiO_2-photocatalysis *[4-6]*. However, for groundwater applications, only certain AOTs are applicable. These include the dark Fenton Reagent and other dark-based AOTs, such as the systems proposed in this study.

One of the most established homogeneous AOTs, even at a large scale, is Fenton Reagent. However, for groundwater remediation, this technology faces certain limitations. First, Fe (II) reacts very rapidly with H_2O_2 resulting in the generation of high concentrations of hydroxyl radicals that are not effectively utilized due to their short half-life. Second, the highly unstable nature of H_2O_2 leaves the system without any residual oxidants for post-treatment contamination events. These process limitations can be overcome by replacing H_2O_2 with a more stable oxidant such as persulfate or peroxymonosulfate.

Persulfate has recently been studied as an oxidant alternative for treating organic contaminants in contaminated soil and groundwater *[7]*. Persulfate anions ($S_2O_8^{2-}$) can be thermally or chemically activated by transition metal ions to produce sulfate free radicals ($SO4^{\bullet-}$) which are very powerful oxidants capable of degrading numerous organic contaminants. High aqueous solubility and stability in the subsurface, relatively low cost and benign end products makes persulfate-based oxidation a promising alternative among the advanced oxidation process (AOPs) for remediation of contaminated soil and ground water applications *[8]*.

Peroxymonosulfate (PMS) is used as a powerful oxidant for a wide variety of industrial and consumer applications *[9]*. Peroxymonosulfate often oxidizes faster than hydrogen peroxide and it is slightly more powerful as an oxidant ($E^0_{HSO5^-/HSO4^-}$ = +1.82V; $E^0_{H2O2/H2O}$ = +1.76V) *[10]*. Anipsitakis et al. recently studied the cobalt (Co) based activation of peroxymonosulfate for degradation of chlorophenols (CPs). Co-PMS system was found to be superior than Fenton reagent and showed no pH limitation for degradation of 2, 4-DCP and atrazine *[11]*. However, use of cobalt may adversely affect the quality of environmental systems.

In this study, we evaluated the performance of iron based activation of PMS and PS for the destruction of numerous ground water contaminants namely $Fe^{2+/}$PMS, Fe^{3+}/PMS, Fe^{2+}/PS and Fe^{3+}/PS. Hydrogen peroxide based activation of persulfate and peroxymonosulfate was also studied to develop an alternative advanced oxidation process for contaminant removal. These technologies are based on the generation of hydroxyl and sulfate radicals, which are among the most powerful oxidizing species found in nature. Degradation of series of chlorophenols (4-CP, 2,4-CP,2,4,6-CP, 2,3,4,5-CP), naphthalene (a PAH) and 2-chlorobiphenyl (a PCB) were evaluated using Fe/PMS and Fe/PS system. Further, the iron availability in the solution was manipulated with chelating agents and by utilizing thiosulfate-oxidant redox couples.

Project Objectives

The primary objective of this study was to develop a novel and versatile class of advanced oxidation processes based on iron mediated activation of peroxymonosulfate and persulfate for the degradation of a variety of ground water contaminants. The objectives include evaluation of:

1) Activation of PS and PMS individually by Fe (II), Fe (III) and H_2O_2.
2) Effect of molar concentration of oxidant and iron on contaminant and TOC removal efficiencies.
3) Feasibility of using chelating agent, phosphate buffer and thiosulfate-oxidant redox couple to avoid iron precipitation commonly observed in such catalytic systems.
4) Versatility of catalytic systems by
    a. Testing the degradation of variety of priority contaminants with widely different properties.
    b. Investigating long term application of catalytic process.

Merits of the project

A novel class of sulfate radical based AOTs (Fe(II)/PS and Fe(II)/PMS) was successfully tested for degradation of variety of ground water contaminates including a series of chlorophenols (4-CP, 2,4-CP, 2,4,6-CP, 2,3,4,5-CP), naphthalene and 2-chlorobiphenyl. In the proposed technologies, the kinetics of the reaction of iron with PMS or PS are slower compared to that of Fenton Reagent. The stable nature of oxidants allows efficient use of such chemicals for significantly longer duration giving new direction to the development of modern AOTs. Application of citric acid, an environmental friendly chelating agent, as reported in this study was found to reduce the precipitation of iron and can be used to improve the degradation efficiency significantly.

Methods, Procedure and facilities

Chemical Used:
The following chemicals were used as received:
2-chlorobiphenyl (99+%, AccuStandard), naphthalene (99+%, fisher Scientific), $Na_2S_2O_8$ (98%, Sigma Aldrich), Methanol (99%, Fisher Scientific), Acetonitrile (Fisher Scientific), $FeSO_4.7H_2O$ (98%, Fisher Scientific), $Fe_2(SO4)_3.4H_2O$ (99+%, Fisher Scientific) and Oxone (95%, Aldrich, manufactured by DuPont). 4-chlorophenol (99.5% , suplco), 2,4-chlorophenol (99.5% ,Supelco), 2,4,6- chlorophenols (99.5%, Supelco) , 2,3,4,5-chlorophenol (99%, Supelco), hydrogen peroxide (30% v/v, Fisher science), sodium phosphate, phosphoric acid, citric acid (99.8%, Sigma Aldrich), sodium thiosulfate (99.5%, Fisher Scientific), methanol (HPLC grade, Fisher), sodium nitrite (99.99% , Fisher), starch (Fisher Scientific), potassium iodide (99.5%, Fisher), acetonitrile (HPLC grade, Fisher).

All chlorophenols were analyzed with an Agilent 1100 series HPLC system with a Quart Pump and UV-diode array detector. The column used for the analysis of chlorophenols was Eclipse XDB-C8 column, obtained from Agilent. Different mobile phase composition and wavelength was used for individual chlorophenol analysis. Naphthalene was also analyzed by Agilent 1100 series HPLC system. A discovery RP amide C-16 column from Supelco was used to analyze naphthalene concentration.

In case of experiments with 2-chlorobiphenyl samples were extracted using hexane/acetone mixture (hexane: acetone = 70:30 v/v) and analyzed by GC/MS (Hewlett-Packard 6890) in accordance with EPA method for chlorinated biphenyl analysis.
Total organic carbon (TOC) in samples was analyzed using a Shimadzu TOC 5050A analyzer equipped with VCSH-ASI system.

The concentration of remaining oxidant (persulfate, peroxymonosulfate) was analyzed using iodometric procedure described by Kolthoff and Carr [12]. 10 ml sample was transferred in a 50 ml conical flask and top of flask was sealed with paraffin after addition of 2 gm of potassium iodide. After vigorous shaking to dissolve potassium iodide, flask was left aside for 15 minute. Finally approximate 1 ml of glacial (~6.5 M) acetic acid was added to the flask and the amount of evolved iodine was determined by titration with standardized thiosulfate solution. Starch indicator was used for a clear end point in titration.

Two different types of batch experimental procedure were used for degradation experiments. In first type of procedure, contaminant concentration was monitored with time (kinetic batch experiment) whereas in second type of experiment procedure (batch experiments) only initial and final samples were taken.

All kinetic batch experiments were conducted in 500-ml narrow neck flask at ambient room temperature. After addition of chemicals, the flask was sealed from the top using Teflon cap with a sampling port. Sampling was performed by withdrawing 5 ml solution from sampling port of the reactor by using gas-tight syringe. The sample was placed in 10 ml borosilicate vials with Teflon caps. To stop the catalytic reaction in sample, excess amount of methanol or sodium nitrite was added as quenching agent. In most of the cases degradation was monitored for four hours.

40 ml clean EPA vials with Teflon cap were used for batch experiments. Prior to experiment, predetermined amount of SQ-water was transferred into the vial and then appropriate amount of contaminant, oxidant and iron stock was added to achieve the predefined molar ratios of contaminant, oxidant and iron. To achieve continuous mixing, vials were placed in the tumbler (30 rpm). Initial and final samples were taken to find the efficiency of the process. After four hours samples were quenched with excess amount of methanol, a well known quenching agent for sulfate and hydroxyl radicals, to stop the chemical oxidation reaction. In case of TOC analysis of samples, sodium nitrite was used as quenching agent, which shows similar quenching properties as of methanol.

In all the experiments, oxidant and iron was added at predetermined molar ratios with respect to the contaminant. It is represented as molar ratio of **contaminant: oxidant: iron**. As an example, if one of the degradation experiments has molar ratios 1:10:5, this means that molar ratio of contaminant and oxidant is 1:10 and molar ratio of contaminant and iron is 1:5.

In most of the degradation experiments, initial concentration of 4-chlorophenol was 50 mg/L (0.389 mM). In case of comparative degradation runs of chlorophenols, initial concentration of 0.194 mM was used for all the chlorophenols. The initial concentrations of other contaminants were 5 mg/L (26.5 μM) for 2-chlorobipehnyl and 20 mg/L (156 μM) for naphthalene.

Results:

Activation of oxidants

In our previous studies *[13]*, Fe (II) was found to be an effective catalyst for the activation of PS/PMS for sulfate radical generation. The capability of Fe (III) for activating H_2O_2 is well documented. Hence, the activation of oxidants using Fe (II) and Fe (III) was investigated in an attempt to gain further insights on these transition metal-based catalytic systems. It has also been reported that H_2O_2 can activate persulfate to produce sulfate radicals *[14]. H*ence, this investigation was designed to perform a comparative study of the potentials of three different catalysts Fe (II), Fe (III) and H_2O_2 which activate sulfate radical generating oxidants by mechanisms unique to each catalyst.

1. Fe (II) based activation

A set of experiments, as described in materials and method, were performed to evaluate the effect of oxidant and iron concentration on the degradation of 4-CP, one of the target contaminants chosen for this study. These experiments were performed maintaining a constant oxidant (PMS) and Fe (II) molar ratio (1:1) and changing their relative amount with respect to the contaminant. The oxidant and Fe (II) concentrations were varied from 0.389 mM to 19.44 mM which correspond to 1:1 to 1:50 molar ratio of contaminant and oxidant or Fe (II).

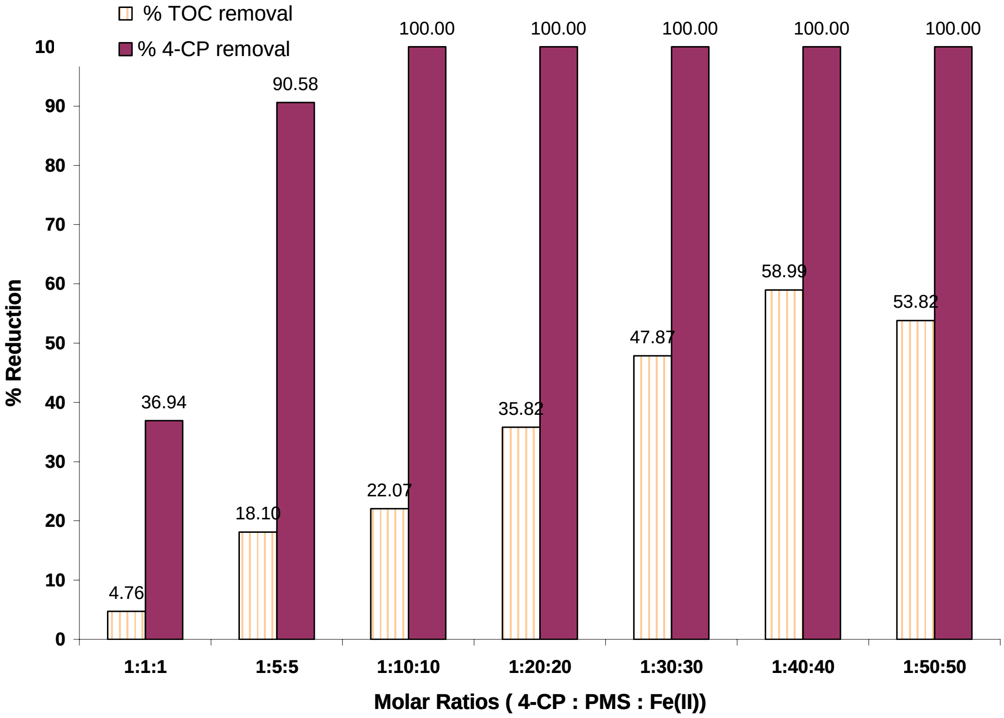


Figure 1: Effect of Fe (II) and PMS amount for 4-CP degradation and TOC removal using Fe(II)-PMS system. $[4\text{-CP}]_0 = 0.389$ mM, $[PMS]_0=[Fe(II)]_0= 0.389 - 19.44$ mM

From Figure-1 it can be seen that Fe (II) is very effective in degrading 4-CP by activation of PMS. It was also observed that with increase in concentration of oxidant and Fe (II), increasing compound degradation and TOC removal was observed. In 4 hours, 58% TOC removal was observed when 19.44 mM PMS and Fe (II) were used. It is interesting to note that the TOC removal was not directly proportional to the oxidant and Fe (II) concentrations. At higher concentrations of oxidant and Fe (II) (11.66 mM – 19.44 mM), the extent of TOC removal increases less than proportionally. This might be occurring due to the increased loss of sulfate radicals to undesirable side-reactions at high concentrations of oxidant (PMS) and Fe (II).

2. Fe (III) based activation

Activation by Fe (III) was tested by maintaining a constant oxidant (PS or PMS) and Fe (III) molar ratio (1:1) and changing their relative amounts with respect to the contaminant. In 4 hours, a maximum degradation of 33% was observed indicating that activation of PMS by Fe (III) is less effective than by Fe (II) where 100% removal was observed in all but one case. A similar trend in degradation was observed for activation of PS by Fe (III). PS performed slightly better than PMS for degrading 4-CP when activated by Fe (III) (Figure-2).

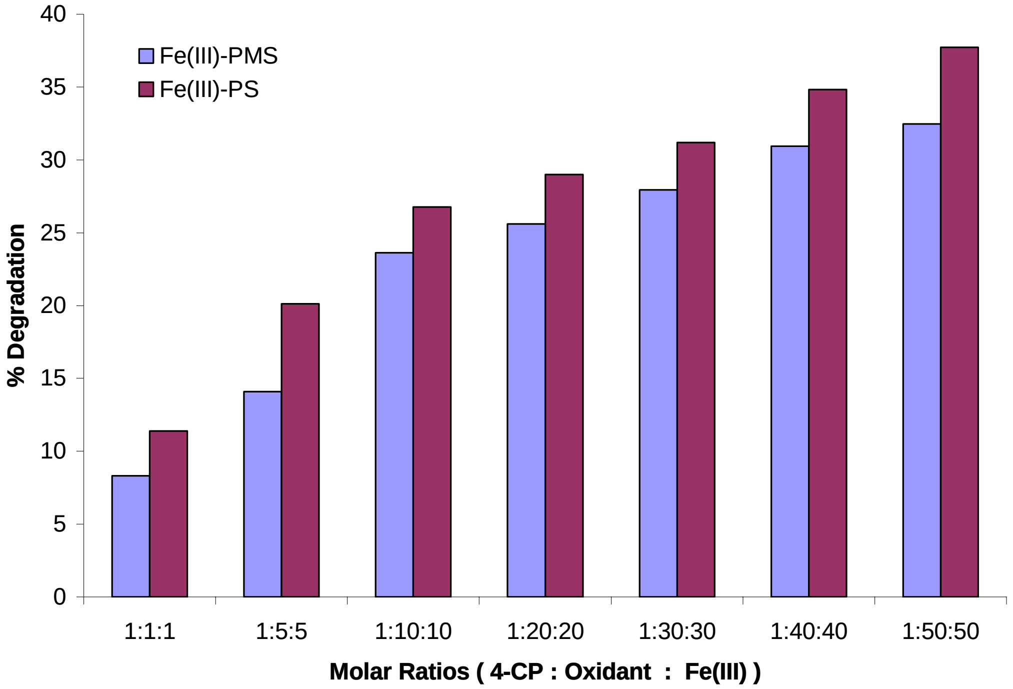


Figure 2: Degradation of 4-CP using Fe (III)-PMS and Fe (III)- PS based catalytic systems. $[4\text{-CP}]_0 = 0.389$ mM, $[\text{Fe(III)}]_0 = [\text{PMS}]_0 = [\text{PS}]_0 = 0.389 – 19.44$ mM. (All molar ratios are based on the initial concentration of the contaminant)

3. Hydrogen peroxide based activation

Based on a previously reported study *[14]*, a feasibility of using H_2O_2 for activating PS and PMS was performed. A control test using only H_2O_2 or persulfate showed no significant loss of contaminant in 4 hours of reaction time. As seen in Figure-3, in H_2O_2 / PMS systems, less than 15 % to 65% degradation of 4-chlorophenol was observed at low (0.39 mM – 3.9 mM) and higher H_2O_2 (19.44 mM) concentrations respectively (Figure-3). Systems with PS yielded 20% more degradation than those with PMS. A higher amount of hydrogen peroxide and oxidant will be required to achieve degradation of contaminants comparable to levels as seen for Fe (II).

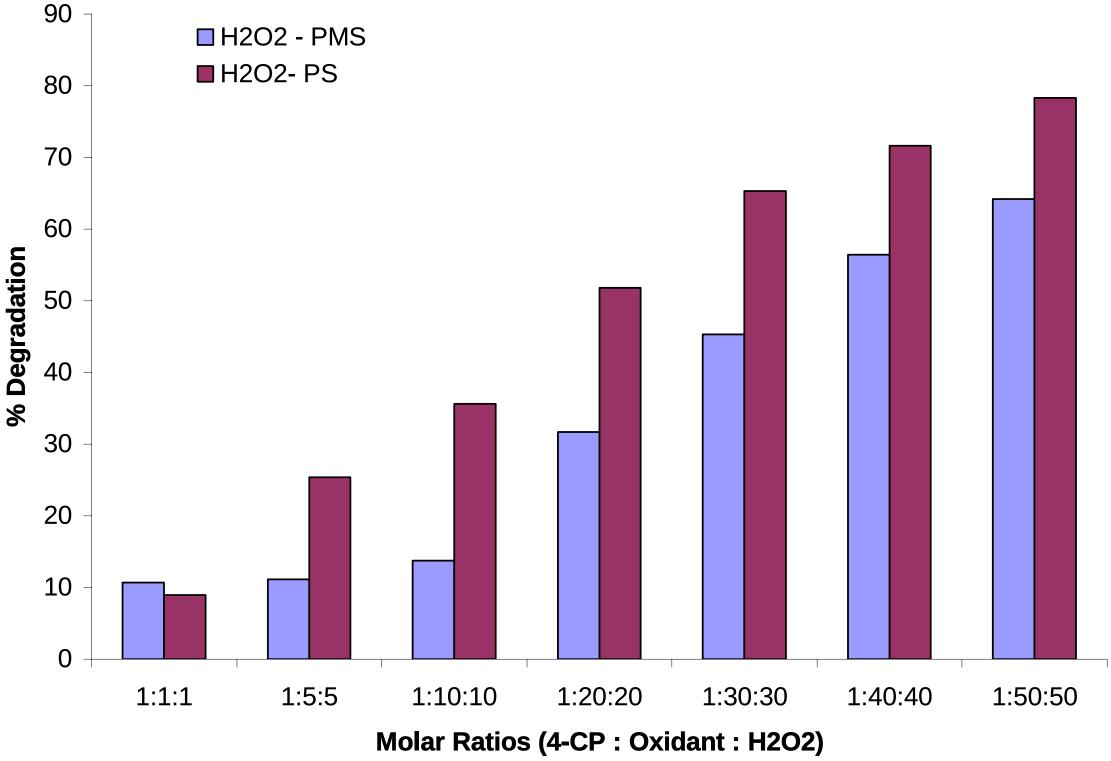


Figure 3: Degradation of 4-CP using H_2O_2 -PMS and H_2O_2- PS based catalytic systems. $[4\text{-CP}]_0 = 0.389$ mM, $[H_2O_2]_0 = [PMS]_0 = [PS]_0 = 0.389 – 19.44$ mM

Effect of molar concentration of Fe (II) and oxidant

It was determined from the previous sets of experiments that Fe (II) is most effective in activating the oxidants (both PS and PMS) for degradation of target contaminants. To further determine the variation in effectiveness of Fe (II) as an activator, the Fe (II): oxidant ratio was progressively changed in the following experiments to gain more insights into the role of each component.

Preliminary experiments were performed using constant oxidant concentration and different Fe (II) concentrations to evaluate the effect of the latter on degradation efficiency. 35% degradation of 4 –CP was observed in a system with PMS: Fe (II) with 5:1 *($[Fe (II)]_0=0.389$ mM)* molar ratio. Increasing the molar ratio of oxidant (PMS) and Fe (II) from 5:1 to 5:5 *($[Fe (II)]_0=1.94$ mM)* led to 95% removal of 4-chlorophenol (Figure – 4). This indicates that a comparable amount of Fe (II) with respect to oxidant is required for achieving higher degradation efficiency.

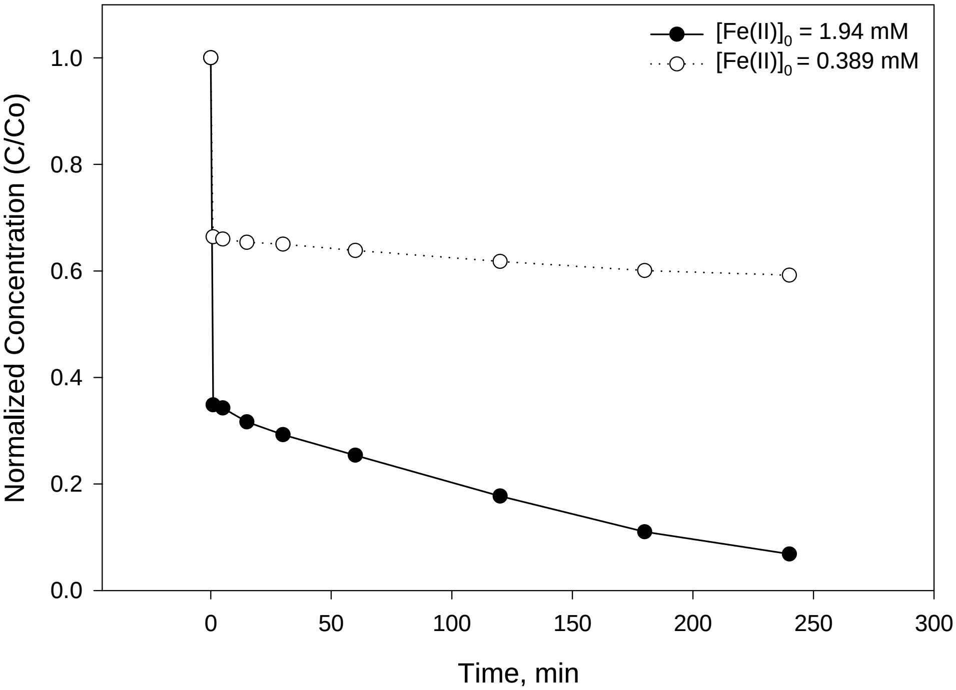


Figure 4: Effect of Fe (II) concentration in degradation of 4-CP using Fe (II)-PMS system. $[4\text{-CP}]_0=0.389$ mM, $[PMS]_0 = 1.94$ mM

Experiments were conducted to determine the effect of Fe(II) concentration on degradation efficiency by changing Fe (II) molar concentration from 0.39 mM to 19.44 mM (corresponding to 1:1 to 1:50 molar ratio of 4-CP : Fe(II)) while keeping the oxidant concentration constant (3.9 mM). Increased degradation efficiency and TOC removal was observed when Fe (II) concentration was increased from 0.39 mM to 3.9 mM. Further increase in Fe (II) concentration drastically reduces the degradation efficiency and TOC removal as seen in Figure-5. Radicals generated through the activation of PMS may be getting consumed in the oxidation of Fe (II) to Fe (III) at high Fe (II) concentrations leading to reduced availability of radicals for oxidation of contaminant and TOC removal from the system. These experiments strongly suggest that an optimum amount of Fe (II) is required to effectively activate the oxidant for contaminant removal.

Experiments were conducted to determine the effect of oxidant concentration on degradation efficiency by changing oxidant molar concentration from 0.39 mM to 19.44 mM (corresponding to 1:1 to 1:50 molar ratio of 4-CP: oxidant) while keeping the Fe (II) concentration constant (3.9 mM). Contaminant removal was found to increase with increasing concentration of oxidant in solution (Figure-6). TOC removal was seen on initially increasing the oxidant concentration (from 0.389 to 7.78 mM). However, on increasing oxidant concentration any higher (11.67 mM – 19.44 mM) resulted in a decreasing trend in TOC removal. Based on the results of these experiment, 2:1 molar ratio of PMS and Fe (II) was found to be optimum. The minimum oxidant concentration for complete removal of 4-chlorophenol was 3.9 mM which corresponds to 1:10 molar ratio of 4-CP and oxidant.

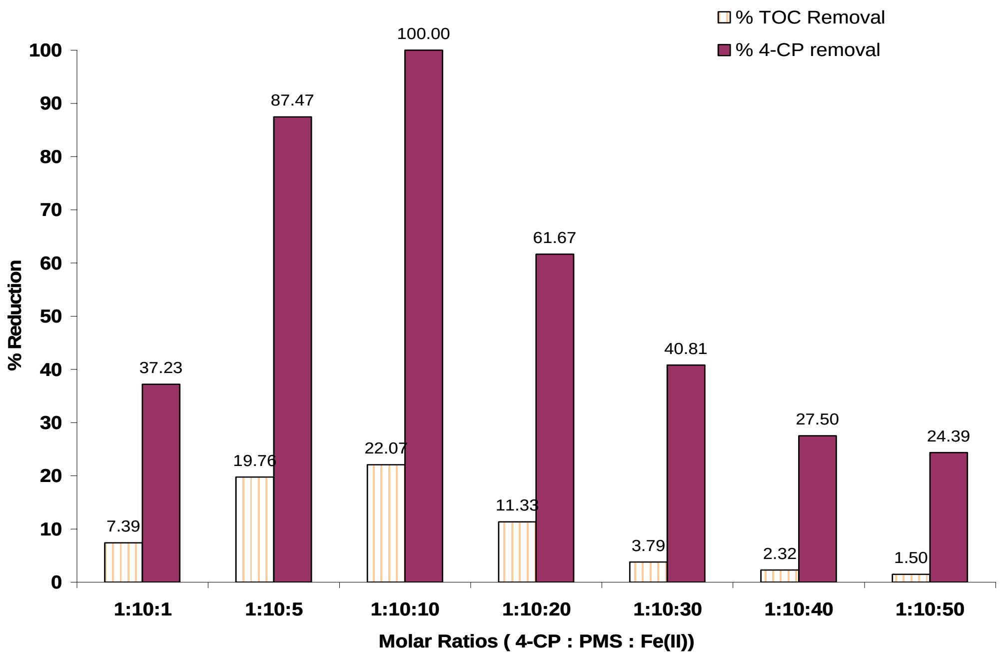


Figure 5: Effect of Fe (II) concentration for 4-CP degradation and TOC removal using Fe (II)-PMS system. $[4\text{-CP}]_0$ = 0.389 mM, $[\text{PMS}]_0$=3.89 mM, $[\text{Fe (II)}]_0$= 0.389 – 19.44 mM

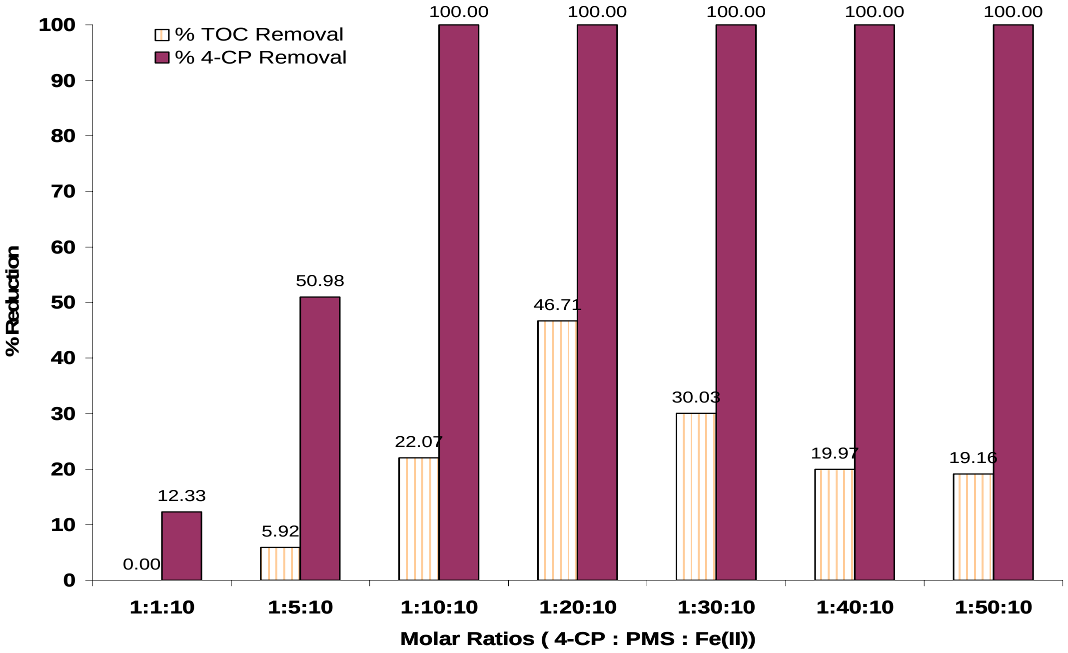


Figure 6: Effect of PMS concentration for 4-CP degradation and TOC removal using Fe (II)-PMS system. $[4\text{-CP}]_0 = 0.389$ mM, $[\text{Fe (II)}]_0 = 3.89$ mM, $[\text{PMS}]_0 =$ 0.389 – 19.44 mM

In the process of activation, Fe (II) changes to Fe (III). However, even at moderate concentrations Fe (III) tends to precipitate out as oxides and hydroxides as these have very low solubilities at most of pH values. Iron in precipitated form is effectively removed from the system as it does not take part in any reactions rendering the crucial re-conversion of Fe (III) to Fe (II) impossible. Hence, to maintain the iron in the solution, different approaches were tested.

1. Effect of phosphate buffer

The effect of phosphate buffer on contaminant removal efficiencies was studied using 100 mM phosphate buffer in Fe (II)-PMS system. In the presence of phosphate buffer, heavy precipitation accompanied with decrease in degradation efficiency. Removal of catalyst leads to decrease in efficiency of contaminant removal as it can be seen in Figure-7. It can be assumed that practically all the catalyst was removed from the system in less than one hour as no further degradation was observed after that.

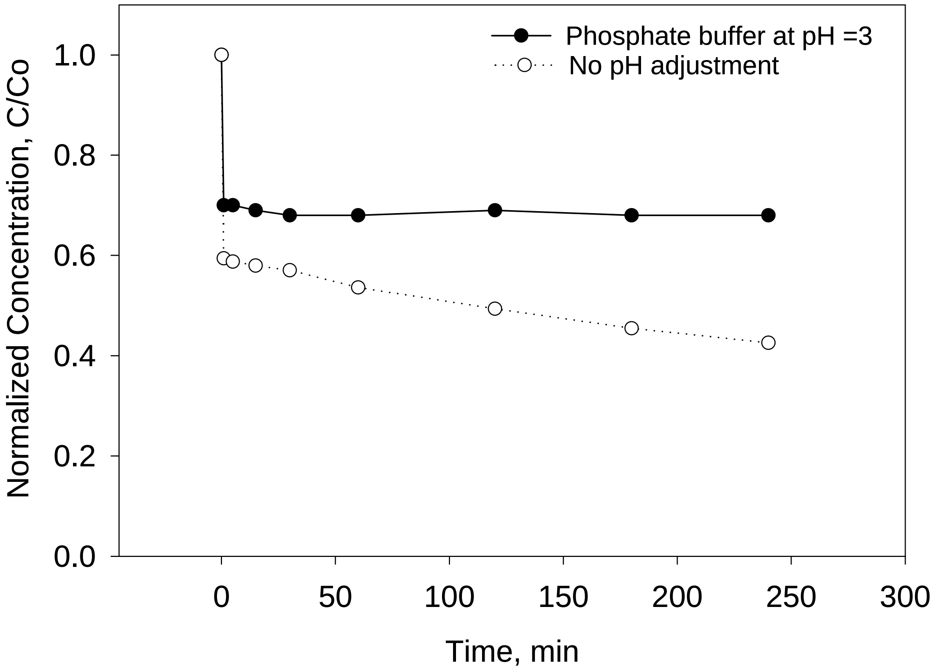


Figure 7: Effect of phosphate buffer on degradation of 4-CP using Fe (II)-PMS system. $[4\text{-CP}]_0 = 0.389$ mM, $[\text{Fe (II)}]_0 = 1.94$ mM, $[\text{PMS}]_0 = [\text{PS}]_0 = 1.94$ mM, buffer concentration = 100 mM

2. Effect of thiosulfate

The addition of a reducing agent such as sodium thiosulfate to a persulfate solution can form a persulfate- thiosulfate redox system, which has been reported to promote persulfate oxidation in polymerization processes *[15]*. The activation of persulfate-thiosulfate system by metal ions can be explained by redox cycle dependent upon the valence state of the metal. Liang et al. *[7]* postulated the mechanism of persulfate-thiosulfate activated by a complex anion containing ferrous ion to produce the sulfate free radical.

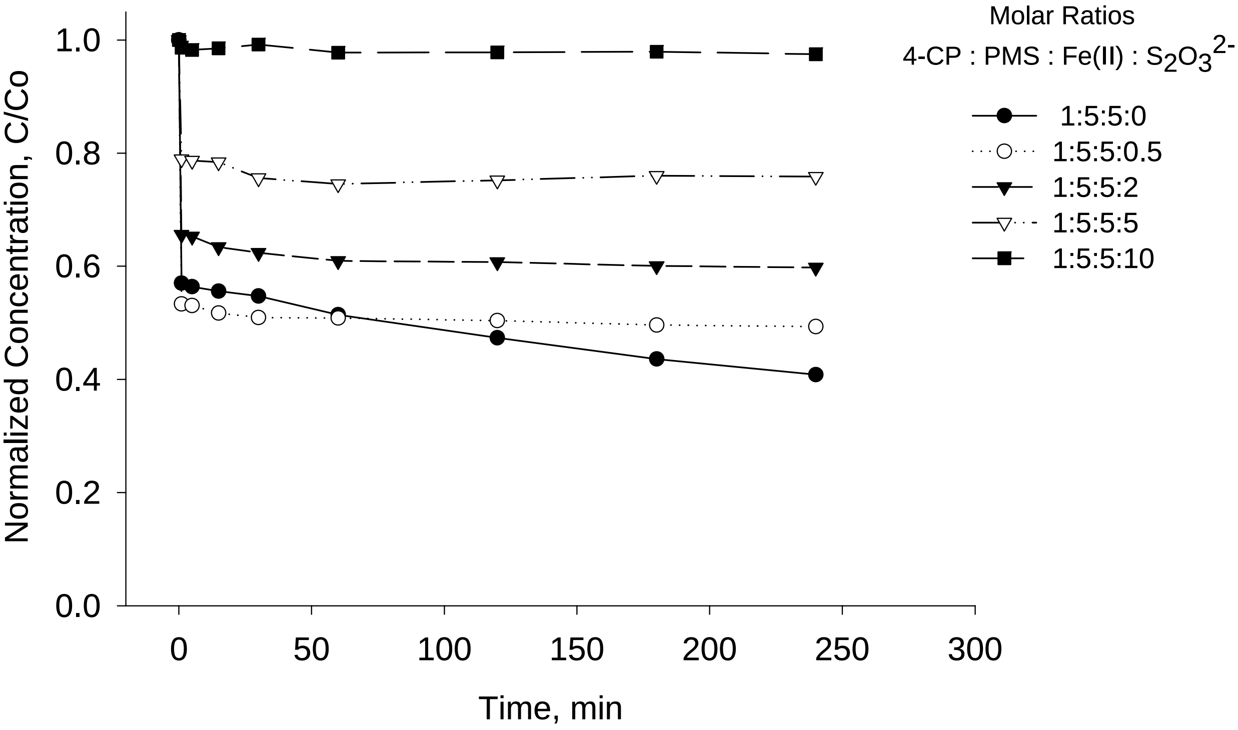
$$Fe^{3+} + S_2O_3^{2-} \longrightarrow Fe^{2+} + \tfrac{1}{2} S_4O_6^{2-}$$

$$x\,Fe^{2+} + y\,S_2O_3^{2-} \longrightarrow \text{Complex anion}$$

$$S_2O_8^{2-} + \text{Complex anion} \longrightarrow SO_4^{\bullet -} + SO_4^{2-} + Fe^{3+}$$

Since the formation of the complex ion which ultimately leads to the generation of sulfate radicals does not involve the oxidant, this activation, though proposed for PS, should theoretically be valid for PMS too. The effect of thiosulfate concentration for activating both oxidants was studied by changing the molar concentration of thiosulfate from 0.2 mM to 3.9 mM and maintaining constant concentrations of the oxidants and Fe (II).

From Figure-8 it can be seen that increasing the thiosulfate concentration leads to decrease in degradation of 4-chlorophenol. Normally in Fe (II)-PMS system, the solution color changes to orange/brown due to formation of Fe (III). At high thiosulfate concentration, no color change in solution was observed. It seems that presence of thiosulfate prevents the oxidation of Fe (II) to Fe (III) hence indirectly reducing the activation of oxidant and decreasing the degradation efficiency. Similar trend of decrease in efficiency was observed in case of Fe (II)-PS system.



3. Effect of chelating agent

Iron chelating agents have been used in Fenton's reaction to control the rate of reactive hydroxyl radical formation *[16]*. A complexing agent functions by making coordinate bond(s) with metals and thus maintaining the metal ions in solution. The obstacle of keeping ferrous ion available in solution can be overcome by employing complexing agents in conjugation with Fe (II). Citric acid has been used by many researchers as complexing agent since it is a natural multidentate organic complexing agent which is environmentally friendly and readily biodegradable *[17]*.

- **Fe (II) – Persulfate system**

Citric acid was used in this study to maintain the slow availability of Fe (II) in the solution for activation of oxidant. Five different molar concentrations of citric acid were used to test the effect of citric acid concentration on the degradation of 4-chlorophenol using Fe (II)-PS system. These concentrations were selected such that metal: ligand ratio was in range of 1:0.02 to 1:2.

From Figure-9 it can be seen that increase in degradation of 4-chlorophenol was observed in presence of citric acid. Increasing trend in degradation was observed up to metal: ligand ratio 1:0.2, after which the increase in citric acid concentration led to a decrease in % removal. This happens because when the chelating agent is present in relatively high concentrations, it binds the metal and reduces its availability in solution. A lower amount of chelating agent, even after binding to some of the Fe (II), leaves considerable amount of Fe (II) in solution for the activation reaction.

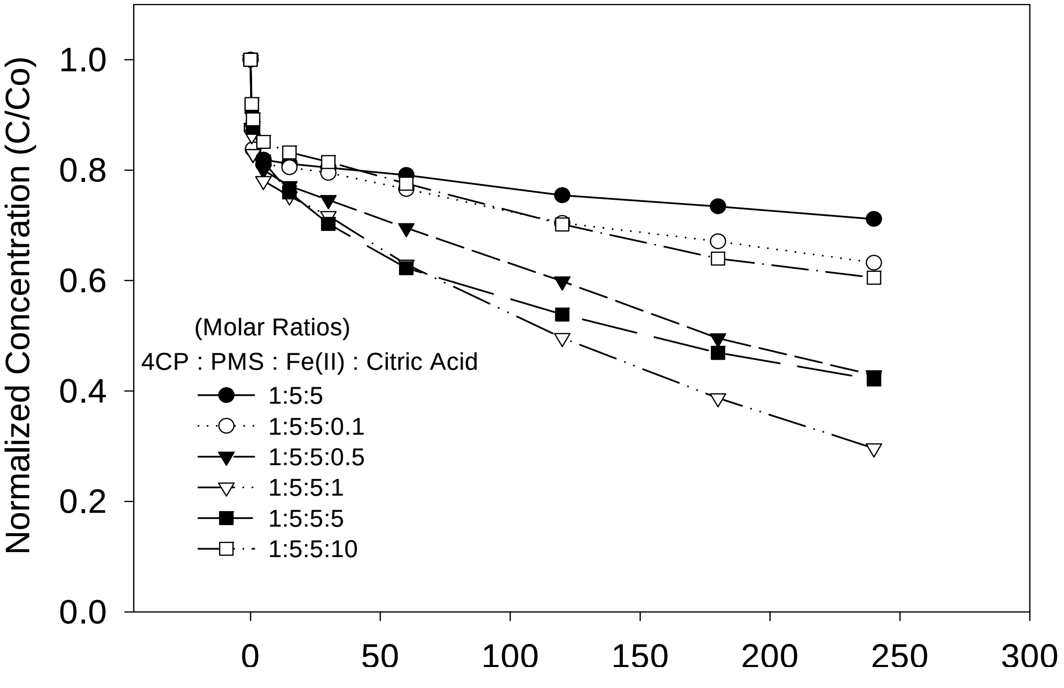


Figure 9: Effect of chelating agent concentration (citric acid) on degradation of 4-CP using Fe (II)-PS system. $[4\text{-CP}]_0 = 0.389$ mM, $[\text{Fe (II)}]_0=1.94$ mM, $[\text{PS}]_0=1.94$ mM, $[\text{Citric Acid}]_0 = 0.0389 - 3.89$ mM

- **Fe (II) – PMS system**

A different type of degradation pattern was observed when citric acid was used in Fe (II)-PMS system. A significant influence of the order of chemical addition was observed.

In Figure-10, when citric acid was not present, degradation of 4-CP continued after 4 hours. In presence of citric acid, degradation of 4-CP reduced drastically after only one hour. In the Figure-10 it can be seen that presence of citric acid only improved the initial degradation. After 1 minute, the degradation curve starts to flatten rapidly most likely due to binding of citric acid with the available catalyst preventing any further degradation of 4-chlorophenol.

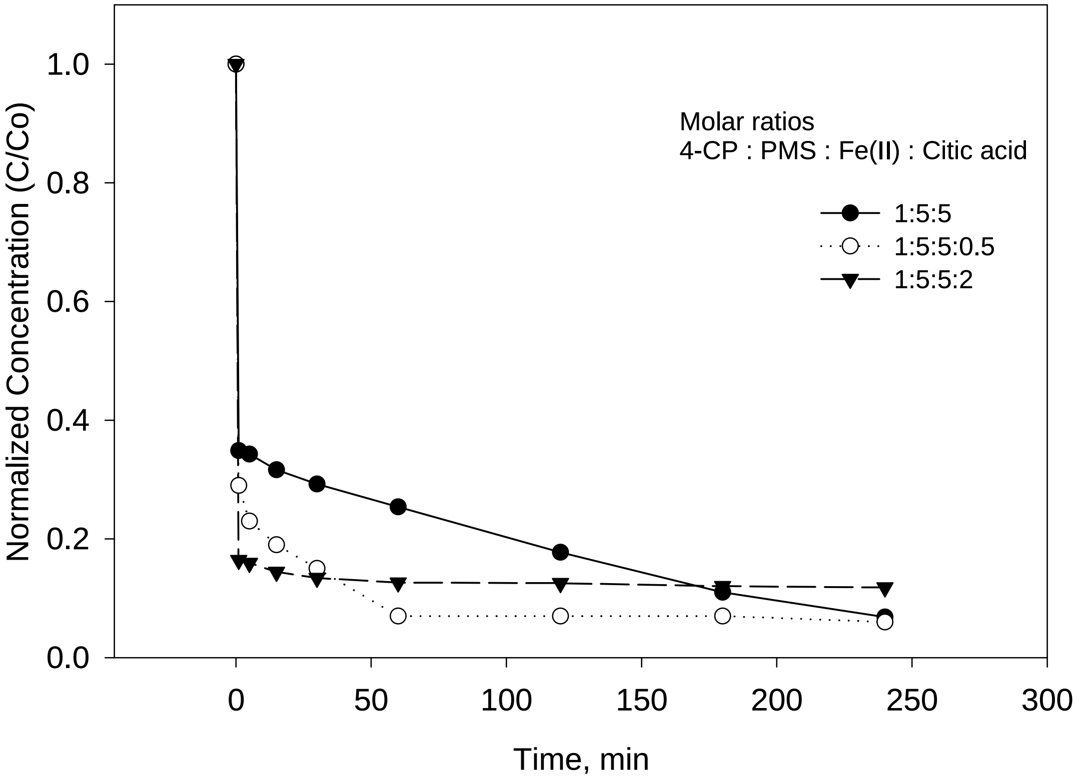


Figure 10: Effect of chelating agent concentration (citric acid) on degradation of 4-CP using Fe (II)-PMS system. $[4\text{-CP}]_0 = 0.389$ mM, $[\text{Fe (II)}]_0 = 1.94$ mM, $[\text{PMS}]_0 = 1.94$ mM, $[\text{Citric Acid}]_0 = 0.194 – 0.778$ mM

Versatility of catalytic systems

The catalytic systems were tested for chlorophenols with increasing degree of chlorination and with other priority contaminants like PCBs and PAHs with widely different structures and properties. This variety of contaminants was selected to test the versatility of the catalytic system under study. The performance of the system was also tested for long term degradation of model organic contaminants and was compared to other established AOTs like Fenton reagent.

a) Long term experiment using various catalytic systems

Owing to their stable nature, persulfate and peroxymonosulfate should be available in the system for long time. Experiments were run for 8 days comparing the three different catalytic oxidation systems under study: Fe (II)-PMS, Fe (II) –PS, and Fe (II)-H_2O_2.

With Fe (II) concentration constant at 1.94 mM in all three units, 50 % TOC removal was observed with Fenton reagent as opposed to 75 % and 93 % in Fe (II)-PMS and Fe (II)-PS systems. Higher Fe (II) concentration led to a decrease in TOC removal in the Fe (II)-PS and Fe (II) –PMS systems whereas no major change in TOC removal (~ 50%) was observed in the system with Fenton reagent. In both PMS and PS based system highest TOC removal was observed when oxidant and Fe (II) was used in 2:1 molar ratio.

In case of Fe (II)-PS, highest TOC removal per unit oxidant consumption was observed. Close to 60% of oxidant was remaining even after 8 days and 93% TOC removal. This shows the superiority of Fe (II)-PS system over other catalytic systems for long term application.

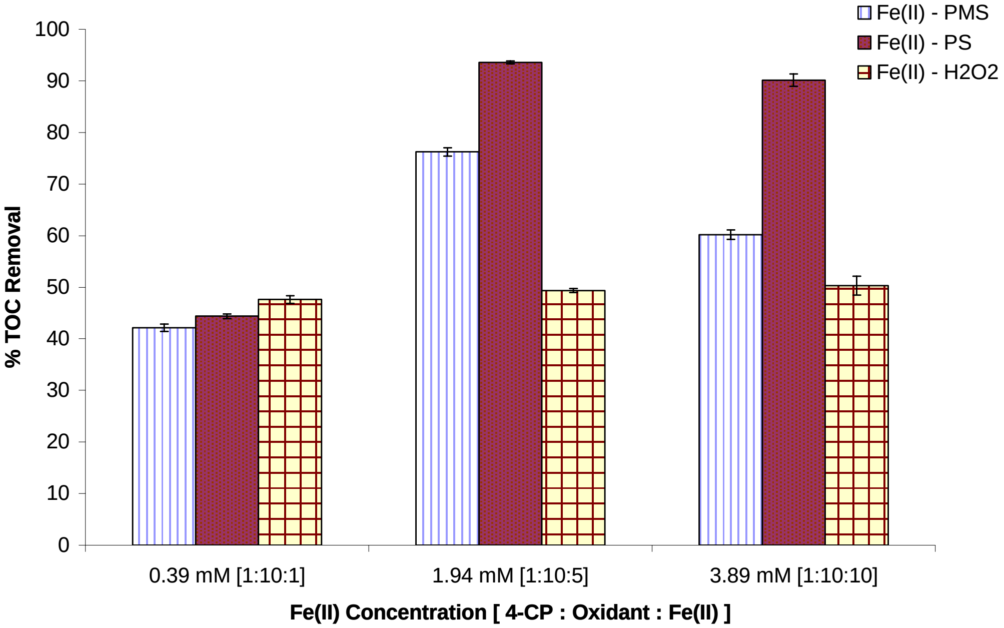


Figure 11: TOC removal efficiency for three different catalytic systems. Experiment duration = 8 days. $[4\text{-CP}]_0 = 0.389$ mM, $[H_2O_2]_0 = [PMS]_0 = [PS]_0 = 0.389$ mM, $[Fe(II)]_0 = 0.389 - 3.89$ mM

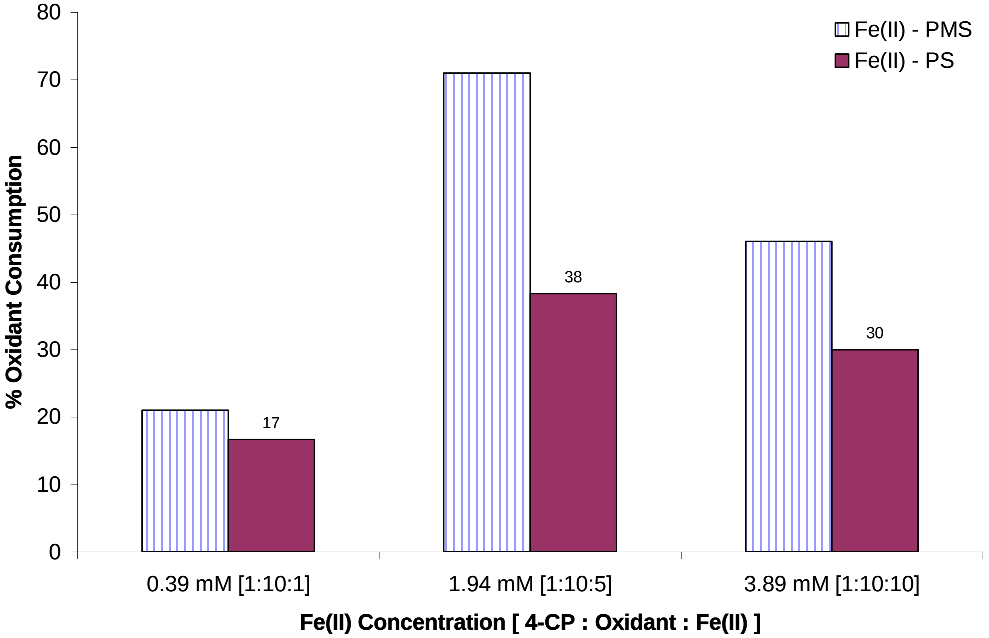


Figure 12: Oxidant consumption for three different catalytic systems. Experiment duration = 8 days. $[4\text{-CP}]_0 = 0.389$ mM, $[H_2O_2]_0 = [PMS]_0 = [PS]_0 = 0.389$ mM, $[Fe(II)]_0 = 0.389 - 3.89$ mM

b) Degradation of series of chlorophenols using Fe (II)/PS, Fe (II)/PMS systems

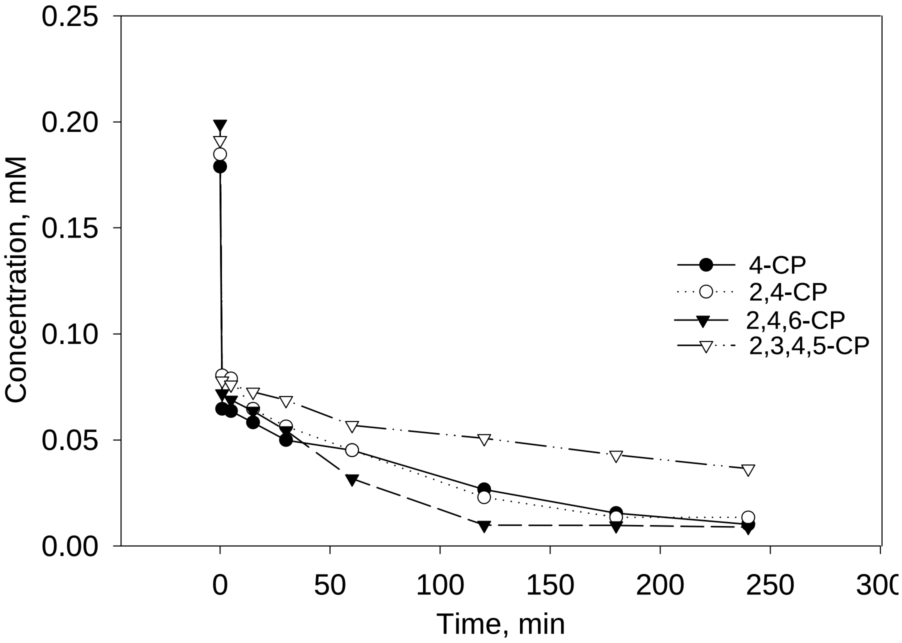


Figure 13: Degradation of series of chlorophenols using Fe (II)-PMS catalytic system. $[4\text{-CP}]_0 = [2,4\text{-CP}]_0 = [2,4,6\text{-CP}]_0 = [2,3,4,5\text{-CP}]_0 = 0.194$ mM, $[PMS]_0 = [Fe(II)]_0 = 0.97$ mM

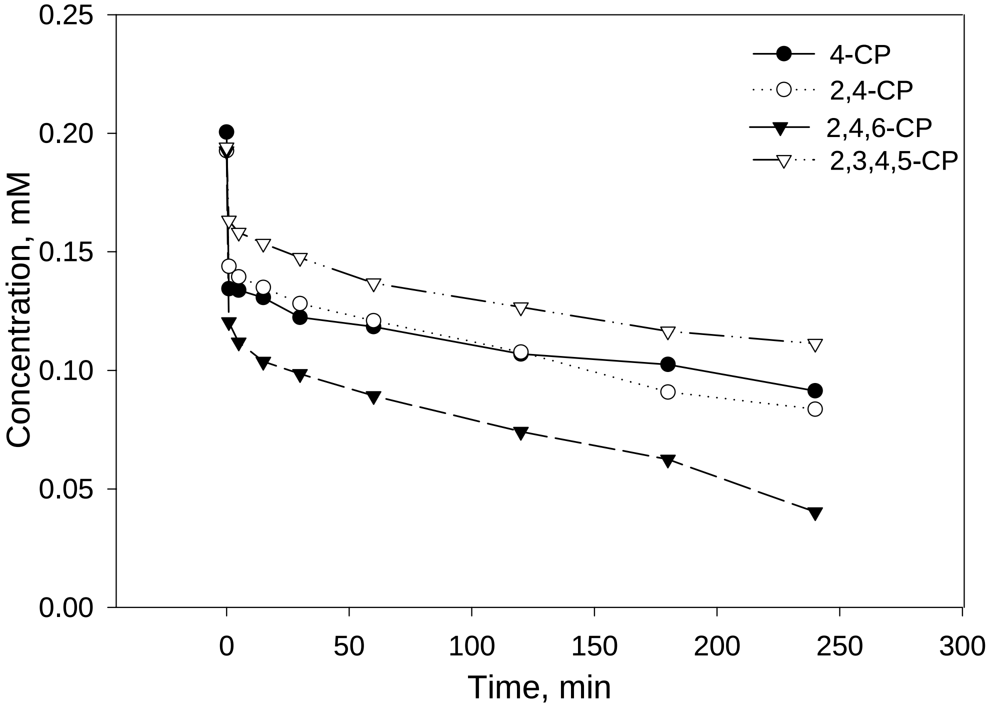


Figure 14: Degradation of series of chlorophenols using Fe(II)-PS catalytic system. $[4\text{-CP}]_0 = [2,4\text{-CP}]_0 = [2,4,6\text{-CP}]_0 = [2,3,4,5\text{-CP}]_0 = 0.194$ mM, $[PS]_0 = [Fe(II)]_0 = 1.94$ mM

To study to applicability of catalytic process for removal of chlorophenols with varying levels of chlorination, degradation of 4-CP, 2,4-CP, 2,4,6-CP and 2,3,4,5-CP was studied using Fe(II)-PMS and Fe(II)-PS system.

From Figure-13 it can be seen that Fe (II)-PMS catalytic system is capable of degrading variety of chlorophenols with comparable effectiveness. It is hypothesized that the degradation of chlorophenols takes place in two distinct steps, first the Fe II) activates the oxidant and generate radicals which destroy chlorophenols. This is a fast step and takes less then 1 min for completion. Then Fe (III) converts to Fe (II) by redox in a slow step, causing degradation which is markedly slower than that seen initially but continues until all the oxidant is consumed.

Degradation of 4-CP, 2,4-CP , 2,4,6-CP and 2,3,4,5-CP using Fe(II)-PS catalytic system, led to varying degradation profiles. Degradation of 4-CP and 2, 4-CP followed similar trends but 2,4,6-TCP degraded with a much faster rate possibly due the less steric hindrance offered by this compound, which facilitates the radical attack.

Overall, it was demonstrated that both the catalytic systems Fe (II)-PMS and Fe (II)-PS are capable of degrading a variety of chlorophenols and the oxidation system performs very comparably with increase in chlorination in phenol ring.

c) Degradation of PAHs and PCBs using Fe (II)/PS, Fe (II)/PMS systems

Preliminary experiments were performed to test the degradation of model polycyclic aromatic compound, naphthalene using Fe (II)-PMS and Fe (II)-PS system. The results are summarized in Table-1. In case of naphthalene, Fe (II)-PS catalytic system was more effective than Fe (II)-PMS system as seen in Table-1. Increasing trends in degradation efficiencies were observed with increase in oxidant concentration under fixed Fe (II) concentration. These preliminary experiments demonstrate the feasibility of these catalytic processes for degradation of naphthalene (a model PAHs). Further experiments will be performed to optimize the degradation of naphthalene using Fe (II)-PMS and Fe (II) - PS process.

Table 1: Summary of naphthalene removal efficiencies by Fe (II)-PMS and Fe (II)-PS systems

Molar Ratio	**% Degradation**	
Naphthalene : Oxidant : Fe(II)	**PMS**	**PS**
1:1:1	41.34	43.6
1:5:1	62.69	75.8
1:10:1	76.87	83.77

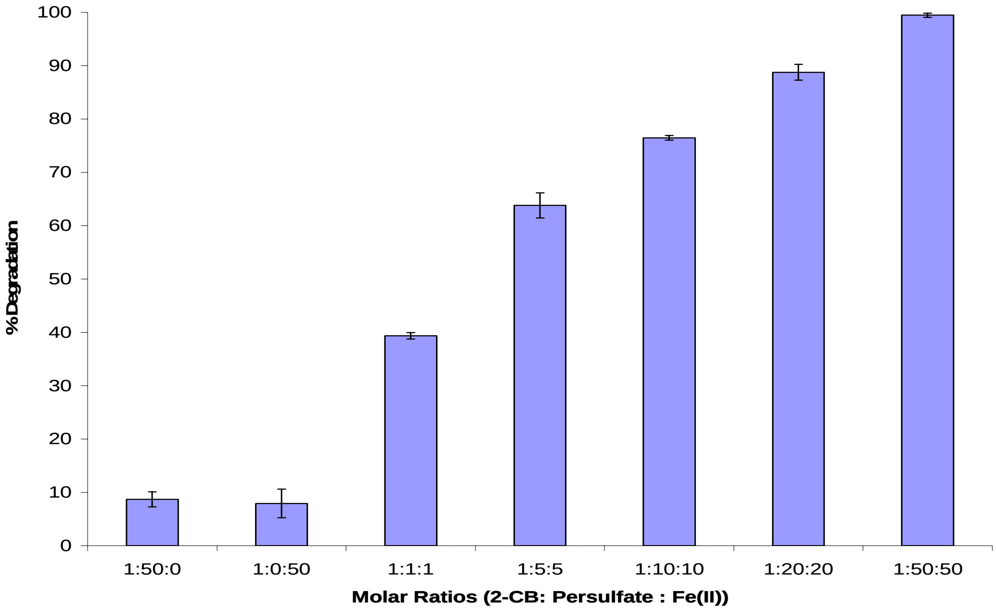


Figure 15: Degradation of 2-chlorobiphenyl using Fe (II)-PS catalytic system. $[2\text{-CB}]_0 = 26.5\ \mu M\ [PS]_0 = [Fe(II)]_0 = 26.5\ \mu M - 1.325\ mM$

Near complete degradation of 2-chlorobiphenyl was achieved in 4 hours, when 1.325 mM oxidant and Fe (II) was used (Figure-15). Similar results were obtained in case of Fe (II)-PMS system. More kinetic experiments will be performed in future to optimize the process with respect to catalyst and oxidant.

Conclusion

Three different kinds of catalytic systems were evaluated for degradation of a variety of contaminants. Fe (II)-PMS catalytic system was found to be superior to other systems in the short term experiments. In general, degradation efficiencies of Fe (II) based catalytic systems were better than Fe (III) based catalytic systems. In both catalytic systems with Fe (II), a 2:1 molar ratio of oxidant (PMS and PS): Fe (II) was found to be optimum for degradation of chlorophenols. Citric acid used as a chelating agent led to a significant increase in degradation for Fe (II)-PS systems, the optimum molar ratio of Fe (II): citric acid being 1:0.2. Contrary to previously reported literature *[7, 15]*, the presence of thiosulfate did not help in increasing the degradation. Highest TOC removal was observed in Fe (II)-PS system in case of long term degradation experiments. The stable nature of persulfate and its slow activation by iron makes the Fe (II)-PS system ideal for longer lasting ground water treatment. Fe (II) based catalytic systems was also found effective in degrading a variety of organic contaminants including chlorophenols, naphthalene and 2-chlorobiphenyl.

References

1) Rivas F. J., Beltran F. J., Frades J., Buxeda P., Oxidation of p-Hydroxybenzoic Acid by Fenton's Reagent, *Water Research*, **35**, 2, 387-396, **2001**.

2) Fernandez J., Bandara J., Lopez A., Albers P., Kiwi J., Efficient photo-assisted Fenton catalysis mediated by Fe ions on Nafion membranes active in the abatement of non-biodegradable azo-dye, *Chemical Communications*, 1493-1494, **1998**.

3) Chamarro E., Marco A., Esplugas S., Use of Fenton Reagent to Improve Organic Chemical Biodegradability, *Water Research*, **35**, 4, 1047-1051, **2001**.

4) Chiron S., Fernandez-Alba A., Rodriquez A., Garcia-Calvo E., Pesticide Chemical Oxidation: State of the Art, *Water Research*, **34**, 2, 366-377, **2000**.

5) Herrera-Melian J. A., Tello Rendon E., Dona Rodriguez J. M., Viera Suarez A., Valdes Do Campo C., Perez Pena J., Arana Mesa J., Incidence of Pretreatment by Potassium Permanganate on Hazardous Laboratory Wastes Photodegradability, *Water Research*, **34**, 16, 3967-3976, **2000**.

6) Xu Y., Comparative studies of the $Fe^{3+/2+}$-UV, H_2O_2-UV, TiO_2-UV/vis systems for the decolorization of a textile dye X-3B in water, *Chemosphere*, **43**, 1103-1107, **2001**.

7) Liang, C., Bruell, C. J., Marley, M. C. & Sperry, K. L., Persulfate oxidation for in situ remediation of TCE. I. activated by ferrous ion with and without a persulfate–thiosulfate redox couple. *Chemosphere* **55**(9), 1213-1223, **2004**

8) Huang, K., Zhao, Z., Hoag, G. E., Dahmani, A. & Block, P. A. Degradation of volatile organic compounds with thermally activated persulfate oxidation. *Chemosphere* **61**(4), 551-560, **2005**

9) Meunier, B. Potassium Monopersulfate - just another primary oxidant or a highly versatile oxygen atom donor in metalloporphyrin-mediated oxygenation and oxidation reactions. *New journal of chemistry****,*** ***16*** (1-2), 203-211, **1992**

10) Betterton, E. A.; Hoffmann, M. R. Kinetics and mechanism of the oxidation of aqueous hydrogen sulfide by peroxymonosulfate. *Environ. Sci. Technol.****,*** ***24*** (12), 1819-1824, **1990**

11) Anipsitakis, G. P.; Dionysiou, D. D. Degradation of Organic Contaminants in Water with Sulfate Radicals Generated by the Conjunction of Peroxymonosulfate with Cobalt. *Environ. Sci. Technol.****,*** ***37*** (20), 4790-4797, **2003**

12) Kolthoff, I. M.; Carr, E. M. Volumetric Determination of Persulfate in the Presence of Organic Substances. *Anal. Chem.****,*** ***25*** (2), 298-301, **1953**

13) Anipsitakis, G. P.; Dionysiou, D. D. Radical Generation by the Interaction of Transition Metals with Common Oxidants. *Environ. Sci. Technol.****,*** ***38*** (13), 3705-3712, **2004**

14) Lunenok-Burmakina, V. A.; Lezina, G. G.; Emel'yanov, V. B., Mechanism of hydrogen peroxide oxidation by peroxydisulphate ions. *Ukrainskii Khimicheskii Zhurnal (Russian Edition)* **54**(12), 1267-9, **1988**

15) Riggs, J.P., Rodrigues, F.,. Polymerization of acrylamide initiated by the persulfate–thiosulfate redox couple. J.Polym. Sci.: Part A-1 **5**, 3167–318, 1967

16) Pignatello, J.J., Day, M.,. Mineralization of methyl parathion insecticide in soil by hydrogen peroxide activated with iron(III)–NTA or –HEIDA complexes. *Hazard. Waste Hazard. Mater.* **13** (2), 237–244, **1996**

17) Francis, A.J., Dodge, C.J.,. Remediation of soils andwastes contaminated with uranium and toxic metals. *Environ. Sci. Technol.* **32** (24), 3993–3998, **1998**

Technology Enhanced Participation for Watershed Planning

Basic Information

Title:	Technology Enhanced Participation for Watershed Planning
Project Number:	2005OH27B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	15
Research Category:	Social Sciences
Focus Category:	Management and Planning, Conservation, Education
Descriptors:	None
Principal Investigators:	Maria Manta Conroy, Steven I Gordon

Publication

USGS WATERSHED FINAL GRANT REPORT
TECHNOLOGY ENHANCED PARTICIPATION FOR WATERSHED PLANNING

Introduction

Watershed management brings to bear a number of integrated issues related to land use, hydrology, biology, policy development, and political feasibility. The scope and diversity of a watershed further challenges the decision making environment. Watersheds often encompass multiple jurisdictions, ecosystems, and span both rural and urban land uses. Such a complex environment can be challenging for farmers and other land owners to understand the impacts of their own actions at the watershed level. Yet, these citizens are the key to watershed management implementation success.

Land use can significantly and negatively impact water quality. Agricultural activities introduce fertilizers, pesticides, and herbicides into the waterways. Traditional farming practices that abut waterways eliminate buffers thereby raising stream temperatures and increasing bank erosion which raises the sediment level in streams. Non-agricultural land uses also impact waterways. Traditional development increases impervious surfaces (e.g., rooftops, parking lots, roadways, sidewalks) resulting in increased amounts of water runoff leading to downstream flooding, and decreased amounts of water percolating into the soil for natural groundwater recharge. The quality of the runoff is degraded due to the emissions, litter, and other wastes that enter the water system as collected by the runoff. Development can also change the physical character of streams and other waterways through channelization and bank erosion.

Best management practices (BMPs) installed along waterways are important to mitigate negative impacts of development and agricultural practices. BMPs include planting along stream banks to curb erosion, establishing a buffer zone of non-activity along a stream, creation of artificial wetlands, and livestock exclusion. Implementation of these practices, however, has been voluntary and requires buy-in from farmers and land owners if BMPs are to be effective. Once BMPs are implemented, it is also critical to establish the relationship between implementation and the biological quality of the watershed. This relationship can not only reinforce the practices, but also to guide watershed plans and related policies.

Farmers and other land owners learn about BMPs through a variety of channels, including extension services and public meetings. Public meetings are also the typical forum in which input is received on watershed planning activities that may incorporate BMP implementation. Public meetings, however, have been characterized as an inefficient means for public learning on a complex topic such as watershed management. The framework of public meetings largely dictates the content and time frame within which participants can learn about issues and express opinions. This institutionalization of the participation process limits the time and depth to which an individual can learn about a complex public issue. Strategies to improve the participation experience through a technology-based, active learning approach have been investigated in the literatures addressing both public policy participation (citizen participation) (e.g., Al-Kodmany, 1999; Macpherson, 1999; Padgett, 1993) and classroom participation (e.g., McIntyre and Wolff, 1998; Oliver and Omari, 2001; Yazon et. al. 2002). Technology-based approaches include, for example, online discussions and resources, as well as computer aided visuals through Geographic Information Systems.

Active learning is an environment whereby knowledge is conveyed through direct experience such as writing, discussing, reading, or acting (Chickering and Gamson, 1987). The student is a participant in the process rather than simply a receiver of information imparted by a lecturer. The literature on active learning, both in general and technology based, typically has focused on an academic learning environment (e.g., McIntyre and Wolff, 1998; Oliver and Omari, 2001; Yazon et al., 2002). This literature provides relevant insights as a public meeting is similar to a classroom in that it is a forum to impart information, though on a condensed exposure scale and to a different audience. The classroom-based active participation literature suggests that an integration of traditional with technology-based participation methods would offer the most satisfying outcome for participants.

Problem and Research Objectives

The Upper Great Miami River Watershed is a fitting location for instituting technology-based active learning participation for watershed planning. The Upper Great includes 10 counties, primarily Shelby, Logan, and Miami. The land uses within the watershed are primarily agricultural, but it also has urbanized areas including Sidney in Shelby County. There are BMPs currently in place in the Upper Great Miami River Watershed. There is, however, no research regarding the relationship between their implementation and the biological quality of the watershed. Stream health ratings in the watershed range from very poor in some areas of Shelby and Logan Counties, to excellent those and other counties of the watershed. Further, the existing means by which to educate the public regarding BMPs and to gain input and insights for related watershed plans and policies is the public meeting which is often both inefficient and ineffective. This research effort attempted to address these issues in the Upper Great Miami River Watershed through the establishment of an online watershed planning participation venue.

There were two primary objectives of this project:

Objective 1: Establish the relationship between implemented BMPs and biological quality in the Upper Great Miami Watershed.

Best Management Practices are a critical means of watershed protection. They rely on typically farmers to establish stream corridor buffers, engage in no or low-tillage activities, and other practices to reduce negative impacts of farming on water quality. As noted previously, however, implementation of BMPs is voluntary. Therefore, it is crucial to understand the relationship that exists between implemented BMPs and biological quality within the watershed. This information can then be used to draft policies for watershed management.

Best Management Practices funding data for the Upper Great Miami Watershed will be used to classify the major areas of study in Logan and Shelby Counties. The data have been compiled by local watershed groups but have not been georeferenced. We undertook an initial classification of watershed areas that are in good condition based on biological data versus and those that are not. We then used land use and BMP data to provide insight into the cause and effect relationships. A preliminary assessment performed by a graduate planning class at OSU has already identified major areas where the quality has improved over the past decade and roughly correlated these trends with the implementation of BMPs (Gordon et al. 2002). The additional analysis should be able to confirm some of those effects as well as point out areas where further study is needed.

Objective 2: Inform public officials, land managers, and other watershed stakeholders of the management choices for their watershed through in person and online participation venues, examining the effectiveness of the integrative approach.

Community outreach is an essential component to any watershed management approach. It serves a number of purposes, primary of which are education and citizen input. Watersheds such as that of the Upper Great Miami in Ohio are complex areas to plan due to their scope and diversity. They encompass multiple jurisdictions, ecosystems, and span both rural and urban land uses. Providing citizens with scientific based pollution and BMP information can be challenging in the limiting format of a public meeting. Public meetings are limiting in who can attend and what can be covered in the time allocated. The intent of the outreach component of this proposal is to utilize a technology enhanced approach to improve the level of citizen participation both in terms of scope and understanding. The outreach will coordinate with established extension groups in the Upper Great Miami Watershed counties of Logan and Shelby.

The incorporation of technology into public planning processes represents an area of great promise to build better relationships between government and its citizenry. Information and communication technology (ICT) relaxes time and geographic constraints faced by citizens who want to participate (Kwan and Weber 2003). Citizens who choose to participate using ICT do so in the location and at the time of their choosing. Governments that harness ICT tools can potentially expand opportunities for citizen participation.

We used two primary forms of participation and education to advance knowledge of the watershed planning effort by stakeholders. First, we held traditional public meetings to introduce our project and gather user pre and post-test information, as well as to provide a training session for potential users of the online participation experience. Padgett (1993) noted that technically savvy citizens may welcome the GIS tool, while “those less knowledgeable will be difficult to convince” (516). Therefore, training sessions on the use of the website and the proposed online discussion tool (Elluminate through an agreement with the Ohio Learning Network Online Community) were deemed important to establish a comfort level with the technology enhanced participation experience. Elluminate provided online discussions and file sharing to allow citizens to continue the dialog begun at the public meeting without regard to the physical limits of time and space; online participants can post questions, suggestions, and the like at their convenience from their own home or wherever they may have access to an Internet connection. Elluminate also has the capacity for streaming video and audio which would allow remote citizen participation in watershed meetings.

Second, we attempted to provide informal education and discussion via the Internet. This technology enhanced participation approach will be used to improve education and awareness of the issues and management plan approaches for the Upper Great Miami Watershed and to test the efficacy of this approach. One of the principle technology enhanced component included a GIS-based decision support tool for education and outreach. This tool allowed users to gather accurate information about the current status of their watershed, as well as current land use and BMP practices and the impacts these have had on the watershed. The tool also provided users the ability to run a limited set of development / watershed management scenarios and graphically observe the anticipated outcomes in various time frames.

Methodology

This project was undertaken in two phases corresponding with the objectives discussed previously. In the first phase, we focused on the relationship between funded BMPs and biological water quality data in the Great Miami Watershed. We began with an initial classification of watershed areas that are in good condition based on biological data versus and those that are not. This classification was based on biological data available through the Ohio EPA. We then correlated that information with existing land use data available through county auditors' websites and with BMP funding information. This information was provided in two online venues; first, a site we created dedicated to the BMP and participation elements of this study (http://uppergreat.knowlton.ohio-state.edu) as well as integrated into an existing website on watershed planning in Ohio (http://tycho.knowlton.ohio-state.edu).

The second phase of this project employed two technology based tools to enhance citizen participation for watershed planning. This phase used the BMP-water quality relationships and corresponding policies established during the first phase of the study. We held public watershed planning meetings in March and April of 2005 to introduce the project to potential participants in Logan and Shelby Counties. These groups were organized with the assistance of the extension offices in those counties; preliminary information was gathered from attendees and they remained on a contact list for the planned online introduction meeting. We then held meetings in both counties in September of 2005 to introduce the policies for consideration as part of a watershed planning effort. The September meetings also served as a training session on the use of the integrated online participation tools. The researchers and assistant demonstrated the technologies, including a step by step example of logging on; navigating pages in the GIS based tool; and utilizing discussion sessions in Elluminate™. Interested participants were given headsets for use with the future online sessions. The training session was intended to reduce technology anxiety that may inhibit use of the participation tools.

The online participation tools were made available in late September. Participants were encouraged to schedule one-on-one or small group online sessions with the researchers to become more comfortable using the online participation venues. A follow up meeting was planned for 6 weeks after the introductory meeting. However, due to the lack of participants for the online sessions, this meeting was never held.

Principal Findings and Significance

Though the funded portion of this project has been completed, the project itself is ongoing. Delays were encountered which prevented us from getting through the full scope of the participation and BMP mapping phases. Therefore, the discussion which follows provides findings at this point in the research.

BMP Relationship to Water Quality

The georeferenced BMP information was incorporated into GIS files with water quality data; primarily, IBI information. However, due to the timing of the BMP adoption versus that of the IBI sampling, it was not consistently possible to propose a relationship between the two. The most extensive recent sampling of the streams in our study area were done in 1994; BMP data was as recent as 1999. Analyses were done on a subwatershed, HUC 14 level. In some cases, BMP data did not exist in the subwatershed. Figure 1 below shows the HUC 14 subwatersheds in the Upper Great. More detailed information on those analyzed follows. This information is also provided at the project website: http://uppergreat.knowlton.ohio-state.edu/ (under Analysis of Watershed Conditions).

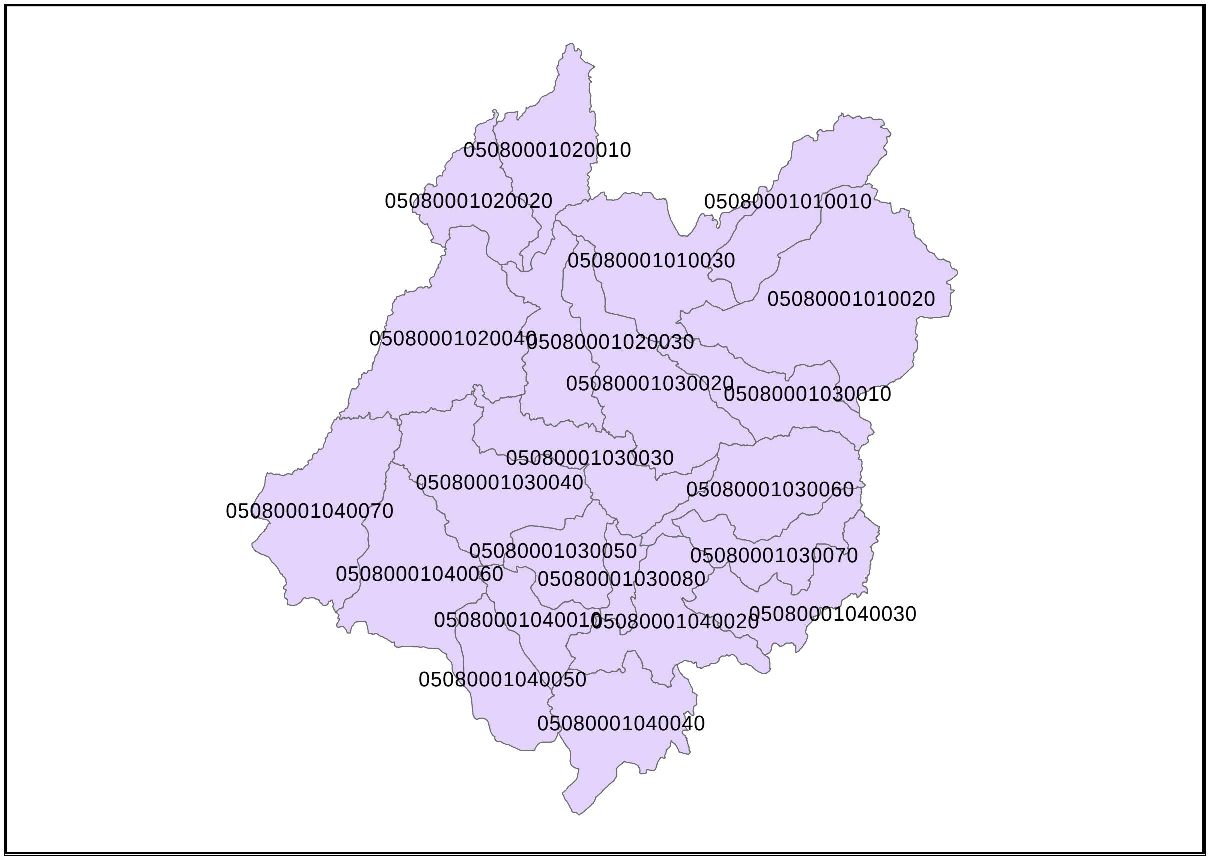


FIGURE I

As mentioned previously, the data used in the research is from a 1994 sampling of multiple streams in many of the HUC 14 drainage basins by Ohio EPA. This data has been analyzed to find possible reasons to explain fluctuations between different water quality indicators. These quality indicators include IBI, QHEI, temperature, chemical levels, oxygen levels, and substrate. Point sources were also analyzed in order to examine their effect on water quality. BMP data from as recent as 1999 has also been noted for possible future study.

The following scale was used to rate the IBI value of water quality:

- Exceptional 50-60
- Very good 42-49
- Good 34-41

- Fair 27-33
- Poor 17-26
- Very poor <17

Analysis

10010

The average IBI value for this sub-watershed is 28.33, which is considered fair but is below the EPA standard for warm water habitat. In other words, this subwatershed is substandard. The apparent cause of these problems here are related to land use and habitat. The average QHEI score of 39.33 is the lowest of any subwatershed in the Upper Great Miami. The 90-meter riparian zone land cover is 86% agricultural and only 12% forest. This sub-watershed also has a very low average DO Probe at 4.80 ppm (parts per million). A healthy stream would have a DO level above 6 ppm. The temperature is 21.75 C which is average for the watershed. None of the Best Management Practices (BMPs) that have been added to the watershed are in this area. There do not appear to be major point sources of pollution in this area. The main source of the problem appears to be habitat problems from the land cover in the 90-meter riparian zone. *Figure II and III compare the average IBI levels to forest land cover and agricultural land cover.*

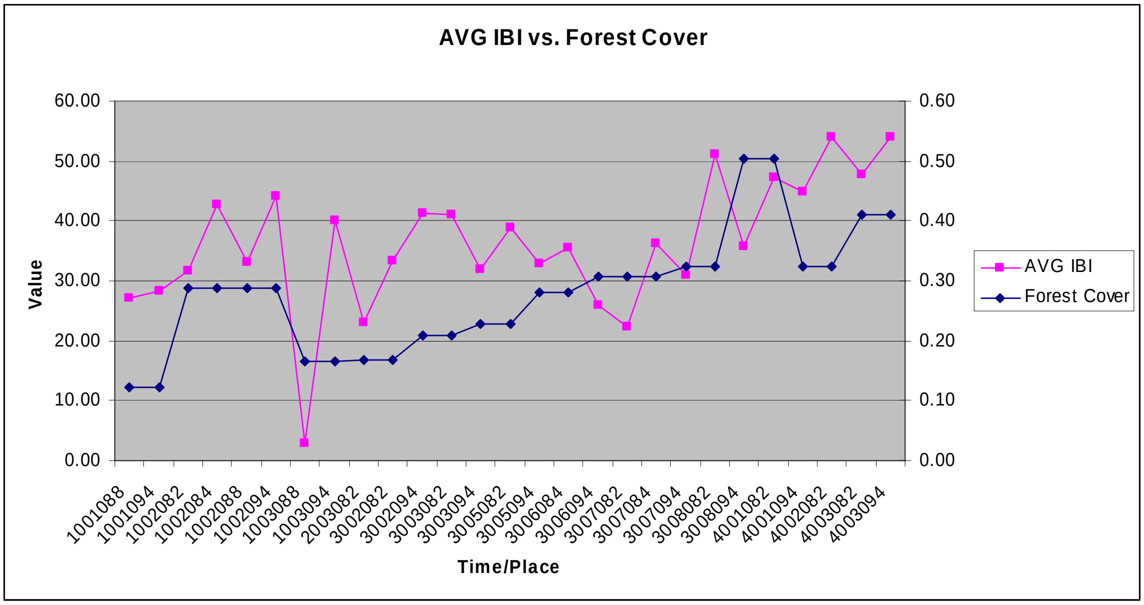


FIGURE II

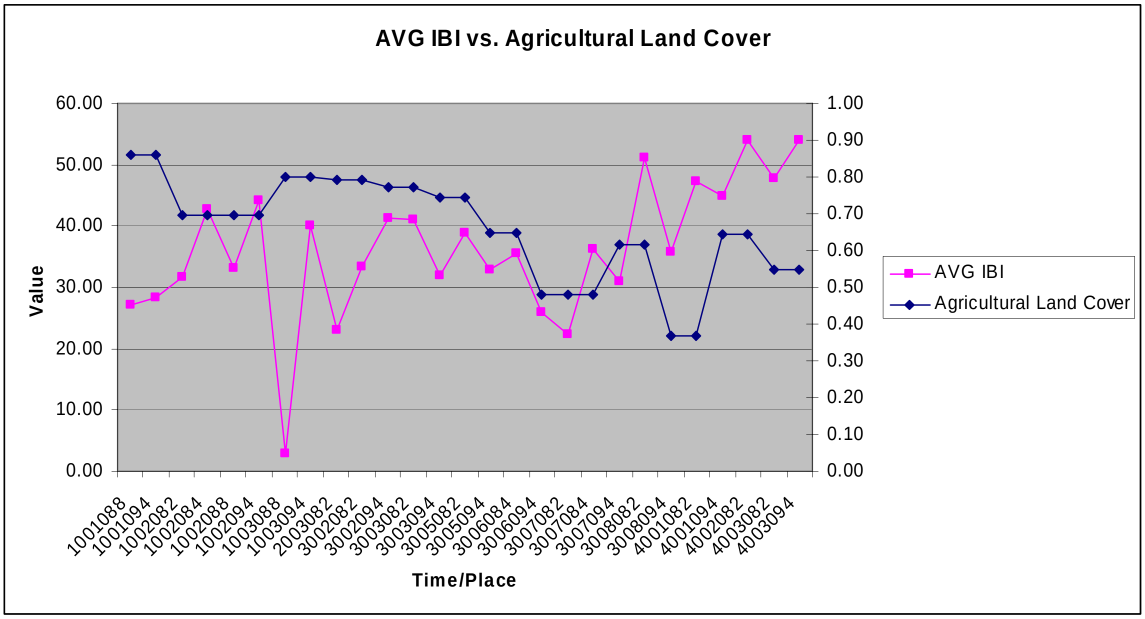


FIGURE III

This subwatershed has the worst average IBI and QHEI values in the entire watershed. However, these values are actually a slight improvement from the previous sampling in 1982. Average IBI increased from 27.00 to 28.33 and average QHEI increased from 31.00 to 39.00. The subwatershed has also experienced decline, as average substrate (an important component of the QHEI) dropped significantly from 13.00 to 8.33, as well as DO Probe from 7.79 to 4.80.

10020

The Great Miami River South Fork to Indian Lake has a very good water quality ranking with an average IBI of 44.25. Thus, this area meets the aquatic life use standard of EPA. This is an improvement from the last sampling data taken from 1988, when the IBI value was 33.14. The QHEI, last taken in 1984 decreased significantly from 71.00 to 49.40. The Ammonia, Biochemical Oxygen Demand (BOD5, a measure of organic waste), maximum Chemical Oxygen Demand (COD, another measure of how much oxygen might be consumed), and Nitrate N are all relatively low. The land cover here is 70% agricultural and 29% Forest. There is one point source on record, Northwood Stone and Asphalt. The increased amount of forest land seems to be helping to protect this area and the point source does not seem to have too great a negative impact. There are no records of BMPs put in place in this subwatershed.

10030

The Great Miami headwaters to above Cherokee Mans Run [except North & South Forks] subwatershed has an IBI value of 40 and is categorized as Good but below the standard. The QHEI in the subwatershed is low at 44.00. The temperature is higher than average at 22.13 C and increased significantly from the samples taken in 1982 (13.52 C). The average DO is low at 6.73 a decrease from the 1982 level of 10.10. There is a high level of agricultural land use in the 90-meter riparian zone at 80% while 1% is urban and 16% is forest. There are no records of BMPs or point sources in the subwatershed. It appears that the low percentage of forest cover in the riparian zone has a negative effect on the water quality.

30020

Basin 30020 is the only other subwatershed in our study area with a fair ranking. This subwatershed has had to deal with multiple point sources in the area including, Heartland of Indian Lake Reservoir, Indian Lake Local Schools, Indian Lake Sanitary Sewer District, Russells Point Water Plant, and Bellemar Parts Industries. Basin 30020, which is the Great Miami River below Cherokee Mans Run to above Munchinippi Creek, has shown great improvement between 1982 and 1994. The average IBI has increased from 23.11 to 33.33. Ammonia levels have dropped from 1.2 to .05. BOD 5 dropped from 3.78 to 2.70. Total Kjedhal N dropped from 1.90 to 1.20. One major reason for these improvements, as cited by the 1996 Upper Great Miami Watershed Report by the Ohio EPA, is that the Indian Lake WWTP was upgraded in 1985. This has helped reduce the ammonia-nitrate loads.

However, even with these improvements, the watershed still struggles. From 1982 to 1994, DO decreased from a low 5.43 to a lower 5.10. The 90-meter riparian zone has only 17% forest cover, as well as 2% urban cover. Figure IV below is an image of the average IBI at sampling points and the point sources in the sub-watershed. The point sources near the IBI sampling points undoubtedly affect the IBI values. The IBI sampling point away from the point sources is a much healthier 41. There are no BMPs on record in this subwatershed. Multiple Point sources could be affecting the area as well as the low percentage of forest (17%).

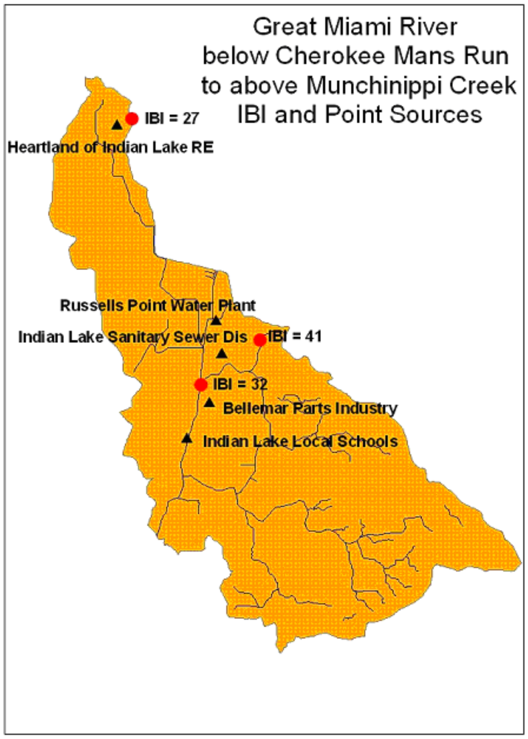


FIGURE IV

30030

With an average IBI of 41, this sub-watershed is considered good. Still the QHEI in this area is lower than average at 48. There is no point source data, but some BMPs are in place including Grass Filters and Livestock exclusion. There is a high level of COD hi (50.00) and a low DO Probe of 5.10. There is a high Residue Total non-filterable of 53.00; the average is 24.43.There is also a high level of Nitrate N at 0.04. There is 77% agricultural land cover in the region and 21% Forest cover. *Figure V shows the average level of Nitrate N in HUC 30030 compared to the average of Nitrate N in other HUCs.*

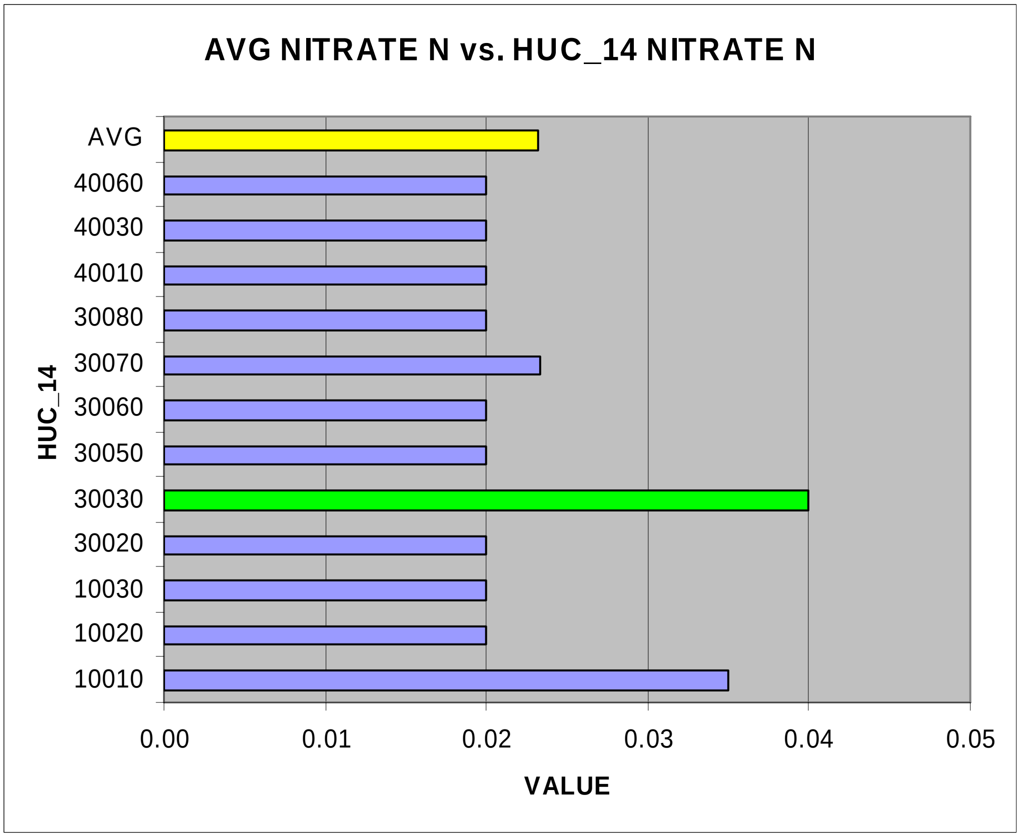


FIGURE V

<u>30050</u>

HUC 30050, the Great Miami River below Rum Creek to above Bokengehalas Creek, has an average IBI of 39. This subwatershed is considered good but does not quite meet the standards. It has a low QHEI of about 47 and a low average substrate of 2.00 out of possible score of 20. The BOD5 and maximum COD are much higher than the averages for other subwatersheds with BOD 5 at 4.00 and COD Hi at 58.00. This is an increase from the 1982 levels when BOD 5 was measured at 3.38 and COD Hi was 27.75 The DO is slightly lower than average at 6.30, a rise from 4.95 in 1982. Total residue (a measure of sediment) is also very high at 73.00 and the temperature is above the average. The area is 74% agricultural and 21% forest. There are BMPs in the area, but the habitat problems along with organic wastes seem to be the major causes of degradation.

Figure VI shows average IBI and average QHEI compared to the COD Hi levels in each HUC at different time periods. You can see the high level of COD Hi in 3005094. Figure VII shows Average IBI vs. Average Substrate and you can see the low level of substrate in HUC 30050.

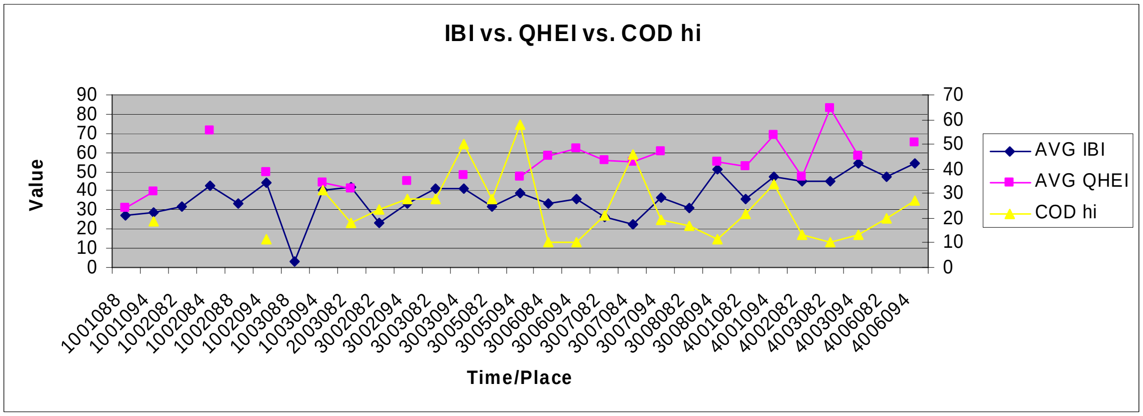


FIGURE VI

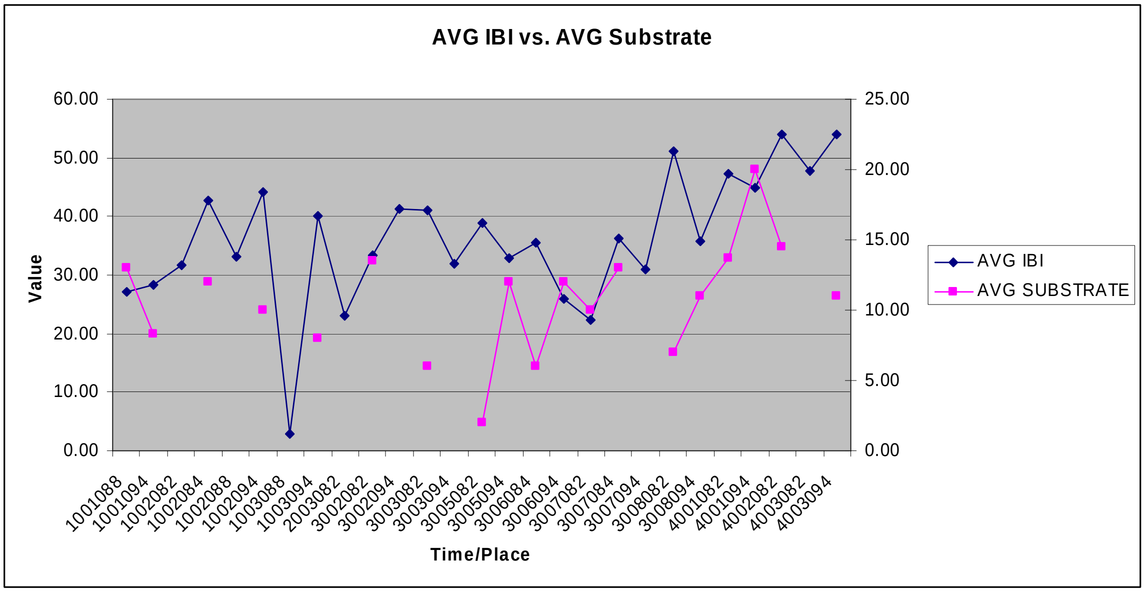
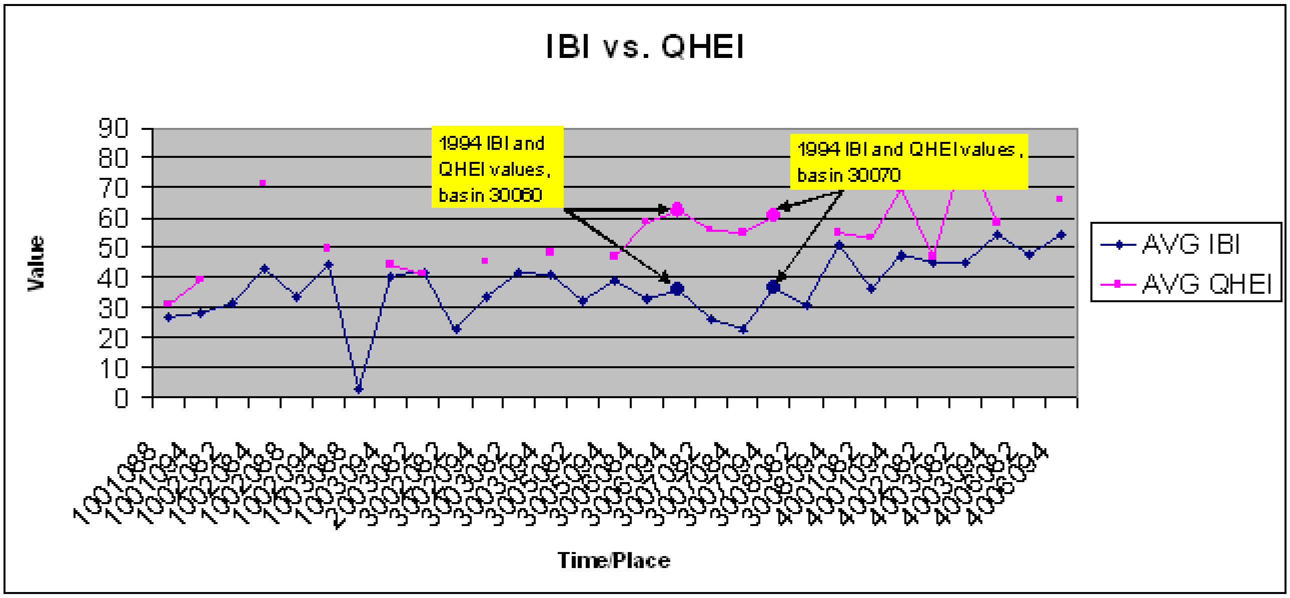


FIGURE VII

While analyzing the sub-watersheds with good water quality, a discrepancy was noticed between average IBI and average QHEI. Some sub-watersheds seemed to have strong QHEI values, but weak IBI values. Figure VIII below depicts the analysis.



1994 IBI and QHEI values, basin 30060

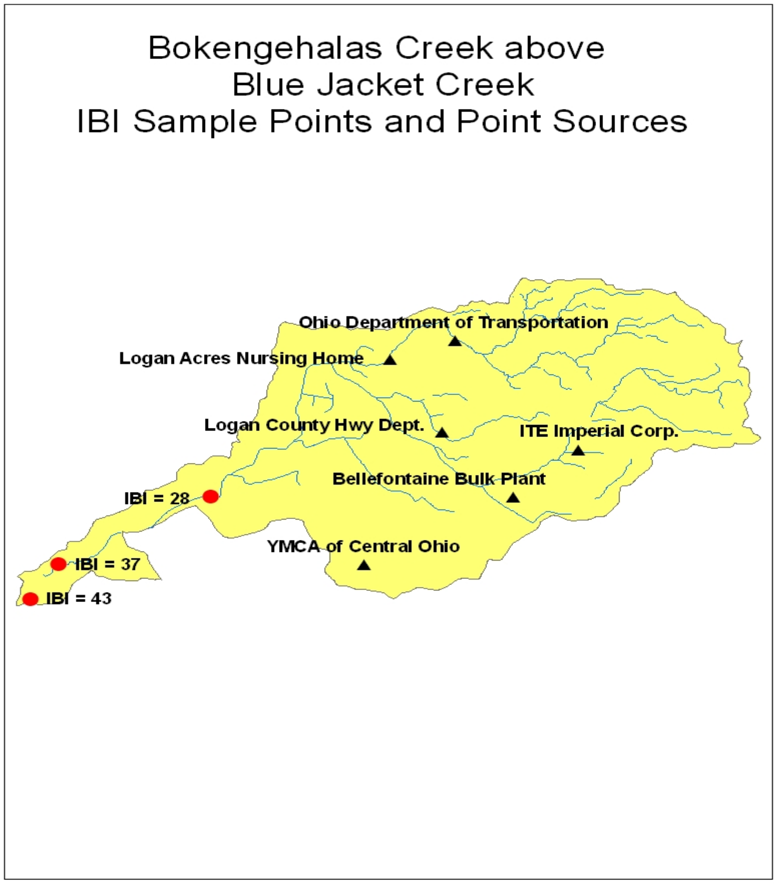
1994 IBI and QHEI values, basin 30070

FIGURE VIII

Two sub-watersheds, HUC 30060 and 30070, were studied in an attempt to understand what caused the discrepancies. It was determined that both point sources and urbanization were the cause.

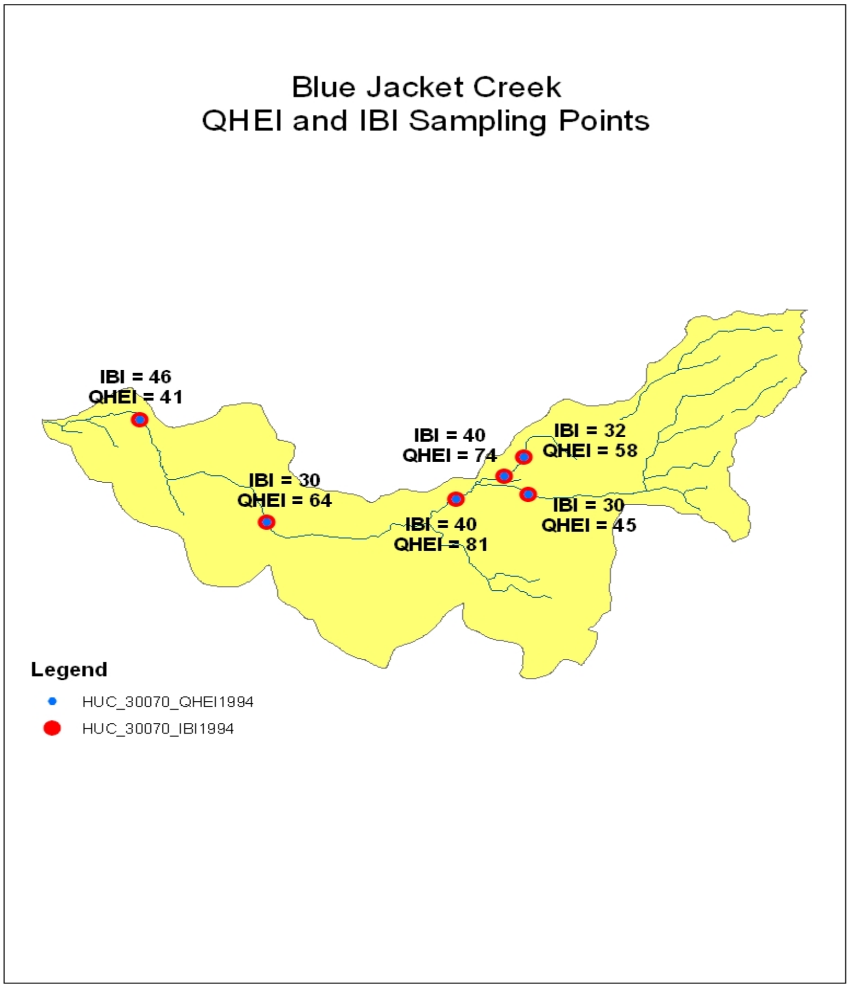
30060

Basin 30060, Bokengehalas Creek above Blue Jacket Creek, has seen a mild improvement from 1982 to 1994. Average IBI improved from 33.00 to 35.50 and QHEI improved from 58.50 to 62.00. The current QHEI is very healthy compared to the current IBI. Average substrate has declined from 12.00 to 6.00. Ammonia and Nitrate N levels have not changed. Average DO levels have improved from 7.95 to 9.40. The temperature in the watershed has also stayed cool; it has risen slightly from 15.5 C to 17.00 C. The 90-meter riparian zone helps the water quality with 28% forest cover. Urban and Agricultural cover are 5% and 65% respectively. Point sources in the subwatershed include including YMCA of Central Ohio, BP OIL Bellefontaine Bulk Plant, ITE Imperial Corp., Logan Co. HWY Dept., Ohio Dept. of Transportation, and Logan Acres Nursing home, which might explain why the IBI level is much lower than the QHEI level. The image below shows the improvement of IBI quality the further away it is from the point sources.



30070

The Blue Jacket Creek sub-watershed has experienced a great deal of improvement from 1982 to 1994. In 1982, the sub-watershed was rated poor with an average IBI of 22.33. Now, with an average IBI of 36.33 it is considered good. The QHEI did not improve much, but it did improve from 55.00 to 60.50. Again, the QHEI is much higher relative to the IBI. Ammonia levels in the area have dropped from 0.27 to 0.05. The BOD 5 levels dropped from 9.64 to 1.15. COD Hi dropped from 46.09 to 19.50. DO levels were good and improved slightly from 8.77 to 9.82. The riparian zone has good forest cover of 31%, but also deals with 18% urban land cover. The subwatershed also has two point sources which include Bellefontaine Municipal Treatment Plant and Westinghouse Electric Corp. According to the 1996 EPA Ohio Report, the Bellefontaine Plant went through two upgrades, one in 1988 and another in 1993, this contributed to the improvements in the sub-watershed. The impacts of urban land runoff continue to cause a problem in this subwatershed.



There are grass filters and septic upgrades in this sub-watershed.

30070

This watershed has a good IBI rating of 36.33. The QHEI is also above average at 60.50. The BOD 5, COD Hi, and Ammonia are all lower than average. The DO Probe is also a healthy 9.82. In this area there is a high amount of urbanization at 18%, forest cover makes up about 31% of the land. The temperature is lower than average at 19.10 C. BMPs are in place, including constructed wetland, septic upgrades, and strip till equipment. There are also point sources in the region including City of Bellefontaine Municipal Treatment Plant, and Westinghouse Electric Corp. Both the point sources and the urbanization undoubtedly affect the IBI levels.

30080

This sub-watershed has exceptional water quality with an IBI value of 51. The QHEI is also 55. The area has low BOD 5, COD hi, Ammonia, and Total Kjedhal N. The temperature is around the average at 20.95. There are BMPs in the area including Grass Filters. The area benefits from 32% forest land cover, however 4% of the land cover is urban and 62% is agriculture. There is no point source data. *Figure IX shows average IBI vs. average QHEI vs. average BOD 5, at*

HUC 30080 you can see the low BOD 5 and the high IBI.

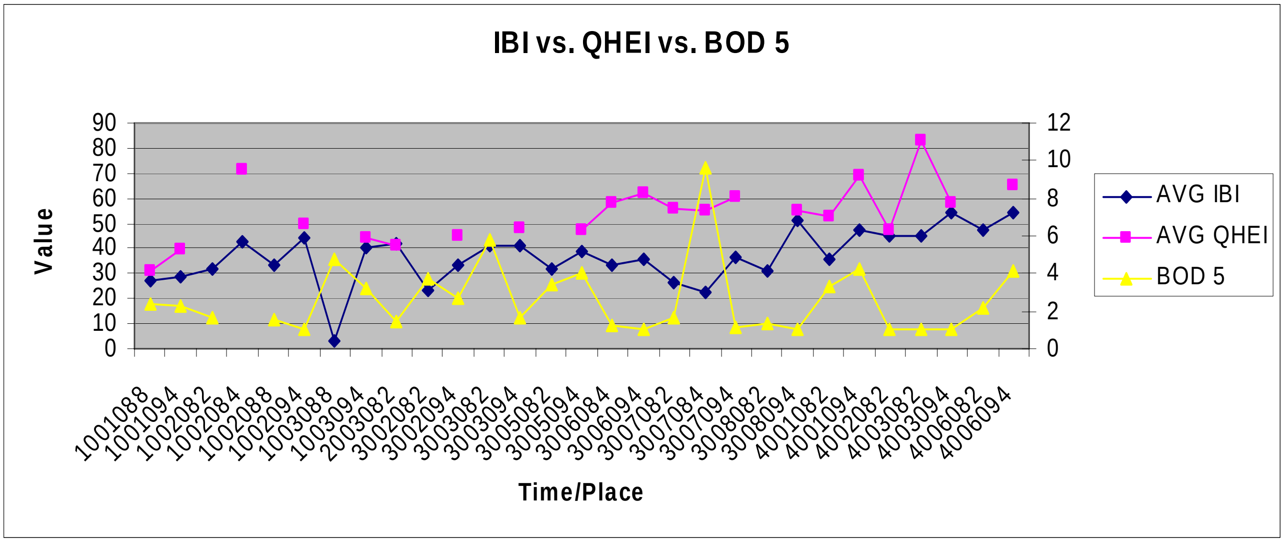


FIGURE IX

40010

This sub-watershed has an IBI level of 47.33 and is considered very good. The QHEI is one of the highest at 69.33. The BOD 5 and COD Hi seem high (4.27 BOD 5 and 33.67 COD Hi). The DO Probe is 11.17. This drainage basin has the highest level of Unlodized Ammonia in the watershed at 0.00739. There is 50% forest land cover in this sub-watershed as well as only 37% agricultural. There are septic upgrades in the area. There is one point source, Quincy STP, which might explain the high BOD 5, Unlodized Ammonia, and COD Hi levels. The point source could be keeping this area from reaching its highest potential. *Figure X compares the unlodized ammonia levels to average IBI and QHEI levels.*

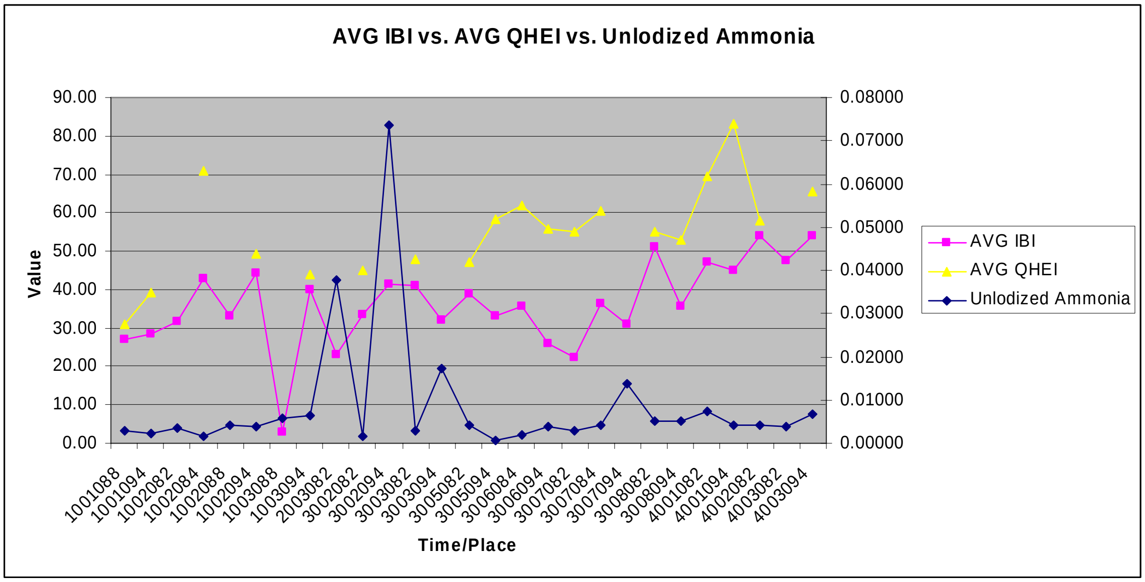
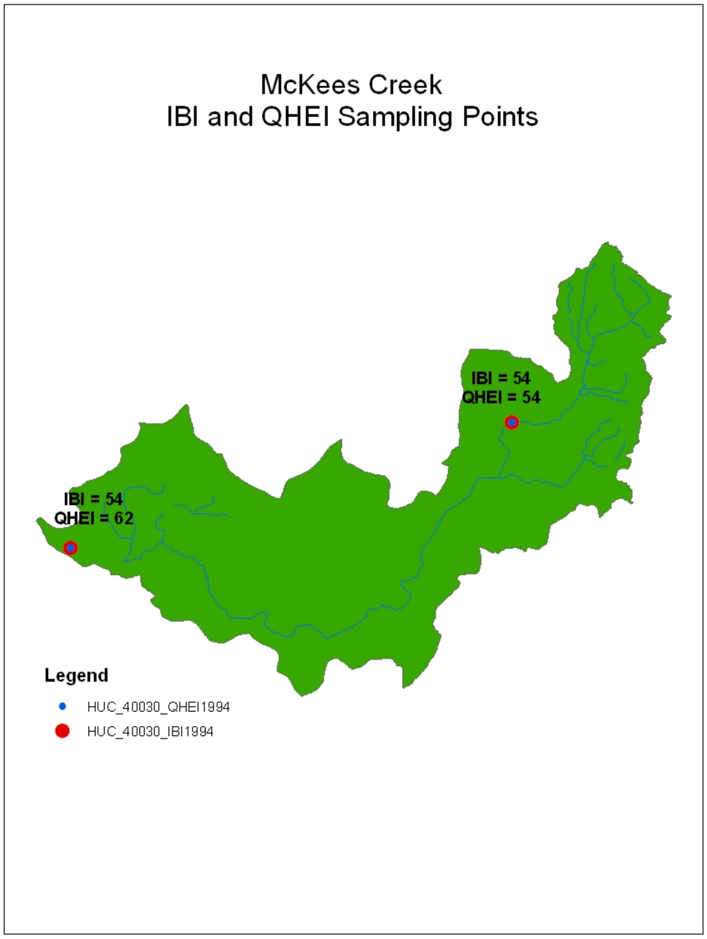


FIGURE X

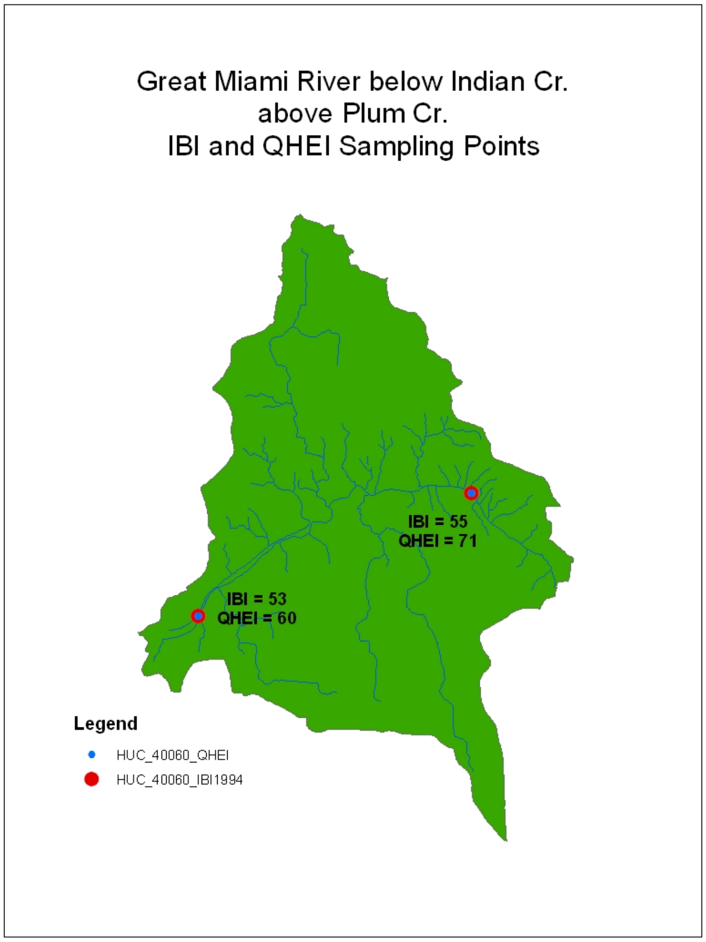
40030

McKees Creek sub-watershed also improved from a very good to an exceptional rating. From 1982 to 1994, the average IBI increased from 45.00 to 54.00. In the case of basin 40030, the QHEI decreased from 83.00 to 58.00. Substrate also decreased from 20.00 to 14.50. Ammonia, BOD 5, and COD Hi levels remained consistent. The temperature of the sub-watershed increased, but by only 1.7 degrees C from 18.00 C to 19.70 C. The 90-meter riparian land cover consists of 32% forest, 64% agricultural, and 1% urban.



40060

Basin 40060, the Great Miami River below Indian Creek and above Plum Creek has exceptional water quality with an IBI value of 54.00. The subwatershed improved from its 1982 rating of very good. In 1994, the QHEI was 65.50. BOD 5 increased from 2.15 to 4.10, and COD increased from 19.75 to 27.00. DO improved from 7.67 to 10.30. Like in many other of the sub-watersheds, the average temperature increased. The average temperature from samples rose almost four degrees from 19.25 to 23.00 C. The subwatershed benefits from 41% forest cover in the 90-meter riparian zone; only 55% of the riparian zone is agricultural. There are BMPs in place which include strip-til equipment and grass filters. *Figure XI shows the DO Probe levels over time and place compared to the average IBI and QHEI over time and place.*



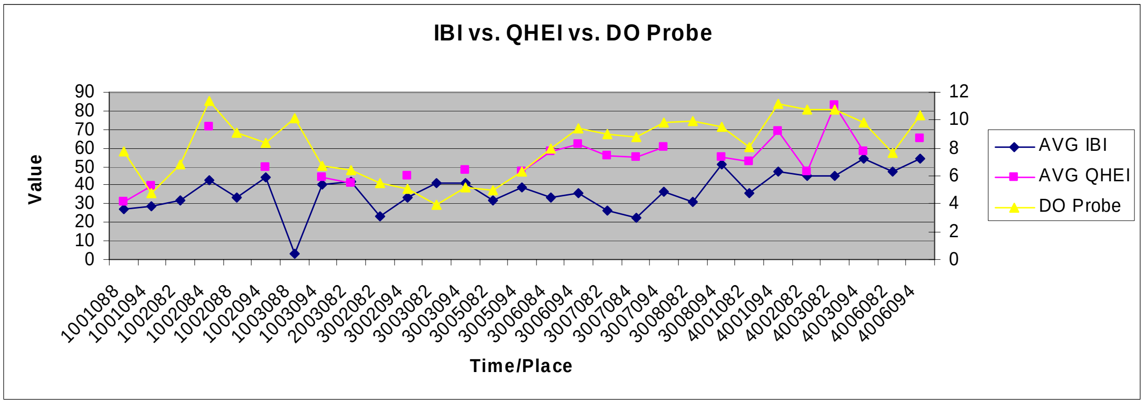


FIGURE XI

Summary of Water Quality Issues in the Subwatersheds

Based on the existing data available for the watershed, some parts of the watershed have improved in quality because of the installation of new sewage treatment plants. Other areas are still of substandard quality from a variety of possible causes. These causes include:

1. Destruction of the habitat in the riparian zone by using that land for urban and agricultural uses or otherwise altering the stream channel
2. Point source pollution from sewage treatment plants and other facilities
3. Non-point source runoff from agricultural and urban areas
4. Excess runoff causing bank erosion and stream sedimentation

The quality of the watershed as measured by the biological indicators is generally very good, but there are clearly some areas that could be improved in quality. In addition, the current data can guide the efforts that can protect the high quality areas from degradation. The issues the communities in the watershed need to discuss are what types of policies and programs are best suited to protect and improve the water quality in the Upper Great Miami Watershed. These discussions will be the subject of the future deliberations with watershed residents.

Technology Enhanced Participation

Preliminary meetings held in March and April of 2005 in the study area gave insight into both the level of interest and accessibility to online participation opportunities. Ohio State University Extension services in Shelby and Logan Counties organized the meetings through their watershed interest listings. Potential participants were notified through phone calls and public notices in the local papers and at Extension offices. Despite these efforts, a total of 15 persons attended the meetings; three people from Logan and twelve from Shelby attended the meetings. A preliminary survey was distributed asking about computing capacity, meeting availability and interest, and online forum topic interest. Of the total attendees, 14 said they would attend additional in person and online meetings. Online meeting interest ranged from weekly to monthly. Five participants said they would attend an online audio conference. All attendees noted access to the Internet from work and/or from home; connection types included dial up, DSL, high speed wireless, and cable modems. Topical interest for the online meetings included general BMP information, state and federal programs, and water quality. Despite the low attendance at these meetings, we felt the interest that did exist might be sufficient to have a core group for a first round of online meetings in the fall.

County level meetings were held again in September; this time period was suggested based on the availability of farming people in our study area. This meeting was to focus on both the mapping information that had been completed since the start of the study as well as to provide a tutorial for participants on Elluminate, the online discussion and meeting tool. Meetings were again organized with the County Extension offices. Unfortunately, turnout at these sessions was lower than the original sessions. When invitations were emailed for the online meetings, only five people registered to participate. The project could not move forward as intended with this number of participants. We contacted the Extension offices in both counties and decided to attempt sessions in the late winter or early fall of 2006. At this time, we discovered through discussions with extension contacts that feedback to the contacts indicated some hesitation on the part of potential participants with the technological aspects of the study. There was also some dissatisfaction with the scope of the study on the entire Upper Great Miami Watershed, rather than on smaller subwatersheds in the counties in question.

We also developed a mail survey instrument to better understand the participation motivation challenges at issue for this project. The survey instrument asked twenty-seven questions related to factors which influence participation (e.g., timing of decision making process, familiarity with topic, familiarity with attendees, type of meeting), as questions on typical meeting habits and demographic information. The mail survey was sent out in April of 2006 to 154 persons identified by County Extension contacts as having interest in watershed planning issues. This represented the same database of contacts used for the in person meetings in March/April and September of 2005. Thirteen surveys were returned due to address issues or, in one case, a deceased addressee. Thirty-two of the remaining 141 surveys (23%) were returned. Summaries of the responses are presented in the tables below (note: in some cases, the % totals do not sum to 100% because not all respondents answered these questions):

Table 1: Percent agreement with participation factors

I am more likely to participate if	Fully Agree 1	2	3	4	5	6	Do not agree at all 7
Comfortable with associated topic technical issues	19%	34%	22%	13%	6%	3%	0%
Meeting times are convenient	44%	31%	13%	6%	3%	0%	0%
Meeting topic is of significant personal concern	53%	25%	6%	0%	6%	3%	0%
There is a **concrete and action-oriented outcome**	47%	34%	16%	0%	3%	0%	0%
I can **influence the decision making process**	28%	38%	19%	9%	6%	0%	0%
Topic is a current crisis in the community	38%	38%	3%	9%	6%	6%	0%
It is **early in the decision making process**	3%	47%	25%	19%	3%	3%	0%
It is in **the middle of the decision making process**	0%	19%	31%	28%	13%	0%	0%
It is the **final decision of a decision making process**	9%	19%	28%	6%	9%	13%	16%
If I **personally know the meeting organizer**	9%	31%	25%	13%	13%	3%	6%
If I **personally know others planning to attend**	6%	47%	13%	13%	3%	6%	9%
It is an **opportunity to gain new information**	28%	34%	31%	3%	3%	0%	0%
It is an **opportunity to share personal knowledge**	16%	28%	31%	22%	3%	0%	0%
I receive **at least two weeks of advanced notice**	34%	31%	16%	6%	0%	13%	0%
The **meeting location** is convenient	25%	38%	19%	13%	3%	3%	0%
It is a **single meeting versus a series of meetings**	13%	25%	25%	22%	9%	0%	3%
There are a small number of committed participants rather than a larger number of folks not as interested.	9%	22%	22%	9%	9%	19%	3%

Table 2: Level of influence of meeting formats on likelihood to participate

Meeting Format	Significant Influence 1	2	3	4	5	6	No Influence at all 7
Traditional public meeting	6%	31%	28%	22%	3%	3%	3%
Online (Internet based) meeting	6%	3%	3%	25%	13%	19%	28%
Panel discussion	6%	16%	22%	25%	13%	9%	6%
“Town Hall” style meeting	9%	22%	31%	19%	3%	9%	3%
Participating on an advisory board	13%	47%	22%	3%	0%	9%	3%

Survey (mail, telephone, online)	0%	9%	34%	16%	13%	9%	3%
Email/phone call input	3%	6%	19%	16%	9%	28%	16%

In a summary follow on question, respondents noted that the three most important factors on their willingness to participate were topic knowledge, meeting time convenience, and topic immediacy (e.g., crisis). For the purposes of this study, the challenge existed that while most people stated they wanted to be involved early in the decision making process, that often is at odds with the immediacy issue. For example, watershed planning efforts in the Upper Great Miami are not currently at a crisis stage. The Ohio EPA has this watershed on its TMDL planning horizon for 2010. Therefore, even though decisions made now will be of value for the 2010 TMDL plans, it was still a challenge to get people to come to meetings to discuss related issues. Additionally, given that an online format had little to no influence on respondents' likelihood to participate in meetings, the anticipated convenience factor for this study did not materialize. An advisory board format, which may incorporate online aspects, may be a better approach based on survey responses.

When asked about extra factors that might positively influence likeliness to participate in a public meeting or similar opportunity, 14 of the 32 respondents provided input. Food (5 of 14) and other factors were the highest responses (6 of 14), while excused time (3 of 14) and nominal monetary incentive (4 of 14) were least selected. Other factors included "treated like my participation is needed" and "meetings that are two hours or less in length." The nominal monetary amount suggested ranged from $0 to $60; the mean was $10. Providing small incentives may have most appeal to those people who are "on the fence" with respect to participating in a public decision making opportunity.

Finally, when asked about the primary reasons respondents are unable to attend meetings, the two most frequent responses were that the meetings "do not address topics in which I am interested" (50%) and they were "unable to fit the meetings into my schedule" (38%). Interestingly, the intent of this project was to address each of these factors through the anticipated convenience of topic selection and personal online scheduling.

This survey will serve as the foundation for a journal submission in 2006.

Future Direction

Survey responses and discussions with county extension agents highlighted two ongoing challenges with this project. First, there remains a technology barrier with the online participation tool used in this study. We feel this barrier is not insurmountable and will be lessened with additional exposure to the tool, a broader participant pool, and enhanced online elements that make the participation process more convenient. One of the ways in which the online tools can be made more convenient to participants is through streaming live and archived video and audio recordings of traditional public meetings throughout the watershed. This would allow for interested participants to "virtually attend" meetings they could not attend physically. Equipment needed for this portion of the project (digital video recorder and accessories, digital audio recorder, and related software) has been purchased and will be utilized as watershed related meetings are scheduled for the fall and winter 2006/2007. Journal submissions based on this component of the study are anticipated in late 2007.

A second challenge with this project has been to generate interest across the entirety of the watershed. While the benefit of an online participation tool is that it can transcend jurisdictional boundaries, a reality encountered in this project is that many interested parties do not see the connection between their subwatershed issues and the larger watershed planning process. In conjunction with the lack of a planning imperative due to the distant Ohio EPA TMDL planning horizon, this lack of a "watershed perspective" has led to surprisingly low turnout for our meetings. We feel that the enhanced technological approach discussed above as well as an expanded participant recruiting effort throughout the watershed will help overcome this problem. Additionally, as the TMDL horizon nears and interested citizens in the watershed become aware of changes proposed in neighboring watersheds, there may be heightened interest in a preemptory planning effort.

References

Al-Kodmany, K. (1999) Using Visualization Techniques for Enhancing Public Participation in Planning and Design, Landscape and Urban Planning, 45, pp. 37-45.

Ball, D.L. & Cohen, D.K. (1999) Developing Practice, Developing Practitioners, in: L. Darling-Hammond & G. Sykes (Eds.) Teaching as the Learning Profession (San Francisco, Jossey-Bass).

Chickering, A.W. & Gamson, Z.F. (1987) Seven Principles for Good Practice AAHE Bulletin, 39, pp. 3-7.

Conroy, M. M.; & Gordon, S.I. (2004) Utility of Interactive Computer Based Materials for Enhancing Public Participation. *Environmental Planning and Management* 47(1): 19-33.

Dorworth, L.; & McCormick, R. (No date) Impacts of Development on Waterways. Planning with POWER (Protecting Our Water and Environmental Resources) at Purdue University Cooperative Extension Service: ID-257, IISG-01-4.

Gordon, S.I.; J. Bishof; K.Dixon; S.Ghosh; A.Iqbal; J. Kim; M.Leatherman; J.Lee; A.Lococo; J. Musson; & S. Zhang. (2003) Preliminary Plan for the Upper Great Miami Watershed. Columbus, OH: Knowlton School of Architecture, The Ohio State University, report for City and Regional Planning, Regional Planning Studio, June, 2003.

Macpherson, L. (1999) Joystick Not Included: New Media Technologies are Ideal Tools for Gaining Stakeholder Interest, Acceptance, Water Environment & Technology, 11(9), pp. 51-53.

McIntyre, D.R. & Wolff, F.G. (1998) An Experiment with WWW Interactive Learning in University Education, Computers & Education, 31, pp. 255-264.

Miller, B.; & McCormick, R. (No date) The Relationship between Land Use Decisions and the Impacts on Our Water and Natural Resources. Planning with POWER (Protecting Our Water and Environmental Resources) at Purdue University Cooperative Extension Service: ID-260, IISG-01-19.

Oliver, R. & Omari, A. (2001) Student Responses to Collaborating and Learning in a Web-Based Environment, Journal of Computer Assisted Learning, 17, pp. 34-47.

Padgett, D.A. (1993) Technological Methods for Improving Citizen Participation in Locally Unacceptable Land Use (LULU) Decision-Making, Computers, Environment and Urban Systems, 17(6), pp. 513-520.

Simons, D. (1987) Communicating with the public: an examination of national park planning workbooks, The Journal of Environmental Education, 19, pp. 9-167.

Yazon, J.M.O., Mayer-Smith, J.A. & Redfield, R.J. (2002) Does the Medium Change the Message? The Impacts of a Web-Based Genetics Course on University Students' Perspectives on Learning and Teaching, Computers & Education, 38, pp. 267-285.

Information Transfer Program

Program Administration Project

Basic Information

Title:	Program Administration Project
Project Number:	2005OH45B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	15
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Earl Whitlatch, 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 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	2	0	0	0	2
Masters	0	0	0	0	0
Ph.D.	1	0	0	0	1
Post-Doc.	0	0	0	0	0
Total	3	0	0	0	3

Notable Awards and Achievements

We used data collected in this grant as preliminary results, and received additional funding from the USDA-Watershed Competitive Program.

Nitrogen removal in agricultural watersheds: ecological interactions associated with forested and agricultural headwater streams. USDA/NRI Watershed Processes and Water Resources. $176,000, 09/15/05-09/14/08. PI: Virginie Bouchard. Co-PI: Kyle Herrman.

Publications from Prior Projects