Institute of Water Resources
Annual Technical Report
FY 2001

Introduction

In fiscal year 2001, the Connecticut Institute of Water Resources continued to be administered by Dr. Glenn Warner, Director, and Dr. Patricia Bresnahan, Associate Director, both in the Department of Natural Resource Management and Engineering, in the College of Agriculture and Natural Resources at the University of Connecticut.

While located at the University of Connecticut, Institute's mission is to cooperate closely with all colleges and universities in the state to resolve state and regional water related problems, and provide a strong connection between water resource managers and the academic community. CT IWR responds to environmental issues in Connecticut through a statewide Advisory Board and through its involvement with state water resource committees. Membership reflects the main constituency groups for the Institute: government agencies, environmental groups, the water industry and academic researchers.

Research Program

Each year, the Connecticut Institute conducts a competitive RFP process to solicit proposals for funding under the USGS 104B program. Announcements are sent to every water resource related academic program in the state. Proposals received are sent out for peer review, and a further technical review is conducted by members of the CT IWR Advisory Board and others with relevant technical expertise. The Advisory Board then reviews the relevance of the proposals to state water research needs, and makes funding recommendations to the Institute Director.

This year three research projects were selected for funding:

Smets and Chandran: "Development of Predictive Tools to Infer Inhibition of Biological Nitrogen Removal at POTWs via Long Term Bench-Scale and Full-Scale Monitoring."

Meyer: "A Characterization of the Discontinuous Nature of Kriging Digital Terrain Models."

Robbins: "A Tracer Dilution Method for Deriving Fracture Properties in Crystalline Bedrock Wells."

Development of Predictive Tools to Infer Inhibition of Biological Nitrogen Removal at POTWs vi Long Term Bench-Scale and Full-Scale Monitoring

Basic Information

Title:	Development of Predictive Tools to Infer Inhibition of Biological Nitrogen Removal at POTWs vi Long Term Bench-Scale and Full-Scale Monitoring
Project Number:	2001CT621B
Start Date:	3/1/2001
End Date:	2/28/2002
Funding Source:	104B
Congressional District:	2nd
Research Category:	Not Applicable
Focus Category:	Nitrate Contamination, Nutrients, Treatment
Descriptors:	water quality, water chemistry, wastewater treatment, toxic substances wastewater, organic compounds, nutrients, nitrogen,denitrification eutrophication, biological treatment, bacteria,activated sludge
Principal Investigators:	Barth Smets, Kartik Chandran

Publication

1. Hu, Z., K. Chandran, D. Grasso and B. F. Smets. 2002. "A comparative study of nitrification inhibition by heavy metals: the influence of metal exposure time on biological effect." in 8th Annual Industrial Waste Technical and Regulatory Conference, Atlanta City, NJ.
2. Chandran, K., Hu, Z, and B. F. Smets 2001. "Optimal Experimental Design for Estimating Ammonia and Nitrite Oxidation Biokinetics from Batch Respirograms". in 74th Annual Water Environment Federation Conference, 2001. Atlanta, GA.
3. Hu, Z, Chandran, K., B. F. Smets and Grasso, D 2001. "Evaluation of Nitrification Inhibition by Heavy Metals Nickel and Zinc". in 74th Annual Water Environment Federation Conference, 2001. Atlanta, GA.
4. Hu, Z. 2002. "Nitrification inhibition by heavy metals and chelating agents." PhD. Dissertation, University of Connecticut, Storrs, CT.
5. Hu, Z., K. Chandran, D. Grasso, and B. F. Smets. 2002. Effect of nickel and cadmium speciation on nitrification inhibition. Environmental Science and Technology 36:3074-3078.

6. Hu, Z., K. Chandran, D. Grasso, and B. F. Smets. 2003. Impact of metal sorption and internalization on nitrification inhibition. Environmental Science and Technology 37:728-734.
7. Hu, Z., K. Chandran, D. Grasso, and B. F. Smets. 2003. Nitrification inhibition by ethylenediamine-based chelating agents. Environmental Engineering Science:Accepted for Publication.
8. Hu, Z., K. Chandran, D. Grasso, and B. F. Smets. 2003. Comparison of nitrification inhibition by metals in batch and continuous flow reactors. Water Research: In Preparation.

Title: Development of Predictive Tools to Infer Inhibition of Biological Nitrogen Removal at POTWs via Long Term Bench Scale and Full Scale Monitoring

Statement of Critical Regional of State Water Problem. The Long Island Sound , bordered by Long Island, Connecticut, and New York, is a vast recreational (e.g., boating) and economical (e.g., fish and shell fish harvesting, navigation) resource. Unfortunately, the Sound's ecosystem continues to be under tremendous stress, jeopardizing its current uses for the future. Although the reasons for the Sound's fragile ecosystem health are manifold, nutrient discharge in the Sound, especially nitrogen, is generally recognized as a key contributor to ecosystem deterioration [1]. **P**ublicly **o**wned **t**reatment **w**orks (POTWs) in Connecticut and New York present major point sources for nitrogen loads that can enter the local watershed and the Sound, resulting in hypoxic conditions in the Sound during late summers [2]. The Long Island Sound Comprehensive Conservation Management Plan requires that both Connecticut and New York reduce their nitrogen discharges to Long Island Sound by 58.5 % [1]. In an attempt to meet these new regulations, the Environmental Protection Agencies of Connecticut and New York are investing multi-million dollar amounts to upgrade wastewater treatment plants for **b**iological **n**itrogen **r**emoval (BNR) with the aim of improving water quality in the Long Island Sound. Unfortunately, many POTWs that have already installed these BNR processes are experiencing intermittent and extended periods when there is a loss of either nitrification or denitrification [2]. Not only does this result in permit violations for the municipality, but also in high total nitrogen discharges to Long Island Sound.

In order to insure that the water quality in Long Island Sound is improved and to protect this major investment, it is vital to understand and identify the cause of failures of BNR processes and to identify the factors preventing individual treatment plants from establishing BNR. The goal of the proposed research is to provide this critical information to regulatory and policy setting agencies in the states of NY and CT as well as to the professionals responsible for the treatment of domestic and industrial waste streams in these two Long Island Sound bordering states.

Statement of Research Results or Benefit. The primary focus of this research is to identify the causes of poor biological nitrogen removal (BNR) in POTWs. This research will compliment an ongoing study on nitrification inhibition study to help identify determinants of N-removal failure at POTWs due to process control deficiencies and waste stream characteristics (*Inhibition of Biological Nitrogen Removal: Microbiology, Physical Chemistry and Process Engineering, by B. F. Smets, D. Grasso, and J. Semon-Brown, March 1999-March 2001*). Driven by an exhaustive literature review, and the results of the ongoing study, we have implicated nitrification, the biochemical oxidation of ammonium-N to nitrate-N, as the bottleneck in BNR. This study will permit the validation of developed assays to rapidly measure the kinetics of the nitrification reaction using mixed liquor from a full-scale treatment plant. Part of this validation will entail a comparison of measured kinetics with observed reactor performance of bench-scale and full-scale BNR reactors across several seasons. Validation of the developed nitrification kinetics assay will yield a rapid tool to measure kinetics of the appropriate BNR rate-limiting step in full-scale POTWs, hitherto not available.

In addition, this study will permit the validation of several analytical assays that are currently being developed to identify and quantify the presence of possible nitrification inhibitors in the complex reactor influents (raw domestic wastewaters) to full scale POTWs. These assays are geared towards measuring total heavy metal content, total cationic surfactant content, and total chelating agent content of a wastewater, expressed in terms of an appropriate normalizing equivalent. Such rapid tools will prove invaluable for rapid and intermittent screening of wastewaters to assess inhibitory character. Both kinetic and inhibitor quantification assays will be developed for transfer to wide use by POTWs across the state and region to rapidly identify and mitigate BNR inhibition.

Nature, Scope & Objective of Research. Under a LISS funded program, the University of Connecticut and the City of Stamford Water Pollution Control Authority (WPCA) are examining the contributions of process engineering (hydraulics, aeration, carbon and nutrient limitation), microbiology (kinetics and stoichiometry) and physical chemistry (nitrogen speciation, availability and matrix chemistry) to BNR limitation (*Inhibition of Biological Nitrogen Removal: Microbiology, Physical Chemistry and Process*

Engineering, by B. F. Smets, D. Grasso, and J. Semon-Brown, March 1999-March 2001). One of the primary objectives of that study is to develop predictive analytical and numerical tools that permit a rapid evaluation of BNR limitation. Consequently, with bench-scale nitrifying reactors at the University of Connecticut, fed with a defined inorganic medium, we are studying reactor performance and nitrification kinetics under undisturbed operation and in response to system perturbations, such as a transient load of toxic chemicals. We have developed and optimized batch respirometric assays to measure nitrification biokinetics from continuously operated bench-scale nitrifying reactors at the University of Connecticut [3, 4]. In addition, we are conducting shock load tests to the nitrifying reactors at UCONN to validate the biokinetic assays as rapid indicators of nitrification inhibition. Further, to enable examination of the complex dynamics of different microbial populations and substrates in actual wastewater treatment bioreactors and varying influent conditions and biocatalyst activity, we propose to monitor nitrogen removal in full-scale and bench-scale activated sludge bioreactor treating actual wastewater.
Nitrification, the first requisite step in BNR, is predominantly catalyzed by autotrophic bacteria and involves the oxidation of ammonium-nitrogen (NH_4^+-N) to nitrite-nitrogen (NO_2^--N) and nitrate-nitrogen (NO_3^--N) [5]. Denitrification, the second requisite step in BNR, is primarily mediated by heterotrophic bacteria, which biochemically reduce ionic nitrogen oxides such as NO_3^--N and NO_2^--N to gaseous nitric oxide (NO), nitrous oxide (N_2O) and nitrogen (N_2) and sometimes even to NH_4^+-N under extremely anaerobic conditions [6]. Due to their different substrate requirements, (*e.g.*, nitrification requires a minimum O_2 : NH_4^+-N ratio of around 4.3, minimum alkalinity (as $CaCO_3$) : NH_4^+-N ratio of around 8.6 and denitrification requires a minimum COD : NO_3^--N ratio of approximately 2.9), the presence and growth of nitrifying and denitrifying bacteria depends somewhat on wastewater composition. BNR can be promoted by engineering reactors to ensure robust nitrifying and denitrifying populations. For instance, a commonly used Modified LÜdzack Etinger (MLE) configuration for BNR consists of an anoxic reactor for denitrification fed with influent carbon and recirculating NO_3^--N from a downstream aerobic nitrification reactor [7]. The effect of process engineering on BNR efficacy can be evaluated and optimized based on certain key indicator stoichiometric ratios. As part of the ongoing project, we developed stoichiometric ratios that will permit a ready evaluation of different causes for the limitation of biological nitrogen removal. While some indicator ratios are either based on the wastewater composition, others arise from the design and operation of the biological nitrogen removal reactor (Tables 1-2). The effect of a range of the indicator stoichiometric ratios was evaluated by performing simulations of a Modified LÜdzak Ettinger process using BIOWIN 32™ (EnviroSim Associates, Flamborough, Canada) using default model parameters and wastewater composition.

Table 1 : Indicator stoichiometric ratios based on wastewater composition

Ratio (units)	Ratio describes
sCOD/NO_3^--N (mg sCOD/mg NO_3^--N)	Effect of influent soluble COD on denitrification
S_{alk}/NH_3-N (mg HCO_3^- alkalinity/mg NH_3-N oxidized to NO_3^--N)	Effect of influent alkalinity on nitrification
f_{na} (mg NH_3-N/mg tTKN)	Effect of nitrogen availability on nitrification

Table 2 : Indicator stoichiometric ratios based on process operation

Ratio (units)	Ratio describes

$\frac{O_2}{K_{O,A}+O_2}$ (mg O_2/mg O_2)	Effect of dissolved oxygen concentration in the aerobic zone on nitrification
$\square_{C,}$ / $\square_{C,minimum}$ (Aerobic SRT provided/Minimum aerobic SRT required for nitrification)	Effect of reactor sizing on nitrification
f_{na} (mg NO_3^--N produced/mg NH_3-N oxidized)	Extent of nitrification under uninhibited or peak operation

It is commonly believed that nitrification is the bottleneck in BNR due to the slow growth kinetics and high susceptibility of nitrifying bacteria to numerous environmental disturbances [8]. Because of the inherent variability of wastewater composition and the dynamics of microbial communities, it is critical to develop tools to measure the activity of that fraction repeatedly, thereby necessitating an easy, rapid, yet accurate assay for routine monitoring. Further, in the same context, there is also a need for tools to rapidly screen a wastewater for potential inhibitors.

- Under the purview of the ongoing BNR limitation study, we have optimized a rapid respirometric nitrification assay to yield nitrification kinetic parameter estimates in a continuously operated bench-scale reactor containing an enriched nitrifying consortium [3, 4]. The developed assay relies on automated measurements of stoichiometric oxygen consumption in response to oxidation of a transient ammonia or nitrite spike. The resulting oxygen uptake profile is fit to Monod-based kinetic expressions to determine the respective kinetic constants q_{max} (maximum specific substrate consumption rate, 1/time) and K_S (half saturation coefficient, mg-N/L) [3, 4]. In the proposed study, we will validate application of the batch respirometric assay to measuring nitrification kinetics in a full-scale BNR reactor treating actual domestic and industrial wastewater, across a wide range of seasonal, wastewater composition and biocatalyst activity dynamics, during a prolonged monitoring campaign.
- In addition, we will develop rapid screening tools to measure wastewater composition and correlate bulk composition measures to nitrification inhibition. Initially, we will focus on metals (cadmium, zinc, nickel and copper, moderate to high toxicity to nitrifying microorganisms [5]), metal binding agents (EDTA, CDTA, NTA, high susceptibility of copper cofactor based ammonia monooxygenase due to copper non-availability [9, 10]), anionic surfactants (sodium lauryl sulfate, found in influent to the Stamford WPCA, Operations Management Inc., New Haven , CT, Personal Communication). The inhibitory character of several classes of compounds will be related to bulk measurable properties using artificial neural networks (ANN). (See Section 13 for details). During the next few months, prior to the start of the monitoring study, we will optimize and validate the bulk chemical characterization tool in an synthetic matrix, such as the cultivation medium for nitrifying bacteria [11]. Subsequently, a more stringent assessment will be conducted using the primary effluent to the treatment train at the Stamford WPCA, subject to the seasonal changes in wastewater composition.

Methods, procedures, and facilities

Respirometric Assay to Measure of Nitrification Kinetics . The kinetics of nitrification and nitrification inhibition will be measured using an extant respirometric assay developed in our laboratories [3, 4]. The developed assay measures the kinetics of nitrification exhibited by biomass derived from a continuously operated nitrifying enrichment culture [12]. The developed respirometric technique is based on stoichiometric consumption of oxygen in response to ammonia and nitrite oxidation [13]. In contrast to nitrification kinetic assays that depend on analytically involved and chemical-specific time-series measurement of nitrogen depletion (for *e.g.*,[14, 15]), the respirometric is rapid, reproducible and facile since oxygen measurements can be accurately performed and can be fully automated. An additional feature of this method is that it allows distinction in activity of ammonia oxidizing and nitrite oxidizing microorganisms from a mixed nitrifying culture [12]. We are currently applying this technique to determine nitrification kinetics during undisturbed operation and during an imposed disturbance (Figs 1 and 2).

Reactor dynamics as measured by effluent concentrations (Fig 1) are strongly correlated with measured kinetic estimates (Fig. 2, SOUR is a measure of maximum NH_4^+-N and NO_2^--N oxidation capacity) : an SOUR increase in SOUR is accompanied by a decrease in effluent NH_4^+-N concentrations.

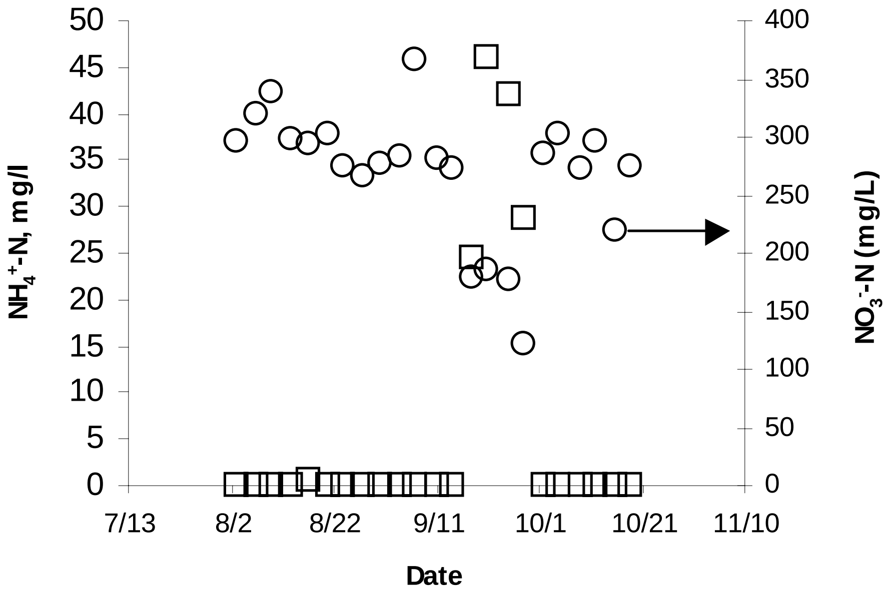

Figure 1 : Performance Profiles for Bench Scale Nitrifying Reactor. ( ) : NH_4^+-N concentrations and (O) : NO_3^--N concentrations.

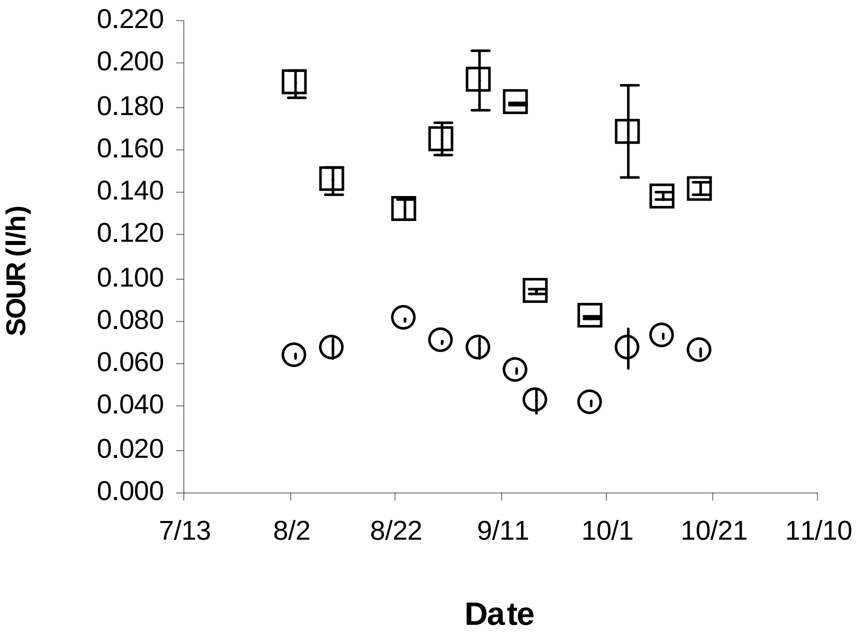

Figure 2 : Biokinetics Profiles for Bench Scale Nitrifying Reactor. ( ) : NH_4^+-N oxidation rate and (O) : specific NO_2^--N oxidation rate.

In addition, we have demonstrated in our laboratory that the proposed assay even permits determination of ammonia and nitrite oxidation kinetics estimates using actual activated sludge samples from a POTW, which contains a variety of microbial groups. We have optimized the developed respirometric assay to yield nitrification kinetic parameter estimates in a continuously operated reactor containing an enriched nitrifying consortium. In addition, in the proposed study, we will validate the method for activated sludge BNR reactors using an ASM2 model based simulation package (BIOWIN®, EnviroSim Asoociates Inc. Flamborough, Ontario, Canada) by evaluating the congruence of kinetic estimates against observed reactor performance.

Chemical analtyical MEASURES OF Nitrification Inhibitory character. We propose to develop quantitative structure-activity relationships (QSARs) that are based on measurable bulk properties of a wastewater sample, (*e.g.*, for metal binding capacity (chelating agents) surface active properties like critical micelle concentration (surfactants), anion binding capacity (metal ions)).
Different bulk characteristics will be developed to measure the presence of the above chemical classes in wastewater. The inhibitory action of heavy metals is due to interaction with enzymes containing thiol groups and formation of metal sulfide complexes [16]. The metal content of a wastewater matrix will be determined by titrating against excess sulfide (in an anoxic environment) and measuring remaining sulfide concentrations. The bulk measure of heavy metal content will be expressed in terms of a lumped metal-sulfide solubility product of the constituent metal-sulfide solubility product (Table 3).

Table 3 : Solubility Products of Metal Sulfides [17]

Metal	Log Solubility Product
Cadmium	-26.1
Zinc	-23.8 (□), -21.6 (□)
Nickel	-18.5 (□), -24 (□), -25.7 (□)
Copper	-47.6

Some metal chelating agents are postulated to function by rendering copper, (part of the ammonia monooxygenase cofactor) unavailable [10]. The presence of chelating agents in wastewater will be tested by titrating against copper or an alternate heavy metal (to be ascertained and optimized) and measuring residual ionic free concentration using ion selective electrodes. The bulk measure of chelator content will be expressed as an effective stability constant(s) for the metal-chelator complex, based on individual chelator-metal stability constants (Table 4).

Table 4 : Log Stability Constants for Chelator-Metal Complexes [18]

Chelator **Metal**	**EDTA**	**CDTA**	**NTA**
Ba^{2+}	7.76	7.99	4.82
Ca^{2+}	10.7	12.5	6.41
Mg^{2+}	8.69	10.32	5.41
Zn^{2+}	16.26	18.67	10.45

The toxicity of cationic surfactants has been expressed in terms of their individual critical micelle concentrations (CMC) [19]. A similar approach will be followed for anionic surfactants. The bulk measure for the presence of surface active agents will be the ratio of the total surfactant concentration to the bulk CMC (via contact angle measurements).

The inhibitory character of several classes of compounds will be related to bulk measurable properties using artificial neural networks (ANN). The ANN will be trained using toxicity-property data obtained from batch biokinetic tests. The ANN QSAR model will be validated and verified by its ability to predict the toxicity due to mixture of different classes of compounds and an untested wastewater matrix.

We believe that our approach is superior to existing QSAR models, which are restricted to classification of organic compounds in terms of their homologous series, for *e.g.*, alcohols, halogenated aliphatics, alkanes, aromatics etc (for *e.g.*, [20]). While such a simplified classification is adequate for deterministic toxicity modeling of a well defined waste-stream, it is of limited application when dealing with a typical wastewater sample, wherein the constituent classes of compounds are unknown.

Operation of Bench-Scale BNR Reactors. To verify proposed measurement techniques, two bench scale bioreactors initiated during our current Long Island Research Foundation funded study, will be operated in parallel at the Stamford WPCA. The bioreactors have an operating volume of 40L, and a flow rate of 10 gallons per day. The reactors consist of one anoxic basin followed by three aerated basins, followed by an internal clarifier and were constructed at the Technical Services Center, University of Connecticut. These reactors will be operated under identical HRT, SRT, aeration and mixing regimes as the full-scale treatment WPCA (*i.e.* as a Modified LÜdzack Ettinger configuration). The bench-scale reactor operation was commenced in October 2000 on a side stream of the actual Stamford POTW wastewater influent. Once established, baseline nitrification and denitrification performance and kinetics in each of these reactors -operated in tandem- will be measured using chemical specific assays (Details can be found in Table 5) [21] and respirometric assays, respectively [3, 4].

Table 5 : Sampling Specifications for Bench-scale Reactors at Stamford WPCA

Name of Chemical or Method	Measurement Classification			Sample Location	Sample Preservation	Maximum Holding Time (Days)
	Type	Frequency (1/d)	Sample Equipment			
pH (Bench scale Reactor)	C	Not applicable	Not applicable	Reactor	NA	None, online
Chemical Oxygen Demand : Colorimetric	I, C	2/7 d	35 ml glass vial	Reactor	4^{o}C	1
NH_3-N Colorimetric	I, C	2/7 d	200 ml glass beaker	Reactor effluent	4^{o}C$^\Psi$	1
NO_2^--N Colorimetric	I, C	2/7 d	200 ml glass beaker	Reactor effluent	4^{o}C$^\Psi$	2
NO_3^--N Colorimetric	I, C	2/7 d	200 ml glass beaker	Reactor effluent	H_2SO_4, pH < 2	28
TKN Colorimetric	I,C	2/7 d	200 ml glass beaker	Reactor effluent	H_2SO_4, pH < 2	28
Biomass concentration (Mixed liquor suspended solids)	I, C	2/7 d	500 ml Erlenmeyer flask	Reactor	4^{o}C	1
Biomass concentration (Mixed liquor volatile suspended solids)	I,C	2/7 d	500 ml Erlenmeyer flask	Reactor	4^{o}C	1
Nitrification kinetics (Extant Respirometry)	I	As required	100 ml respirometric vessel	Reactor	4^{o}C	1
Dissolved oxygen (Bench scale Reactor)	C	Not applicable	Bench scale Reactor	Reactor	NA	None, Online

[*] : The tabulated sample volume is twice that required for routine duplicate analysis and is apportioned into two sample containers. The additional volume is collected to determine quality control measures such as accuracy (analysis of spiked samples), precision (duplicate analysis) and to account for potential sample loss while handling or analysis. (Also see section 1.7.5)

C : continuous measurement; I : intermittent measurement; Frequency of measurement applies only to continuous measurements

$^\Psi$: Storage at 4^{o}C. However, the biomass is removed from the sample via centrifugation at 3500 g for 10 minutes. Biomass removal arrests further biochemical oxidation of NH_4^+-N and NO_2^--N.

NA : Not applicable

** : Performed at the University of Connecticut
Frequency of measurement applies only to continuous measurements

Subsequently, one reactor will be subjected to different levels of a disturbance, (*e.g.* selected inhibitors will be added to the influent at several concentrations). Initially, we will choose anionic surfactants, such as sodium lauryl sulfate, since these have resulted in significant nitrification inhibition in POTWs in Stamford [2] and metal chelating agents (high susceptibility of metal cofactor based ammonia monooxygenase enzyme to compounds such as allylthiourea [9, 10]). In addition, as part of a parallel research investigation on heavy metal inhibition of nitrification, the bench-scale reactors will be dosed with nickel, copper, zinc and cadmium. During the imposed process disturbance, the BNR performance will be recorded. In addition, the proposed surrogate chemical measure of inhibitory character and biokinetics of nitrification and denitrification will be measured. The measured biokinetics will be input into the ASM2 model structure of BIOWIN®. The biokinetics and surrogate chemical measurement techniques will be confirmed by comparing measured nitrogen removal performance with that simulated by BIOWIN®. In the validation study, known nitrification inhibitors (e.g., metals, surfactants, metal chelators, and other compounds likely to occur in sewage waste streams) will selectively be added to one of the bench scale reactors. The ability to predict the effect of these inhibitors on nitrification kinetics via the bulk chemical measurements and developed QSARs will be assessed, while the kinetic assays will be verified to predict deterioriating reactor process performance prior to onset of reactor failure.

Evaluation of Full-Scale BNR performance. The treatment train at the Stamford Water Pollution Control Authority consists of two series of 2.46 million gallons volumetric capacity each. The total influent flow (average 20 million gallons per day) is equally split between the two trains. Each train consists of the equivalent of one anoxic and three aerobic reactors of 0.615 million gallons each. While bench scale testing is ongoing, the treatment train of the full scale Stamford POTW will be periodically sampled and analyzed (Details can be found in Table 6).

Table 6 : Sampling Specifications for Full-Scale Treatment Train at Stamford WPCA

Name of Chemical or Method	Measurement Classification			Sample Location	Sample Volume (ml)	Sample Preservation	Maximum Holding Time (Days)
	Type	Frequency (1/d)	Sample Equipment				
pH	C	8	1 L polypropylene bottle	1-5	10	Not applicable	Within 15 min of sampling
Chemical Oxygen Demand – Colorimetric	C	8	1 L polypropylene bottle	1-5	1000	$4^{o}C$	7
NH_3-N Colorimetric	C,G	8,1	1 L polypropylene bottle	1-5	100	$4^{o}C^{\Psi}$	1
NO_2^--N Colorimetric	C,G	8,1	1 L polypropylene bottle	1-5	100	$4^{o}C^{\Psi}$	2
NO_3^--N Colorimetric	C,G	8,1	1 L polypropylene bottle	1-5	100	H_2SO_4, $pH < 2$	28
Soluble TKN Colorimetric	C,G	8,1	1 L polypropylene bottle	1-5	100	H_2SO_4, $pH < 2$	28
Biomass concentration Total suspended solids	C,G	8,1	1 L polypropylene bottle	1-5	1000	$4^{o}C$	7
Nitrification Kinetics (Extant Respirometry)	C	As required	1 L polypropylene bottle	2-5	200	$4^{o}C$	1
Biomass concentration Volatile suspended solids	C,G	8	1 L polypropylene bottle	1-5	1000	$4^{o}C$	7

Sample Location (See Figure 3) : 1 - influent, 2 - primary effluent, 3 - final effluent, 4 and 4' - anoxic tank (trains 1 and 2), 5 and 5'- aerobic tank 3 (trains 1 and 2)

* : Conducted at the University of Connecticut

C : composite samples are flow weighted samples composed of grab samples obtained every 3 h. Four composite samples are taken every week.

G : Grab sample

$^{\Psi}$: Storage at 4°C. However, the biomass is removed from the sample via centrifugation at 3500 g for 10 minutes. Biomass removal arrests further biochemical oxidation of NH_4^+-N and NO_2^--N.

Flow proportioned composite samples will consist of samples taken every three hours over a twenty four hour period by plant operators. The average dynamics of nitrogen removal will be based on analysis of the flow proportioned composite samples. Grab sampling will also be performed to determine time-varying dynamics of biological nitrogen removal. By periodic sampling and nitrification kinetics testing, the baseline kinetics will be determined. Trends and variability in kinetic parameter estimates for the Monod constants describing nitrification and denitrification will be ascertained and input to the simulation and modeling package BIOWIN®. The model performance output will be correlated to actual measured performance. In addition, we will conduct retrospective sampling, wherein samples taken during episodes of nitrogen removal failure will be subject to the bulk chemical parameter characterization and inhibition kinetics estimation. This sampling effort will assist in the validation of the bulk measurements, QSARs, and the kinetic assays.

Facilities. For conducting the periodic assays required in this study, facilities available in the Environmental Processes Laboratory at the University of Connecticut include :
Batch respirometric station for kinetics measurement, Biological dissolved oxygen Monitor (YSI model 5300), Clark type polarographic dissolved oxygen probes (YSI model 5331), glass jacketed respirometric vessels, constant temperature controller and circulator (Fisher Isotemp 9501), Hach COD Digester (COD Reactor Model 45600), high speed centrifuges (Marathon 22KBR and Sorvall RC-5C+), fixed wavelength spectrophotometer (Spectronic 20+ and 20D+), High performance liquid chromatograph station (Jasco Instruments), Ion chromatograph station (Dionex, Model A500), Perkin Elmer CHNSO analyzer (Series II, Model 2400), Ion specific electrodes for nitrate (Hach) and copper (Orion), gas sensing ammonia electrode (HNU systems).

At the Stamford WPCA, are available a COD (Hach) and nutrients analysis station (SKALAR) and a respirometric station identical to the one at the University of Connecticut. The personnel at Stamford have already been introduced to the extant respirometric technique for measuring nitrification kinetics via a workshop held at the University of Connecticut in August, 2000. Both respirometers at the University of Connecticut and Stamford will be used to monitor nitrification kinetics.

Related Research. The demand for nutrient removal, especially nitrogen, from wastewaters has been a demand placed on publicly and privately owned treatment works for over a decade. The general process engineering requirements to attain nitrogen removal via the concerted activities of nitrification and denitrification are well documented and implemented [7]. Nevertheless, even with apparent adequate process engineering in place, nitrogen removal is often unreliable[1]. Although some site-specific assessment of nitrification and/or denitrification kinetics limitations continue to be performed [22-24], design of such studies permit little generalization. On the other hand, several researchers have studied in great detail the kinetics and inhibition of nitrification in pure culture and clean matrices [9, 10, 25-34]. These studies, although of significant inherent scientific value, are of limited relevance to situations of interest that involve complex matrices and mixed microbial activities. Our kinetic assays [3, 4] are similar to, and compete with similar assays that have been designed by researchers overseas [35-41]; our assays to measure bulk inhibitory character of wastewaters are truly novel. Hence, we believe that our study, commenced with funding from the LISS program, is truly on the forefront for the development of predictive tools to assess nitrogen removal from wastewater in treatment facilities. Our study combines a strong scientific based method development with a full-scale real-world evaluation of our methodology.

- [1] **Chandran, K.**, and B. F. Smets. **2000**. "Factors Limiting Biological Nitrogen Removal : Nitrification Inhibition and Nitrogen Availability". *New England Water Environment Association (NEWEA) Technical Specialty Seminar on* **Biological Nutrient Removal in New England**. *Storrs, CT.*

Principal Results and Significance

Chemical analtyical MEASURES OF Nitrification Inhibitory character

We are developing a rapid assay to determine the total concentration of heavy metal cations in a wastewater. The heavy metal cations are precipitated as metal sulfides by titrating the wastewater sample with sodium sulfide. We quantify the total concentration of metal cations in the wastewater sample by measuring sulfide consumption during the assay.
We have calibrated the bulk metal assay to measure heavy metal concentrations using metal solutions in a deionized water matrix at pH 7.0. We are currently verifying the developed method in the feed medium to nitrifying bench-scale reactors. Subsequent verification will employ primary clarifier effluent at the Stamford WPCA as the test matrix. Following calibration and verification, we will apply test heavy metal solutions to both the bulk metal assay and the nitrification biokinetic assay and correlate the measured total heavy metal concentration to calculated heavy metal speciation and measured nitrification inhibition.

Operation of Bench-Scale BNR Reactors

Fabrication of the bench-scale reactors to be installed at the Stamford WPCA was performed by the University of Connecticut Technical Services Center and completed in March 2001. Bench-scale operation at Stamford is expected to commence during June 2001. Upon installation at the Stamford WPCA, the reactors will be seeded with biomass from the full-scale reactors at the same facility. Continuous monitoring of reactor performance and kinetics to infer biological nitrogen removal performance and BNR inhibition will commence after the reactors attain steady state performance.

Evaluation of Full-Scale BNR performance

Continuous monitoring of the full-scale reactors at Stamford commenced on November 6, 2001 and is being conducted in accordance with the schedule and particulars described in the monitoring proposal. Full-scale reactor monitoring will continue through November 2001 to enable collection of pertinent data across a wide range of seasonal, wastewater composition and biocatalyst activity dynamics.

Project Personnel Supported

Kartik Chandran Ph.D., Post Doctoral Fellow, Environmental Engineering Program, University of Connecticut.
Monika Siwek, Undergraduate student, Microbiology Program, University of Connecticut.
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A Characterization of the Discontinuous Nature of Kriging Digital Terrain Models

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The Discontinuous Nature of Kriging Interpolation for Digital Terrain Modeling

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Abstract

Kriging is a widely accepted method for interpolating and estimating elevations from digital elevation data. Its place of prominence is due to its elegant theoretical and practical properties. From an interpolation point of view, kriging is equivalent to a thin-plate spline and is just one species among the many in the genus of weighted inverse distance methods, albeit with attractive properties. However, from a statistical point of view, kriging is a best linear unbiased estimator and, consequently, has a place of distinction among all spatial estimators because any other estimator that performs as well as kriging (in the least squares sense) must be equivalent to kriging. Therefore, kriging is held by many to be the gold standard of digital terrain model (DTM) elevation interpolation. Even so, as used for DTM interpolation, kriging has an undesirable property that has not been previously documented. Kriging produces discontinuous surfaces along the boundaries of interpolation patches. This paper documents the situation, explains its source, provides bounds on the discontinuity, and provides real-world examples from a digital elevation model of mountainous terrain in central New Mexico.

Keywords: kriging, discontinuity, digital terrain modeling, spatial interpolation.

INTRODUCTION

Kriging (Matheron, 1963) is a popular technique for interpolating and estimating elevation values from digital terrain data. General references on the subject are (Journal and Huijbregts, 1978; David, 1977; Lam, 1983; Isaaks and Srivastava, 1989; Goovaerts, 1997). Bailey (1994) asserts that "there is an argument for kriging to be adopted as a basic method of surface interpolation in GIS as opposed to the standard deterministic tessellation techniques which currently prevail and which can produce artificially smooth surfaces." This argument was supported by Laslett (1994) whose study gives an example of a data set for which certain splines are "too smooth," whereas kriging produced more precise estimations. Declercq (1996) compared polynomials, splines, linear triangulation, proximation, distance weighting, and kriging to test their efficacy to visualize spatial patterns in addition to their performance in predicting unvisited sample locations. Kriging performed among the best in both categories. Katzil and Doytsher (2000) found third-order polynomials to perform comparably with kriging but they did not have either the need to compute a variogram or kriging's complicated matrix computations. Yang and Hodler (2000) found that kriging outperformed four other interpolation techniques in preserving the visual character of digital terrain models. Regarding the "spline vs. kriging" debate, it has been shown (Kimeldorf and Wahba, 1971; Wahba, 1990) that kriging is mathematically equivalent to thin plate splines. Almansa and others (2002) established kriging's place in a more general class of functions, namely, the absolutely minimizing Lipschitz extension. Although kriging is not without its critics (Philip and Watson, 1986), there is no question that its use is widespread.

The properties of any mathematical surface being used as a terrain model define the properties imbued to the model. The onus is on the modeler to choose the surface model wisely to properly match the properties of the surface with the desired traits of the terrain. Continuity properties are of paramount importance. Discontinuous surfaces have "holes" or "tears" in them, so to speak. A continuous surfaces might not be smooth, meaning that the surface might have "creases" in it, such as with a triangulated irregular network (TIN). It is important to catalogue surface model continuity properties and this paper establishes these properties for kriging interpolation.

Surface Models

In their seminal work, Miller and LaFlamme (1958) suggested, "The digital terrain model (DTM) is simply a statistical representation of the continuous surface of the ground by a large number of selected points with known xyz coordinates in an arbitrary coordinate field." A DTM was envisioned to be a set of height samples, that is to say, a set of points. We will denote this set of sample locations by $s = \{(x_i, y_i)\}$ and denote the set of heights measured at those locations by $h = \{z(x_i, y_i) \,|\, (x_i, y_i) \in s\}$. Miller goes on to say, "Just as the engineer must interpolate on the topographic map, the computer will have to interpolate with the DTM." The mathematical scheme used for this interpolation is what we call a **surface model.** We formally define a surface model to be a real–valued function of two variables, $f : \mathbf{p} \in \mathcal{R}^2 \to \mathcal{R}$, or $z = f(x, y)$, where $\mathcal{R}$ denotes the set of reals.

Some surface models are defined upon all the sample points in s. Examples include Lagrange polynomials, Fourier transformations, and kriging.

Such functions are said to have **global support**, meaning that every point in s contributes to the formulation of f. Global support is generally not desirable for digital terrain modeling for several reasons. Global support imposes relatively heavy computational burdens, especially for large data sets. Also, it has the counter-intuitive property that, for certain techniques such as Lagrange polynomials, making a small change in any particular sample can produce large changes over the entire surface. This runs contrary to Tobler's Law of Geography, that everything is related to everything, but closer things are more related. Also, polynomial global support surface models that interpolate all the points in s must be of an order equal to the cardinality of s, or greater. This can produce unwanted behaviors such as extreme surface departures and unrealistic undulations.

Although kriging is defined with global support, in practice, it is not typically used that way for terrain modeling. Instead, s is subdivided into **neighborhoods**, being subsets of s with relatively few elements that roughly (or strictly) partition s. Then, kriging is used to interpolate over these neighborhoods in the following way. Suppose we want to interpolate a surface value at the point $\mathbf{p} = (x, y)$ and $\mathbf{p} \notin s$. Let n_j denote a neighborhood containing $\mathbf{p}$. Then, the height estimate at $\mathbf{p}$ is a weighted sum of the heights of the points in n_j. The weights are related inversely to the distance from the sample to $\mathbf{p}$ in such a way that minimizes the variance of the estimate. The surface produced over a neighborhood is called a **patch**.

There are several heuristics for choosing neighborhoods for a point of interest (e.g., Isaaks and Srivastava, 1989, p. 338). Some of the heuristics include using all samples within some circle or ellipse enclosing $\mathbf{p}$, using all samples within some convex polygon enclosing $\mathbf{p}$, using a limited number of samples from the four quadrants enclosing $\mathbf{p}$, or using Voronoi nearest neighbors.

Continuity

Although the physical surface of the Earth is arguably not mathematically continuous (Meyer, 1999), it is generally modeled as if it were. The Earth's surface is seen as being piece-wise continuous, meaning that, on the whole, the surface is continuous but it is possible that there are local discontinuities such as knick points and cliffs. Consequently, piece-wise continuity is commonly considered a desirable property in terrain surface models.

Any surface model that is based on polynomials (i.e., not a fractal) will be smooth within a patch. This is a direct consequence of the infinite differentiability of polynomials. However, the piece-wise continuity of surface patches cannot be taken for granted. There is a huge body of literature in the Computer Aided Geometric Design (CAGD) community devoted to creating piece-wise continuous surfaces of various orders with first and second order being the most common (e.g., see Lancaster and Šalkauskas (1986); Farin (1993, 1995); Dierckx (1995)). These patches are smooth in their interiors

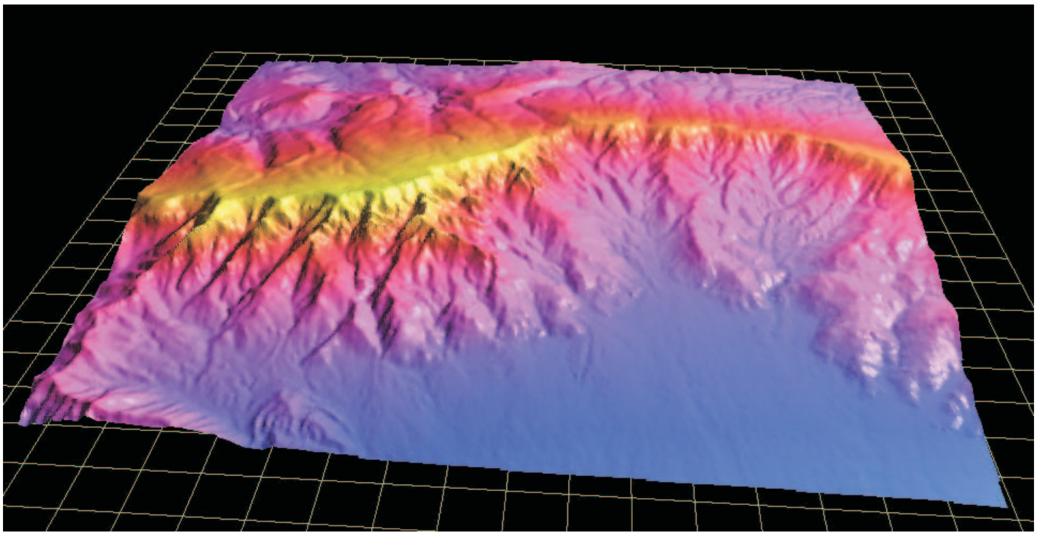

Figure 1: DEM of the Sandia Mountains in north-central New Mexico.

and form, say, a first-order continuous surface on the whole. The remainder of the paper will document that kriging creates a zero-order, piecewise continuous surface model.

Kriging Continuity

The equivalence of kriging and thin–plate splines guarantees that, within a patch, kriging produces a continuous surface. The question then becomes what continuity can be expected along the border between two neighborhoods?

Claim: When used with local support, kriging is in the class of piecewise, zero-order continuous surfaces.

Proof: To establish the claim, it suffices to produce a single example. The proof proceeds as follows.

1. Choose a sample height data set.
2. Subdivide the data set into neighborhoods.
3. Select a border between two abutting neighborhoods.
4. Interpolate the border twice, once for each neighborhood.
5. If the two interpolated borders differ in elevation, then kriging is discontinuous along the border.

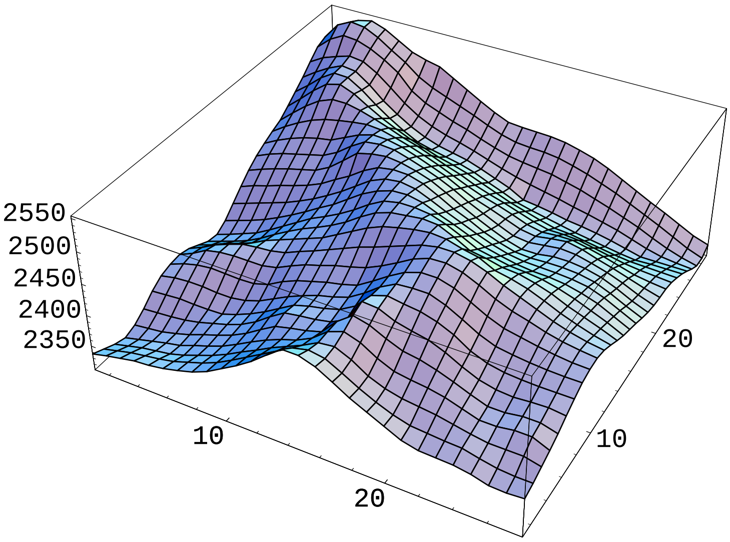

Figure 2: The topographic data set.

The data set and its covariance function

The topographic data set comes from the the Sandia Mountains of north–central New Mexico, see Fig. 1. This DEM was chosen because of the wide variety of topography within a single DEM, from flat tails of alluvial planes to sheer cliffs. These mountains, although quite rugged, are not remote in the sense that Albuquerque, New Mexico, is built up to and around them. Therefore, surveyors can encounter terrain of this type in their work.

The data for this proof comes from the foothills of these mountains, see Fig. 2. The site is located in UTM zone 13 with corner coordinates (e364140, n3900690) and (e364980, n3901590) and measures 840 meters east to west and 810 meters north to south. The corners and extent of the site were chosen to coincide with elevations available in the USGS Sandia Crest $7\frac{1}{2}$ minute digital elevation model of the area.

The omni–directional variogram of the data set was computed using relational database queries as described in (Maggio and others, 1997). The result is shown in Fig. 3. There is no discernable anisotropy for distances less than two hundred meters, a distance greater than the largest nearest neighbor distance. Therefore, the omni–directional variogram was judged to be an adequate model and no directional variograms were computed. The variogram was deemed to be Gaussian and, thus, be of the form

$$\gamma(h) = 1 - e^{-3h^2/a^2},$$

where h is the lag distance and a is the practical range. In this case, a was

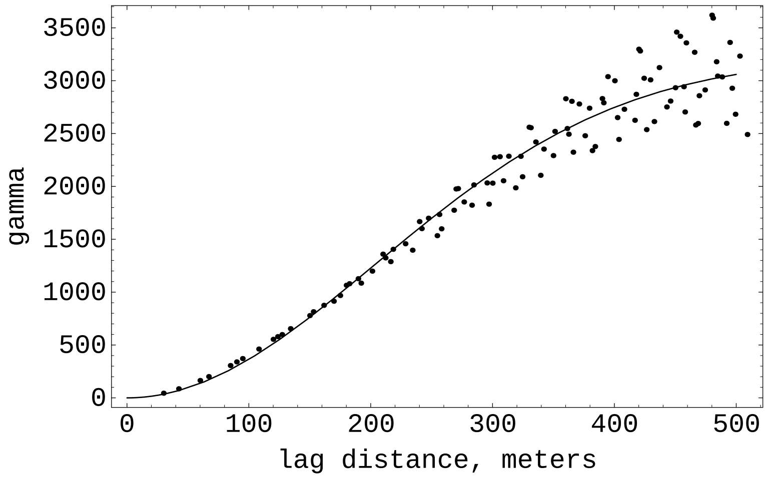

Figure 3: The omni–directional variogram and its least squares model.

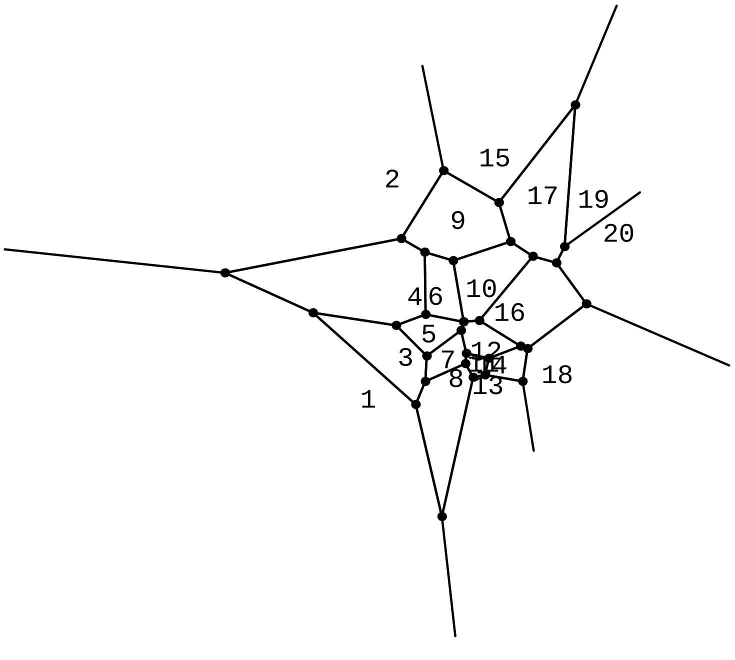

Figure 4: The Voronoi diagram for the study area. Individual sample points are indicated by numbers. The polygons are subregions of R such that every point in a polygon corresponds to the same interpolation neighborhood.

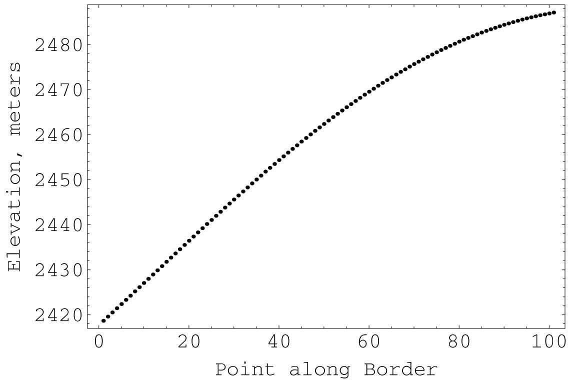

Figure 5: The border as interpolated with the nearest neighbors of point 6.

chosen to be 500 meters. A least squares fit yielded the model

$$\gamma(h) = 3219.67 \left(1 - e^{-3h^2/250000}\right).$$

The model and the data are depicted in Fig. 3.

By assuming stationarity, the covariance function is related to the variogram by

$$cov(h) = \sigma^2 - \gamma(h), \tag{1}$$

where σ^2 is the variance of the data set and has a value of 2352.829 m^2.

Patches

Having created a covariance function with which to krige, the next task was to tessellate the region into neighborhoods. It was decided to create neighborhoods using Voronoi nearest neighbors. This choice is arbitrary; any other neighborhood scheme would confirm the claim. Twenty *easting, northing* pairs were generated randomly from a uniform distribution. These pairs were constrained to fall within the study area. Figure 4 shows the points and the Voronoi diagram of the points.

Proof by example

Consider the border between the polygons generated by points 6 and 10. The nearest neighbors of point 6 are $\{10, 9, 4, 5, 12\}$. The nearest neighbors of point 10 are $\{6, 12, 16, 17, 9\}$. The two Voronoi vertices defining the common border between points 6 and 10 are (285.4, 466.7) and (320.5, 261.3). The border between the polygons was defined by kriging the surface at 100 points distributed evenly between these two Voronoi vertices. The ordinary kriging was done using Mathematica v3.0 by constructing the matrices and

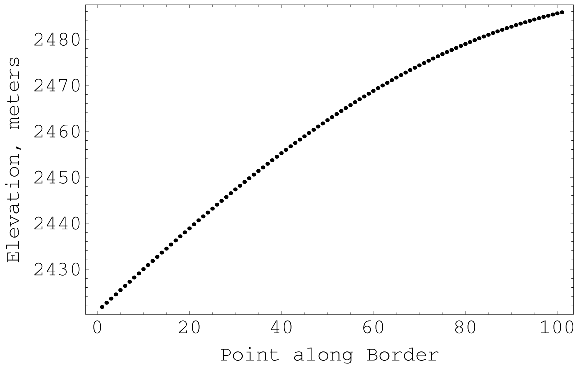

Figure 6: The border as interpolated with the nearest neighbors of point 10.

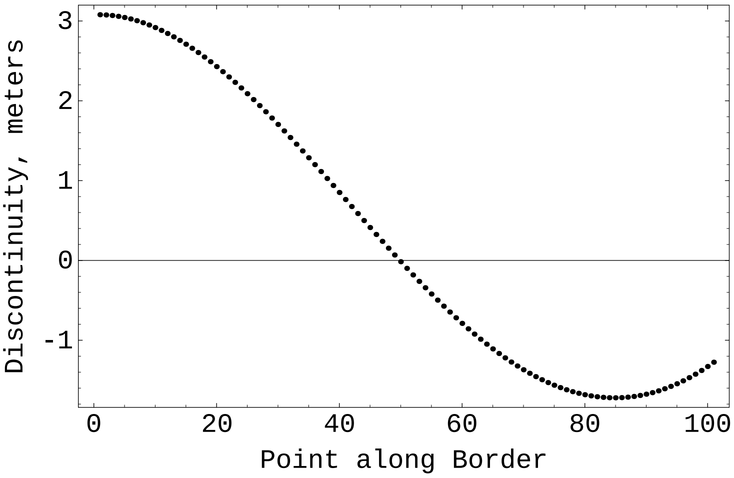

Figure 7: The difference of the two interpolated borders. Any value not equal to zero indicates a discontinuity.

computing their inverses. However, the other types (universal kriging, kriging with a trend, block kriging, and cokriging) have the same basic structure and the argument applies equally to them, as well.

The results are shown in Fig. 5 and 6. The visual similarity of the two borders confirms that the interpolation is working correctly; one could expect them to be very similar. However, the difference of the interpolated values shown in Fig. 7 clearly depicts the discontinuity. The discontinuity ranges in value from 3.08 meters to -1.72 meters. This completes the proof.

Causes

The source of the discontinuity comes from the observation that the border is being interpolated via two different covariance matrices. The matrices

Gap (m)	Count
0-1	206939
1-2	102100
2-3	13383
3-4	3449
4-5	1047
5-6	450
6-7	228
7-8	132
8-9	85
9-10	49
10-11	40
11-12	20
12-13	15
13-14	17
14-15	5
15-16	8
16-17	2
17-18	1
18-19	1
19-20	1

Table 1: Distribution of Discontinuity Magnitude (m).

are different because the interpolation neighborhoods are different. If the samples are not reflective symmetric, then there is no reason to expect the patches to match on their borders. Therefore, this is a completely general result; it is not specific to the chosen data set.

This property of polynomial surfaces is essentially why CAGD exists. Global support has long been known to be undesirable for reasons listed above. These drawbacks lead to using piecewise curves and surfaces that have local support. However, it is usually desirable to have surface-wide continuity of first or second order. If the piecewise curves are not constructed to be continuous, in general, they will not be (de Boor, 1978). The central theme of CAGD is to develop piecewise curves and surfaces that enjoy continuity across their borders, in addition to other properties as well.

Examination of a DEM

To explore the range of possible discontinuities further, the entire Sandia Crest DEM was analyzed in the manner described above. That is to say, random points were generated to cover the entire DEM and the borders between all adjacent neighborhoods were interpolated. This resulted in the analysis of 327972 borders. 94.2% of the borders had a maximum absolute discontinuity (gap) of one meter or less. The maximum gap observed was 19.48 meters. The average maximum gap was 0.54 meters with a standard deviation of 0.62 meters. See Table 1.

We observed a correlation between slope and increasing discontinuity size so we grouped the tests by slope and created histograms of the discontinuity size. Slope was computed using a technique specifically designed for irregularly spaced data (Meyer and others, 2001). The gaps were grouped by slope. Table 2 shows the distributions of the gaps for four particular slope values. For 0°, meaning flat ground for both neighborhoods, 86% of the gaps are between zero and one meter in magnitude, with the overall shape of the distribution appearing to be a decreasing exponential. Interestingly, there was a single instance in which flat ground produced a nine meter gap. We next show the results for the next slope group, those less than 3.75°. Again, the distribution appearing to be a decreasing exponential. We skip to the results for 49.7°. Notice that the distribution now appears to be lognormal with a mean around 3 meters. Finally, the distribution for the steepest sloped neighborhoods has very few samples but appears to be roughly uniform.

Conclusions and Discussion

We note several trends in the gap distributions. Overall, the distributions of the gaps appear to be lognormal. Next, the average gap size steadily increases with slope. Third, the variability of gap size increases with slope.

(m)	0°	3.75°	49.7°	52.7°
0	1901	38765	1	
1	288	3644	7	
2	9	89	18	2
3	5	12	13	1
4		4	14	2
5		2	12	4
6			7	1
7			7	
8			3	
9	1		4	
10			3	
11			0	
12			2	
13				
14				
15			3	
16				
17			1	
18				
19				
20			1	

Table 2: Slope (degrees) vs. Discontinuity Magnitude (m).

This suggests that kriging with a trend might perform better than the ordinary kriging used in this study because kriging with a trend removes trends (slope) in the data, which can arguably be violating the stationarity assumption upon which kriging is based. This is a subject for future research.

The ramifications of this discontinuity depend largely upon the needs of the user. Discontinuities such as the one presently above will be clearly visible on high–accuracy topographic maps. Survey maps frequently have one–foot contour lines and discrepancies of three meters will be significant. In contrast, these data were taken from a digital elevation model developed from a map with 40 foot contour lines. These discontinuities do not compromise such a map's conformance with the National Map Accuracy Standards and, therefore, could be ignored in its compilation.

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A Tracer Dilution Method for Deriving Fracture Properties in Crystalline Bedrock Wells

Basic Information

Title:	A Tracer Dilution Method for Deriving Fracture Properties in Crystalline Bedrock Wells
Project Number:	2001CT741B
Start Date:	3/1/2001
End Date:	2/28/2002
Funding Source:	104B
Congressional District:	2nd
Research Category:	Not Applicable
Focus Category:	Groundwater, Water Supply, Solute Transport
Descriptors:	well hydraulics, water quality, water levels, solute transport, hydrogeology, fracture hydrology, contaminant transport, bedrock fractures,aquifer characteristics
Principal Investigators:	Gary Robbins

Publication

1. Brainerd, Richard J.; 2002, "A Stepwise Discharge Tracer Dilution Method for Deriving Fracture Properties in Crystalline Bedrock Wells", "MS Dissertation", Department of Geology and Geophysics, University of Connecticut, Storrs, CT, 162pp.

Title: A Tracer Dilution Method for Deriving Fracture Properties in Crystalline Bedrock Wells.

Statement of Critical Regional or State Water Problem:

Most rural domestic wells in New England derive their water from fractured crystalline rocks. Unfortunately, our knowledge of the hydraulic characteristics of subsurface, water-bearing fractures is sparse. Such information is critical in evaluating ground water supplies, in conducting wellhead protection, and in preventing and remediating ground water contamination in crystalline rock. In recent years, the U.S. Geological Survey (USGS) has developed cutting edge techniques to perform downhole fracture testing. These techniques, however, may be cost prohibitive to be applied on a large scale. This research is aimed at developing more cost-effective methods for conducting downhole fracture characterization. As such, it should aid the rural community and state and local environmental regulators in assessing the availability of ground water and the source and transport of contamination in fractured crystalline rock.

Statement of Results or Benefits:

The goal of this research is to develop a cost effective, technically sound method for conducting downhole fracture characterization using tracers. The research is focused on developing a unifying method that can identify water bearing fractures that intersect a well, that can provide information on the interconnectiveness of fractures in relation to a well (recharging and discharging fractures), that can be used to determine the transmissivity of fractures, used to determine the hydraulic head in fractures, and that can quantify fracture water quality (including contamination). Uniquely, we have an opportunity to compare our tracer results with those of the U.S. Geological Survey, derived using their integrated downhole geophysical and hydraulic packer test methods. If brought to fruition, the tracer test method may make downhole testing more practical. As such, it can help in assessing the availability of ground water in fractured crystalline rock and in protecting the ground water resource.

Nature, Scope and Objectives of the Research:

Most rural domestic wells in New England derive their water from fractured crystalline rocks. Unfortunately, our knowledge of the hydraulic characteristics of subsurface, water-bearing fractures is sparse. As such, drilling productive domestic wells in crystalline rock is a hit or miss proposition that could result in consumers laying out thousands of dollars for a “dry hole”. This lack of information also prohibits performing, in any quantitative fashion, ground water resource estimates that can be used in guiding developers or land use planners. A lack of information also inhibits applying the concepts of wellhead protection to municipal wells founded in rock. Importantly, when bedrock wells are impacted by contamination, the absence of fracture information complicates evaluating contaminant sources, and means to remediate these problems.

Over the last several years, the USGS has conducted geophysical and hydrologic research aimed at developing techniques to characterize fracture hydrology as part of their *Toxic Substances Hydrology Program*. This research has shown that that superficial investigations of ground water conditions in bedrock wells (that basically entail water level measurements and well sampling) can be highly misleading owing the nature of fracture flow. Their research has shown that fracture rock assessments requires detailed characterization. In that light, they have developed “tool boxes” of techniques that can be applied in characterizing fracture hydraulics and water quality. A detailed borehole investigation might entail the use of the following tools: a downhole television camera that provides a 360 degree digital image of the borehole wall for defining rock characteristics and location of fractures, an acoustic televiewer that provides magnetically oriented borehole wall images for determining fracture dip and strike, and a high resolution flowmeter for discerning water bearing fractures and identifying inflowing and outflowing fractures under both pumping and static conditions. These logging techniques would then be followed by packer testing to determine the hydraulic head in individual fracture zones, to conduct hydraulic testing for fracture transmissivity, and to collect water quality samples. Although the information derived by applying the USGS methods is comprehensive and definitive, it is also costly. The costs and the timeframe associated with the approach can inhibit its practicality.

The objective of this proposal is to develop a tracer technique to derive fracture information downhole, as a cost-effective compliment to the USGS "tool box" methods.

Methods, Procedures and Facilities:

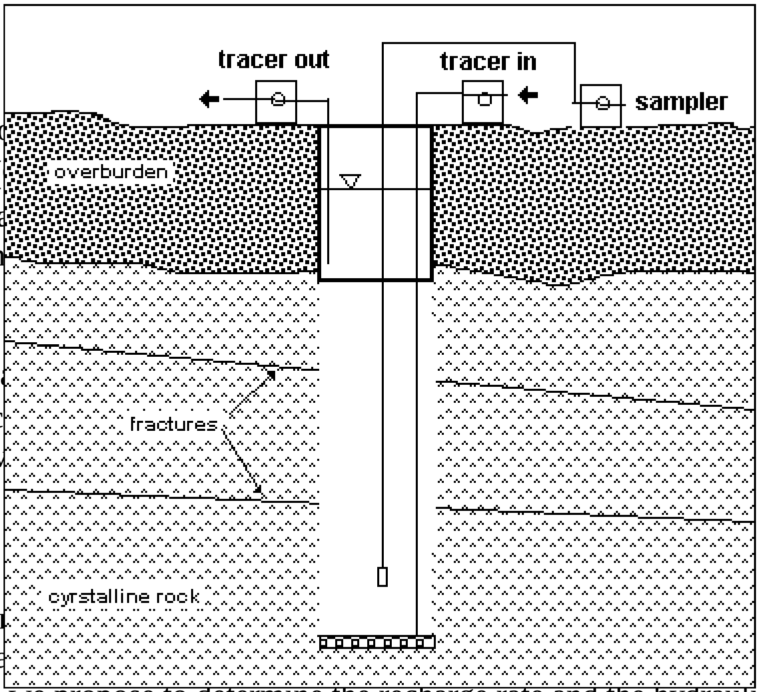
The research will be divided into three tasks:

Task 1 Literature Review

A literature review will be conducted to summarize past research on the use of chemical tracers downhole in crystalline fractured rock. The review will derive an annotated bibliography of methods, procedures and results. Also, it will aid in developing our test technique in task 2.

Task 2. Field Tracer Test

The USGS Branch of Geophysical Applications and Support is located on the University of Connecticut's, Mansfield Depot Campus. The Mansfield Campus is underlain by crystalline metamorphic bedrock. The USGS drilled three 6'' diameter bedrock wells, ranging in depth between 223 and 443 ft., on the Campus. These wells will be used to test the tracer method. A conceptual model of the tracer method is shown on Figure 1.



The method c xic tracer will be pumped at a
constant rate (ll be pumped out the top of the
well but at a r low into the well from fractures.
The tracer con stant. Then the tracer
concentration dure will then be repeated at
different flow and recharge rate (Q_I) of
fractures. As The concentration of tracer
below the frac was contributing flow to the
well, just abov

Equation 1 pe e well would permit determining
the fracture tr .g., in Hvorslev (1951). To be
more rigorous we propose to determine the recharge rate and the hydraulic head in the well at three different pumping rates. By continuing to sampling up the well, one can determine the recharge rates of each inflowing fracture using equation 2.

(2) $C_i = C_{in} * Q_{in} / (Q_{in} + Q_1 + Q_2 \ldots Qi)$

Again, given the recharge rates and the head in the well, the transmissivity of fractures can be calculated.

To be successful in identifying outflowing fractures that intersect a well, the head in the well must be lowered below that of the lowest head of any outflowing fracture. Under static conditions, the head in the well represents a weighted average head with respect to inflowing and outflowing fractures and their transmissivities, as shown in equation 3

$$(3) \qquad h_w = \Sigma(h_i * T_i)\ \Sigma/(T_i)$$

where h_w = hydraulic head in the well, h_i = hydraulic head in fracture i, and T_i is the transmissivity of fracture i. By monitoring the tracer concentration profile at different flow rates, one can determine when a fracture is converted from outflowing to inflowing. This approach also permits determining the hydraulic head in fractures. By pumping tracer in at the top of the well and out at the bottom at a rate that causes the head in the well to rise, one can determine the head in the inflowing fractures through tracer profiling.

A number of details are still to be worked out. For example, what should the optimum flow rates be for pumping and sampling, how should the tracer be delivered at the bottom of the well, how should the tracer be sampled so as not to disturb the vertical tracer profile, and what water treatments are needed following experiments.

Presently, we are considering the use of a dual tracer approach using bromide for field measurement and rhodamine for laboratory measurement. The bromide would be measured in the field using ion specific electrodes. The analytical sensitivity for rhodamine is several orders of magnitude, which would permit identifying fractures having several orders of magnitude difference in transmissivity. We have available to us in our Department or on campus all the field and analytical equipment to perform this research including water level sounders, peristaltic pumps, ion specific electrodes and meters and a florescence spectrometer. Additionally, we have access through cooperative efforts with QED Environmental Incorporated, to downhole sampling pumps if needed.

Task 3 Comparison to USGS Methods

The tracer tests will be performed without knowledge of any fracture information about the wells. Our results will then be compared to downhole tests performed by the USGS using the methods cited above. This will provide a unique opportunity to evaluate the tracer test results with those derived by the USGS methods.

If successful, this research would put us in a position to seek NSF, EPA or private sector funding to conduct a joint study with the USGS on the use of the tracer method at contamination sites. Here, we could conduct comparative testing as well as evaluate the use of the method for discerning which fracture may be contaminated.

Related Research

The use of tracers has long been used to characterize hydraulic properties in fractured rock. Methods that have been used include conventional well-pumping tests, tracer travel time between wells, and tracer dilution (Lewis et al., 1966). Various tracer dilution tests have been conducted by Raymond and Bierschenk (1957), Moser et al. (1957), Nuemaier (1960), Ochiachi and Rodriguez (1962) Michalski and Klepp (1990), Tsang (1990) and the United States Geologic Survey, to name a few. Although there are similarities in some of these methods with the method we are proposing, there are substantial differences. Most of the previous methods involve injecting a slug of tracer into the borehole, mixing the borehole fluids to achieve a homogeneous state, and then measuring tracer dispersion throughout the well depth. Certain methods also included the use of packers to isolate a specific fracture. The proposed research will involve active pumping of a specific concentration of tracer into and out of the borehole. This greatly simplifies interpreting the tracer data. A brief summary of previous tracer research follows.

Raymond and Beirschenk used hydraulic conductivity logging in 1957, as a means to determine the velocity of ground water passing through a well. Salt solutions were added to the well and then allowed to mix. Conductivity measurements were taken, using two probes, every five minutes, for a certain time period at a specific depth (Lewis et al, 1966).

Moser et al., as well as several others, (Lewis et al., 1966) has implemented the use of radioactive isotopes. The isotopes were introduced to the well. The radioactive activity was monitored for a period from a few hours to a day. The hydraulic conductivity was then computed from the data. The hydraulic conductivity computed was very close to that derived from pumping tests (Lewis et al., 1966).

Ochiachi and Rodriguez refined the radioactive isotope method in 1962 (Lewis et al, 1966). They designed the flow meter such that their model not only determined ground water velocity but also direction of flow.

In 1990, Michalski and Klepp reported on the use of a single well tracer study to compute the transmissivity of fractures intersected by the well (Mickalski and Klepp, 1990). A slug of deionized sodium chloride water was introduced to the well. The solution was introduced to what is considered "upstream", dependent on vertical flow direction. The volume of slug injected was kept to below one well diameter to reduce any hydraulic head or flow change. An electric conductivity probe was lowered into the well and used to measure electric conductivity throughout the depth of the well. From the tracer profiles, not only could intrawell flow and transmissivity of fractures be characterized, but also incoming water quality could be determined.

Tsang, Hufschmied and Hale (1990) also used an electric conductivity method to estimate the transmissivities of intersected fractures within a single well. The water in the well was first replaced with deionized water. Then the well was pumped at a low flow rate. An electric conductivity probe was then lower through the well depth. This was performed a number of times and several conductivity logs were created. Using these logs the inflow characteristics of the fractures could be determined (Tsang et al, 1990).

Recently (1997) the United States Geological Survey as part of their *Toxic Substances Hydrology Program* (USGS, 2000), has also used tracer dispersion methods to determine water predicting and water receiving zones in the Newark basin area in Pennsylvania. (Sloto, 1997) This was a dual method test, using both a brine-tracing method and a heat-pulse flowmeter. 93 boreholes were logged, 83 using the brine-method and 10 using the flowmeter. A slug of high conductivity fluid was injected into the 83 boreholes and vertical movement was tracked using a fluid resistivity tool under nonpumping conditions. By correlating caliper logs with the fluid resistance and fluid temperature logs, it was possible to determine water receiving and water producing fractures (Sloto, 1997).

Similar methods were also used by the USGS in 1997, for the Lockatong and Brunswick Formations in Montgomery County, Pennsylvania. By correlating caliper, natural gamma, fluid-resistivity and fluid-temperature, fluid-movement (brine-tracing or heat-pulse flowmeter), and borehole video logs it was possible to determine water producing fractures (Senior and Conger, 1997).

In 1997 and 1998 the USGS used similar methods at a Superfund site in Chester County, Pennsylvania to determine horizontal and vertical distribution of contaminated water moving from the source area. Fluid temperature and resistivity logs were used to determine water producing and water receiving fractures. Slug tests were then used to determine the transmissivity of those fractures (Conger et al., 1999).

All of this research is similar to the proposed research in that tracer dilution methods were used to measure certain hydraulic properties (i.e. receiving vs. producing fractures, flow direction within those fractures and the fracture transmissivity.) The number of hydraulic properties was limited to about two parameters in each case. Our proposed research characterizes at least four hydraulic properties during one testing period. In addition, the proposed research will be compared to results computed by the United States Geological Survey using downhole tools and packer tests to characterize fractures. This will permit a rigorous evaluation of the accuracy of the tracer method.

Principal Findings and Significance

The results of this study are described in the masters thesis, "A Stepwise Discharge Tracer Dilution Method for Deriving Fracture Properties in Crystalline Bedrock Wells," Richard J. Brainerd, Dept. Geology and Geophysics, University of Connecticut, 2002. The major conclusions of this study include:

* The ability to characterize the flow properties of transmissive fractures in bedrock aquifers is of the utmost importance, not only for water supply but also contamination transport. Throughout the years, many methods have been used to try to gain knowledge of these flow properties. These methods include various geophysical, borehole logging, conventional hydraulic test and tracer test techniques.

* This research evaluated a tracer method to characterize the flow properties of water-conducting fractures intersecting a borehole in fractured crystalline bedrock. This method allows the determination of the fracture hydraulic head directly. Thus, the calculated transmissivity, which is directly related to the effective drawdown of the fracture, is not subject to ambiguities associated with the assumption of a uniform aquifer head.

* Fracture hydraulic head and ambient flow are determined graphically, thus avoiding the use of any of the multiple equations for flow which all require, in some way or another, assumptions to be made. As is known, these assumptions were developed for unconsolidated material and are often invalid when describing fracture flow.

* The tracer dilution test method was able to characterize two fractured bedrock wells. One fracture was identified and characterized in BGAS-3, while four fractures were identified in BGAS-1. Only tow of the fractures in BGAS-1 could be completely characterized.

* The three wells are hydraulically, very connected by a highly transmissive fracture. This is seen in the imeediate response in the observation wells to a change in the water level in the pumping well.

* Several recommendations to improve the developed method are given. These include: lowering the injection rate and concentration, using more accurate flowmeters, and using a different criteria for identifying the presence of a fracture.

* Tracer tests are a valuable tool in helping to characterize flow conditions in fractured bedrock aquifers. They can be used as a preliminary screening tool or as a stand-alone method.

* In recent years great strides have been made in our ability to decipher the subsurface but we have far to go to. It is only with the integration of many such techniques that the pieces of the puzzle of teh subsurface fracture networks will become clear.

* The unknown aspects of fracture interconnectivity will continue to test the ability to put those pieces of the puzzle together. It is for that reason that the ability to describe the interconnectivity of fractures and how that interconnectivity effects flow properties could be one of the most important areas that further research needs to concentrate on.

Citations:

Conger, Randell w., Goode, Daniel J, Sloto Ronald A, 1999. *Evaluation of Geophysical Logs and Slug tests, Phase II, at AIW Frank/Mid County Mustang Superfund Site, Chester County Pennsylvania*, United States Geologic Survey, Open File Report 99-452

Lewis, David C., Kriz, George J., Burgy, Robert H, 1966. *Tracer Dilution Sampling Techniques to Determine Hydraulic Conductivity of Fractured Rock,* Water Resources Research, vol. 2, no. 3, p.533-542.

Michalski, Andrew, Klepp, George M., 1990. *Characterization of Transmissive Fractures by Simple Tracing of In-Well Flow,* Ground Water, vol. 28, no. 2, p. 191-198.

Senior, L.A., and Conger, R.W., 1997. *Use of Borehole Geophysical Logging and Water-Level Data to Characterize the Ground-Water System in the Lockatong and Brunswick Formations*: (abs.), GSA Abstracts with Programs, vol. 29, no. 1, p. 78.

Sloto, Ronald A., 1997. *Use of Borehole Geophysical Methods to Define Ground-Water-Flow Systems in the Stockton Formation, Newark Basin, Pennsylvania*: (abs.), GSA Abstracts with Programs, Northeast Section, vol. 29, no. 1, p. 81.

Tsang, Chin-Fu, Hufschmied, Peter, Hale, Frank V, 1990. *Determination of Fracture Inflow Parameters With A Borehole Fluid Conductivity Logging Method,* Water Resources Research, vol. 26, no. 4, p. 561-578.

United States Geologic Survey, 2000. *Toxic Substances Hydrology Program,* http://toxics.usgs.gov/about.html.

Information Transfer Program

The Institute conducts a number of information and technology transfer activities through its ongoing seminar series and publications program and through cooperative efforts with other water groups in the state.

In 2001, WR collaborated with the CT DEP on the Golf Course Compliance Assistance Project. The Institute facilitated the development of the "Best Management Practices for Golf Course Water" document, and managed an outreach effort that included a one-day conference for industry professionals, "Water Resources Management in a Golf Course Environment."

Also this past year, the CT IWR became involved in the work of the statewide Water Planning Council, created by an act of the state legislature. The Council’s mission is to "... identify issues and strategies which bridge the gap between the water supply planning process and water resources management ..." The Institute contributed technical expertise regarding water resources research needs, methodologies for water resource investigations and decision support strategies.

Seminar Series: The theme of the 2001-2002 series, "Public Health and Water Quality" was chosen based on needs expressed by our Advisory Board. Talks included: "Social Justice and Connecticut’s Water Resources." Senator Donald E. Williams, Jr., Chair, Environment Committee, Connecticut State Senate; "Waterborne Infectious Agents" Dr. David Hill, Professor of Medicine, UCONN Medical School ; "The State Aquifer Protection Area Program" Robert Hust, Planning and Standards, Connecticut Department of Environmental Protection; "Pesticides and Private Residential Wells." Nancy Alderman, President, Environment and Human Health, Inc.; "The Financial Cost of Toxics in the Water Supply." Dr. Edward Rossomando, Director, Waterborne Disease Center, UCONN Health Center, Farmington, CT.; "Monitoring Water Quality in the Willimantic Reservoir and Mansfield Hollow Lake." Dr. George Hoag, Director, Environmental Research Institute, University of Connecticut; "An Introduction to the Source Water Assessment Program." Lori Mathieu, Lead Planning Analyst, Water Supplies Section, CT Department of Public Health

Web Site and Publications: The Institute’s web site contains abstracts of recent research projects, the current year’s seminar series, a publication database, special project information and links to other water related sites. The Institute is scanning many of its older publications for distribution over the web or on CD. We will shortly be publishing a report on updated historical precipitation statistics for Connecticut that shows changes in long-term trends and the probabilities of extreme events.

The Institute also accepts proposals for funded Information Transfer projects as a part of its competitive RFP process explained in the Research Program below. This year, 104B funds were used to support two IT projects:

Clausen: Co-sponsorship of the 8th National Nonpoint Source Monitoring Workshop.

Clausen et al.: Rain Garden Demonstration and Workshop.

8th National Nonpoint Source Monitoring Workshop

Basic Information

Title:	8th National Nonpoint Source Monitoring Workshop
Project Number:	2000CT11B
Start Date:	9/10/2000
End Date:	9/14/2001
Funding Source:	104B
Congressional District:	2nd
Research Category:	None
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	John Clausen

Publication

Rain Garden Demonstration and Workshop

Basic Information

Title:	Rain Garden Demonstration and Workshop
Project Number:	2001CT601B
Start Date:	3/1/2001
End Date:	2/28/2002
Funding Source:	104B
Congressional District:	2nd
Research Category:	Not Applicable
Focus Category:	Education, Non Point Pollution, Surface Water
Descriptors:	rain garden, nonpoint source pollution, education,storm water management
Principal Investigators:	John Clausen, John Alexopoulos, Michael Dietz, Laurie Giannotti

Publication

1. Project number.

2. Title. **Rain Garden Demonstration & Workshop.**

3. Focus categories. EDU, NPP, SW, TRT, WQL, WQN

4. Key words. Storm water management, education, nonpoint source pollution, rain garden.

5. Duration (month/year to month/year). 3/01-2/02

6. Federal Funds. $7,000.

7. Non-Federal Funds. $13,852.

8. Principal investigator's names and university. John C. Clausen, John Alexopoulos, Laurie Giannotti, Michael Dietz, University of Connecticut

9. Congressional district. Second

10. Statement of critical regional or State water problems. In the U.S., nonpoint sources of pollution have been reported to result in use impairments in 37% of the rivers, 40% of the lakes, and 39% of estuary areas (U.S. EPA, 1998). Nationally, urban runoff and storm sewers are responsible for 13% of impaired rivers, 21% of impaired lakes, and 46% of impaired estuaries. In Connecticut, 28% of rivers, 36% of lake areas and 53% of estuary areas do not support drinking, fishing, and swimming uses. The primary causes of impairments in Connecticut are bacteria, PCBs, metals, oxygen demanding wastes, ammonia, nutrients, and habitat alteration (U.S. EPA, 1998). Sources of these pollutants include urban runoff and storm sewers, industrial discharges, municipal sewage treatment plants, and in-place contaminants. Hypoxia is a widespread problem in Long Island Sound (CT DEP, 1989; LISS, 1990). The Long Island Sound is a critical resource to the State which provides annually, a fishery for one million anglers and recreation for 20 million beach goers (Altobello, 1989).

Several practices have been recommended to reduce pollutants in storm water runoff (U.S. EPA, 1993). One such practice is the use of a rain garden, which is a small, shallow depression intended to treat the first flush of runoff from impervious surfaces (U.S. EPA, 1999). Although this practice is in use elsewhere, planning officials and design engineers in Connecticut are not aware of how to design and apply rain gardens to new and existing urban and suburban developments.

11. Statement of results or benefits. The proposed workshop will transfer relatively recent technology to an audience in Connecticut that is primarily responsible for planning and regulating the treatment of storm water runoff. This project will also support development of workshop materials and create a demonstration site at a central Connecticut location. The rain garden has numerous applications as a low technology best management practice in Connecticut and elsewhere.

12. Nature, scope, and objectives of the research.

The overall objective is to develop and conduct a one-day workshop on the design and construction of rain gardens for storm water treatment. A secondary objective would be to construct a demonstration rain garden at the Connecticut Cooperative Extension System Center in Haddam, CT

This workshop is needed because engineers and local officials are unaware of how to design and construct rain gardens and where they are applicable. The actual construction of a rain garden will give a demonstration site for future workshops.

13. Methods, procedures, and facilities.

A "rain garden" is a shallow depression intended to treat the first flush of runoff from impervious surfaces. Larger flows are diverted through or around the rain garden. This urban best management practice was developed in Maryland to provide bioretention of storm water pollutants (Prince George's County, 1993). Biological activity hastens a break down of contaminants into forms that selected herbs, shrubs and trees can take up. By diverting the first flush of contaminated runoff to a rain garden, fewer contaminants enter the storm water system, and the load to local water bodies can be lessened. An additional and important benefit of a rain garden is that 5% to 7% of runoff is infiltrated into the soil rather than contributing to overland flow.

A typical rain garden would be constructed to accept roof or parking lot runoff. A rain garden is usually a maximum of 15 cm (6 in) deep for ponding, has a sand bed over which is placed topsoil and mulch, and is planted with vegetation that can tolerate temporary standing water and fluctuating water levels. The size of a rain garden is determined as 5% to 7% of the drainage area times the "C" coefficient from the rational equation. The coefficient "C" varies with land use and soil types (Chow, 1964). For example, the "C" for asphalt ranges from 0.70 to 0.95, whereas the "C" for lawns ranges from 0.05 to 0.35, depending on the soil type and the slope. Most commonly, rain gardens have been applied in traffic islands in parking lots and on individual lots in residential neighborhoods.

A one-day workshop will be developed. The targeted audience will be local planning officials and engineering consulting firms. Instructors for the workshop will include the principal investigators as well as outside experts in rain garden design. A draft outline for the workshop is given below.

A workbook will be developed for workshop attendees that will assist participants in designing a rain garden with a focus on Connecticut conditions. The workshop will be conducted at the Haddam Cooperative Extension Center. The Center has a conference facility that can hold up to 155 attendees. Lunch can also be served in the conference facility.

A rain garden will be designed by the principal investigators for application at the Haddam Cooperative Extension Center. The rain garden will be mostly constructed prior to the workshop by a local contractor. However the actual planting of the rain garden will be completed by workshop participants at the end of the workshop.

13. Summary of the Information Transfer Activity.

The "Rain Garden Workshop" was held on October 3, 2002, in Haddam Connecticut. Approximately 63 people attended. The workshop consisted of six presentations related to the purpose and design of rain gardens, and concluded with a demonstration. Handouts provided to the attendees included:

From the Prince George's County Department of Environmental Resources, Maryland:

- * "Rain Gardens: The Natural Solution"
- * "How Does Your Garden Grow?"
- * "The Bioretention Manual"

From the University of Connecticut, Middlesex County Cooperative Extension Center:

- * "Planting Design Suggestions"

The Workshop program is shown on the following page.

Rain Garden Workshop - October 3, 2002 - Haddam, Connecticut

Final Schedule

9:00 Introduction and get acquainted
Jack Clausen, Associate Professor
University of Connecticut
Department of Natural Resources Management and Engineering 1376 Storrs Rd. U-87, Storrs, CT 06269-4087
(860) 486-0139
john.clausen@uconn.edu

9:15 Introduction to rain gardens and bioretention
Derek Winogradoff, project manager
Prince George's County Department of Environmental Resources
9400 Peppercorn Place, Suite 610
Largo, MD 20774
(301) 833-5903
dawinogradoff@co.pg.md.us

10:15 NEMO
Laurie Giannotti, NEMO Project CT Coordinator
Middlesex Extension Center
1066 Saybrook Rd. PO Box 70,
Haddam, CT 06438
(860) 345-4511
laurie.gianotti@uconn.edu

10:30 Break

11:00 Rain Garden Design I - hydrology, size and location
Jack Clausen, University of Connecticut

12:00 Lunch (Provided)

1:00 Rain Garden Design II - Soils
Lisa Krall, Soil Scientist
USDA - Natural Resources Conservation Service
24 Hyde Ave. Vernon CT 06066
(860) 785-3881 x. 110
lisa.krall@ct.usda.gov

1:30 Rain Garden Design III - Plants
John Alexopoulos, Associate Professor
University of Connecticut
Department of Plant Science
1376 Storrs Rd, U-67, Storrs, CT 06269-4067
(860)486-1941

2:00 Rain Garden Design IV - Construction supervision
Team

2:30 Planting the Rain Garden

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	2	0	0	0	2
Masters	2	0	0	0	3
Ph.D.	0	0	0	0	0
Post-Doc.	1	0	0	0	1
Total	6	0	0	0	6

Notable Awards and Achievements

Publications from Prior Projects