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"Elements of Ground Water Management: The Unsaturated Zone"

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Elements of Ground Water Management: The Unsaturated Zone

by

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ABSTRACT

Proper management of the transfer of water and dissolved constituents in and through the unsaturated zone requires an accurate conceptual understanding and a quantitative description of all relevant physical, chemical and biological processes and properties in the unsaturated zone. Several conceptual problems and opportunities for modeling vadose zone water flow and solute transport processes are reviewed. Alternatives to classical modeling approaches are also outlined.

INTRODUCTION

Motivation for developing a quantitative understanding of the processes governing the movement and retention of water and dissolved solutes in the unsaturated zone has never been higher than it is today. The public is increasingly focusing its attention on the intentional and unintentional release of surface-applied or soil-incorporated chemical contaminants, their immediate effects on soil and water pollution, and their indirect harm by entering the food chain for all living organisms. Fertilizers and pesticides intentionally applied to agricultural and silvicultural operations inevitably move below the root zone, percolate through the vadose zone and eventually contaminate ground and surface waters. Chemicals migrating from municipal and industrial disposal ites as well as radionuclides from nuclear energy and waste storage facilities lso present environmental hazards. Although the accidental release of chemicals nd wastes onto the land and into surface water supplies enjoys a great deal of otoriety in the public media, of equal importance to the quality of the global nvironment are the subtle, yet enormous releases of organic constituents from ield soils caused by changing land management practices. Cyclic variations in he flux of constituents moving through the vadose zone related to crop rotation nd annual weather patterns are occasionally confounded by irregular perturbaions caused by major changes in land use. An example of this, pertinent to ome areas in California's San Joaquin Valley and many other arid and semiarid egions in the world where irrigated agriculture is practiced, is the problem of oil salinity and the leaching of salts and toxic elements through or from the adose zone into underlying groundwater systems and ultimately also into nearby urface waters. Our ability to control the flow of saline or otherwise contaminated drainage waters, and ultimately to dispose of these waters, may well determine he long-term viability of irrigated agriculture in those areas.

Fortunately, the research community over the years has provided considerable information about the behavior of salts and toxic elements in soils. Much has been learned from elaborate plot and field experiments designed, for example, to estimate salinity-related yield losses and/or groundwater salt loadings for various combinations of crops, soils, irrigation water types, climatic conditions and management schemes. Physically-based simulation models have and will continue to provide convenient tools for analyzing specific experiments, and for extrapolating information from a limited number of field studies to different crop and climatic conditions, and to different soil and water management schemes. Because crop response to transient water and salinity distributions in the root zone is complex and little understood, it is also imperative that all relevant processes operative in the soil-root system be integrated into one model for study of water-salinity-yield interactions. The value of models, and the need to quantify specific processes in those models, should not be underestimated since they eventually will guide research into areas in need of further investigation. At the same time, scientists and engineers, including those in planning and action agencies, need analytical tools (models) for predicting the impact of alternative soil and water management practices on crop yields and groundwater quality. For example, physically-based models of the type discussed in this paper are required for economic analysis of irrigation with saline water (Letey et al., 1985; Solomon, 1985). As pointed out by Dinar et al. (1986), possible applications include the determination of optimal water quantities, irrigation timing, potential for blending water of various sources, evaluation of income losses due to salinization of soils and water supplies, and estimation of water demand. Another application involves the management of irrigated agricultural systems in the presence of high water tables, an extremely timely problem in the San Joaquin Valley of California (e.g., Hanson and Kite, 1984). Similar applications can be easily enumerated for environmental contamination by industrial and municipal pollutants, be they organic trace elements or other toxic substances.

Unfortunately, prediction of the migration of chemicals through the vadose zone is usually complicated by the spatial and temporal heterogeneity of various physical, chemical and biological processes and properties of the soil profile. While much progress in monitoring and analyzing water and solute transport has been attained during the past few decades, a number of challenges remain for both the theoretician and the practitioner. They include (a) how to best deal with preferential flow and transport, (b) how to best model the effects of local and regional spatial and temporal variabilities of soil hydraulic properties on solute transport, (c) how to efficiently couple multi-component geochemical subroutines with available unsaturated-saturated water flow models, (d) how to improve field methods for measuring vadose zone transport parameters, and (e) how to best estimate the long-term consequences of short-term land management decisions regarding the quality of surface and ground waters. The purpose of this presentation is to briefly review some of the conceptual problems and opportunities for modeling transport in the vadose zone and to delineate promising areas for further research and management applications.

The data presented in Figure 1 is a gentle, but sobering reminder of the opportunity that awaits the avid modeler, or the manager who contemplates the application of a model to a field site. The data stem from a uniform application of a soluble chloride salt to the soil surface only to be sampled later. Observations at this spatial scale and their values distributed over time scales of one year offer a glimpse of the complexity of natural field soils. Examples at other scales of observation would be equally revealing and educational. The consequences of such complexity must be considered when developing models and designing sampling schemes. It is also readily apparent that instrumentation to monitor even simple, readily understood soil attributes must be improved. New instrumentation techniques to increase the spatial and temporal frequency of soil observations that address the tradeoffs between accuracy and precision await development. Meanwhile, any modeling venture should proceed with considerable humility.

GOVERNING TRANSPORT EQUATIONS

Classical descriptions of one-dimensional solute transport in the unsaturated zone are usually based on the single-component convection-dispersion equation

$$\frac{\partial \theta c}{\partial t} + \frac{\partial \rho s}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z} - qc\right) + f \qquad (1)$$

where c and s are solute concentrations associated with the liquid and solid phases of the soil respectively, θ is the volumetric water content, ρ is the soil bulk density, D is the dispersion coefficient, z is vertical downward distance, t is time, and q is the volumetric fluid flux given by Darcy's law as

$$q = -K(h)\frac{\partial h}{\partial z} + K(h) \qquad (2)$$

in which K is the hydraulic conductivity and h is the soil water pressure head. For transient flow, q can be calculated from solutions of the unsaturated-saturated flow equation

$$C(h)\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z} - K(h)\right] + g \qquad (3)$$

where C is the soil water capacity, being the slope of the soil water retention curve $\theta(h)$. Functions f and g are sources/sinks of solutes and water, respectively, which stem from one or more physical, chemical or biological processes (e.g., water absorption by plant roots, chemical reactions resulting in an insoluble precipitate, microbial transformation of one solute species into another, radioactive decay of one isotope into another, etc.). The term g in Eq. (3) usually focuses on plant water absorption in the upper reaches of the vadose zone. While a large number of plant water absorption models exist, most or all are empirical relying on parameters that depend upon specific crop, soil and environmental conditions (Molz, 1981).

While deterministic solutions of Eqs. (1) and (3) have been popularly used in contaminant transport studies, they are subject to a number of difficulties that are not easily resolved (Sposito et al., 1986; Nielsen et al., 1986). Among these are the hysteretic nature of the soil hydraulic functions $\theta(h)$ and $K(h)$, the effects of temperature and soil salinity on the hydraulic properties, the extreme nonlinearity of $K(h)$, the neglect of air flow, the assumption that Darcy's law is valid for structured (fractured) soils, constancy of the fluid density, and the assumption that the soil matrix compressibility is constant. Accurate prediction of solute transport in the vadose zone is further complicated by soil heterogeneities at various scales. Our point here is that any model, however complete and refined, remains a simplification of actual processes. This in turn implies that the parameters in Eq. (1) nearly always requires the inclusion of the effects of processes or properties that have been neglected in the governing equations.

An excellent example of over-simplification is the dispersion coefficient D which in concept reflects the macroscropic effects of diffusion and mechanical dispersion, the latter resulting from variations in local fluid velocities inside individual pores and between pores of different sizes, shapes and directions. In practice, however, D includes all of the solute spreading mechanisms that are not explicitly included in the governing transport equations (e.g., transient flow, kinetic phenomena, nonlinear sorption, field-scale variability). Because of our inability to include all key transport mechanisms, most or all previously established relationships between D and certain macroscopic properties (e.g., fluid flux) are therefore essentially empirical and will probably always remain model and site dependent. Notwithstanding this problem, the world's hydrologic community continues its propensity to define D as

$$D = D_o \tau(\theta) + \lambda v^n \tag{4}$$

where D_o is the mulecular diffusion coefficient, τ a tortuosity factor, v an average pore water velocity and λ and n empirical constants. And, because Saffman (1959) showed that n is approximately unity for homogeneous, water-saturated porous media, λ is now known as the dispersivity. Experimentally, λ has been found to range over 3 orders of magnitude depending primarily on the spatial scale of the observations (e.g., Biggar and Nielsen, 1976; and Sposito and Jury, 1985).

While the soil water retention and hydraulic conductivity functions in Eq. (3) are probably the most crucial parameters for predicting flow and transport processes in the unsaturated zone, their theoretical description and measurement remains a continuous and sometimes frustrating challenge for hydrologists and soil scientists. Numerous methods have been developed to evaluate the hydraulic properties using both in situ field and laboratory procedures. The need for accurate, yet economical methods is not likely to diminish in view of recent awareness that the functions are subject to important temporal and spatial variations in the field. Traditionally, these and other parameters in Eqs. (1) and (3), have been determined by imposing rather restrictive initial and boundary conditions so that exact or approximate analytical solutions of the governing equations could be inverted directly. Such direct methods generally lead to specific functional forms of the parameter in terms of measurable soil properties. Klute (1986) gives a recent inventory of such methods applicable to a variety of soil physical processes. Contrary to these direct methods, parameter estimation techniques do not pose inherent restraints on the mathematical form of the governing equations, on the initial and boundary conditions, or on the invoked constitutive relationships. Parameter estimation methods also provide information about parameter uncertainty, a feature that is usually not possible with direct inversion methods. Although parameter estimation techniques have been frequently applied to groundwater flow problems (Cooley, 1985; Yeh, 1986), their use in unsaturated flow and transport studies is relatively new. Nevertheless, a number of laboratory and field applications currently exist that clearly indicate the great potential of optimization techniques for improved designs and analysis of vadose zone flow and transport experiments (Kool et al., 1987; Wagner and Gorelick, 1986).

Application of Eq. (1) to transport through the vadose zone using Eq. (2) to ascertain q remains largely untested and unexplored. Its application to transport through laboratory soil columns or in relatively uniform field soil plots involving non-reactive or only weakly reactive solutes has been fairly successful. On the other hand, Eq. (1) has not performed well in several situations, especially for strongly absorbed chemicals as well as for many structured soils. One reason for this failure is the inadequacy of accurately describing the kinetic nature of sorption and exchange processes. Various chemical-kinetic and diffusion-controlled rate laws have been proposed to describe nonequilibrium transport behavior (Wagenet, 1983). Among these, the most popular and simplest one has been the first-order linear kinetic rate equation

$$\frac{\partial s}{\partial t} = \alpha \ (kC-S)$$

where α is a first-order rate constant. An improvement to this model was the notion that two kinds of sites exist simultaneously - one described by Eq. (3) and another governed by instantaneous, equilibrium adsorption (Selim et al., 1976). Unfortunately, kinetic adsorption parameters in the model, only sparingly tested in laboratory soil columns, have frequently been found to be functions of pore water velocity. An alternative conceptualization is a physical nonequilibrium model that partitions the liquid phase into mobile and immobile regions. For this model the sorption rate is limited by the diffusion rate to reaction sites. Diffusion into and out of immobile regions in generally modeled as an apparent first-order exchange process. Nkedi-Kizza et al. (1984) demonstrated that the two-site and two-region models have the same dimensionless form and showed that effluent curves from laboratory soil columns alone cannot be used to differentiate between chemical and physical phenomena that cause an apparent nonequilibrium condition.

Recent reviews (MacKay et al., 1985; Wagenet and Rao, 1985; and Abriola, 1987) indicate these same problems of apparent nonequilibria also pertain to the transport of organic solutes and are further complicated by volatilization and the potential presence of co-solvents. Indeed, multiphase flow including the migration of partially miscible and immiscible fluids occurring in locations contaminated with only a few or a multitude of organic solvents offers challenges to the hydrologic community which have only begun to emerge theoretically.

Surface and subsurface soil environments are seldom without "structure," and hence, render their transport characteristics highly dependent upon the nature and duration of the localized contamination or infiltration events at the soil surface. Cracks from soil swelling and shrinking, localized macropore geometries derived from naturally occurring soil formation and geochemical processes, and channels derived from the decay of the roots of plants and from the activities of soil fauna are examples of soil structure that complicate the utility of Eq. (1). With water and its constituents being able to move readily through such large, continuous pores and thereby by-passing the majority of the porous matrix, the equation has to be reformulated to account for these geometrically observable structures.

Equation (1) has enjoyed the enviable position of the "cornerstone" of most theoretical descriptions of solute transport since the mid-20th century (e.g., Danckwerts, 1953). Hydrologists and physicists, minimizing the impact of S and ε, have focused their attention on D and the value of v including its distributional make-up. Geochemists have focused on S versus C relations while Geobiologists have emphasized the nature of g. That cornerstone position is now rapidly eroding as the scientific community has unfolded more comprehensive consideration of D, v, S and f as well as recognizing that Eq. (1) is fraught with uncertainties of applicable temporal scale (Skopp, 1986). Resolution of these ambiguities has led to additional conceptualizations some of which are briefly described later.

While criticisms are largely justified when models based on Eqs. (1)-(3) are applied in purely predictive scenarios, the fact remains that they are useful tools, often the only tools, for management purposes - to rank or study alternative management practices in a relative way.

ALTERNATIVE MODELS OR APPROACHES

Monte Carlo Simulations

Monte Carlo simulations of the solution of a deterministic equation such as Eq. (1) allows transport and storage coefficients to be random variables of the nature expected within a heterogeneous or nonhomogeneous field soil. The

variables may be independent, correlated or manifest a variance structure. Based upon a preliminary sampling, parameters selected for the assumed probability density functions (pdf) permit repeated solutions of the deterministic equation [e.g., $C_i(z,t)$]. These solutions $C_i(z,t)$ are then used to calculate sample moments (mean, variance, etc.) which are assumed to represent the statistical properties of the underlying stochastic transport process. Ammozegar-Fard et al., (1982) used Monte Carlo simulations of the solutions of Eq. (1) assuming S and g were negligible for the pdf of D, v and θ taken from the experiment of Biggar and Nielsen (1976). Two kinds of C(z,t) are of interest. The first is that expected at any location within a field, and the second is that obtained by averaging $C_i(z,t)$ from many locations within the field. The former is important because it is commensurate with that solute profile associated with a single crop plant or a small neighborhood of plants. The latter is important because it is the expectation of solute retention and mass emission of solutes across the entire field. C(z,t) expected at any location within the field was calculated with the solution of Eq. (1) using values of D and v from their relatively frequency distributions considered independently and jointly. The average solute concentration $\bar{C}(z,t)$ expected for the entire field was calculated from

$$\bar{C}(z,t) = \int_0^{C_o} C \; f(C|z,t) \; dC \qquad (5)$$

where $f(C)|z,t)$ is the relative frequency distribution of C(z,t). They concluded that the variability of v had the most influence on $\bar{C}(z,t)$.

Future research may allow the determination of autocorrelation and/or cross correlation lengths of the dependent variables in Eqs. (1) and (3). With those lengths known, Monte Carlo simulations of C(z,t) could be associated with a small site or known domain in the vicinity of a particular field location. Without those lengths, the extent of the field characterized by a single simulation is not known. The opportunities afforded by using Monte Carlo simulations of the solutions of Eq. (1) hinge upon the development of methods to measure and ascertain the pdf of the transport coefficients within prescribed limits of vadose zone depth and time.

Stochastic Continuum Approach

This approach was initiated by Gelhar et al. (1979) studying transport processes in water-saturated aquifers. Their interest in the development of a stochastic approach was based upon their recognizing the paucity of solute concentration data usually available to permit calibration of the solution of Eq. (2) for the value of the apparent diffusion coefficient. The stochastic continuum approach considers the hydraulic conductivity as a random field with spatial persistence characterized by its covariance function. Hence, when random variables such as D or K in Eqs. (1) or (2), respectively, are represented by the sum of their mean value plus random fluctuations a mean transport model with additional terms is obtained. By solving these stochastic equations of the local-scale water and solute transport, the functional form of the D for macro-regions is related to the statistics describing the variability. From such an analysis it is hoped that long-term, large-scale transport can be described using the stochastically derived value of D in the deterministic Eq. (1). For example, for an infinitely thick aquifer in which the water velocity varied randomly with depth, Gelhar et al. (1979) showed that the effective value of D in the direction of flow for large times is

$$D = D_t^{-1} \int_{-\infty}^{\infty} \frac{s_{vv}(k)}{k^2} dk \qquad (6)$$

where $s_{vv}(k)$ is the spectrum of the velocity fluctuations with depth, D_t the local scale transverse diffusion coefficient and is is the wave number. Sudicky (1983) showed similar results for a perfectly layered system of finite depth.

Field tracer tests (Sudicky et al., 1983; Freyberg, 1986) have shown that the value of the dispersivity increases with solute residence time and travel distance and gradually approaches a constant asymptote consistent with the continuum stochastic approach. Similar analysis for the vadose zone for steady vertical mean infiltration of water using Eq. (2) are traded for the necessity of estimating the statistics describing the variability of the material comprising the vadose zone.

STOCHASTIC CONVECTIVE APPROACH

Although several stochastic convective models have been suggested, the transfer function model (TFM) of solute transport initiated by Jury (1982) provided the impetus for the more generalized concept to describe movement of a solute that may undergo physical, chemical or biological transformations as it moves through the vadose zone. The general, three-dimensional TFM was derived by Jury et al., (1986) from the principle of superposition and solute mass balance. They showed that any linear solute transport model consistent with the mass balance equation may be expressed as a TFM. Applying the TFM to a transport volume into which solute enters through one surface ("entry surface"), and from which it exits through a second surface ("exit surface"), the relationship between the entry mass flow rate $Q_i(t)$ (the rate of solute entry into the volume devided by the total solute mass input) and the exit mass flow rate $Q_e(t)$ is

$$Q_e(t) = \int_0^t g(t-t'|t')Q_i(t')dt' \qquad (7)$$

where $g(\tau|t')$ is the conditional solute lifetime density function, giving the probability that a solute molecule which enters the volume at t' leaves it between τ and $\tau + d\tau$.

Equation (7) may be simplified when used in specific applications (e.g., steady water flow) when the solute lifetime τ is independent of the entry time t', in which case $g(\tau|t') \rightarrow g(\tau)$. Moreover, the lifetime density function $g(\tau)$ for conservative solutes becomes a travel-time probability density function (pdf). Equation (7) may be expressed in terms of flux concentrations C(t) (Parker and van Genuchten, 1984) by substituting $Q(t) = i(t)C(t)$, to give

$$C_e(t) = \int_0^t g(t-t')i_i(t')C_i(t')dt'/i_e(t) \qquad (8)$$

where i(t) is the water flux. During steady-state water flow the i(t) in Eq. (8) cancel. In cases where the soil water flux cannot be measured, Jury (1982) recommended an approximate TFM for use under transient conditions in which the cumulative net applied water flux,

$$I(t) = \int_0^t i(t')dt' \qquad (9)$$

was the dependent variable. In this formulation Eq. (8) is replaced by

$$C_e(I) = \int_0^I g(I-I')C_i(I')dI' \qquad (10)$$

Equation (10) was used successfully to describe transient solute outflow at five depths averaged over a 0.6-ha surface area by Jury et al., (1982).

White et al. (1986) and Sposito et al. (1986) have provided additional insights into the utility of this stochastic convective approach by applying the TFM to some selected laboratory and field studies, and by developing the two-component chemical nonequilibrium and physical nonequilibrium convection-diffusion equation models as special cases of the generalized TFM.

We illustrate the approach given by Germann and Beven (1985). The mass balance equation for a kinematic wave approach to vertical water flow along macropores that includes a sink function with respect to water sorbance into the soil matrix r is

$$\frac{\partial z}{\partial t} + \frac{c\partial q}{\partial z} + crw = 0 \qquad (11)$$

where q is volume flux density, c is the kinematic wave velocity, r is macropore sorbance as decrease of volume flux density per unit depth, and w is macropore moisture content. The following relationship exists between q and w (Beven and Germann, 1981):

$$q - bw^a \qquad (12)$$

The kinematic wave velocity is (Lighthill and Whitham, 1955)

$$c = \frac{dq}{dw} = ab^{1/a}q^{(a-1)/a} = abw^{(a-1)} \qquad (13)$$

The sorbance function is of the following form

$$r = -1/w(t)\ dw/dt \qquad (14)$$

The wetting front depth z_w, which is the depth where the moisture content jumps from $w = 0$ at $+z_w$ to $w - w_w$ at $-z_w$, moves downward with a velocity c_w, i.e.,

$$c_w = q/w_w = b^{1/a}q^{(a-1)/a} = bw_w^{(a-1)} \qquad (15)$$

where w_w is the moisture content at the wetting front.

Germann and Beven (1986) obtained the frequency distribution of the macropore conductance b by superimposing the predicted drainage hydrographs from that between 0.01 and 0.2 of the input is required to supply water to the macropore system, while a parameter controlling losses to the matrix varies over only a small range. The relationships between antecedent soil moisture and hydraulic properties and the sorbance function r remains poorly defined and not well understood.

SCALING

Scaling theory applied to field-scale transport remains immature and undeveloped. It stems from the pioneering work of Miller and Miller (1956) in which different regions of a heterogeneous field are conceptualized as being scale transformations for a hypothetical reference location. Warrick et al. (1977), Tillotson and Nielsen (1984), Ahuja et al. (1984), and Sposito and Jury (1985) have pursued the scaling concept to identify a scaling factor λ which characterizes the hydraulic properties of a particular region in a field. Bresler and Dagan (1983a,b), assuming that λ is a random variable represented by a probability density function, has relied on scaling to describe water and solute transport in field soils.

OTHER APPROACHES

Chromatographic considerations of solute transport (Dutt and Tanji, 1962) offer possibilities that remain relatively unexplored. Under these considerations the vadose zone can be considered as a finite number of layers with different chemical, physical and biological processes occurring simultaneously within each or any layer. Recently, Knighton and Wagenet (1988a,b) have simulated such solute transport using a continuous time Markov process and even more recently Knighton (personal communication) has extended the analsyis to allow for short-circuiting relative proportions of the water flow and its dissolved constituents from one layer to a distribution of downstream layers in a fashion consistent with the concept of macropore flow.

Fractal distributions of soil heterogeneity and their influence on water and solute transport are emerging opportunities for hydrologists to study the vadose zone. Fractals were originally introduced by Mandelbrot to relate the length of a coastline P to the length of the measuring length ℓ by $P \sim \ell^{1-D}$ where D is the fractal dimension. If a fractal relation is found, a scale invariant phenomenon is implied. Hewett (1986) has discussed the geometric properties and spatial correlation structure of fractal distributions and has reviewed methods for measuring the fractal character of field data and synthesizing fields with a similar correlation structure.

There are, no doubt, other intellectual frameworks available and being developed to understand and manage the quality of water moving through the vadose zone. Basic research on physical and chemical mechanisms and processes affecting solute transport remains important. The relationships between molecular and macroscopic transport requires continual investigation (Sposito, 1986; and Cushman, 1987). The development of a data base on multiphase flow parameters is no less important (Pinder and Abriola, 1986).

An abundance of theories and approaches are available for analyzing water and solute transport through the vadose zone. Computer codes escalate in number as pressures mount for improved management strategies for decreasing the pollution of surface and groundwaters. This trend will likely continue as computer costs decrease and relative cost of carefully designed and executed field experiments increase unless a concerted effort amongst hydrologists is made to provide new methods and additional experimental data for predicting site-specific predictions of solute transport.

THE FUTURE

Many of our current methods for measuring relevant vadose zone water flow and solute transport parameters are largely those that were introduced several decades ago. Thus, new methods and technologies of measurement are needed to keep pace with our ability to simulate field systems. A number of potentially powerful methods based on parameter estimation of various unsaturated flow (Dane and Hruska, 1983; Kool et al., 1985, 1986) and solute transport (Parker and van Genuchten, 1984b; Jury and Sposito, 1985; Wagner and Gorelick, 1986) parameters have recently been introduced. Other papers have contributed significantly to a better technology of measurement (Paetzold et al., 1985; Topp and Davis, 1985; Dasberg and Dalton, 1985). It is imperative that research in these and related areas continue in order to couple specific sampling designs with various parameter estimation methods.

The key to the future is accelerated efforts in field experimentation with the development of management tools at the farm or basin scale providing the greatest challenge. Interdisciplinary educational and research reforms are necessary in graduate research programs while state and federal agencies must provide policies and enhanced opportunities for such field investigations and subsequent development and utilization of the sorely needed management tools.

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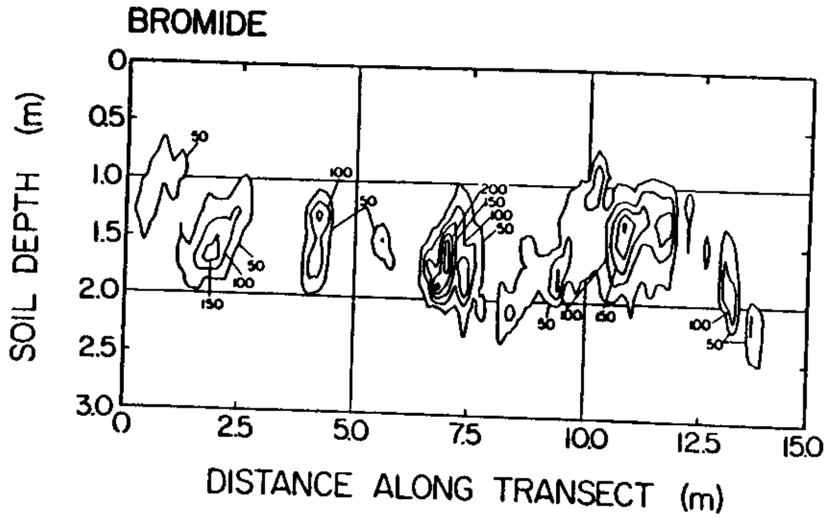

Figure 1. Distribution of bromide within a field soil.