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SOLUTE TRANSPORT IN A HETEROGENEOUS FIELD

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE

OF MASTER OF APPLIED SCIENCE

IN REGIONAL ENVIRONMENTAL SYSTEM ENGINEERING

UNIVERSITY OF REGINA

BY

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REGINA, SASKATCHEWAN

MARCH, 1997

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CERTIFICATION OF THESIS WORK

We, the undersigned, certify that Yili An, candidate for the Degree of Master of Applied Science, has presented a thesis on *Solute Transport in a Heterogeneous Field*, that the thesis is acceptable in form and content, and that the student demonstrated a satisfactory knowledge of the field covered by the thesis in an oral examination held on March 14, 1997.

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谨以此文纪念我的母亲

THESIS DEDICATED TO THE MEMORY OF MY MOTHER

ABSTRACT

The present study analyzes the problem of transport of an inert solute carried by water which flows in a relatively large heterogeneous field by coupling a solute transport model and a regional stochastic approach. In this study, a controlled laboratory experiment was conducted. Twenty one nondisturbed monoliths were sampled from a field plot. The soil structure maintained in the undisturbed soil monoliths, and the spatial distribution of the sampling captures the heterogeneity of the field. Chloride tracer tests were carried out in these monoliths. These tests provided local breakthrough curves at the scale of the individual monoliths. The high degree of variability of downward solute movement at different locations in the site may be illustrated by examining the extremes in the shapes of the solute pulses obtained from different monoliths. A large variability in convective transport was evidenced by the very rapid solute breakthrough at some sites, in contrast to the late arrival and slow passage of solute at others.

A regional stochastic approach was used in the study to investigate the spatial variability (expressed through the semivariogram) of two measured solute transport parameters, velocity (V) and dispersion coefficient (D). These two transport parameters were then used as input parameters to a simplified solute transport model (the one-dimensional convection-dispersion model). The model, when coupled with the stochastic approach, can be used to analyze the effect of the spatial variabilities in V and D on the spatial variability in the solute concentration (C) during leaching. With only 16 sampling points, the semivariogram of a given solute transport

parameter can be only crudely estimated. However, the validation tests of the kriging models showed that the selected semivariograms adequately described the spatial behavior of the transport parameters.

The sensitivity of the present stochastic model was analyzed. Its applicability to agricultural water management and pollution control was examined. Although the results of the present approach for the clay field were encouraging, no attempt was made to generalize the results. It is suggested that the present study be considered primarily as one which presents a methodology to solve solute transport problems which are associated with field spatial variability.

Acknowledgments

Numerous people have made this research possible, and it is impossible to give each one credit. To those persons not mentioned below, I thank you for your time and effort.

First of all, I would like to thank my supervisors Dr. Y. C. Jin and Dr. T. Viraraghavan for their patience and guidance which were invaluable during my graduate studies and in the preparation of this thesis.

This research was supported in part by a research grant to Dr. Jin and Dr. Viraraghavan from the Natural Science and Engineering Research Council of Canada.

I am grateful to the Faculty of Graduate Studies and Research for their financial support during Sep. 1995 to Dec. 1995.

I also like to express my gratitude to Mr. S. L. Ye for his assistance in designing and maintaining the experimental facility.

Deepest gratitude to my parents, whose constant encouragement made this work possible.

List of Symbols

a	Range of the semivariogram.
C_0	Input solute concentration.
C_T	Total solute concentration (mass of solute/soil volume).
C_L	Dissolved solute concentration (mass of solute/volume of solution).
C_s	Adsorbed solute concentration (mass of solute/mass of dry soil).
ρ_b	Soil dry bulk density (mass/volume).
θ	Volumetric water content.
J_w	Water flux (volume flow/ area time).
J	Integral scale.
D	The apparent diffusion coefficient.
erfc	Complementary error function.
m	Lagrangian multiplier.
N	Nugget effect.
PDF	Probability density function
R	Generalized sink term modeled for specific reactions (mass of solute/ volume/time).
S	Sill of the semivariogram.
t	Time.
t_1	Leaching time at which $C/C_0=1$.
V	Effective pore water velocity.
λ	Kriging weight.
μ	Mean value of the samples.
σ^2	Sample variance.
$\sigma(h)$	Covariogram.
$\sigma^*(h)$	Experimental covariogram.
$\gamma(h)$	Semivariogram.
$\gamma^*(h)$	Experimental semivariogram.
$\rho(h)$	Autocorrelation function.

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1 INTRODUCTION

1.1 Background

Public awareness and concerns about groundwater pollution have been heightened through a series of highly-publicized incidents: the accidental application of TCDD (dioxin) throughout Missouri (Esposito et al., 1980), the detection of pesticides like aldicarb and DBCP in groundwater (Pratt et al., 1985), and the controversy surrounding efforts to devise safe storage repositories for nuclear waste (Roy, 1982). Mistakes resulting from poor management or imperfect understanding of soil conditions surrounding hazardous waste storage sites can lead to soil contamination which carries staggering remediation cost. Agricultural land use can also contribute significantly to the chemical loading of soil overlying groundwater or bordering surface water supplies. Pesticide and fertilizer residuals can move below the crop rooting zone and percolate downward as irrigation water or rainfall enters the soil (Pratt et al., 1972). Furthermore, agricultural operations can contribute to lower water quality in general by increasing the dissolved solids concentration in drainage water through water extraction by crops. This is not surprising as more and more evidence points to the pollution of groundwater by hazardous chemicals from various sources.

Given the political, economic, and social implications of widespread water pollution resulting from soil-applied chemicals, prediction of downward

movement of chemicals below land operations become one of the major tasks facing environmental scientists today. These operations, ranging from farming inputs of fertilizers and pesticides, to sludge pond disposal of heavy metals, to shallow burial of nuclear waste, all pose a potential hazard to underlying or adjacent water supplies. For those chemicals which are hazardous even at trace concentrations, the task of prediction must extend to "worst case" behavior, such as might occur through some sites of a highly heterogeneous field.

There is an increasing body of experimental information to suggest that vertical water and chemical transport in the vadose zone can vary significantly from place to place in the horizontal direction in natural soil profiles, even when the input of material at the surface is uniform (Jury et al., 1976; Biggar and Nielsen, 1976; Van de Pol et al., 1977; Starr et al., 1978). Models are needed which can simulate this variability while at the same time requiring only such calibration as may be reasonably performed in situ.

At present, only a few transport models are appropriate for this type of a problem. Most water and solute transport models used in the vadose zone are an outgrowth of laboratory models developed to simulate flow in uniformly packed porous media. As such they are either one-dimensional models which assume vertical flow with no lateral variability (Rose et al., 1982) or are formal three-dimensional models with the transport coefficients represented as tensors which are impossible to calibrate (Duguid and Reeves, 1976; Jury, 1983). Only in recent years have soil scientists turned to the more difficult problem of simulating flow under conditions of natural variability. In this

chapter some recent solute transport field experiments will be briefly reviewed and the major models used currently in the heterogeneous fields will be identified.

1.2 Review of solute transport variability studies

There have been several significant studies performed in recent years which demonstrate the extreme lateral variability of solute applied to the unsaturated zone of soil . Biggar and Nielsen (1976) conducted a steady state ponded flow experiment studying the movement of a solute pulse on 20 subplots of a 150-ha field. They measured water velocity by determining the arrival time lag between adjacent solution sampler depths from the surface to 180 cm. The resulting measurements of water velocity were log-normally distributed with a mean, median, and mode value of 44.2, 20.3, 4.3 cm/day. This variability was much higher than the corresponding variability of the saturated hydraulic conductivity measurements on the same field.

There also have been studies conducted where the input of water at the surface was uniform across the field. Jury et al. (1976) added a tracer dye to the irrigation water on a sprinkler-irrigated potato field and observed a highly nonuniform water infiltration pattern underneath the hill, shoulder, and furrow surfaces of the field even though the infiltration capacity of the sandy soil was very high. Van de Pol et al. (1977) studied the movement of a pulse of chloride added by a trickle irrigation system with a high application uniformity, and measured a lognormal water velocity distribution even though

the system was in steady state and the trickle emitters were only 30 cm apart. Jury (1982) studied movement of a pulse of bromide applied uniformly to the surface and leached by rainfall and again found lognormally distributed velocities. Table 1 shows a summary of these four experiments with each observed velocity distribution fitted to a lognormal distribution. The fifth and sixth columns give the expectation and variance of the log of water velocities. As expected, the variance of the ponded experiment is quite high, reflecting not only variability in the infiltration rate from a various point, but also variability in water transport within the soil. The other studies, however, show substantial variability even though the input of water to the soil was spatially uniform. It is clear from these studies that regardless of the uniformity of the input, a distribution showing variation in water output velocities in the horizontal direction is to be expected.

Table 1.1 Measured solute velocity distribution in field experiments using mobile chemicals

Experiment	Soil type	E(v) cm/d	Var(v) cm ² /d ²	E(lnv)	Var(lnv)	Literature citation
Tracer movement under sprinkler irrigated potato crop	sand	14.4	24.0	2.61	0.11	Jury et al. (1976)
steady state Cl- ponded bare soil plots over 150 ha	clay loam	44.3	62.1	2.01	1.56	Biggar and Nielsen (1976)
Steady state Cl- flow under 2 cm/day trickle irrigation	clay sand	3.9	5.7	1.2	0.32	Van de Pel (1977)
Leaching of Br- pulse by rainfall	loamy sand	1.0 1	0.4	0.15	0.31	Jury (1982)

1.3 Review of field models of solute transport

1.3.1 Deterministic approach

There have been a number of comprehensive reviews of solute transport in soil published in recent literature (Biggar and Nielsen, 1976; Boast, 1973), including an excellent review of all models potentially applicable to waste disposal and modeling (van Genuchten , 1978). The vast majority of all field solute transport models used in the unsaturated zone are based on the convection-dispersion equation, which was developed from laboratory simulations and experiments.

$$\frac{\partial C_T}{\partial t} + R = \nabla \cdot \underline{D} \cdot \nabla C_L - \nabla \cdot \underline{J}_w C_L \quad (1.1)$$

where

$C_T = \rho_b C_s + \theta C_L$ is total solute concentration (mass of solute/soil volume)

C_L is dissolved solute concentration (mass of solute/volume of solution)

C_s is adsorbed solute concentration (mass of solute/mass of dry soil)

ρ_b is soil dry bulk density (mass/volume)

θ is volumetric water content

J_w is water flux (volume flow/ area time)

D is the diffusion- dispersion tensor (area/time)

R is a generalized sink term modeled for specific reactions (mass of solute/volume/time)

1.3.2 Classic stochastic approach

Equation 1.1 has been thoroughly tested under laboratory conditions both for steady state and transient water flow. Predictions obtained with these models have generally been reasonably accurate for miscible displacement experiments involving repacked or undisturbed laboratory soil columns, especially when inert tracers are used (e.g., Danckwerts, 1953; Nielsen and Biggar, 1961; Biggar and Nielsen, 1962, 1967; Lindstrom et al., 1967; Fried, 1971; Bear, 1972; Rao et al., 1980; Nkedi-kizza et al., 1984). Its applicability to the field, however, has been hampered by an inability to predict multi-dimensional water flows using the water flow equation, and a corresponding inability to measure or model the diffusion-dispersion tensor. In fact, the form and size of dispersion is a function of the precision of the representation used for the water flux. For example, if only a one-dimensional average water flux is used in a situation where lateral variations in water flux are present, then solute spreading caused by the variable convective flux will have to be modeled as though it arose from dispersion. For this case, a large and complex form for dispersion would be needed to simulate any observed solute movement (e.g., Bredehoeft and Pinder, 1973; Konikow and Bredehoeft, 1974; Gelhar et al., 1979; Sposito et al., 1986; Jury, 1992).

For this reason, many workers have stopped trying to represent in exact detail transport of solute through heterogeneous soil and have rather proposed approximate procedures for describing flow under conditions of high lateral variability. Several such approaches still utilize aspects of deterministic

flux and meet material balance theory and represent downward vertical flow through a field soil as flow through one-dimensional , parallel, regimes each with its own characteristic set of hydraulic transport and retention parameters. As an alternative to the deterministic approach which uses the convection-dispersion equation and a tensor representation of transport coefficients, several researchers have begun to look at stochastic representations of water movement. One such approach has been to use scaling theory to relate various regions of a field soil. In this method, heterogeneous regions of the field are imagined to be magnified versions of a reference region, related to each other by a macroscopic length parameter or scaling factor. If the assumptions of scaling theory are met in a field, then knowledge of the scaling factor distribution would allow calculations to be made of the transport coefficient at the reference location. Once the distribution of transport coefficients is obtained, laterally variable water and/or solute transport during infiltration, could be modeled by assuming the field to consist of a parallel non-interacting network of soil columns, each with its characteristic scaling factor and corresponding transport properties. Computer simulation of such processes could be simplified through dimensionless calculations (Peck et al., 1977; Warrick and Amoozegar-Fard, 1979). A few field tests of the scaling factor model of variability have yielded mixed results (Warrick et al., 1971; Sharma et al., 1980) when used to compare transport coefficients or processes measured at different locations in a field.

A novel variation in solute transport modeling was achieved by Dagan and Bresler (1979), who combined a piston flow model of downward solute

flow under the influence of gravity at a given point in the field, with a stochastic model for a prediction of the probability of solute movement to given depth. They defined the hydraulic transport properties of any point in the field through a probability distribution for scaling factors. Finally they combined the soil transport model with spatial variations in water application rate defined through a frequency function.

Two years later Bresler and Dagan (1981) incorporated pore-scale dispersion into their earlier model. This had very little effect on the calculated solute distributions, as already had been foreseen in the 1979 paper. Finally, Bresler and Dagan (1983 II) developed expressions for the first- and second-order moments of the concentration distribution as a function of depth and time, using a simplified solution (Dagan and Bresler, 1983 I; Bresler and Dagan, 1983 II) of the non-steady water flow equation. The transient water flow condition provides approximately the same results as the steady- state approach.

Jury(1982) introduced the concept of the transfer function model as a means of describing solute transport in heterogeneous fields. In this approach, a soil system is characterized uniquely by the way in which it transforms an input function into an output function, assuming a log-normal distribution of travel times and no local dispersion. Jury (1986) later gave a more general derivation of transfer function models for transport of solutes in soils. Solutes in the model may be conservative, or may undergo physical-chemical or biological transformations in a soil with spatially or temporally variable flow properties. The authors concluded that any mechanistic solute transport

model which maintains mass balance can be made consistent with the transfer function concept.

Several field studies were conducted in which the transfer function model was used to predict transport of tracers in natural soils. Butters and Jury (1989 a, b) studied the movement of bromide through a 0.64 ha loamy sand field under steady-state flow conditions. While the transfer function model successfully predicted bromide concentration at 0.3m depth, the prediction of bromide concentration at other depths (0.6m-4.5m) was not good. Bowman and Stephens (1991) conducted a comprehensive field experiment to study solute transport in a heterogeneous field. The study area was 10m×10m in size and it was fed with bromide solution at a steady-state flow rate. By examining the average breakthrough curve, they made the conclusion that the application of the transfer function model to predict bromide concentration was only 'partially successful' (Bowman and Stephens,1991). Tseng and Jury (1994) made a comparison between the deterministic and the transfer function models in their ability to predict solute transport in a 10m×10m field under steady-state flow condition and found, both the two models can not provide a good description of solute transport at that field.

Many research efforts have been made in recent years to improve the above mentioned stochastic models. The most important progress is the conditional stochastic approach in which the probability density was calculated by more sophisticated numerical methods. Zhang and Neuman (1995a,b,c,d) used Eulerian-

Lagrangian method to simulate groundwater flow and solute transport. Harter and Yeh (1996a,b) simulated water flow and solute transport under unsaturated conditions using a conditional Monte Carlo method. However, no field test was made to confirm the applicability of these models.

Although the stochastic approaches mentioned above differs widely in working procedures, they share a common assumption that the porous medium may be considered as a single realization of a random field. The application of these models, therefore, relies on a quantification of the spatial variability of the random field that is assumed to represent the pertinent transport properties. A complete characterization of the random field for a given property would require specification of the joint probability function for the property at established coordinate points throughout the system. Unfortunately, because regional statistical processes have been introduced only recently to soil physics and hydrology, all the previously discussed attempts to quantify the spatial variability of a porous medium have been based on a conventional statistical approach. In this approach, field spatial variability was quantified in terms of the first and second statistical moments. An implicit assumption in that analysis is that the observation of a given property is independent of one another, regardless of their locations in the random field.

For most natural porous media, spatial variations are not completely disordered but instead possess a structure (Vauclin et al., 1983; Russo, 1983; Russo and Jury, 1987a, b; Unlu et al., 1990; and Russ and Bouton 1992). By

neglecting this structure, researchers may come up with an incomplete statistical description of the medium and biased estimates of the probability density function (PDF) for the pertinent property, since no account is taken of the correlation between neighboring observations. Jury (1987a, b) examined those previously discussed stochastic models and concluded that the assumption of statistical independence is contributing to less success of these models.

1.4 Objectives and scope of the study

The present study was oriented along the lines of the above discussed stochastic approaches in the sense that the field was represented as a collection of homogeneous vertical columns. However, this study was more practically oriented, and it also differed from the above discussed stochastic approaches in one important aspect.

The spatial structure of the relevant soil hydraulic properties were considered in this study. Thus, by using a spatial stochastic approach, each of the soil hydraulic parameters V and D can be expressed as a realization of a stochastic function, the spatial variability of which is expressed through the semivariogram.

Once the semivariogram was developed, the kriging technique was applied to map parameter which was spatially variable and showed a definable spatial structure. Therefore, by use of a number of sampling points, the method provides, at any given point in the field, the best linear unbiased

estimate of the soil hydraulic parameters V and D . With this approach, not only the response of an entire field can be estimated, but also that of specific sites in the field.

The objective of this study was therefore to characterize the inherent spatial variability of the soil hydraulic properties, and to analyze their effect on the predicted solute profiles during leaching under steady state flow rate.

To achieve this purpose, a controlled laboratory experiment was conducted. At the first stage of the study, 16 nondisturbed monoliths were sampled from a field plot. The soil structure maintained in the undisturbed soil monoliths, and the spatial distribution of the sampling captured the heterogeneity of the field. Chloride tracer tests were carried out in these monoliths. These tests provided local breakthrough curves at the scale of the individual monoliths, from which the transport parameters V and D at each sample point can be optimized. Using the limited number of measured parameters V and D , a regional stochastic model was developed to predict solute transport throughout the entire field. The accuracy of the model was then tested by comparing predicted solute concentration with the data measured from another group of monoliths. At the second stage of the study, another five monoliths were sampled at the same field plot and tracer breakthrough experiments were carried out under the same irrigation load. The accuracy of the present model was then tested by comparing the predicted solute concentration with the data measured from these five monoliths.

2 THEORY

2.1 Basic assumptions

The present study analyzed the problem of transport of an inert solute carried by water which flows in a relatively large heterogeneous field by coupling a solute transport model and a stochastic approach. The soil properties which were considered in the study varied in space. These variations were characterized by length scales which were much larger than the pore scale. The main concern was the influence of these variations on flow of solutes, and pore-scale variability was therefore neglected and the soil was regarded as a continuum medium, the properties of which were continuous functions of the space coordinates. At a given point x of the horizontal plane (ζ, η) , the elementary volume representing the properties of the field is characterized by a macroscopic scale (where Darcy' law is relevant), which is large compared with the pore scale but small compared with the scale of the field heterogeneities. In the particular case of a cultivated agricultural field, dimensions in the horizontal plane (hundreds of meters) are much larger than the vertical dimensions (the root zone) . Therefore as a first- order approximation the possible variations of a given soil property with respect to depth were neglected, and average (over depth) values of the soil properties were considered.

Consider the vertically downward leaching from a soil profile comprised of soil particles which neither sorb nor repel the solute species. If we neglect the transient nature of the water flux during initial stages of leaching and assume the value of pore

water velocity v is independent of soil depth and equal to $\frac{J_w}{\theta}$, where θ is the average soil water content from the soil surface to depth z , Equation 1.1 can be changed into the following simple equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} \quad (2.1)$$

where D is the apparent diffusion coefficient, V the pore water velocity, z the vertical coordinate measured positively downward from the soil surface, and t time.

Therefore at each point x of the coordinates (ζ, η) in the field, the knowledge of V and D enables one to calculate the solute concentration profile for that point for a given set of boundary and initial conditions.

2.2 The lognormal distribution

Transport properties measured near the soil surface have often been found to be skew-distributed—their sample frequency distributions are not well represented by a Gaussian distribution. Although the distribution of a given property cannot be inferred solely on theoretical grounds, the lognormal distribution has been found to describe adequately the distribution of skewed properties. In general, the lognormal distribution will provide a representation superior to the normal distribution for properties that (1) have a large coefficient of variation (CV), and (2) have a positively skewed probability density function (i.e., the sample mean is larger than the mode and

median). In addition, as the sample CV approaches the value 0.1, the lognormal distribution approaches symmetry and can adequately represent a normal distribution.

Many studies show that solute transport properties measured in the field are described better by a lognormal distribution than by a normal distribution (Biggar and Nielsen 1976; Freeze 1975; Hoeksema and Kitanidis 1985; Jury, Stolzy, and Shouse 1982; Nielsen, Biggar, and Erh 1973). So in the present study it was assumed that the solute transport parameters of V and D were lognormally distributed.

2.3 Regionalized variables

The term 'regionalized variable' was proposed by Matheron (1971) to describe a phenomenon which is spread out in space and which shows a certain structure. A variable which characterizes such a phenomenon is called a 'regionalized variable'. In fact, all of the variables describing the subsurface environment may be considered as regionalized variables (Russo and Jury, 1987).

From a mathematical stand point, a regionalized variable is simply a function $z(x)$ which gives the value at point x (in a 1, 2, or 3-dimensional space) of a characteristic z of the natural phenomenon being studied. The theory of regionalized variables covers all the possibilities from the smoothest variables to the roughest. The functions of regionalized variable are as follows:

- 1) to establish the theoretical grounds for expressing the structural properties of natural phenomena in a mathematical form; and
- 2) to provide a practical means for solving various problems of estimation.

2.4 Covariogram

2.4.1 Definitions

Let $z(x_i)$ be the value of the regionalized variable z at a point x in the entire field Ω , and $z(x_i+h)$ the value of z at a point x_i+h at a distance h from x , also in Ω . The covariance between $z(x_i)$ and $z(x_i+h)$ in Ω for a given h is:

$$\sigma(h) = E\left\{\left\{z(x_i) - E[z(x_i)]\right\}\left\{z(x_i+h) - E[z(x_i+h)]\right\}\right\} \quad (2.2)$$

where $E[\cdot]$ is the expected value of $[\cdot]$ when both x and x_i+h remain in Ω .

The function $\sigma(h)$ is the covariogram of the regionalized variable z in the field.

In practice, however, it is not possible to take two samples at the same place. If we value the same sample twice, we do not obtain the same results because of valuation errors. If we analyze two samples next to each other we obtain different values, not only because of sampling errors, but also because of variations in soil properties on a micro-scale, or because of micro-structures which cannot be detected in practice. In consequence, a discontinuity is usually observed in the covariogram near the origin, which is called the nugget effect N :

$$N = \sigma^2 - \lim_{h \rightarrow 0} [\sigma(h)] \quad (2.3)$$

2.4.2 Estimation

Let $n(h)$ be the number of pairs of samples at distance h apart taken in the field to be studied. Let x_i and x_i+h be the positions of the two samples in the i th pair, and $z(x_i)$ and $z(x_i+h)$ the corresponding values of z . We define:

$$\sigma^*(h) = \frac{1}{n(h)-1} \sum_{i=1}^{n(h)} \{ [z(x_i) - \mu] [z(x_i+h) - \mu] \} \quad (2.4)$$

where μ the expected sample value, $\sigma^*(h)$ is the observed or experimental covariogram of z .

2.4.3 Conditions of application: second order stationary

In any field Ω it is possible to calculate a covariogram $\sigma^*(h)$. The model obtained is not necessary valid, however, for local valuation, we must make the assumption that the general covariogram estimated in Ω is representative of the smaller section of Ω which is considered for valuation. As a rule, the covariogram can be used for local valuation only if the following second order stationary conditions are satisfied:

- 1) the expected value of $z(x_i)$ is independent of the point z ;

$$E[z(x_i)] = \mu \quad \text{for any value of } x_i. \quad (2.5)$$

2) the covariogram is independent of the point z for any vectorial distance h ;

$$E\{[z(x_i) - \mu][z(x_i + h) - \mu]\} = \sigma(h) \quad \text{for any value of } x_i \text{ and } h. \quad (2.6)$$

The first condition implies that there is no drift (trend) in values, but does not preclude the presence of high and low value areas.

2.5 Variogram and semivariogram

2.5.1 Definition

Instead of using the covariogram $\sigma(h)$ to measure the relationship between sample values at distance h , a more powerful tool, the variogram, has been proposed by Matheron (1971). By definition, the value of the variogram $2\gamma(h)$ for a given distance h in a field Ω is the expected squared difference between the values of the samples separated by h ;

$$2\gamma(h) = E\left[[z(x_i) - z(x_i + h)]^2\right] \quad (2.7)$$

The function $\gamma(h)$ is the semivariogram,

$$\gamma(h) = \frac{E\left[[z(x_i) - z(x_i + h)]^2\right]}{2} \quad (2.8)$$

The variogram is also a measure of the mean squared error (or variance) of estimation of $z(x_i+h)$ by $z(x_i)$. If we assume that the sample at position $x+h$ has the same value as the sample at position x , we make an error $z(x_i)-z(x_i+h)$ whose average squared value is $2\gamma(h)$.

If the second order stationary conditions are satisfied, the semivariogram and covariogram are related as follows:

$$\gamma(h) = \sigma^2 - \sigma(h) \quad (2.9)$$

2.5.2 Estimation

Using the definitions given in 2.5.1, the estimator $\gamma^*(h)$ of the semivariogram $\gamma(h)$ is

$$\gamma^*(h) = \frac{1}{2n(h)} \sum_{i=1}^{n(h)} [z(x_i) - z(x_i + h)]^2 \quad (2.10)$$

where $z(x_i)$ are the experimental values at points x_i such that data are available at x_i and x_i+h , and $n(h)$ is the number of pairs of data points separated by a gap equal to h .

2.5.3 Conditions of application: intrinsic hypothesis

The semivariogram can be used for local valuation provided the intrinsic hypothesis is satisfied:

1) The expected value of the difference $z(x_i) - z(x_i + h)$ is independent of the point x for any distance h :

$$E[z(x_i) - z(x_i + h)] = m(h) \quad (2.11)$$

where $m(h)$ is a function of h independent of x_i .

2) The semivariogram is independent of the point x for all possible distance h :

$$\frac{E\left[\left[z(x_0) - z(x_0 + h)\right]^2\right]}{2} = \gamma(h) \quad (2.12)$$

where $\gamma(h)$ is a function of h independent of x_i .

The first condition implies the absence of drift, or the presence of linear drift. The intrinsic hypothesis can be satisfied even in field in which a priori variance σ^2 does not exist. Note that the intrinsic hypothesis is less restrictive than the second order stationary conditions and will always be satisfied whenever the second order stationary conditions are satisfied.

2.6 Fitting a theoretical model

Once the experimental semivariogram is obtained, it has to be fitted to a theoretical model of a semivariogram. The mathematical models of semivariograms can be classified according to whether or not they correspond to situations where the second order stationary conditions are satisfied. If second-order stationary conditions exist, for large distances h such that $z(x)$ and $z(x+h)$ are not correlated, the semivariogram $\gamma(h)$ will reach a value equal to σ^2 . This limiting value is called the sill S of the semivariogram, and the distance at which $\gamma(h)$ reaches the sill is called the range. The range of the semivariogram obtained from a given type of a sample corresponds to the distance of influence of these samples. If only the intrinsic hypothesis is satisfied, the sample variance is an increasing function of the size of the area or volume in which the samples are located, and the semivariogram $\gamma(h)$ will be a continuously increasing function of h .

The most commonly used semivariogram models are described in Table 2.1.

Table 2.1 Models of semivariograms in widest use(Delhomme, 1978)

Type	Formula	Range
Classical	$\gamma(h) = \sigma^2$	0
Monomial	$\gamma(h) = \sigma^2 h^a$	∞
Spherical	$\gamma(h) = \begin{cases} \sigma^2 \left[\frac{3}{2} \left(\frac{h}{a} \right) - \frac{1}{2} \left(\frac{h}{a} \right)^3 \right] \\ \sigma^2 \end{cases}$	a
Exponential	$\gamma(h) = \sigma^2 \left[1 - \exp\left(-\frac{h}{a}\right) \right]$	a
Gaussian	$\gamma(h) = \sigma^2 \left[1 - \exp\left(-\frac{h^2}{a^2}\right) \right]$	a

2.7 Kriging

The number n of sample points x_i is relatively small in practice. Therefore, in order to quantify the spatial behavior of the soil properties from fragmentary sampling, it is desirable to estimate the values of these properties at unmeasured points x_0 . The kriging technique is an interpolation model

based on a stochastic approach and is especially suited to mapping properties which are spatially variable and show a definable spatial structure. Detailed descriptions of the kriging algorithm were provided by Journel and Huijbregts (1978), and therefore it is appropriate here only to summarize the characteristics of the method. When a number of sampling points are used (x_i , $i=1, 2, \dots, n$), the method provides, at any given point in the field x_0 , the best linear unbiased estimate:

$$z^*(x_0) = \sum_{i=1}^n \lambda_i z(x_i) \quad (2.13)$$

where n is the number of measured values $z(x_i)$ involved in the estimation of the unrecorded point, x_0 , and λ_i are the weights.

Therefore, our problem is to find the weights λ_i such that the estimator $z^*(x_0)$ is unbiased. Hence,

$$E\{z^*(x_0) - z(x_0)\} = 0 \quad (2.14)$$

and

$$\sigma_k^2(x_0) = \text{Var}\{z^*(x_0) - z(x_0)\} = \text{Minimum} \quad (2.15)$$

Where σ_k^2 is the variance of kriging error.

Development of Equation 2.13 yields

$$\sum_{i=1}^n \lambda_i = 1 \quad (2.16)$$

The condition for minimum variance expressed in Equation 2.15, subject to Equation 2.16, can be shown to be

$$\sigma_k^2(x_0) = \sum_i \sum_j \lambda_i \lambda_j \sigma(x_i, x_j) + \sigma(0) - 2 \sum_i \lambda_i \sigma(x_i, x_0) \quad (2.17)$$

which in terms of semivariograms becomes

$$\sigma_k^2(x_0) = - \sum_i \sum_j \lambda_i \lambda_j \gamma(x_i, x_j) + 2 \sum_i \lambda_i \gamma(x_i, x_0) \quad (2.18)$$

where (x_i, x_j) represents a vector with origin on x_i and extremity on x_j . It is preferable to work on the form expressed by Equation 2.18 since only the intrinsic assumption is required rather than that of stronger second-order stationary assumption.

Equation 2.18 is minimized under the constraint that

$$\sum_{i=1}^n \lambda_i = 1 \quad (2.16)$$

This minimization involves Lagrangian techniques in which all the n partial derivatives

$$\frac{\partial \left[\sigma^2(x_0) - 2m \sum_i \lambda_i \right]}{\partial \lambda_i} \quad (2.19)$$

are set equal to zero where μ is a Lagrangian multiplier. Thus

$$2 \sum_j \lambda_j \gamma(x_i, x_j) = 2\gamma(x_i, x_0) - 2m \quad (2.20)$$

Canceling the factor 2, rearranging, and combining with Equation 2.17 yields the kriging system

$$\sum_{j=1}^n \lambda_j \gamma(x_i, x_j) + m = \gamma(x_0, x_i), i = 1 \text{ to } n \quad (2.21)$$

$$\sum_{j=1}^n \lambda_j = 1 \quad (2.22)$$

The kriging system can be written using a matrix notation, as follows:

$$A = \begin{vmatrix} \gamma_{11} & \gamma_{12} & \cdots & \gamma_{1n} & 1 \\ \gamma_{21} & \gamma_{22} & \cdots & \gamma_{2n} & 1 \\ \vdots & & & & \\ \gamma_{n1} & \gamma_{n2} & \cdots & \gamma_{nn} & 1 \\ 1 & 1 & \cdots & 1 & 1 \end{vmatrix} \quad B = \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \vdots \\ \lambda_n \\ m \end{bmatrix} \quad C = \begin{bmatrix} \gamma_{01} \\ \gamma_{02} \\ \vdots \\ \gamma_{0n} \\ 1 \end{bmatrix} \quad (2.23)$$

A is a symmetric matrix which is a function of the samples only and independent of the point to be evaluated. For usual values of the semivariogram this matrix will have an inverse A^{-1} . B is a column vector of the coefficients λ_i ($i=1, 2, \dots, n$) and m . C is a column vector which is a function of the samples.

The general kriging system can be written as follows:

$$AB=C \quad (2.24)$$

with solution:

$$B=A^{-1}C \quad (2.25)$$

3. MATERIALS AND METHODS

3.1 Soil sampling sites

The proposed study (Figure 3.1) is located in a sparsely grassed area at southeastern part of the University of Regina campus.

Figure 3.1 Location of study area

3.2 Soil sampling

The main objective of the experimental study was to address flow and transport processes that occur in a naturally heterogeneous soil. Therefore the experimental investigations had to be based on intact soil monoliths, which represent the soil structure that prevail in the field.

A number of techniques have been proposed for collecting undisturbed soil monoliths. Cassel et al. (1974), Brown et al. (1985), Khan and Jury (1990), Persson and Bergström (1990), and Tindall et al.(1992), among others, have proposed a combination of drilling and driving, while Reeves and Beven (1990), Andreini and Steenhuis (1990), and Wildenschild et al. (1994) have isolated undisturbed blocks by hand excavation. Because the clay soil at the site was sufficiently cohesive to allow for stable soil monoliths during hand excavation, undisturbed soil columns were isolated by hand excavation in this study.

The field sampling started by carefully removing the vegetation and few centimeters of the humus layer from the selected sampling site. The sampling unit (a steel cylinder which is 80cm in length and 20cm in diameter) was placed vertically at the shaped surface. As the cylinder was hammered down 10-15 cm by a hammer, shovels were used to remove the soil around the exterior of the cylinder to lower soil resistance and reduce soil compaction and boundary effects near the monolith edge. After the cylinder was hammered into designed depth(70 cm), a knife was used to separate it from the surrounding soil and it

* ----- First Group Sampling Points
 O ----- Second Group Sampling Points

Figure 3.2 Study area showing sampling points

was lifted from the pit. A grass screen was attached to the bottom of each cylinder by a wide rubber band to prevent the soil from falling out.

A total of 21 monoliths were sampled in a systematic network as shown in Figure 3.2. The sampling area was approximately 64m×64m in size, with sampling locations systematically established in order to enable testing for spatial correlation structures.

In the laboratory the monoliths were wrapped with dark plastic bags in a room of fairly constant temperature and then mounted one after another on a wooden rack for the transport experiments.

3.3 Tracer selection

In this study a tracer test was conducted to measure the velocity of flow and dispersion. To achieve this purpose, the most suitable tracer was selected based on three aspects.

Detectability. Injected tracers should be easily detected. The lower the detection limit for instruments, the better.

Mobility. Conservative tracers used to measure transport parameters should be 1) stable (i.e., not subject to transformation by biodegradation or nonbiological processes during the length of the test and analysis), 2) soluble in water, and 3) of a similar density and viscosity, and not subject to adsorption or precipitation.

Economics. The tracer or the instrumentation to analyze samples may be expensive. In this situation, another less-expensive tracer with somewhat less favorable characteristics may suffice.

Chlorides has been used as tools for a wide range of hydrologic problems dealing with the determination of flow paths and residence time and the measurement of transport parameters. Yule and Gardner (1978) used chloride as a tracer to determine longitudinal and transverse dispersion coefficients in unsaturated plain field sand; Khan and Jury (1989) used chloride as a tracer to study the longitudinal dispersion in both undisturbed and packed columns containing Tujunga loaming sand; and Destouni et al. (1992) studied chloride migration in heterogeneous soil through 29 undisturbed soil monoliths.

In most cases, chlorides are not affected by the porous medium. They do not decompose or precipitate and thus are not lost from the system, neither they are subject to adsorption by the soil. Although chlorides may be subject to transformation by biodegradation processes resulting from the trace organics and rootlets in the monoliths, this can be controlled by pretreatment of the clay soil by adding $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Another advantage of chlorides is that they can easily be detected by a titrator at any chemical laboratory with relatively higher accuracy. A commonly used titrator can detect chloride at 0.05 mmol/l by using KMnO_4 as an indicator.

Therefore chloride was chosen as tracer in this experiment. The concentration of chloride was fixed at 350 mg/L. The density difference

between this solution and deionized water (0.0047g/cm^3) was slightly greater than that recommended by James and Rubbin (1972).

3.4 Experimental setup

The laboratory setup (Figure 3.3) consisted of a support base, which was constructed as a wooden rack fixed with a metal funnel for diverting the effluent water. The inflow into each monolith was controlled by a micro-pump. The outflow from each monolith was collected in a plastic vial.

For each test, the monolith was first fed with 0.3g/L of reagent-grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to control biological activity and 15 mmol/L reagent grade $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to prevent particle dispersion. After steady state flow at the desired flow rate was achieved, the soil was then feed with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution. The effluent was collected every hour to analyze for chloride concentration.

All the monoliths were irrigated with the same flow rate of 1cm/h. , this flow rate was chosen because most of the irrigation rate and rain intensity rates are between 0.5 to 4 cm/hr.

The feed solution was passed through a dispenser fixed on top of the solution and then distributed over the surface of soil evenly. Several layers of cheesecloth were placed on the soil surface beneath the dispenser to prevent soil disturbance and the core was sealed with plastic to prevent evaporation.

Because the flow rate was quite low, no ponding occurred during the experimental period.

I: Solution container, II: Pump, III: Soil sample, IV: Funnel, V: Wooden rack.

Figure 3.3 Experimental setup

4 RESULTS AND DISCUSSION

4.1 Local breakthrough curves

The high degree of variability of downward solute movement at different locations in the field site may be illustrated by examining the extremes in the shapes of the solute pulses obtained from different monoliths. Experimental breakthrough curves for monoliths 8 and 15 are illustrated in Figure 4.1 in terms of relative chloride concentration in the effluent. The fact that the minimum and maximum curves occurred at different sites at the same depth indicates that the solutes were following very tortuous paths as they moved downward. The large variability in convective transport was evidenced by the very rapid solute breakthrough at some sites, in contrast to the late arrival and slow passage of solute at others. For example, the chloride in monolith 8 moved rapidly through the soil, and almost all the injected mass was recovered in the effluent after approximately 12 hours, while the mass recovery for monolith 15 was only 50% after almost 25 hours.

Figure 4.1 Experimental breakthrough curves of Monolith 8 and Monolith 15.

4.2 Transport parameters optimization

Given the one dimensional convection and dispersion model:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} \quad (4.1)$$

For initial and boundary condition

$$\begin{aligned} C(z, 0) &= 0 \\ C(0, t) &= C_0 \\ C(\infty, t) &= 0 \end{aligned} \quad (4.2)$$

where C_0 is the input solute concentration.

The solution of the convection-dispersion equation is given by Biggar and Nielsen(1961)

$$\frac{C}{C_0} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{z - Vt}{2\sqrt{Dt}} \right) + \exp \left(\frac{Vz}{D} \right) \operatorname{erfc} \left(\frac{z + Vt}{2\sqrt{Dt}} \right) \right] \quad (4.3)$$

The second term is very small compared to the first one and may be neglected; thus

$$\frac{C}{C_0} = \frac{1}{2} \operatorname{erfc} \left(\frac{z - Vt}{2\sqrt{Dt}} \right) \quad (4.4)$$

If the following approximation is used (Luckner, 1991)

$$\left(\frac{z - Vt}{2\sqrt{Dt}}\right) = -\frac{z}{\sqrt{\frac{4Dz}{V}}} \ln \frac{t}{t_{50}} \quad (4.5)$$

where $t_{50} = \frac{z}{V}$

The following solution results (Luckner, 1991):

$$\operatorname{inverfc}\left(\frac{2C}{C_0}\right) = -\frac{z}{\sqrt{\frac{4Dz}{V}}} (\ln t - \ln t_{50}) \quad (4.6)$$

This means that $\operatorname{inverfc}\left(\frac{2C}{C_0}\right)$ depends approximately linearly on $\ln(t)$ and if $\operatorname{inverfc}\left(\frac{2C}{C_0}\right)$ versus $\ln t$ is plotted, the pairs of values $(\ln(t), \operatorname{inverfc}\left(\frac{2C}{C_0}\right))$ will also be arranged approximately on a straight line. The intercept of the line with y axis will be $\ln(t_{50})$, and the slope of the line will be $-\frac{z}{\sqrt{\frac{4Dz}{V}}}$. Therefore, the

transport parameters V and D can be obtained by the following calculation:

$$V = \frac{z}{\ln t_{50}} \quad (4.7)$$

$$D = \frac{Vz}{4\alpha^2} \quad (4.8)$$

where α is the slope of the straight line.

Figures A.1 through A.16 show the agreement between the theoretical and experimental breakthrough curves for each monoliths, and Table 4.1 lists the values of the calibrated local transport parameters V and D.

Table 4.1 Values of fitted transport parameters V and D

Monolith	V (cm/h)	D(cm ² /h)	Monolith	V (cm/h)	D (cm ² /h)
1	4.07	11.1	9	3.86	10.3
2	3.95	10.7	10	5.54	14.8
3	7.16	19.13	11	8.06	21.54
4	6.5	17.39	12	3.55	9.47
5	5.98	15.99	13	3.22	8.61
6	4.5	14.81	14	4.02	10.9
7	9.58	25.6	15	2.86	7.65
8	10.3	28.7	16	2.41	6.44

4.3 Estimation of the semivariograms γ

When there is a constant trend, an unbiased estimate for γ is obtained by using the available data:

$$\gamma^*(h) = \frac{1}{2n(h)} \sum_{i=1}^{n(h)} [z_i(x_i) - z_i(x_i + h)]^2 \quad (2.11)$$

where $n(h)$ is the number of pairs of observation points separated by distance h .

Since both V and D were assumed to be approximately lognormally distributed, the experimental semivariograms of both V and D were constructed using logarithms of the original data, i.e., $Z_1 = \ln(V)$ and $Z_2 = \ln(D)$. The experimental semivariograms of both $\ln(V)$ and $\ln(D)$ are given in Figure 4.2. For both $\ln(D)$ and $\ln(V)$, $\gamma^*(h)$ passes through the origin as increments are obviously nil at a zero distance. $\gamma^*(h)$ increases rapidly until it reaches the sill at $h \approx 30.7$ m and $h = 29.8$ m for $\ln(V)$ and $\ln(D)$ respectively. Each of the semivariograms had to be fitted to an appropriate theoretical semivariogram. And the appropriate theoretical semivariogram for this study should be the one for which a minimum mean square deviation (MSD) is calculated between the values of the experimental semivariogram and its values. The results of the MSD method are summarized in Table 4.2 .

Table 4.2 Results of MSD method to select the most appropriate theoretical semivariograms for solute transport parameters V and D

Model type	MSD (lnV)	MSD (lnD)
Spherical	0.037	0.038
Exponential	0.123	0.137
Gaussian	0.071	0.077

Figure 4.2 Experimental and theoretical semivariograms of (A) $\ln(V)$ (Equation 4.9) and (B) $\ln(D)$ (Equation 4.10).

It was found (Table 4.2) that the minimum MSD criterion led to an spherical semivariogram for both $\ln(V)$ and $\ln(D)$.

For $\ln(V)$, the semivariogram can be written as

$$\begin{aligned}\gamma(h) &= 0.191 \left[\frac{3}{2} \left(\frac{h}{30.7} \right) - \frac{1}{2} \left(\frac{h}{30.7} \right)^3 \right] & h \leq a \\ \gamma(h) &= 0.191 & h \geq a\end{aligned}\tag{4.9}$$

For $\ln(D)$, the semivariogram can be written as

$$\begin{aligned}\gamma(h) &= 0.191 \left[\frac{3}{2} \left(\frac{h}{29.8} \right) - \frac{1}{2} \left(\frac{h}{29.8} \right)^3 \right] & h \leq a \\ \gamma(h) &= 0.191 & h \geq a\end{aligned}\tag{4.10}$$

Noting that the autocorrelation function $\rho(h)$ of a given property is related to the semivariogram $\gamma(h)$ of that property by

$$\rho(h) = 1 - \gamma(h) / \sigma^2\tag{4.11}$$

and using the expression of Russo and Bresler (1981 a) for the integral scale J of a two-dimensional isotropic stationary stochastic process, i.e.,

$$J = \left[2 \int_0^{\infty} \rho(h) h dh \right]^{\frac{1}{2}}\tag{4.12}$$

The following values of $J=14.5$ m and $J=13.9$ m were calculated for $\ln(V)$ and $\ln(D)$, respectively. For a given property the value of J can be interpreted as the largest average distance $h=x_2-x_1$ for which the values of z at x_1 and x_2 are correlated. The range, on the other hand, is interpreted as the distance for which the values of z at x_1 and x_2 bear no relation to one another.

4.4 Validation of the stochastic approach

To test the accuracy of the present stochastic approach, another group of monoliths were sampled throughout the field and chloride tracer tests were performed under the same conditions. Transport parameters of V and D at these five points were kriged using the semivariogram shown in Equations 4.10 and 4.11. Then these parameters were substituted into the convection-dispersion equation (Equation 4.4) to calculate the relative solute concentration C/C_0 . The theoretical breakthrough curves were then used to compare with the experimental breakthrough curves.

As shown in Figures 4.3, 4.4, and 4.5, a good agreement was found between the experimental breakthrough curves and theoretical breakthrough curves. These results suggest that the stochastic approach can describe the solute transport in the tested field very well.

Figure 4.3 Experimental and predicted breakthrough curves of Monolith 17 and Monolith 18.

Figure 4.4 Experimental and predicted breakthrough curves of Monolith 19 and Monolith 20.

Figure 4.5 Experimental and predicted breakthrough curves of Monolith 21.

4.5 Sensitivity of the stochastic model

Because of the uncertainty associated with the behavior of h in the neighborhood of the origin, another function for the semivariogram of $\ln(V)$ and $\ln(D)$ was examined. This time, a regression line was fitted to the first three values of h . This led to the following semivariogram.

For $\ln(V)$

$$\begin{aligned}\gamma(h) &= 0.014 + 0.0059h & h \leq a \\ \gamma(h) &= 0.191 & h \geq a\end{aligned}\tag{4.13}$$

For $\ln(D)$

$$\begin{aligned}\gamma(h) &= 0.014 + 0.006h & h \leq a \\ \gamma(h) &= 0.191 & h \geq a\end{aligned}\tag{4.14}$$

As it is shown in Figure 4.6, the difference between the two semivariograms (Equations 4.9 and 4.13, Equations 4.10 and 4.14) were relatively small as indicated also by the similar values of the range (For $\ln(V)$, 30.7 m as compared to 28.6 m for the spherical and linear semivariograms, respectively; For $\ln(D)$, 29.8 as compared to 27.7 m for the spherical and linear semivariograms, respectively). It should be noted, however, that the spherical semivariogram (Equations 4.9 and 4.10)implies a regular variable (differentiable by mean square convergence) while the linear semivariogram (Equations 4.13 and 4.14) with the discontinuity at the origin , means that the variable is very irregular (not continuous in mean square convergence).

Figure 4.6 Experimental and theoretical semivariograms of (A) $\ln(V)$ (Equation 4.9) and (B) $\ln(D)$ (Equation 4.10). The dashed line is calculated from Equation 4.13 (A) and Equation 4.14 (B) respectively.

The sensitivity of this stochastic approach can be analyzed by comparing the theoretical breakthrough curves obtained by using different semivariograms . As shown in Figures 4.7, 4.8 and 4.9 , the good agreement between the theoretical breakthrough curves calculated by using a spherical semivariogram of $\ln(V)$ and $\ln(D)$ and the theoretical breakthrough curves calculated by using a linear semivariogram suggests that both the semivariograms can be used to obtain kriging estimates of $\ln(V)$ and $\ln(D)$ with essentially the same results.

Figure 4.7 Experimental and predicted breakthrough curves of Monolith 17. Prediction1, calculated by using spherical semivariogram; Prediction 2, calculated by using linear semivariogram.

Figure 4.8 Experimental and predicted breakthrough curves of Monoliths 18 and 19. Prediction 1, calculated by using spherical semivariogram; Prediction 2, calculated by using linear semivariogram.

Figure 4.9 Experimental and predicted breakthrough curves of Monoliths 20 and 21. Prediction 1, calculated by using spherical semivariogram; Prediction 2, calculated by using linear semivariogram.

4.6 Response of specific sites in the field

With the present stochastic approach, not only the response of the entire field can be evaluated, but the response of specific sites in the field can be estimated as well.

1) The entire field is divided into 256 equivalent cells, each is $4 \times 4 \text{ m}^2$ in size. Kriging the values of V and D at the central points of each cell by using semivariogram expressed in Equation 4.10 and 4.11 respectively.

2) The average solute concentration of the field at a depth $z=70 \text{ cm}$ can be approximated by the following equation:

$$\overline{C_z} = C_0 \int_0^{70} \frac{1}{2} \operatorname{erfc}\left(\frac{z - vt}{2\sqrt{Dt}}\right) dz \quad (4.15)$$

where $\overline{C_z}$ the solute concentration averaged from the surface of the soil to a depth of 70 cm.

A contour map of the mean $\overline{C_z}/C_0$ is shown in Figure 4.10 (for $t=20 \text{ h}$). Note that although the values of $\overline{C_z}/C_0$ were considerably increased throughout the field, the response of different sites in the field is quite different. For example, for $t=20 \text{ h}$, compare the northeastern corner of the field ($C=0.7-1.0$) with the southern portion of the field ($C=0.0$). The distinct response of the two sites is clearly demonstrated.

Figure 4.10 Contour map of $\bar{C}_z/C_0$ after 20 hours of continuous leaching

5 APPLICATION

Two fundamental goals of agricultural water management must be met. One is the wise and economical use of irrigation water. Another is the protection of soil and groundwater from being polluted by agricultural use.

Irrigation is the only method that takes full advantage of agricultural soils in areas where rainfall is insufficient for all or part of the year. This is the situation in many areas in the world. For many countries, groundwater is the main source of irrigation water supply. A worldwide increase in demand for water by agricultural practices resulting primarily from population growth and an improved standard of living, has placed great importance on water management practice. Unlike other raw material, water has no substitute, it is absolutely essential. The future development of agriculture in many countries will depend decisively upon how the increasing demand for water will be satisfied, and how the economic and environmental cost for that demand will be met. Hence, wise and economical use of irrigation water to protect soil water and groundwater resources against depletion has developed into one of today's foremost problems worldwide.

Fertilizers have long been seen as an important means of producing the food needed by the population as they replace the nutrients removed by crops and maintain soil fertility. However, the environmental implications of fertilizer use cause growing concern as evidence shows that the application of agrochemicals and fertilizers is reducing the quality of water, particularly in

terms of the nitrate content in drinking water. In recent years a significant upward trend in the nitrate content in drinking water has been recorded, especially in groundwater resources underlying arable land (Ronen et al., 1984). Moreover, recent reports have indicated that the concentration within aquifers can be expected to intensify as a result of the continuous accumulation of nitrogen in the soil profile (Jollans 1985, Ronen and Magaritz 1985).

The various sources and pathways of nitrogen through the soil which finally lead to the contamination of groundwater with nitrate were clearly described by Conrad (1986). Fertilizer is one main source of nitrogen contamination of groundwater.

Although there is no conclusive evidence that high nitrate consumption is positively linked with the blue baby syndrome and gastric cancer (Jollans 1985, Conrad 1986), it is generally agreed that some limit should be applied on nitrate content in water. In accordance, most countries have already adopted standards for nitrate content in drinking water and have adopted national policies and regulations to control it.

The need for intensive agriculture requiring large quantities of fertilizer will increase over time. Therefore, in addition to administrative measures, which have been suggested to reduce the amounts of nitrate in run-off, emphasis should be placed on adopting appropriate agrotechniques as a way of increasing the efficiency of nitrogen application. In this way it may well be possible to achieve the necessary environmental improvement without penalizing the farming community.

To achieve this purpose, three requirements must be satisfied :

- 1) satisfy the minimum demand of fertilizer and irrigation water .
- 2) save water and fertilizer to their full extent.
- 3) minimize the fertilizer residuals in order to reduce the possibility of groundwater pollution by nitrate.

Unfortunately, the most often used irrigation procedure is the deterministic procedure, which leaches the entire field for maximum time. This procedure will lead to the result that in most areas of the field the fertilizer and water are over applied . Furthermore, the potential of groundwater pollution by fertilizer residuals is increased.

An intuitive approach therefore is to apply different amounts of water to different sites (for a trickle irrigation system) in order to meet a prespecified value of solute concentration uniform throughout the field. Assuming an average concentration of fertilizer from the surface of the field to a depth of 70 cm $C=C_0$ is required, the procedure can be performed by the following steps:

- 1) The entire field was divided into 256 equivalent cells, each is $4 \times 4 \text{ m}^2$ in size. Obtain the values of $\ln(V)$ and $\ln(D)$ by kriging at the central points of each cell by using semivariogram Equation 4.10 and 4.11 respectively.
- 2) The depth averaged solute concentration can be calculated using

$$\bar{C}_z = C_0 \int_0^{70} \frac{1}{2} \operatorname{erfc}\left(\frac{z-vt}{2\sqrt{Dt}}\right) dz \quad (5.1)$$

where $\bar{C}_z$ the solute concentration averaged from the surface of the soil to a depth of 70 cm.

3) For each of the $M=256$ nodal points of the field, the values of $t^1=t$ ($C/C_0=1$) was obtained by constructing a table of the calculated $\bar{C}_z/C_0$ versus t ($t>0$). The value of t^1 was evaluated from this table by using $\bar{C}_z/C_0$ as the argument and t as the function. Linear interpolation was used to evaluate values falling between tabular data. A contour map of t^1 was then plotted (Figure 5.1).

4) For the tested field, the field was divided into four equal subplots, each 32×32 m² in size. By superimposing these four subplots on the map of t^1 and by selecting the maximum value of t^1 for a given subplot, an operational scheme for the leaching of the field can be obtained. This "worst case" approach (i.e., using a maximum value of t^1 for a given subplot) ensures that, for a given subplot, the constraint of $C/C_0 = 1$ will be met throughout the subplot. From this operational scheme the average amount of leaching water is given by

$$Q_w = q_0 A_p \sum_{i=1}^4 t \quad (5.2)$$

and the amount of applied fertilizer is given by

$$M_w = C q_0 A_p \sum_{i=1}^4 t \quad (5.3)$$

in which A_p is the area of a given subplot .

Note that if the spatial structures of C was not considered and the entire field was leached with a deterministic amount of water, uniform throughout the field, then this amount can be calculated from Figure 4.8 . From this figure the time required to obtain $C/C_0=1$ for the entire field will be about 45 h. If 45 h was used, then the amount of applied fertilizer and irrigation water required to obtain $C/C_0=1$ will be

$$Q = t^1 q_0 A_T \quad (5.4)$$

$$M = t^1 q_0 A_T C \quad (5.5)$$

in which A_T is the total area of the field.

The expected water saving and fertilizer saving will be 25%. In other words, not only 25% of applied fertilizer was saved, but the potential of groundwater pollution by these fertilizer residuals will be significantly reduced.

Figure 5.1 Contour map of time t^1 (hour) required to obtain $C/C_0=1$ uniform throughout the field.

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

A knowledge of the nature of the spatial variability of the soil transport properties is important for irrigation management and pollution control in natural fields. In this study, a stochastic approach was used to investigate solute transport in heterogeneous fields. The main findings of results of this study may be summarized as follows:

1. It was found that downward solute movement at different locations in the study area exhibited a high degree of variability. This large variability in convective transport in the study area was evidenced by the very rapid solute breakthrough at some sites, in contrast to the late arrival and slow passage of solute at others. For example, the fitted solute transport velocity of monolith 8 was four times that of monolith 15.

2. The spatial variability of two measured transport parameters velocity (V) and diffusion coefficient (D) can be represented through a set of spherical semivariograms. These two transport parameters were then used as input parameters to a simplified solute transport model (the one-dimensional convection-dispersion model). This model, when coupled with the stochastic approach, was found to predict

successfully solute concentration at unrecorded sites of the study area. With only 16 sampling points, the semivariogram could be only crudely estimated. However, the validation tests of the kriging models showed that the selected semivariograms adequately described the spatial behavior of the solute transport parameters V and D.

3. A different set of semivariograms was selected for the two transport parameters V and D to test the sensitivity of the stochastic interpolation to the selected semivariograms. A comparison of the theoretical breakthrough curves obtained by using different semivariograms showed that both the spherical and linear semivariograms can be used to obtain kriging estimates of V and D with essentially the same results.

4. With a stochastic approach, it was found that not only the response of the entire field can be evaluated, but the response of specific sites in the field can be estimated as well. An analysis of the spatial structure of solute concentration showed that the response to leaching at different sites in the field was quite different. For example, after 20 hours of continuous leaching, the average solute concentration at 70-cm depth at the northeastern corner of the field was far higher than that at the southern end of the field.

5. The application of the results of this study to agricultural water management and pollution control was examined. Practically, by dividing the field area into equal regular subplots based on engineering and economic constraints, the

total amount of applied fertilizers and irrigation water required to obtain $C/C_0=1$ was reduced by 25% relative to the amount had the entire field been considered as one unit for water and fertilizer application.

In summary, although the results of the present approach for the clay field were encouraging, no attempt was made to generalize the results. The present study may be considered primarily as one which presents a methodology to solve solute transport problems which are associated with spatial variability.

6.2 Recommendation

This study was limited to one-dimensional solute transport under steady state conditions. Therefore, lateral dispersion was neglected and transport velocity was assumed to be constant. However, solute transport in natural fields is much more complicated, the flow is multi-dimensional and the convective velocity changes with time. More soil hydraulic and transport parameters are needed to describe multi-dimensional water flow and transport processes,. These include: saturated hydraulic conductivity, volumetric moisture content, pressure head potential, and lateral dispersion coefficient. A comprehensive study of the spatial variability of these parameters and their influence on solute transport is therefore strongly recommended.

The semivariogram was found to be sensitive to the sample size and nugget effect (Russo and Jury 1987a, b). However, no attempt was made to evaluate the sensitivity of the selected semivariograms to sample size because only sixteen samples were used in this study. Although the sensitivity of selected semivariograms to the nugget effect was examined, the results showed that the selected semivariograms were generally not sensitive to the nugget effect. This may be because the sampling distance was too large that the spatial structure of the transport parameters at a small scale can not be detected. Therefore, it is recommended that a large sample size and a small sampling distance be adopted for further studies.

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APPENDIX A

EXPERIMENTAL RESULTS

Figure A.1 Experimental and fitted breakthrough curves of Monolith 1.

Figure A.2 Experimental and fitted breakthrough curves of Monolith 2.

Figure A.3 Experimental and fitted breakthrough curves of Monolith 3.

Figure A.4 Experimental and fitted breakthrough curves of Monolith 4.

Figure A.5 Experimental and fitted breakthrough curves of Monolith 5.

Figure A.6 Experimental and fitted breakthrough curves of Monolith 6.

Figure A.7 Experimental and fitted breakthrough curves of Monolith 7.

Figure A.8 Experimental and fitted breakthrough curves of Monolith 8.

Figure A.9 Experimental and fitted breakthrough curves of Monolith 9.

Figure A.10 Experimental and fitted breakthrough curves of Monolith 10.

Figure A.11 Experimental and fitted breakthrough curves of Monolith 11.

Figure A.12 Experimental and fitted breakthrough curves of Monolith 12.

Figure A.13 Experimental and fitted breakthrough curves of Monolith 13.

Figure A.14 Experimental and fitted breakthrough curves of Monolith 14.

Figure A.15 Experimental and fitted breakthrough curves of Monolith 15.

Figure A.16 Experimental and fitted breakthrough curves of Monolith 16.

IMAGE EVALUATION TEST TARGET (QA-3)

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