New York State Water Resources Institute

Annual Technical Report

FY 2000

Introduction

None

Research Program

The New York State Water Resources Institute's (NYSWRI) FY2000 activity under the Federal Water Resources Research Act consisted largely of nine research projects funded during FY1998, FY1999, and FY2000. The FY1998 projects had been funded in northeast regional competitions, one of the FY2000 projects was funded in a national 104G competition, and the remainder were funded within 1999 and 2000 New York competitions. The FY1998 projects had eclectic themes due to their derivation from a competition covering the diverse Northeast US that allowed many possible topics. These projects covered remediation of solvent-contaminated aquifers, and leaching of heavy metals from sludge-amended soils. Principals completed both regional projects during the FY2000 reporting period.

The FY2000 104G project, covering watershed nutrient modeling, began in late 2000; only a recapitulation of its goals and methods is included in this report. Subsequent annual reports will include results and student involvement. Two FY1999 104B projects had schedules that overlapped into the FY2000 fiscal years. These dealt with Cryptosporidium oocyst settling with applications in stormwater treatment, and fine-detailed Cryptosporidium oocyst transport modeling.

Four FY2000 104B projects resulted from an in-NY competition whose topic focus reflected NYS WRI's long-term priority on nonpoint source pollutant management. The projects study methods for river habitat assessment, Cryptosporidium and phosphorus management on farms, subsurface water quality monitoring methodology, and riparian buffer evaluation for water supply source protection.

All nine projects were completed except possibly for future journal publications.

Basic Information

Title:	Watershed Management: Optimizing the Location of Riparian Buffers				
Project Number:	B-08				
Start Date:	3/1/2000				
End Date:	2/28/2001				
Research Category:	Social Sciences				
Focus Category:	Economics, Surface Water, Models				
Descriptors:	Riparian buffers, Economics, Stochastic models, Water supply source protection, Optimization				
Lead Institute:	New York State Water Resources Institute				
Principal Investigators:					

Title: Watershed Management: Optimizing the Location of Riparian Buffers

Principal Investigator: Jon M. Conrad, Professor of Resource Economics, Department of Applied Economics and Management, Cornell University, Ithaca, New York.

Problem and Research Objectives:

Develop binary optimization problems that might be used to optimize the selection of parcels for a riparian buffer. Apply these models to sub–watersheds that drain into Skaneateles Lake.

Methodology:

Research was conducted into the way that riparian parcels might be ranked to determine their desirability for inclusion in a riparian buffer. Based on parcel ranking and the importance of different pollutants, several binary optimization problems were developed and applied to the Shotwell Brook and Harold Brook Sub–Watersheds that drain into Skaneateles Lake, which serves as the source of drinking water for the City of Syracuse. In addition, research was initiated on a way to integrate non–point source pollution models, that would generate "with and without buffer" pollutant loadings, and to use those loadings as inputs into a buffer optimization model. Given the expected loadings from a parcel with and without buffer status, it was possible to formulate the buffer selection problem as a binary optimization problem which sought to maximize the weighted sum of reduced loadings by acquiring conservation easements to riparian parcels, subject to a budget constraint.

Principal Findings and Significance:

In the application to the Harold Brook Sub– Watershed, eight variations of the Parcel– Pollutant Weighting (PPW) Model were solved. There were 10 parcels common to all eight buffers. These parcels might be regarded as having high priority for buffer acquisition. The cost of easement acquisition for these 10 parcels was estimated at \$560,300. This approach, based on a binary optimization problem, seems well–suited to cities wishing to establish riparian buffers to protect surface waters that serve as a source for drinking water.

Basic Information

Title:	Improved Sampling Methods for Soil Water and Groundwater				
Project Number:	B-09				
Start Date:	3/1/2000				
End Date:	2/28/2001				
Research Category:	Water Quality				
Focus Category:	Groundwater, Water Quality, Methods				
Descriptors: Water quality monitoring, Groundwater quality, Vadose zone, Solute transport, Field methods					
Lead Institute:	New York State Water Resources Institute				
Principal Investigators:	Tammo Steenhuis, Ellen Z. Harrison				

Title: Improved Sampling Methods for Soil- and Ground-Water

Principals: Tammo S. Steenhuis, Dept. of Agricultural and Biological Engineering, and Ellen Z. Harrison, Center for the Environment, Cornell University

Problem and Research Objectives

One of the critical shortcomings in the evaluation of land management practices (such as BMP=92s, land application of biosolids, septic tanks, etc) is the lack of effective methods to evaluate impacts on ground water quality. Research to date (Boll et al. 1992; Kung 1988; Ozaki 1999) demonstrates that sampling methods can have a significant impact on monitoring results. This is especially true for soils that have significant preferential flow such as occur throughout New York State. These soil types have a perched water table only during the winter to early spring, and concentrations in conventional sampling wells during this time are highly variable (i.e. two orders of magnitude). Other sampling devices such as wick pan lysimeter, gravity pan and horizontal wells (or field drains) show much grater promise for accurately monitoring the soil water.

The overall goal of the research was to examine different soil and water sampling techniques for their capability to capture the transport of water and contaminants in soil typical of the northeast.

Methodology

The study was carried out on the Dickson Farm near Bath where on wastewater sludge has been land applied on a portion of the farm since 1978. Wick pan samplers, suction cup samplers, piezometers, vertical wells and a drainage tile have been installed on the two sites for the purpose of comparing the results of the different sampler types. The wick pan samplers were installed 1 m apart, 0.6 m below the soil surface in 0.7 m long, horizontal tunnels excavated in the side of a trench. The pan consists of a 5 by 5 grid of individually sampled compartments and was pressed against the native soil with springs The undisturbed soil above each cell of the wick pan was sampled under continuous suction applied by a 0.4 m long, 95 mm diameter fiberglass wick. The upper end of the wick was spread over an acrylic plate and each plate was seated on a compression spring (65 mm tall, 24 mm in diameter) assuring good contact with the soil. Each wick was encased in 13 mm (i.d.) tygon tubing and was suspended well above a collection bottle to prevent upward movement in the wick.

The 10 cm diameter tile line (or horizontal well) is installed at a depth of 90 cm. Gravel is put around the tile line. Samples can be collected at the outlet of the tile line.

Porous cup samplers consists of a ceramic cup having an outside diameter of 48 mm, cemented to a 70–100 cm long PVC pipe plugged with a two–hole stopper. Plastic tubing is put through the stopper holes: A short length to apply the vacuum and a longer section reaching into the cup for sample retrieval. Each sampler will be installed through vertical augered holes backfilled with a slurry of the original soil mixed with a small amount of bentonite. All holes were sealed with a 250 mm layer of bentonite and/or

expanding foam to prevent leakage from the surface. In each field six porous cup samplers will be installed at a depth of 0.6 m and six at a depth of 90 cm.

Four piezometers have been installed to a depth of 1 meter. Backfilling will be same as for the porous cup samplers.

Principal Findings and Significance

Samples have been taken four times since January of this year. Samples have been analysed for trace metals and phosphorus. Results are being analysed currently and will be reported in the next year progress report.

Samples will be collected and analyzed over the next fall/winter percolation season. In addition two other similar sampling sites will be installed to evaluate the movement and monitoring of pesticides.

References

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Kung, K–J.S., Ground truth about water flow pattern in a sandy soil and its influence on solute sampling and transport modeling, in *International Conference and Workshop Proc.: Validation of Flow and Transport Models for the Unsaturated Zone*, Wierenga, P.J. And Bachelet, D., Eds., Ruidoso, NM, May 23–26, 224, 1988. (Also Research Report 88–SS–04, Department of Agronomy and Horticulture, New Mexico State University, Las Cruces, NM, 1988.)

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Basic Information

Title:	Evaluation and Management of Cryptosporidium parvum and Phosphorus Contributions in the Town Brook Watershed: Laboratory Experiment			
Project Number:	B-10			
Start Date:	3/1/2000			
End Date:	2/28/2001			
Research Category:	Water Quality			
Focus Category:	Non Point Pollution, Agriculture, Nutrients			
Descriptors:	s: Solute transport, Phosphorus, Cryptosporidium parvum, Nonpoint pollution, Livestock agriculture, Best management practices			
Lead Institute:	New York State Water Resources Institute			
Principal Investigators:	Tammo Steenhuis, Murray B. McBride			

- 1. Geohring L.D, O. L. McHugh, M. T. Walter, T. S. Steenhuis, M. S. Akhtar, M. F. Walter, 2001, Phosphorus transport into subsurface drains by macropores after manure applications: Implications for best management practices. Soil Sci. (accepted for publication, 2001).
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- Walter, M.T., M.F. Walter, E.S. Brooks, T.S. Steenhuis, J. Boll, and K.R. Weiler. 2000. Hydrologically Sensitive Areas: Variable Source Area Hydrology Implications for Water Quality Risk Assessment. J. Soil Water Cons. 3:277-284.
- 4. Walter, M.T., E.S. Brooks, M.F. Walter, T.S. Steenhuis, C.A. Scott, and J. Boll. 2000. Evaluation of Soluble Phosphorus Loading from Manure-Applied Fields Under Various Spreading Strategies. J. Soil Water Cons. (In press.)
- Christophe J. G. D. 2000. Preferential Flow and Transport of Contaminants Through the Vadose Zone. Ph.D. Dissertation. Department of Agricultural and Biological Engineering. Cornell University. Ithaca, NY
- 6. DeGroot, M.F. 2000. Factors Affecting the Sub-Surface Transport of Soluble Phosphorus: A Scientific Analysis and Farmers Perspectives. MS thesis. Department of Agricultural andBiological Engineering. Cornell University. Ithaca, NY

Title: Evaluation and Management of *Cryptosporidium parvum* and Phosphorus Contributions in the Town Brook Watershed: Laboratory Experiment

Principals: Tammo S. Steenhuis, Dept of Agricultural and Biological Engineering, Murray B. McBride, Dept of Crop and Soil Sciences, and Saleem M. Akhtar.

Problem and Research Objectives:

The USEPA s Surface Water Treatment Rule generally requires filtration to remove pollutants from drinking water supplies. New York City (NYC) was granted an exemption from the filtration rule, providing that an acceptable watershed program plan and protective measures can be achieved. A panel of scientists convened by the National Research Council (NRC) recently carried out an independent scientific review of the completed, comprehensive NYC Watershed Program s plan. The NRC panel recommended that NYC put its highest priority and resources on demonstrating that best management practices (BMPs) will remove phosphorus and pathogens (NRC, 1999). A major portion of the steam water originates from base and interflow. Although the effect of BMP s on phosphorus and Cryptosporidium in overland flow is relatively well understood, many questions remain; the effectiveness of BMP s on subsurface transport is not well known.

The objective of this research was to investigate process–based factors of C. parvum and P subsurface transport at the laboratory scale. In the first year we focused on P transport due to experimental difficulties (now being resolved) with determining C. parvum in the leachate.

Methods

Phosphorus movement (both ortho–and organic P) was studied in five different soils with widely–varying structural properties under low rainfall intensity and under ponded conditions. The soils were characterized for the magnitude of macropore flow using both chloride tracer breakthrough curves as well as dye staining of flow paths. Phosphorus adsorption isotherms were determined to correlate the adsorption potential with transport/retention of solute P.

Intact columns were obtained of five soils from New York state with structures ranging from massive to moderate coarse prismatic. The soils series included in the study were: (1) Hudson silt loam/silty clay loam (firm, moderate coarse prismatic parting to medium subangular blocky structure); (2) Honeoye loam (weak medium subangular blocky); (3) Lackawanna channery silt loam (weak medium subangular blocky parting to medium granular); (4) Genesee silt loam (granular, friable); and (5) Arkport sandy loam (massive to friable weak medium subangular blocky). All soils are moderately– to well–drained, and occur in udic moisture regimes. The columns had a diameter of 35 cm with a target length of

Both saturated and unsaturated flow experiments were carried out. For the unsaturated flow experiments, water and solutes were applied using a rainmaker 3 m above the soil surface, delivering drop sizes of approximately 3.2 mm. To mitigate raindrop impact and

consequent surface sealing, the surface of the columns were covered with multiple layers of plastic mesh with 1 mm openings. Saturated flow experiments were carried out by maintaining a constant head of 0.5 cm ponded on the soil surface by a Mariotte bottle–feed system.

The leachate was collected, immediately filtered (0.45 m nominal porosity), and stored in closed bottles at 4 o C until analysis (usually within 48 hours for ortho–P and organic P). Leachate wasnot filtered for the chloride breakthrough tests.

Over the course of several months, five leaching experiments were completed with various solutes and rainfall rates. Experiments were sequenced so that they would minimally interfere with each other. First, baseline P concentrations were assessed for 12 days. After establishing steady state, movement of ortho–P through the same columns was then examined. After 13 days organic P in the form of phytic acid was applied twice to the same columns at two different flow rates. Chloride breakthrough curves were then determined for all the columns over the course of 12 days. Finally, a 1% solution of brilliant blue dye was added to indicate flow paths. Infiltration characteristics for these soils were determined under steady unsaturated conditions during the period. On a separate set of six columns (two each from Hudson, Honeoye and Genesee), P transport was determined under steady saturated conditions.

Results

[Figures are omitted from this submission due to word processor format conversion problems.]

Figure 1 shows the distribution pattern of blue dye under unsaturated flow conditions in the undisturbed soil columns after application of 0.5 cm (Hudson) or 2.5 cm (all other soils) dyed rain at 0.2 cm/hr. Clearly visible in the Hudson are the 5–10 cm distribution zone and two preferential flow paths to a depth of 30 cm (Fig. 1). Preferential flow paths followed worm channels as well as intrapedal voids. In the Honeoye soil, dye followed ped surfaces but diffused radially as the peds were not firm. The Arkport wetted uniformly in the distribution zone, similar to but more uniformly than the Hudson. Below the distribution zone a 10 cm finger formed that

moved slightly upward after it reached a coarse lens (Fig. 1). The Lackawanna (not shown) and Genesee had diffuse flow with no signs of preferential dye movement through macropores, as both soils had basically granular structure. For the Genesee soil a wetting front with two finger– like features formed.

At the 0.2 cm h–1 rain intensity, significant ortho–P breakthrough occurred only in those Hudsoncolumns in which P appeared in the leachate shortly after application, i.e., <1 cm percolate depth (Fig.2a). Percolate P then steadily increased to a relative concentration of 0.5–0.65 after 60 cm rain application (Fig. 2a). This P breakthrough was as fast or faster than chloride, indicating no retardation. After phytate–P was added at 62 cm rain, the Hudson leachate ortho–P concentration initially decreased, followed by an increase (quickly for Hudson replicate 1 (Hud1) and gradually for Hud2). The ortho–P in the Hud2 increased sharply after the second phytate–P addition at 158 cm rain whereas the

other columns showed minor breakthroughs (Fig 2). The Arkport had an elevated (relative to the baseline) ortho–P concentration throughout the experiment while both the Honeoye and Lackwanna occasionally had elevated concentrations at 30 and 60 cm rain. concentrations in outflow water for ponded conditions.

Under saturated conditions, ortho–P appeared immediately in the first few centimeters of drainage water of Hudson, Genesee and Honeoye (Fig 2b). The maximum relative P concentration (C/Co) attained in the runoff water differed between soils. In the Honeoye and Genesee soils series the relative effluent concentration was between 0.5 to 0.75 even after 250 cm effluent depth. One Genesee column was close to 0.5 indicating, as discussed later, a greater portion of matrix flow compared to the others soils. After the influent P was halted, effluent P concentration dropped more rapidly in Hudson columns than the Honeoye and Genesee columns (Fig. 2b). In one Honeoye column the decrease in concentration after termination of the tracer influent was as fast as that of the Hudson columns.

Using the convective dispersive equation we found that the adsorption partition coefficient can at best partially explain the movement of P through the soil. Instead we found that phosphorus leaching depended on both soil structure and moisture content. Under saturated conditions P was transported by preferential flow paths in all soils tested, whereas in unsaturated conditions P was transported preferentially only in the more strongly structured Hudson soil. This has important implications for modeling P in the landscape

Saturation occurs in the landscape when the groundwater is near the surface, or when there is a perched water table near the surface. In agricultural soils these saturated areas are usually drained by tile lines. Observations of elevated P concentrations in tile lines shortly after application of manure during rainfall events (Simard et al. 2000; Jensen et al. 2000; Geohring et al. 2001) are in agreement with our experimental findings.

Soil surveys do not contain assessments of the occurrence of preferential flow, and direct collection of these data is impractical, so it is important to find a surrogate that might indicate the amount of preferential flow that might be expected to occur under different flow rates. It appears that soil structure could fulfill this role as the surrogate for indicating preferential flow in the subsoil, since classical descriptions of soil structure include degree of development or distinction, shape of peds, relative size, and firmness of the structural units.

The structures of the soils tested in this experiment were, as is typically the case, more strongly developed in the subsurface (Bw2, Bt, BC) horizons than the surface (A, Ap) horizons (Table 1). At one extreme, the Arkport subsoil is friable, weak fine granular structure or massive and at the other extreme, Hudson subsoil had firm, moderately developed very coarse prismatic structure parting to firm, moderate, medium sub– angular blocky. The Honeoye, Genesee, and Lackawanna subsoils had friable, weak to moderately developed medium sized subangular blocky structure parting to weak, fine to medium friable granular structure. The description of the Hudson subsoil as firm indicates that the matrix in the subsoil is dense and does not conduct water even at low flow rates, thus the water flow can occur only between the structural units. Hence the

description of structure (in terms of degree of development, size, shape, and stability) can be used for finding soils that at prevailing rainfall rates will experience preferential flow.

In upland settings where soil saturation rarely occurs soil structure would be a dominant factor for predicting preferential P transport, while the extent of saturation is likely a predominant factor in bottom lands. Currently we are testing this proposition under actual field conditions.

References

Geohring L.D, O. L. McHugh, M. T. Walter, T. S. Steenhuis, M. S. Akhtar, M. F. Walter. 2001. Phosphorus transport into subsurface drains by macropores after manure applications: Implications for best management practices. Soil Sci. (in press).

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Simard, R.R., S. Beauchemin, P.M. Haygarth, 2000. Potential for preferential pathways of phosphorus transport. J.Environ. Qual. 29:97–105

Basic Information

Title:	River Scale Instream Flow Simulation (RIFS)
Project Number:	B-11
Start Date:	3/1/2000
End Date:	2/28/2001
Research Category:	Biological Sciences
Focus Category:	Surface Water, Ecology, Methods
Descriptors:	Streams, Global positioning system, Aquatic habitat, Field methods
Lead Institute:	New York State Water Resources Institute
Principal Investigators:	

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Title: River Scale Instream Flow Simulation

Principal: Piotr Parasiewicz

Problem and Research Objectives:

Physical habitat simulation is a part of the Instream Flow Incremental Methodology, which was developed in the early 1970s as a planning tool for the negotiation of in– and out–of–stream water use. This method uses high–precision measurements of physical conditions to predict flow–related changes of habitat potential. Recently, this technique has been criticized as being too narrowly focused on local–scale issues, and therefore inadequate for modern, more holistic management of running waters. In the process of generalizing the results to a scale relevant to construction planning, this high precision is rapidly being lost. On the other hand, this technique deals with the functional relationship of physical attributes and biology, making it highly attractive for large–scale applications.

The scope of our study was to design and test modeling techniques that allow for a better assessment of habitat conditions on a larger scale and integration with river basin methods. Keeping technical considerations in mind, two objectives were defined:

- Development and evaluation of overall sampling strategy.
- Testing of sampling techniques combining GPS-supported survey equipment with GIS background data and modern hydraulic sensors.

Methodology

This methodological study was conducted to support the ongoing river restoration project on the Quinebaug River in Massachusetts and Connecticut. A 38 km–long study area frequently changes due to geological, hydrological, and human influences. The Quinebaug River is therefore considered representative of upcoming issues of large–scale river restoration projects in highly urbanized areas of the United States. In the first step, a theoretical concept of the large–scale survey was developed. An analytical process was subsequently simulated, using available and extrapolated data. The survey instruments were purchased and tested under field conditions. We applied our refined method to map the Quinebaug River under three different flow conditions. Data obtained to determine fish community composition was used to establish the habitat model for the study area. The performance of this method was analyzed and the objectives and strategy of the survey were modified to accommodate the findings.

Principal Findings and Strategy

The elaborated survey strategy builds upon hydro-morphological features (pools, riffles, etc.) as basic spatial habitat units. By reducing spatial resolution from the micro- to mesohabitat level, one is able to survey river sections much longer than would be possible using the standard approach. Supported by the application of a real-time GPS positioning system and aerial photographs, we determined the location and estimated the character of each hydro-morphological unit. Through the examination of the quantitative

distribution of such units in the first survey, one can delineate specific sections and identify representative sites to be re–sampled at different flow conditions. The habitat suitability of each unit can be determined by a multivariate analysis of fish community response to specific combinations of physical conditions. The collective area of all units suitable for fish is a measurement of habitat quality at observed flows. It can be used to produce a rating curve of habitat quality vs. flow. This rating curve indicates fish community response for a variety of river restoration scenarios.

The application of the above sampling strategy to the Quinebaug River has shown that the hydro–morphological mosaic is a sensitive indicator of flow–dependent fish–habitat fluctuations (Figure 1). The biological–response models constructed at the same level of resolution had highly predictive values and corresponded with known life history patterns. We were able to survey the Quinebaug at an average rate of 1 km per day. The use of real–time differential GPS (Ashtech Z–Surveyor) did not provide as precise data as had been expected, however; problems caused by multipathing and canopy cover resulted in unnecessary delays and inaccuracy.



The greatest significance of the elaborated system (MesoHABSIM) has been its successful closure of the gap between large– and small–scale assessment techniques. It permits quantitative analysis of impact across multiple scales, connecting the river– management scale with the scale relevant to biota. This makes the quantitative evaluation of restoration measures both possible and easy. The elaborated technique also has very high potential as a research tool, allowing for a multitude of analytical procedures

previously unavailable at such a level of effort. Already during the evaluation process on the Quinebaug River, findings such as an unexpectedly high sensibility of hydro– morphological configuration to flow were documented. In our future studies, we hope to use MesoHABSIM to address a number of issues critical to a more complete understanding of the function of running–water ecosystems.

Our system will be applied in Summer 2001 for two other Department projects on the Mill River in Massachusetts and at Beaver Kill in New York. MesoHABSIM will also be used by the EPA for the bioassessment of seventy streams in New England.

Basic Information

Title:	A Watershed-Scale Biogeochemical Loading Model for Nitrogen and Phosphorus		
Project Number:	G-12		
Start Date:	9/1/2000		
End Date:	8/31/2003		
Research Category:	Water Quality		
Focus Category:	Hydrology, Models, Nutrients		
Descriptors: denitrification, ecosystems, hydrologic models, geographic information systems and-water interactions, land use, mathematical models, rainfall-runoff processes, watershed management			
Lead Institute:	New York State Water Resources Institute		
Principal Investigators:	Robert W Howarth, Elizabeth W. Boyer, Dennis Swaney		

Title: A Watershed–Scale Biogeochemical Loading Model for Nitrogen and Phosphorus

Principal: Robert W. Howarth, Dept. of Ecology and Evolutionary Biology, Cornell University

[This three–year project was approved toward the end of the FY2000 reporting period. Material below is excerpted from the proposal. Progress will be reported in subsequent years.]

Problem and Research Objectives:

Two recent reports from the National Academy of Sciences have concluded that eutrophication is the biggest pollution problem in the coastal marine waters of the United States (NRC 1993, NRC 2000). Eutrophication lowers biotic diversity, leads to hypoxic and anoxic conditions, facilitates harmful algal blooms, causes dieback of seagrass beds, and can lead to changes in ecological food webs that lower fishery production (NRC 2000). Over 40% of the estuaries in the country are degraded from eutrophication, with the problem being particularly severe in the northeastern and mid-Atlantic regions (Bricker 1999). For most estuaries in these regions, eutrophication is caused primarily from over-enrichment with nitrogen; phosphorus is a secondary contributor (Howarth 1988; Nixon 1995; NRC 2000). Most of the nitrogen delivered to coastal waters in the US, including the northeastern and mid-Atlantic regions, comes from non-point sources in the watershed (Howarth et al. 1996). Agricultural sources are important in some watersheds, dominating the flux in the Mississippi River basin and contributing to the flux of some estuaries in the mid-Atlantic region, but atmospheric deposition of nitrogen from fossil-fuel combustion is an even greater source of nitrogen to estuaries for most of the mid-Atlantic region and for the northeastern US (Howarth et al. 1996; Smith et al. 1997; Jaworski et al. 1997; Goolsby et al. 1999; NRC 2000).

In regions subject to changes in land use and in atmospheric deposition of nitrogen, the processes that control nutrient loads to the coastal zone are complex. Variability of these hydrological and biogeochemical processes is increasing as weather and climate change. Understanding how these processes affect the magnitude and transformations of the nutrient loads is necessary in order to manage the environmental resources of the coastal zone. Further, it is important for those living in and managing coastal watersheds to understand the impacts of their activities and policies on these nutrient loads. A relatively simple modeling tool that can estimate the impacts of various activities in the watersheds can greatly enhance, at low cost, our ability to manage these regions effectively and to communicate the effects of human activities and environmental processes on nutrient loads. The report of the National Academy of Science s Committee on Causes and Management of Coastal Eutrophication concluded that no model currently available to managers fulfills this need for estimating the controls on nitrogen loads (NRC 2000). They noted in particular that most models used by watershed and estuarine managers fail to deal adequately with nitrogen deposition onto the landscape with subsequent export downstream, even though this is the number one input of nitrogen to many estuaries. The Committee further concluded that the development of such a model particularly one that deals with atmospheric deposition -- is one of the most pressing priorities for solving the problem of coastal eutrophication (NRC 2000). We propose to develop such a model.

To mitigate the effects of human activities on the supply of nutrients to surface waters, managers are tasked with gaining an understanding of the landscape source areas delivering nutrients to receiving waters. We propose to develop an easy-to-use model for calculating loads of N and P to coastal watersheds, targeted toward management applications. Our model will describe flow paths of water and nutrients through landscapes to receiving waters, and will characterize biogeochemical reactions that occur as water moves along these flow paths (e.g., from an upland hillslope through the riparian zone to the river). Our goal is to create a model structure that will be used widely; thus we develop the model in a commonplace spreadsheet (Excel) and will provide an optional module to make use of spatial data to calculate model input parameters and to visualize spatial elements of the model output using the Arc/View GIS. Both Excel and Arc/View can be run on PC or Macintosh platforms, and are among the most popular software of their types.

Our model will combine the event-based dynamics of a simple, lumped hydrologic model (Generalized Watershed Loading Function (GWLF) (Haith and Shoemaker, 1987) with biogeochemical dynamics suggested by statistical analyses of spatially-referenced data (the SPARROW model; Smith et al., 1997) and with information derived from spatially referenced data using GIS. GWLF is a parsimonious, event-based model that has been used successfully to analyze the hydrology, sediment, and nutrient loads of several mixed watersheds in the United States, including the New York City reservoir system, the Hudson River (Howarth et al., 1991; Swaney et al., 1996), the Tar–Pamlico (Dodd and Tippett, 1994), and the Choptank River drainage of the Chesapeake Bay (Lee et al., 2000). The model uses daily historic or synthetic temperature and precipitation data to simulate monthly discharge, sediment load, and nutrient transport. It is not a spatially-explicit model, but rather compartmentalizes the watershed into land-use/soiltype categories and considers the loads from each category separately. While groundwater and runoff are both considered, no biogeochemical dynamics of nutrients are considered; nutrients are transported passively in streamflow and sediment. Atmospheric deposition of nutrients is not considered explicitly. Sediment is generated by a variation of the Universal Soil Loss Equation, and then transported from the watershed using a nonlinear relationship with streamflow. Within-stream processes are not considered. Although the model has limited biogeochemical capabilities, it captures seasonal and annual streamflow and sediment dynamics and is sensitive to land use and management parameters.

We propose to utilize the streamflow and sediment transport components of GWLF, but to add modules that will allow improved estimation of loads to the coastal zone. These proposed modifications include: "Addition of biogeochemical dynamics for carbon, nitrogen, and phosphorus, including within-river and riparian-zone denitrification and other transformation processes. "Representation of spatially-variable atmospheric deposition "Characterization of residence times of water in the landscape and travel times of water in stream channels, and their implications for evolution of water chemistry (N and P) along flow paths. "Representation of the potential for phosphorus saturation in some soils.

We intend to incorporate the major biogeochemical processes that control nutrient exports into the model structure. Our goal is that of parsimony to keep the model as simple as possible while still retaining enough complexity to provide a satisfactory estimate of N and P fluxes. Processes that we will quantify are: 1) retention and export of nitrogen from atmospheric deposition from forested ecosystems; 2) denitrification within wetlands, streams, and rivers; and 3) retention and export of nitrogen and phosphorus from agro–ecosystems.

Methodology:

Sampling and nutrient analyses. Hydrology, sediment, and nutrient load data are necessary to calibrate and validate the model. Currently, the USGS Hudson NAWQA program samples for TN on a monthly basis at 2 sites: Mohawk at Cohoes and Canajoharie Creek and has historical data for TN at about 10 sites in the Hudson Basin (Phillips and Hanchar, 1996). Because total nutrient load is heavily dependent on storm events, it is imperative to have an intensive sampling program to enable characterization of the response to these episodes. NAWQA currently has automatic samplers in place at three main tributaries to the Hudson estuary; time–composited sample splits will be taken from these and analyzed for nutrients at Cornell to develop a dataset describing the watershed nutrient response to hydrologic events. This dataset can be used to calibrate the model to improve our understanding of extreme–event behavior.

Model calibration, validation and testing. In the model development phase, uncertainty analysis will be conducted to obtain variance estimates on the model parameters. A bootstrapping technique will be used (Smith et al., 1997) in which the calibration data are subsampled (with replacement) to develop distributions on the model parameters from which confidence intervals can be obtained. Sensitivity analyses will also be performed to evaluate the effect of particular model parameters on model predictions. A powerful aspect of modern spreadsheet software is its ability to perform relatively sophisticated fitting of models to data. The SOLVER add-in built into EXCEL permits iterative variation of parameters until model fits are optimized. We will use the SOLVER tool in the model calibration phase to fit model parameters to existing hydrological datasets. A hierarchical procedure will be followed in which hydrologic parameters will be optimized first, then erosion/sediment transport parameters, and finally biogeochemical process parameters. The rationale for this hierarchy is that those processes later in the sequence cannot be understood properly unless the earlier processes are being modeled reasonably. While this tool will not be used to perform uncertainty analyses (which require many more runs to estimate variance), incorporating the fitting capability of SOLVER into the modeling tool is seen as a benefit to future users. Note that errors recently attributed to some of the statistical functions of EXCEL (McCullough and Wilson, 1999) do not apply to the SOLVER package. The model will be evaluated in several ways by comparison against data (independent of data used in the calibration phase) and results of the SPARROW model. SPARROW and the modified-GWLF model compare in the following ways: "The exact specification of biogeochemical processes by the models will likely differ, but land use, soils, principal nutrient sources, and river hydraulics remain important predictors in both models. Similar sources of these data will likely be used. It would seem that SPARROW model coefficients and

predictions would have some transfer value at least to provide guidelines on a range of possible values to try in the optimization. "The spatial scale of the models is similar, although the spatial domain (i.e., Hudson vs U.S. watersheds) differs considerably. Both models will rely on 30-m land-cover and standard river reach network data; however, the extent of lumping of the transport pathways and model parameters may differ. "Parameter estimation entails the use of iterative optimization procedures in both; SPARROW relies on a nonlinear spatial regression procedure that is applied to estimate simultaneously all model parameters, whereas the proposed optimization routine for GWLF will be applied separately in a staged manner to fit parameters for hydrology, sediment, and biogeochemical processes. Several types of comparisons will be possible, at both the annual and seasonal time scales: "Analysis of bias and precision of model predictions of nutrient export through comparisons with monitoring data at various stream locations, including a spatial analysis of errors similar to that in a recent method comparison paper (Alexander et al. 2000b). "Comparisons of distributions of model and literature predictions of nutrient export by source and land-use type. "Comparisons of streamflow, nutrient export, and source contributions to export for specific inland watersheds, including the quantity and timing of nutrients delivered from these locations to the estuary. "Comparisons of the effects of streams and reservoirs on nutrient loss at locations throughout the watersheds.

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Basic Information

Title:	Estimating the Risk of Water Contamination by <i>Cryptosporidium parvum</i> oocysts and other colloidal pollutants			
Project Number:	B-07			
Start Date:	10/1/1999			
End Date:	9/30/2000			
Research Category:	Water Quality			
Focus Category:	Water Quality, Non Point Pollution, Solute Transport			
Descriptors:	Cryptosporidium, Solute transport, Mathematical models, Animal waste, Nonpoint source pollution			
Lead Institute:	New York State Water Resources Institute			
Principal Investigators:	Carlo D. Montemagno			

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Title: Estimating the Risk of Water Contamination by *Cryptosporidium parvum* oocysts and other colloidal pollutants

Principal: Carlo D. Montemagno, Dept. of Agricultural and Biological Engineering, Cornell University.

[Note: This project was a 12–month FY1999 project that overlapped into FY2000. NYS WRI failed to contact this principal for an additional progress report in time for one to be submitted in this FY2000 report. This project will be revisited in NYS WRI's FY2001 report. (Student and publication data are updated for FY2000.)]

Problem and Research Objectives

Many municipalities world–wide provide their citizens with finished drinking water whose source is surface waters. Recent outbreaks of cryptosporidiosis (a gastrointestinal disease caused by oocysts of *Cryptosporidium parvum*) raise grave concerns about the quality of raw surface waters, and watershed management of the risk of contamination by pathogens.

Cryptosporidium parvum is a protozoan pathogen that is found in high concentrations in animal feces. High intensity agriculture such as cattle feedlots and land application of sewage and manure may be the source of these pathogens in drinking water. The transmissive form of *C. parvum*, its oocysts, may not be eliminated by filtration and standard disinfection methods. *C. parvum* oocysts thus challenge the long–standing engineering approaches to public health risks from water supply contamination, and little is known about the transport of the oocysts in natural systems.

Our primary objective is to develop an accurate method for the quantitative determination of the effect of watershed management practices on the risk of human health caused by the transport of *C. parvum* oocysts into municipal water supplies. This goal will be achieved through development and verification of an integrated model of the transport of *C. parvum* oocysts in environment. While the study considers *C. parvum*, our strategy can be applied to any pathogenic microorganisms or colloidal particles that share the specifics and transport of *C. parvum* on the soil surface.

Methodology:

The project consists of two major components: a modeling and an experimental study. The modeling study identifies the key measurements necessary to fully describe the processes. The experimental study will provide the data necessary to verify and drive the model in practical applications.

The model has the following features:

- 1. ability to predict low probability events
- 2. temporal and spatial distribution of pathogenic microorganisms in runoff
- 3. pathogenic microorganism partitioning in soil, sediments, and the aqueous phase

4. sensitivity analysis of microorganism yield with respect to land management and environmental factors

To verify the model, we will

* carry out plot experiments with various vegetation, slope and soil types. Experimental plot studies will be designed and built to simulate field conditions * analyze the microorganism partitioning in water, soil, and sediments of varying sizes

* employ immunofluorescence assay (IFA) to estimate microorganism concentrations in water, soil and sediments, and dye permeability assay to carry out viability analysis.

Principal Findings and Significance:

[see FY1999 report]

Basic Information

Title:	Settling Characteristics of As-Deposited Cryptosporidium Oocysts
Project Number:	B-06
Start Date:	3/1/1999
End Date:	2/28/2001
Research Category:	Water Quality
Focus Category:	Water Quality, Treatment, Agriculture
Descriptors:	
Lead Institute:	New York State Water Resources Institute
Principal Investigators:	Simeon J. Komisar

Title: Settling Characteristics of As–Deposited Cryptosporidium Oocysts.

Principal: Simeon J. Komisar, Rensselaer Polytechnic Institute, Dept. of Environmental and Energy Engineering

Problem and Research Objectives:

Understanding the transport and fate of *Cryptosporidium* in the environment is especially critical to the protection of unfiltered water sources and treated sources with the potential for large protozoan inputs from their watersheds. Watershed Best Management Practices (BMPs) have been designed to mitigate the inputs of farm-generated pollutants to surface and ground water. Many of these practices serve to remove the solids from farm runoff, relying on sedimentation as a removal mechanism. Although the effectiveness of BMPs for removal of solids and nutrients has been documented (e.g. NYSDEC, 1992; Edwards et al., 1996; Meals et al., 1996), to our knowledge, no studies have assessed the effectiveness of agricultural BMP s for the removal of *Cryptosporidium*. The use of BMP s m NYS watersheds as a means of controlling potential inputs of Cryptosporidium oocysts to reservoirs may or may not be effective. Understanding the settling characteristics of Cryptosporidium oocysts in the environment, then, is critical to the rational design of BMP s that rely on sedimentation for removal of Cryptosporidium. In addition, oocyst settling is a key parameter in modeling and predicting the fate of Cryptosporidium in reservoirs. The rate at which Cryptosporidium oocysts settle is an important element in our efforts to understand and control oocyst transport to and in NYS reservoirs.

This study examined the settling velocity of oocysts under controlled laboratory conditions using oocysts that were, as much as possible, unaltered from the form in which they occur in the environment. By using freshly obtained oocyst–infected feces in settling column experiments, we hoped to overcome the experimental bias of previous investigations by other researchers into oocyst settling. The results of this study will contribute to our understanding of the associations of oocysts with other particles in fecal matter and whether these associations can significantly impact the sedimentation of oocysts from the water column. Our objectives in conducting this investigation were:

- 1 . to determine the settling velocity for oocysts, as deposited in infected fecal material, when this material is introduced to a column of quiescent water with known constituents; and
- 2. to examine the effect oocyst age, ionic strength of the suspending medium, and the presence of magnesium (Mg) and calcium (Ca) on the experimentally-determined settling velocity of *Cryptosporidium* oocysts.

Knowledge of the settling velocities of *Cryptosporidium* oocysts under various conditions, then, will provide a more rational basis for risk assessment, regulation and monitoring as well as design of BMP s to enhance oocyst removal.

Methodology:

Source of as-deposited Cryptosporidium *oocysts.* Bovine fecal material containing *Cryptosporidium parvum* oocysts was obtained from Excelsior Sentinel, Inc., Ithaca, NY. Three batches of fecal material were used in this study. Batch 1 was collected from a 10– day–old calf, which was asymptomatic for cryptosporidiosis. Batch 2 was from a 9–day– old calf and Batch 3 from a 7–day–old calf. The percent solids was determined for all batches of fecal material by weighing samples before and after drying at 105°C until a stable mass was obtained. Percent solids was calculated as the percent of wet weight. Fecal material was stored at 4°C Oocysts described as fresh in this study were from feces that had been stored 5 weeks or less; aged oocysts were from feces that had been stored for 13 weeks or more.

The concentration of oocysts in each batch of feces was determined by preparing suspensions of known dilution of the fecal material in distilled (DI) water. 100 µl subsamples of these suspensions were filtered onto 13 mm Whatman Nucleopore membrane filters, pore size 0.8 µm. A filtered sample was incubated for 40 minutes in the dark at room temperature with 100 µl of fluorescein isothiocyanate (FITC)conjugated monoclonal antibody for Cryptosporidium parvum (Aqua-Glo, Waterborne Inc., LA) diluted 120 with AusFlow® mAbBuffer (0.89 g tetra-sodium pyrophosphate, 500 µl 0.05% w/v Tween 80 solution, 500 µl 0.05% w/v sodium azide, and 5 g BSA albumin, in 1 1 DI water, adjusted to pH 8 with HCl and filtered through 0.2 µm filter). At the end of the incubation period, the filter was rinsed with a few drops of AusFlow® FlowBuffer (same as AusFlow® mAbBuffer without the BSA albumin added), then placed on 5 µl of AusFlowB mounting medium (2 ml glycerol, 2.4 ml DI water with 100 mg/ml DABCO, 4.8 ml 1 M TRIS buffer, 0.5 ml formalin, and 0.5 ml 5 M NaCl, adjusted to pH 8.6 using 1 M HCl) on a glass microscope slide. Entire filters were examined for oocysts at 400x magnification using a Nikon epifluorescent microscope (excitation at 480/30 nm and emission at 535/40 nm). Oocysts were identified as bright apple-green fluorescing ovoid to spherical objects, $3 - 6 \,\mu\text{m}$ in diameter, with brightly highlighted perimeters.

Viability of Cryptosporidium oocysts. Viability of the oocysts in the fecal material and in the samples drawn from the settling columns was determined using a dye permeability assay, as described by Anguish and Ghiorse (1997). Briefly, 100 µl samples were incubated with 10 µl each of solutions of 4',6-diamidino-2-phenylindole (DAPI) (2 mg/ml in high-pressure liquid chromatography-grade methanol) and propidium iodide (PI)(1 mg/ml in 0.1 M phosphate buffered saline (PBS) (8.1 mM Na₂HPO₄·12 H₂O, 1.47 mM KH₂PO₄, 0.138 M NaCl, 2.7 mM KCl at pH 7.4)) at 37°C for 1.5 hours, then with 100 µl of diluted Aqua-G10 for an additional 0.5 hours. Samples were washed twice in 0.1 M PBS and resuspended in 100 µl of 0.3 M 1,4-diazabicyclo[2.2.2]octane in 0.1 M PBS. 100 µl samples were pipetted onto 0.1% agar-coated microscope slides for examination under the epifluorescent microscope. Oocysts identified by FITC staining were examined with appropriate microscope filter sets for inclusion of DAPI (excitation 330 - 380 nm and emission 420 nm) and PI (excitation 5 10 - 560 nm and emission 590 m-n). FITC-positive oocysts that did not exhibit inclusion of DAPI or PI were further examined under differential interference contrast (DIC) for the presence of internal structures. Oocysts with internal structures were classified as intact (I), while those without internal structures were identified as nonintact (NI). DAPI-PI-, I and DAPI+

PI-, I oocysts were considered viable; DAPI+ PI+, I and DAPI- PI-, NI oocysts were considered nonviable.

Settling Columns. Sedimentation rates for Cryptosporidium oocysts in fecal material were measured in side-by-side duplicate settling columns. Each column was constructed of. glass tubing mounted vertically in a polyvinyl chloride (PVC) and metal gate valve sealed with a PVC base (overall dimensions for each column: 10.5 cm inside diameter (ID.) x 114 cm high). Glass side ports (10 mm I.D. x 35 mm long) were located 5, 20, 40, and 70 cm from the top surface of water in each column (two ports at each level). Each side port was plugged by a rubber stopper into which a 14-gauge canula was inserted so that the tip of the canula extended 2.5 cm into the column. The canula was attached to two syringes by way of a 3-way stopcock. The settling columns were clamped to metal stands, which were mounted on a pneumatically damped vibration-free table (Melles Griot StableTop 150 optical table). Each column was wrapped with vinyl tubing through which 26°C water was pumped by a circulating water bath (Neslab model RTE221). Fiberglass insulation encased each apparatus to further aid thermal stability. A temperature probe was inserted in a port 50 cm from the top of each column. Tubing connected to ports 85 cm from the top of each column allowed the upper column contents to be drained at the end of an experiment.

Settling experiment procedure. 2–3 g of oocyst–containing fecal material was gently stirred into 200 ml of DI water along with 2.977 (±0.101) μ m, 3.92 (standard deviation N/A) μ m, 5.75 (±0.262) μ m or 5.895 (±) μ m fluorescent latex microspheres (2.977, 5.75 and 5.895 μ m spheres manufactured by Polysciences, Inc., Warrington, PA; 3.92 μ m spheres by Spherotech, Inc., Libertyville, IL). Density of all latex microspheres was reported to be 1.05 g/cm. To facilitate analysis, amounts of oocysts and latex beads were selected to result in final concentrations in the settling column of approximately 200–300 particles/100 μ l. Approximately 10.5 L of DI water was warmed to 26°C then NaHCO₃, KCl, MgSO₄, and CaCl were added to produce the test conditions of ionic strength and divalent cation concentration. Ionic strength was formulated to simulate the ionic strength of fresh water (low) or that of domestic wastewater (high). When present, divalent cations Ca⁺² and Mg⁺² were in concentrations typical of a low alkalinity surface water. In Test #7, 0.1X Hank's Balanced Salt Solution (HBSS) was used as the suspending medium.

The suspension of fecal material and latex microspheres was added to the test water and gently stirred for approximately 3 minutes. Conductivity of the suspension was measured at this time. The suspension was then quickly poured into the settling column to a depth 5 cm below the top of the column. The gate valve at the base of the column was initially open. The top of the column was . capped with a Styrofoam stopper and then covered with additional fiberglass insulatron. After flushing 0.5 ml of column contents through the sample needles, 1.5 ml of sample was immediately drawn from a sample port at each depth in the column. This procedure was repeated for the second column. 45 minutes after the start of a test, the gate valve in the base of the column was left over after filling the columns was placed on ice for subsequent pH and oocyst viability measurements.

24, 48, 72, and 96 hours after the start of a test, 0.5 ml of column contents was evacuated from the sample needle at each port into a waste syringe, and 1.5 ml was drawn from each port on the column. As initial results indicated that there was no significant difference between concentrations of oocysts or latex beads at the various depths for a given sample time, the eight samples drawn from a column at a given sample time were combined into a single glass vial.

After the 96 hour sample had been collected, the column contents were drained through the drainage port. Approximately 500 ml of this portion of the column contents (upper column) were reserved for measuring final pH, conductivity and oocyst viability. After shaking the column to resuspend the particles that had settled onto the closed gate valve, the suspension remaining between the drainage port and the gate valve (middle column) was poured from the column, and its volume was measured. After shaking the column again, the gate valve was opened, and the contents of the column below the gate valve (lower column) were collected separately and measured. All samples were immediately placed on ice until analysis. Concentrations of oocysts and latex microspheres were determined in the fractions collected from the upper, middle, and lower column to calculate a mass balance for these particles in the settling column, and thereby assess if particles had been lost to the test apparatus.

Sample analysis. Concentrations of oocysts in settling column samples were determined using an immunofluorescent assay as described earlier for the analysis of the fecal material. After vortexing the sample, at least four 100 μ l subsamples were examined for each initial sample, and at least three 100 μ l subsamples were examined for each time interval. Two to three 100 μ l subsamples were examined from each of the middle and lower column samples. Viability of the oocysts in the initial samples, the 96 hour samples and the lower column samples was assessed using DAPI, PI and DIC, as described earlier. Fluorescent latex microspheres were enumerated using the appropriate filter sets on the epifluorescent microscope.

Principal Findings and Significance:

Settling velocities of unprocessed *Cryptosporidium* oocysts in bovine fecal material (asdeposited) were measured in settling columns, assessing the impact of oocyst age, ionic strength, and calcium and magnesium ion concentration in the suspending medium. The results of this study support the following conclusions:

1.) Based on a model for settling in a completely mixed column of fluid, derived settling rates for as-deposited Cryptosporidium oocysts ranged from 0.39-1.78 µm/s. Derived settling velocities for oocyst-sized latex microspheres settling concurrently in test columns were approximately 1.1 times faster than predicted by theory. Slowest settling rates characterized populations of oocysts that had been stored for > 11 weeks. Settling velocity of oocysts was fastest for aged oocysts in a high ionic strength suspension with calcium and magnesium ions and low PH.

2.) When the presence or absence of internal structures in the test population of oocysts was accounted for, the settling velocity of aged intact oocysts (mean = $1.39 (\pm 0.42) \mu m/s$) was greater than that for fresh intact oocysts (mean = $0.99 (\pm 0.13) \mu m/s$). The effect of oocyst age on settling velocity was independent of ionic strength and the presence of Ca and Mg in the suspending medium, but may be enhanced by low pH conditions.

3.) Although some clumps of oocysts in fecal material were observed in this study, the number of oocysts that might settle quickly due to association with large, faster settling particles in fecal material is not significant.

4.) Even under conditions producing the highest settling rates in this study, the percent removal of oocysts from suspension due to sedimentation was only 48% after 96 hours. Other environmental conditions that may enhance the agglomeration of oocysts into larger, faster settling particles, such as higher particle counts and increased mixing, were not examined in the laboratory settling columns in this study. However, it is likely that natural flow regimes will be more turbulent than the nearly-quiescent conditions provided in this study, contributing to slower settling velocities and resuspension of oocysts in the environment. Further research should examine the potential for oocyst agglomeration and settling under natural conditions (e.g. in the presence of soil particles and under turbulent regimes). The results of this study suggest that a high percentage of Cryptosporidium oocysts introduced to waterways in fecal material can remain suspended in the water column for a long time, and therefore have the potential to be significantly transported by water in the environment. In addition, the potential for transport is greater for slower settling nonintact oocysts, emphasizing the importance of assessing the viability of Cryptosporidium oocysts detected at the drinking water intake.

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Basic Information

Title:	Preferential flow and organic enhancement of metals transport to groundwater from land-applied biosolids in the northeastern U. S.			
Project Number:	NY98-C-05			
Start Date:	10/1/1998			
End Date:	2/28/2001			
Research Category:	Ground-water Flow and Transport			
Focus Category:	Solute Transport, Toxic Substances, Models			
Descriptors: Contaminant transport, heavy metals, leaching, phosphorus, pollutants, preferential flow, sludge, soil physics, unsaturated flow, water quality, water quality modeling				
Lead Institute:	New York State Water Resources Institute			
Principal Investigators:	Tammo Steenhuis, Murray B. McBride			

- 1. McBride, M. B., B. K. Richards, T. S. Steenhuis and G. Spiers, 2000, Molybdenum Uptake by Forage Crops Grown on Sewage Sludge-Amended Soils in the Field and Greenhouse. JOURNAL OF ENVIRONMENTAL QUALITY 29,848-854.
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- Qureshi, S., B. K. Richards, M. S. Akhtar, T. S. Steenhuis, M. B. McBride, and P. Baveye, 2000, Facilitated Transport of Sludge Soluble Heavy Metals Affected by Temperature and Micro-organisms. ASA-CSSA-SSSA Annual Meetings, Minneapolis, MN. Nov. 5-9, 2000.

Title: Preferential Flow and Organic Enhancement of Metals Transport to Groundwater from Land–Applied Biosolids in the Northeastern US

Principals: Tammo S. Steenhuis, Department of Agricultural and Biological Engineering and Murray B. McBride, Department of Crop and Soil Sciences, Cornell University

Problem and Research Objectives:

Application of municipal wastewater sludges (biosolids) to land is being widely promoted as a cost–effective management practice. Agricultural land, forest land, and land reclamation sites are increasingly being used for land application. In addition to beneficial components such as organic matter and nutrients, sludges also contain trace metals (such as Cd, Cu, Hg, Ni, Pb and Zn) which in groundwater or agricultural products present human and/or animal toxicity risk. Current USEPA regulations governing sludge application assume little or no mobility of sludge–applied metals to groundwater. Many field studies are unable to account for a substantial fraction of sludge–applied trace metals when the receiving soil is examined several years after application. Losses from the soil profile via leaching is a potential mechanism for the apparent losses. Relatively few studies report water quality data, and results can be complicated by instrumental detection limits and by the potential for sampler interactions.

Our overall research objective is to obtain a better understanding of the potential risks to water quality posed by land application of sludges, and to contribute to the base of knowledge needed to define land application practices that are protective of water quality in the Northeast. The specific goal of the grant was to study metal movement though the vadose zone with undisturbed laboratory soil cores, field observation and modeling.

Methodology:

Laboratory, field and modeling studies were carried out to study the metal movement in the soil. Because each of these studies had a separate methodology, it is listed with each study description in the section "Principal Findings and Significance."

Principal Findings and Significance:

The studies carried out with partial support of this grant are listed according to the objectives as: laboratory, field and modeling:

Laboratory studies: The effects of sludge processing (digested dewatered, pelletized, alkaline–stabilized, composted, and incinerated), soil type, and initial soil pH on trace metal mobility are being examined using undisturbed soil columns. Soils tested are Hudson silt loam (Glossaquic Hapludalf) and Arkport fine sandy loam (Lamellic Hapludalf), at initial pH levels of 5 and 7. Sludges were applied during four accelerated cropping cycles (215 t/ha cumulative application for dewatered sludge; equivalent rates for other sludges), followed by four post–application cycles. Also examined (with no sludge applications) are Hudson soil columns from a field site that received a heavy

loading of sludge in 1978. Romaine (*Lactuca sativa*) and oats (*Avena sativa*) have been planted in alternate cycles, with oats replaced by red clover (*Trifolium pratense*) from cycle 7 on. Soil columns are watered with synthetic acid rainwater; percolates are collected and analyzed for trace elements (by ICP spectroscopy), electrical conductivity and pH.

Twelve cropping cycles have been completed, with metals data from the most recent cycle still being processed. Leachate and soil pH levels were substantially depressed in dewatered and pelletized sludge soil columns due to oxidation of sludge-borne S and N. pH levels increased for alkaline-stabilized and ash treatments. In addition to these effects, a general trend towards acidification is occurring in all columns due to accelerated leaching with synthetic acid rainfall. Columns with a target initial soil pH of 6.5–7 were thus limed after cycle 7 and again after cycle 11 to counter this; the columns with initial soil pH of 5 are being allowed to acidify, simulating unmanaged conditions; soil pH levels in dewatered and pelletized sludge columns are dropping to or below 4.0 as a result.

Percolate metal concentrations continue to vary with sludge and soil treatments. Composted sludge and incinerated sludge ash have the lowest overall metal mobilities. Dewatered and pelletized sludge had notable leaching of Ni, Cd and Zn in Arkport soils, especially at low pH. Percolate Zn concentrations are again increasing in the low pH columns as a result of the ongoing acidification. Alkaline–stabilized sludge had the greatest number of metals appearing in percolate, including Cu, Ni, B and Mo. While Cu and Ni mobility peaked shortly after application, B and Mo mobility peaks lagged from alkaline–stabilized sludge continues to increase as of Cycle 11. In general, mobilities are greater in the coarse–textured Arkport soil than in the fine–textured Hudson soil. Old site column percolate concentrations showed good agreement with previous field data. Little leaching of P was observed in all cases. Samples from this study are being shared with Dr. Anthony Hay of Cornell University, who is investigating the distribution and fate of nonylphenols present in sludge.

Research by Qureshi et al. is investigating the role of facilitated transport and microbial activity in the release and mobility of sludge–borne trace elements. The first set of experiments (presented in 2000 by Qureshi et al.; currently being submitted for publication) examined the role of temperature and biocide (silver) in limiting metals release by altering microbial activities. Ongoing work is isolating the roles of microbial activity vs. microbial–induced pH effects (S oxidation leading to acidification) in metals mobilization.

Field studies: Two different papers were published examining the metal movement under field conditions.

The study by Richards et al. (1998) was undertaken to determine the present distribution and mobility of sludge–applied metals at an old land application site. Trace metals concentrations were determined for soils (using 4M HNO3 extracts), soil leachates (collected with passive wick lysimeters over a 2.5–year period), and plant tissue from a held site which received a heavy loading of wastewater sludge in 1978 and an adjacent control plot. Blue dye was used to indicate preferential percolate flowpaths in the sludge plot soil for sampling and comparison with bulk soil metals concentrations. After nearly 20 years, metals in the sludge plot leachate were found at significantly greater concentrations than in the control plot, exceeding drinking water standards for Cd, Ni, Zn, and B. Annual metals fluxes were only a fraction of the current soil metal contents, and do not account for the apparent substantial past metals losses determined in a related study. Elevated Cd, Cu, and Ni levels were found in grass growing on the sludge plot. Despite heavy loadings, fine soil texture (silty clay loam) and evidence of past and ongoing metals leaching, examination of the bulk subsoil indicated no statistically significant increases in metals concentrations (even in a calcareous subsoil horizon with elevated pH) when comparing pooled sludge plot soil profiles with controls. Sampling of dyed preferential flow paths in the sludge plot detected only slight increases in several metals. Preferential flow and metal complexation with soluble organics apparently allow leaching without easily detectable readsorption in the subsoil. The lack of significant metal deposition in subsoil may not be reliable evidence for immobility of sludge–applied metals.

McBride et al. (1999) examined leachate samples from the same site by using a more sensitive method (ICP-MS), which revealed elevated concentrations of Cu, Zn, Sr, Rb, Mo, Cd, As, Cr, Ni, Sb, W, Ag, Hg, and Sn compared with a nearby control site. Enhanced leaching of some elements from this near-neutral, fine-textured (silty clay loam) soil could be explained by exchange of soil-bound elements by components of the added sludge. For most of the heavy metals, however, increased leaching was a response to the high metal loadings in the soil, probably facilitated by higher dissolved organic matter in the leachate. Laboratory determined distribution coefficients, K–D, for the metals in newly prepared sludge/soil mixtures were lower than K–D values of the field-aged sludge-treated soil, suggesting that metal mobility may have been substantially higher shortly after sludge application than many years later. Cumulative losses of certain trace elements from the topsoil have been estimated relative to Cr, a comparatively immobile element. These suggest that relative long-term losses range from 20 to 80%, with the order being: Sr, Mo, Sb > Ni, Cd, Cu > Zn, Ag. Generally, those elements with the smallest K-D values (most soluble) measured recently in the soil had the largest loss estimates. However, present leaching loss rates are too low to explain the estimated relative losses of several of these elements from the topsoil over the 15 or more years since sludge application.

Model development: Steenhuis et al. (1999) examined the first–order model used by the USEPA for predicting losses from the zone of incorporation as part of the risk assessment that undergirded the development of Part 503 regulations. We found that when empirical adsorption partition coefficients from the site are used as model inputs, the EPA model for the incorporation zone is similar to that derived from preferential flow theory and simulates well the loss of metal from the surface soil layer at an orchard site where sludge was applied 15 years earlier. The EPA model and the preferential flow model were clearly different for the remaining part of the unsaturated soil below the incorporation zone.

Basic Information

Title:	Developing comprehensive criteria for dehalorespiratory bioremediation of chlorinated ethenes in a contaminated aquifer				
Project Number:	NY98-C-04				
Start Date:	10/1/1998				
End Date:	2/28/2001				
Research Category:	Water Quality				
Focus Category:	Ecology, Toxic Substances, Groundwater				
Descriptors:	Biodegradation, Reductive dechlorination, Trichloroethene, Detoxification, Intrinsic bioremediation, Groundwater, Technology				
Lead Institute:	New York State Water Resources Institute				
Principal Investigators:	Eugene Madsen				

- Hohnstock-Ashe, A. M., Scott M. Plummer, P. Baveye, and E. L. Madsen, Submitted, Further Biogeochemical Characterization of a TCE-Contaminated Fractured Dolomite Aquifer: Geochemical and Microbial Controls on in situ Reductive Dechlorination, submitted to Environmental Science and Technology.
- Committee on Intrinsic Remediation, Water Science and Technology Board, Board on Radioactive Waste Management, and Commission on Geosciences, Environment, and Resources, 2000, Natural Attenuation for Groundwater Remediation, National Academy Press, Washington, DC. 274 pp.
- Madsen, E. L., 2001, Natural Attenuation of Organic Contaminants, in J. K. Frederickson and M. Fletcher ed., Subsurface Microbiology and Biogeochemistry, New York, NY, John Wiley and Sons.
- 4. Madsen, E. L., 2000, Verifying Bioremediation: How do I know if it is taking place? in J. J. Valdes ed., Bioremediation, Kluwer Academic Publ., The Netherlands, 101-122.

Title: Developing comprehensive criteria for dehalorespiratory bioremediation of chlorinated ethenes in a contaminated aquifer

Principal: Eugene L. Madsen, Dept. of Microbiology, Cornell University

Problem and Research Objectives:

Industrial operations in past decades led to significant groundwater pollution with chlorinated solvents (especially trichloroethene, TCE). This family of solvents (which includes perchloroethene, PCE) is among the most widespread groundwater contaminants, regionally and nationally. Conventional pump-and-treat cleanup technology, designed to keep a corporation in Niagara Falls (Textron Inc.) in environmental regulatory compliance, constitutes a major financial liability. But more importantly, TCE-impacted groundwaters threaten human and ecosystem health throughout the Northeastern US and current treatment technologies constitute a significant drain on the financial resources of municipalities and private enterprises. Dehalorespiration by naturally-occurring groundwater microorganisms has the potential to supplement or replace pump-and-treat technology at some of these sites. The goal of this project is to implement a series of laboratory and field procedures (stable isotopic analyses of key carbon pools in the contamination site, analysis of site samples, physiological assays examining competing biodegradation pathways) that document the variety of processes that influence the effectiveness of naturally-occurring microorganisms in detoxifying chlorinated ethenes in groundwater. A key goal of this investigation is identifying the site geochemical component (the physiological electron donor) that derives and sustains reductive dechlorination.

Methodology:

Procedures involved iterative progression from field to the laboratory and back again. We gather site groundwater samples from wells inside and outside the contaminant plume and analyze them chemically and microbiologically. Aseptically gathered groundwaters are brought back to the laboratory where they are used for physiological assays aimed at identifying the degree to which the naturally occurring microbial community has adapted to various potential electron donors (e.g., H2, yeast extract, hexadecane native to the aquifer formation). We also use laboratory incubations of groundwater and rock samples from the field site to assess the impact of competing physiological regimes (electron accepting processes that include methanogenesis, sulfate reduction, iron reduction, manganese reduction, nitrate reduction) on dehalorespiration. These incubations include microcosms that document the potential of groundwater microorganisms to metabolize vinyl chloride (the most toxic of chlorinated ethenes daughter products) under iron-reducing and other conditions. We have discovered that pulverized aquifer material added to laboratory microcosms accelerates reductive dechlorination of TCE. We are using GC/MS analysis to attempt to identify petroleum compounds in the rock that may drive the dehalorespiratory process in situ. In addition, recently-developed molecular biological procedures for characterizing the identity of the microbial community (by sequencing the 16S rRNA genes) are being employed. Furthermore, we are using stable isotopic analyses of the inorganic and organic carbon pools in the contaminated field study site to trace the sources and fates of carbon

transformation processes. Characteristics signature in 13C to 12C ratios will allow in situ electron sources and sinks to be identified. Overall the procedures are designed to create a diverse, comprehensive chemical, microbiological, and physiological understanding of the interactions between site geochemistry and microbial detoxification processes.

Principal Findings and Significance:

Yager et al. (Environ. Sci. Technol. 31:3138–3187) presented site geochemical and microbial activity data establishing metabolic adaptation and in situ reductive dechlorination of trichloro-ethene (TCE) in a fractured dolomite aquifer. This study was designed to further explore site conditions, microbial populations, and explain previously reported enhancement of reductive dechlorination by the addition of pulverized dolomite to laboratory microcosms. A survey of groundwater geochemical parameters (chlorinated ethenes, ethene, H₂, CH₄, DIC, DOC, and d13C values for CH₄, DIC, and DOC indicated that in situ reductive dechlorination was ongoing and that an unidentified pool of organic carbon was contributing, likely via microbial respiration, to the large and relatively light on site DIC pool. Petroleum hydrocarbons associated with the dolomite rock were analyzed by GC/MS and featured a characteristically low d13C value. Straight chain hydrocarbons, were extracted from the dolomite previously found to stimulate reductive dechlorination; these were particularly depleted in hexadecane. Thus, we hypothesized that hexadecane (HD) and related hydrocarbon might be anaerobically respired and thus serve both as the source of on-site DIC and support reductive dechlorination of TCE. Microcosms amended with pulverized dolomite demonstrated reductive dechlorination; whereas a combusted dolomite amendment did not. HD treatments were also inactive. Thus, the stimulatory-factor in the pulverized dolomite was heat labile, but not HD. Amplified Ribosomal DNA Analysis (ARDRA) of the microbial populations in well waters indicated that a relatively low diversity, sulfurtransforming community outside the plume was shifted towards a high diversity community including *Dehalococcoides ethanogenes* –type microorganism inside the zone of contamination.

Information Transfer Program

Basic Information

Title:	e: Director's Office, Information Transfer and Student Project			
Start Date:	3/1/2000			
End Date:	2/28/2001			
Descriptors:	Information transfer, Education, Water quality management			
Lead Institute:	New York State Water Resources Institute			
Principal Investigators:	Keith S. Porter			

Over the past year WRI has promoted specifically the engagement of the wider academic community in water resource management issues in New York State. Opportunities to pursue this aim were sought through the New York State Soil and Water Conservation Committee, the New York State Agricultural Environmental Management Committee and the New York State Non point Source Management Coordinating Committee. With the encouragement of the three committees, WRI engaged SUNY-Buffalo faculty in an exploration of Food and Water Safety challenges presented by the high value vegetable and fruit production systems in Genesee and Orleans Counties. WRI created and inter-agency committee which explored research and outreach needs of the food industry related to water. A result was a 'first phase' proposal, which was subsequently funded through the New York State Non point Source Abatement and Control Program. The proposal was ranked fourth out of 84 proposals. Through this success WRI successfully fostered interest in similarly engaging academic resources in other counties in New York State. The NYS Soil and Water Conservation Committee is now prepared to formally invite universities and colleges to form a partnership with the committee, and its member state agencies in shared research and educational ventures.

USGS Summer Intern Program

Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 RCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	9	0	0	0	0
Masters	9	0	0	0	0
Ph.D.	8	0	0	0	0
Post-Doc.	0	0	0	0	0
Total	26	0	0	0	0

Notable Awards and Achievements

As a notable achievement, WRI has continued to play a lead scientific and educational role in the New York City Watershed Program. The high environmental and economic significance of this program attract a high degree of national and international interest. With the assistance of WRI, Delaware County has now obtained over \$2.0 million to conduct scientific and technical work on the Cannonsville Reservoir Basin. A particular success is the innovative integrated nutrient management program that WRI has facilitated through these funds. This program, led by faculty at Cornell University, is developing and applying integrated models for animal nutrition, field crops, soil and water. By using the models, imports of phosphorus can be reduced by up to 50% and the amount of phosphorus in manure reduced by 25%. This environmental gain is accomplished with economic benefits to the farmer. The models also improve the recycling of nutrients on the farm and promote more efficient applications of manure resulting in greatly reduced looses of the nutrients to watercourses. WRI is also assisting in extending the adoption of the management methods elsewhere in New York State through the NYS Agricultural and Environmental Management Program. It may also be noted that the Cannonsville Reservoir Program conducted through Delaware County is receiving a high level of acknowledgement. The recognition is due in large part to the solid scientific credentials upon which the watershed program is based. This is now an excellent example of how the academic scientific community: faculty, staff and students, can assist in meeting a critical water resources challenge.

Publications from Prior Projects

None