Quantitative Prediction of the Leaching of Organic and Inorganic Solutes in Soil [and Discussion]

R. J. Wagenet, P. H. Nye, John Nowland, I. G. Burns, D. J. Greenwood, T. M. Addiscott and I. J. Graham-Bryce

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Quantitative prediction of the leaching of organic and inorganic solutes in soil

R. J. WAGENET

Department of Agronomy, Cornell University, Ithaca, New York 14853, U.S.A.

SUMMARY

The quantitative description of chemical leaching in soil, long a focal point for soil science research efforts, is being pursued with increased intensity. Although much is known of the physics and chemistry of well-defined, homogeneous soils studied under controlled situations, only recently have there been attempts to apply these concepts to the description of field conditions. The interpretation of results is a challenging task, as field-scale variability and non-equilibrium processes are proving to be substantial issues in natural systems. New models of leaching are required to describe the macropore flow of water and chemicals, kinetic-equilibrium sorption processes and the inherent spatial variation in soil hydraulic properties and biological and chemical processes. Development of these models depends upon increased understanding of leaching processes in the field, that can only come from increased numbers of experimental studies in which appropriate parameters are recorded. Until improved models are available, those currently available will be used by a variety of individuals to estimate the environmental fate of chemicals. Defining the proper use of such models is the responsibility of soil scientists. This is a new responsibility that they must assume if quantitative estimation of chemical leaching is to be accomplished in an accurate and meaningful manner.

1. INTRODUCTION

Water and chemical movement in the environment is increasingly the focus of society's attention. The broad spectrum of concerns include the mobility, persistence and ultimate fate of both organic and inorganic chemicals in the soil profile. Accordingly, soil scientists are being asked to extrapolate their previous experience, which derives primarily from agricultural chemicals and practices, and to provide regulators and managers with guidance on the environmental impact of a wide range of agricultural and non-agricultural chemicals introduced to soils. Organic solvents, heavy metals, and radioactive wastes are examples of the solutes that now require attention, in addition to an increasing array of pesticides. The ability to predict quantitatively the fate of these chemicals in soil would provide us with increased capability to manage intelligently a portion of the environment. Soil scientists and hydrologists have therefore invested substantial effort in understanding the processes that influence chemical leaching, and in devising a broadly applicable theory that will allow quantitative prediction of it.

Classical concepts of water flow and chemical leaching have been refined over the past 30 years through exhaustive study of well-defined experimental systems. Basic principles derived from application of elementary physics and chemistry have been identified, and the first-generation models of soil leaching processes have been constructed and tested, principally in the laboratory and for similarly well-controlled lysimeter cases. The relatively recent application of these models to field soils has produced mixed results, indicating that the first-generation models may not include a description of all processes that influence leaching at the field scale. As a result of these studies, several issues are now clear. First, extension of classical theories of water flow and solute transport are required to describe leaching in spatially variable soils and in situations where non-equilibrium physical and chemical processes prevail. Secondly, new procedures are required to apply existing models to those other cases in which basic processes in fact operate as described by classical concepts. Thirdly, pressure is building for soil scientists to provide tools that can be used to predict chemical leaching in assessments of the fate of chemicals in the environment. The third area, more an issue of technology than science, is not discussed here, but is comprehensively discussed by Wagenet & Rao (1990). A review of the evolution of leaching models will provide perspective on current activities in the first two areas.

2. CLASSICAL CONCEPTS OF LEACHING IN HOMOGENEOUS SOILS

Leaching models have evolved from two general approaches: those models that are empirical and those that begin from some consideration of mass balance.

(a) *Empirical relations*

The reclamation of salt-affected soil in the semiarid western United States focused attention in the early 1950s upon the leaching of soluble salts. Data from

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field studies in the Coachella Valley of California (Reeves *et al.* 1955) suggested that salt leaching from soil followed a general pattern. The empirical equation derived to describe the amount of water required as a function of the desired change in salt content was among the first leaching models:

$$D_w/D_s = [0.20(EC_e)_o/(EC_e)] + 0.15, \qquad (1)$$

where D_w is the depth of water leached through a depth of soil D_s, $(EC_e)_o$ is the average saturation extract electrical conductivity of the soil to a depth D_s before leaching, and EC_e is the average saturation extract electrical conductivity of the soil after leaching.

These and similar subsequent equations showed some utility in field reclamation studies in several semiarid areas, and represented a first attempt at integrating irrigation, evaporation and the leaching of soil salts. However, these equations are restricted by factors that limit all empirical approaches, and are as a result rather non-quantitative with respect to masses of chemicals leached. Yet, they were (and are) particularly useful in cases where only a few measurements could be done, when only approximate estimates were needed, and when no other estimation tool was available. As will be discussed below, a similar approach is being used for a large class of leaching models currently being developed. However, where more detailed estimates are required, or when an objective is to use the leaching model to learn about basic processes, these approaches have generally been replaced by the mass balance models reviewed below.

(b) Models based on conservation of mass

Leaching models based upon mass balance considerations evolved simultaneously from two different directions, although the philosophies of the two were quite similar. One path had its roots in salinity and reclamation issues, and represented an attempt to summarize leaching processes more universally than was done in equation (1). The other path originated in the column chromatography literature and provided the basis for development of equations that describe simultaneous physical and chemical processes influencing solute displacement.

The general mass balance equation for downward salt movement in a soil profile in situations where no sources or sinks of salt exist is:

$$\begin{bmatrix} \text{change in mass} \\ \text{of salt in} \\ \text{soil} \end{bmatrix} = \begin{bmatrix} \text{mass of salt in} \\ \text{added water} \end{bmatrix} - $$
$$\begin{bmatrix} \text{mass of salt in} \\ \text{drainage water} \end{bmatrix} \quad (2)$$

This can be expressed for a uniform soil profile as:

$$D_s \Delta\theta(\Delta C_{sw}) = (C_{iw} D_{iw}) - (C_{dw} D_{dw}), \qquad (3)$$

where $\Delta\theta$ is the change in profile volumetric water content, ΔC_{sw} is the change in salt concentration in the soil solution, C_{iw} is the salt concentration in the irrigation water, D_{iw} is the depth of added irrigation water, and C_{dw} and D_{dw} are similar with respect to the

drainage water. For non-uniform soils, in which D_{iw} is sufficient to lead to drainage, equation (3) can be written as:

$$\sum_i D^i(\theta^i_{fc} C^i_{fc} - \theta^i_o C^i_o) = C_{iw} D_{iw} - C^i_{dw}[D_{iw} - \sum_i D^i (\theta^i_{fc} - \theta^i_o)], \quad (4)$$

where superscript i refers to the ith soil layer, D^i is the thickness of a soil layer, subscript fc refers to field capacity water contents and salt concentrations, and subscript o refers to the initial water content and salt concentration.

Equations (3) and (4) served as the basis for early leaching models. With several assumptions about the nature of the leaching process, description was possible of the release of readily soluble salts from a saline soil during leaching. These approaches accounted for approximately 80–90 % of the accumulation of total salt in the profile, but were limited in their ability to describe the concentration of salt in drainage waters.

The concentration of the drainage water C_{dw} is often of critical interest to non-point-source pollution of groundwater. Early models (Van Der Molen 1956; Bresler 1967; Bresler & Hanks 1969) divided the soil into layers through which water flow was estimated by using equation (4), with the objective of estimating salt distributions in soil during leaching. These models suffered from the lack of consideration of mediating processes (such as precipitation and dissolution or ion exchange), yet were useful as most early salinity studies were accomplished in soil systems at or near equilibrium between solution and exchangeable or precipitated phases. A further weakness of these approaches was that time was not included as a variable in the equations. Leaching was event-driven, not a continuous process (as in nature) of infiltration and redistribution of water and solutes. Additionally, these early models included a built-in dispersion process, as the selection of depth intervals influenced the calculated transport of salt. This problem still remains today with some leaching models, and now takes the form of numerical dispersion resulting from approximations in finite difference solutions. Nevertheless, the early leaching models were useful first approximations of the movement of inorganic salts in relatively saline soils. But this approach was insufficient for a description of leaching in systems characterized by transient fluxes of water and solute.

The parallel path of development of leaching models based upon conservation of mass originated in the field of column chromatography. Chromatographic models can generally be classified as either plate theories or rate theories, with an excellent review of the distinctions being given by Frissel & Poelstra (1967).

Plate models (Martin & Synge 1941; Mayer & Tompkins 1947) consider a chromatographic (or soil) column as being divided into a large number of equal-sized increments (plates). Two solute phases are presumed in each plate, sorbed and dissolved, with equilibrium between the two. The thickness of the plate (plate height) is an important parameter characterizing flow through the column. In these models, flow occurs consecutively through adjacent

plates, with equilibrium in each plate achieved before flow passes to the next plate. This approach suffers the same weaknesses with respect to simulation of soil leaching processes as do the simple layer-type models used in early salinity studies. That is, the simplification of transport (leaching) to 'discontinuous' plate flow can lead to serious cumulative errors as the number of plates or time increases. This has prevented much of the early chromatographic literature based on plate theories from being directly applicable to soil leaching processes. The few studies that applied this theory (Dutt & Tanji 1962; Rible & Davis 1955; Bower *et al.* 1957; Thomas & Coleman 1959) failed to consider the mixing that takes place as a result of pore water velocity distributions (resulting from pore size and shape variations). Additionally, in all of the above cases displacement and ion exchange under partially water-saturated conditions, which normally prevail in soil, were not considered. Although fairly good agreement between measurement and prediction was obtained for the few cases considered, this approach was scientifically unsatisfying and limited in its applicability.

The advantage of the plate theory is also its limitation. That is, whereas the optimum plate thickness can easily be determined experimentally, the approach does not lend much insight into basic processes, nor does it allow one to predict the effects of changing one or more of the controlling soil-water variables, such as water flow velocity. By contrast, in the rate theories that followed, a physical model of the system was defined, with each parameter in the model either known beforehand or measured experimentally. Early models of this type were developed by DeVault (1943), Heister & Vermeulen (1952) and Lapidus & Amundson (1952). These models form the basis of the diffusion theory now used in many contemporary leaching models. Reviews of the development of these theories exist elsewhere (Wagenet 1983; Nielsen *et al.* 1986).

3. CONTEMPORARY DESCRIPTION OF WATER FLOW AND CHEMICAL LEACHING

The first step in accurate prediction of chemical leaching is accurate description of water movement. Water flow in porous media was first quantified by Henri Darcy (Darcy 1856). Darcy's law describing the relation between soil-water potential energy gradients and the resulting water flux density is now a common beginning point in the study of water flow in porous media. That is:

$$q_w = -K \frac{dH}{dz}, \tag{5}$$

where q_w is the water flux density, defined as the quantity of water moving through a cross-sectional area in a unit time; H† is the hydraulic potential energy, consisting principally of the sum of matric potential energy (denoted as h, and derived from interaction of water molecules and soil mineral surfaces), and gravitational potential energy; K is the

† Measured in water head units.

soil hydraulic conductivity, a proportionality constant inversely related to resistance to flow, and z is distance. Note that flux density and conductivity are dimensionally equivalent, but conceptually quite different. Darcy's law describes steady-state conditions, in which q_w and dH/dz are constant with time. As such its direct application is limited to rather special cases, usually occurring under laboratory conditions.

The space and time continuity of water flow is expressed by Richards' equation (Richards 1931), that was developed using Darcy's law and a continuity equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\theta)\frac{\partial H}{\partial z}\right], \tag{6}$$

where θ is the volumetric fractional water content of the soil, $K(\theta)$ is soil hydraulic conductivity, now dependent on water content, and partial derivatives have been introduced since water flow varies with both depth and time. Richards' equation has been widely used as the fundamental equation describing the transient state of water in soil. It is almost always necessary to solve it by numerical methods to provide estimates of $\theta(z, t)$. For example, the integral of equation (6) with depth

$$\int_{z_1}^{z_2} (\partial \theta / \partial t) \, dz = K(\theta)\frac{\partial H}{\partial z}, \tag{7}$$

provides an estimate of the time-dependent local water flux, $q_w(z, t)$, between two positions z_1 and z_2. Knowledge of $q_w(z, t)$ is required to predict chemical leaching, as explained below.

A number of reviews have treated the strengths, weaknesses, application and solution of equation (6) (Towner 1989; Wagenet 1986; Nielsen *et al.* 1986). In general, the Richards' equation is a useful tool in any coordinate dimension $(x - y - z)$ in which the soil can be assumed homogeneous. That is, when water flow through a porous matrix occurs vertically or horizontally in response only to a gradient in hydraulic potential energy. In such cases, the $K(\theta)$ relation may be in fact be spatially variable in the horizontal dimension, as well as changing with depth according to soil horizonation. The limitation of the use of the Richards' equation in such cases in the lumping of soil heterogeneity into a macroscopic $(K)(\theta)$ relation. On a small scale a Darcy-type equation is probably always valid; at larger scales one lumped equation fails to describe and reflect the real variation in fluxes.

This shortcoming aside, the quantitative description of water flow has been very successful for well defined systems in which equation (6) is most applicable. Water flow has been predicted accurately in a large number of laboratory soil columns and in fewer field soils provided that homogeneity criteria are met (usually apedal sands or sandy loams). These experiments, conducted in the laboratory since 1950 and in the field since the early 1970s, have reinforced our understanding of the basic physics of well-defined systems. However, equation (6) does not apply directly to flow in non-homogeneous soils, which are characterized by non-matrix water flows, such as water

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movement down wormholes, structural cracks, and similar such 'preferred pathways' (see, for example, Beven & Germann (1982)).

Many field soils are characterized by large voids, commonly referred to as macropores, that provide the opportunity for flow to by-pass the small pores of the bulk soil matrix. This short-circuiting of the matrix microporosity is difficult to describe quantitatively, yet has substantial implications for such important processes as groundwater recharge and the rapid movement of chemicals to soil depths much deeper than would be predicted by the use of equation (6). Recognition of the importance of macropore flow is relatively recent, and is providing soil scientists with one of their greatest challenges as they attempt to treat it both theoretically and experimentally.

Quantitative description of chemical leaching is most often described with the dispersion-convection equation. Since the early 1960s (Nielsen & Biggar 1962) this approach has been widely applied to a variety of solutes in homogeneous soils. The theory presumes that chemical movement is the result of the combined processes of chemical diffusion in response to a concentration gradient and physical convection (mass flow) in response to the movement of the bulk liquid phase in which the chemical is dissolved. For steady-state conditions, in which water flow and concentration gradients are time-independent, the classical concept of transport of a solute that only dissolves in water is usually expressed as:

$$q_S = q_{DL} + q_{CL} \tag{8}$$

$$q_S = -D_P \frac{dc_L}{dz} + \left[D_M \frac{dc_L}{dz} + q_W c_L \right], \tag{9}$$

where q_s is the solute flux density, or mass of chemical moving through a cross-sectional area per unit time; q_{DL} and q_{CL} are the fluxes moving by diffusion and convection in the liquid phase; D_P is the ionic or molecular diffusion coefficient adjusted for the water content and tortuosity of the porous media, D_M is a mechanical dispersion coefficient that describes the effect of local variations in water flow velocities between large and small pores, and c_L is chemical concentration in the liquid phase.

For complete description of the leaching of chemicals (especially those of environmental concern, such as pesticides, fertilizers and miscible organics), equation (8) must be expanded to include the possible flux of chemical in the gas phase, interaction of solute with soil solids, and transformation and plant uptake processes. Equation (8) then becomes:

$$q_S = q_{DL} + q_{CL} + q_{DG} + q_{CG} \pm \phi, \tag{10}$$

where q_{DG} and q_{CG} are diffusion and convection in the gas phase, and ϕ indicates processes that increase or decrease the mass in solution. Diffusion in the gas phase is represented by Fick's law, and gas-phase convection arising from cyclical changes in the pressure of the soil atmosphere has been shown to be conceptually of the same effect as an enhanced gas-phase diffusion (Scotter *et al.* 1967).

For a chemical that partitions between three phases

(sorbed, liquid, gas), the total mass of chemical in the soil (T) is:

$$T = \theta c_L + \rho c_S + \epsilon c_G, \tag{11}$$

where ρ is the soil bulk density, c_S is sorbed phase concentration, ϵ is air-filled soil porosity and c_G is chemical concentration in the gas phase. Appropriately formulated to describe non-steady state cases, equations (9), (10) and (11) are combined to give:

$$\frac{\partial (\theta c_L + \rho c_S + \epsilon c_G)}{\partial t}$$
$$= \frac{\partial}{\partial z} \left[D(\theta, q_W) \frac{\partial c_L}{\partial z} - q_W c_L + D_G \frac{\partial c_G}{\partial z} \right] \pm \phi, \tag{12}$$

where D_G is the gas-phase diffusion coefficient that includes the effect of convection in the gas phase, and $D(\theta, q_W)$ combines the effects of both chemical diffusion and mechanical (hydrodynamic) dispersion upon chemical transport.

Equation (12) forms the basis of quantitative description of chemical movement in soil where the chemical partitions between three phases, is transported through a homogeneous media, and undergoes transformation or uptake. In most previous agricultural applications, where leaching of aqueous solute was the only transport pathway (partitioning between only two phases), equation (12) was simplified to:

$$\frac{\partial (\theta c_L + \rho c_S)}{\partial t} = \frac{\partial}{\partial z} \left[\theta D(\theta, q_W) \frac{\partial c_L}{\partial z} - q_W c_L \right] \pm \phi, \tag{13}$$

or when applied to cases where water flow was constant, and solute concentrations were transient:

$$\frac{\partial c_L}{\partial t} + \frac{\rho}{\theta} \frac{\partial c_S}{\partial t} = D \frac{\partial^2 c_L}{\partial z^2} - v \frac{\partial c_L}{\partial z} \pm \phi \tag{14}$$

where v is the interstitial, macroscopically averaged pore-water velocity. Equation (13) has been extensively used as the basis of models of field-scale chemical leaching (Nielsen *et al.* 1986), whereas equation (14) has been used to interpret numerous laboratory leaching studies (van Genuchten & Cleary 1979) that examine in detail the processes of sorption, dispersion and transformation.

As with equation (6), equation (14) works well in controlled or laboratory situations where the functional relation between c_S and c_L, the nature of ϕ, and v and D are known or can be measured. As with water flow models, the more interesting and perplexing results arise from attempts to describe field-scale leaching. One of the first such experiments still provides the best illustration of the issues. Nielsen *et al.* (1973) used equation (14) simplified further to describe a non-sorbing, non-degrading solute (chloride). They conducted a field experiment on a relatively unstructured soil in which large (0.01 ha†) plots at multiple locations were continuously ponded with unamended water until steady-state water flow was achieved. A pulse of water containing chloride was then added, followed by continued leaching of the chloride with unamended

† 1 hectare = 10^4 m².

water. In this way, undisturbed field soil profiles acted as soil columns. By using a porous cup vacuum extractor system, the soil profiles were repeatedly sampled for chloride. Multiple breakthrough curves of the chloride concentration were thereby obtained to soil depths of 240 cm. The analytical solution to the simplified form of equation (14) was applied to each breakthrough curve, with the objective of determining D and v at each point of field measurement.

Quite surprisingly (at least in 1973), the values of D and v were found to be spatially variable, both populations being logarithmic-normally, rather than normally, distributed. The measured steady-state infiltration rate was also log-normally distributed and the $K(\theta)$ relation was variable by orders of magnitude at a particular water content. This variability has been confirmed in numerous subsequent studies, with important consequences for the application of field-scale models based on both equations (6) and (13). Today, even when a particular soil can be assumed to be reasonably homogeneous (without macropores or preferred pathways), the spatial variability in $K(\theta)$, and the resulting variability in v and D, preclude the use of a single application of equations (6) and (13) to estimate chemical leaching, and strategies to account for variability are essential.

One strategy recognizes that although models based on equations (6) and (13) are deterministic, such models can be used in an 'ad-hoc' stochastic manner to estimate leaching. By definition, the deterministic approach used in classical numerical models of leaching based on equations (6) and (13) presumes that definition of an initial soil profile condition of $h(z, t)$ (or $\theta(z, t)$), combined with the knowledge at each depth of the $K(\theta)$ and $h(\theta)$ relations presumed to describe the soil properties, will allow estimation of $q_w(z, t)$ and $\theta(z, t)$, so long as the system boundary conditions are defined. This assumption does not allow direct consideration of the variability of $K-\theta-h$. As a means of including such variability in the analysis, it is possible to use a multiple execution scheme to estimate the stochastic behaviour of the system. When used in such an 'ad-hoc' stochastic manner, each execution of the deterministic model utilizes a different $K(\theta)$ and $h(\theta)$ relation selected from possible realizations of the soil hydraulic properties within the spatially variable domain being considered. The multiple executions each provide a different, but possibly real, estimate of q_w, θ, q_s and c_L for the system. With enough executions, a frequency distribution of, for example, c_L can be estimated for each soil depth at each time of interest. The statistical moments of this distribution can then be compared with the moments of a population of measured c_L obtained from field sampling.

The above exercise, although not yet accomplished in enough cases, has been shown to describe $c_L(z, t)$ and $\theta(z, t)$ in homogeneous, but spatially variable soils where equations (6) and (13) are properly applied. However, this approach presumes that in homogeneous soils all variability in solute leaching derives from variability in transport processes. This is clearly naive, as sorption and degradation processes also vary horizontally and vertically in soil. Although vertical

variability has been considered through development of models that distinguish soil horizons of different character, the influence of horizontal spatial variation in sorption and degradation, and the sensitivity of the models to such variation, have not yet been fully considered in the 'ad hoc' stochastic use of deterministic leaching models. Attention to this issue will help identify the relative importance of different sources of variability upon chemical leaching.

4. QUANTIFICATION OF LEACHING IN NON-HOMOGENEOUS SOILS

Leaching processes in structured soils, or in soils that have pores, which are large and continuous, are not well described by equations (6) and (13). These non-homogeneous soils can be considered as composed of two domains, one of which is the bulk matrix, in which flow is by classical processes describable by equation (6). The other domain, the macroporosity, is usually irregularly distributed and may comprise only a few percent ($< 5 \%$) of the soil volume. Yet this second domain may allow movement of water and chemicals to much greater depths than would be predicted by equations (6) and (13). Although the importance of such pores has long been recognized, there remains no comprehensive or practically useful theory that adequately describes such systems.

Staining techniques and morphological studies have provided insight into the physical structure of macropores, yet they have not led to quantitative prediction of water flow velocities and chemical leaching through macropores. Velocities can be calculated from hypothetical macropore geometries, but these values are seldom observed in nature because of the discontinuity and irregular configuration of pore space, the effect of air entrapment on water entry into macropores and the infrequence and short duration of ponded conditions that are most conducive to maximum macropore flow. With such limitations, the mathematical descriptions of macropore flow that have been developed are numerous and ingenious, ranging from adaptations of the convection-dispersion equation for describing chemical movement to more empirical, though perhaps more useful, approaches. A contemporary review of the modelling of macropore systems is presented by Germann (1989).

One of the most comprehensive models for describing flow of water in macropores was proposed by Beven & Germann (1981). They recognized that any model combining micropores and macropores should reduce to a Darcy-type model when no macropores are present. A two-domain concept was adopted with the micropore system being the domain that behaves according to classical hydraulic principles as summarized in Darcy's law. The macropores were recognized as a second domain requiring separate treatment. The two domains had to be linked so that they could interact in a physically realistic manner. This was accomplished by describing the micropore system as in equation (6), but including an additional term describing the exchange of water between micropores and macropores. The macropore system was assumed to

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be so complex so that it could not be defined on a purely theoretical basis, but required empirical relations. Assumptions about macropore geometry and flow led to relations between pore dimensions and macropore water flux. Interaction between the domains was defined in terms of a hydraulic gradient between micropore and macropore systems, where the gradient depends on the water contents in micropore and macropore regimes. The resulting model was capable of handling a wide range of conditions, and provides a good beginning for future efforts. Description of chemical movement was not included. A similar approach was used earlier by Edwards *et al.* (1979), but was less mechanistic and involved less rigorous consideration of the difference between the two domains.

The concept of two domains underlies other models of both water and chemical movement in non-homogeneous soils. Although there are a number of such models, the conceptual approaches can be shown with three examples. Van Genuchten & Wierenga (1976) arbitrarily divided the soil-water between 'mobile' and 'immobile' water with the proportions of each dependent upon soil properties and rate of flow. This concept was applied to chemical movement and models derived from it consist principally of analytical solutions to appropriate formulations of the convection-dispersion equation. The analagous forms of equation (8) by this approach are, for the mobile region:

$$\frac{\partial c_{Lm}}{\partial t} + \frac{f\rho}{\theta_m}\frac{\partial c_{Sm}}{\partial t} = D_m\frac{\partial^2 c_{Lm}}{\partial z^2} - v\frac{\partial c_{Lm}}{\partial z} - \frac{\alpha}{\theta_m}(c_{Lm} - c_{Lim}) \quad (15)$$

and for the immobile region:

$$\frac{\partial c_{Lim}}{\partial t} + \frac{(1-f)\rho}{\theta_{im}}\frac{\partial c_{Sim}}{\partial t} = \frac{\alpha}{\theta_{im}}(c_{Lm} - c_{Lim}), \quad (16)$$

where subscripts m and im refer to the mobile and immobile regions respectively, f is the fraction of the solid phase that equilibrates instantly with the mobile region, and α is a first-order mass transfer coefficient describing the rate of transfer between the mobile and immobile regions. This approach works well for steady-state water flow conditions, so long as α can be determined from the measured data. It has not been developed in detail for the transient water flow conditions of most field cases.

A similar conceptual approach was used by Addiscott *et al.* (1978) to describe chloride and nitrate measured in the field in the drain gauges first used by Lawes *et al.* (1882). The Addiscott model assumes that the incoming water moves in the mobile phase but that chemical equilibrium between mobile and immobile phases is approached slowly. This model is much more empirical than equations (15) and (16), but also includes a description of the water regime. The approach is useful in describing macropore flow, but as it is quite empirical, it provides only hints as to the basic processes that may operate in such systems.

The model of White (1985) was used to predict nitrate leaching during unsaturated flow through a soil containing macropores. The assumption is made that water infiltrating the soil surface mixes incompletely with resident water to form a mixed transport volume, the size of which can vary with time. Changes in chemical storage within the mixed transport volume can occur by diffusion and biological transformations. The mobile and immobile soil solution volumes into which the system is divided are analogous in concept to those of van Genuchten. The model utilizes a straight-forward algebraic, bookkeeping approach to construct a description of chemical leaching between adjacent soil-depth increments. The model was tested in experiments that describe measured nitrate concentrations in both the soil solution and in effluent from leached core samples. Although the results were generally encouraging, it was recognized that two parameters, the interfacial wetted area of the soil (ped surface wetted as water flows through interpedal voids) and the chemical diffusion coefficient, needed to be known to use the model. It remains to be seen whether this approach has long-term utility, although it appears promising.

The absence of a comprehensive, generally accepted model of macropore flow is currently limiting the ability of soil scientists to estimate chemical leaching in numerous important field situations. As a result, this is currently one of the most active areas of research in leaching processes. The best efforts to develop such a model that show not only the greatest chance of success but also the greatest possible flexibility, are those which include the combined efforts of soil physicists and soil morphologists. Only a model that considers soil morphological characteristics, structural patterns and utilizes broadly available data bases (such as soil survey information), will be able both to represent properly the extremes of flow, and be flexible and useful enough to describe a variety of field situations.

5. COUPLING OF PHYSICAL, CHEMICAL AND BIOLOGICAL PROCESSES

Progress in the understanding of soil processes has produced ever more comprehensive descriptions of the non-transport processes that influence chemical leaching. One of the most important of these is sorption, which is the distribution of the chemical between the solution and solid (sorbed) phases of the soil. Recent developments in such studies challenge the current formulation of chemical leaching models, particularly for miscible organic chemicals such as pesticides.

It is usually assumed that simple equilibrium isotherms adequately describe the partitioning of organic compounds between solution and sorbed phases. This has led to the use of Freundlich-type sorption isotherms of the general form:

$$c_S = k_F c_L^n, \quad (17)$$

where k_F and n are coefficients describing a non-linear, but equilibrium, partitioning process. For pesticides, n is usually assumed to be one, and

$$c_S = k_D c_L, \quad (18)$$

where k_D is a linear distribution coefficient. One of the assumptions that has made both (17) and (18) attractive is that they can be determined in batch-type

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liquid phase

$$\frac{\partial \theta c}{\partial t} = -\frac{\partial j_{\mathrm{S}}}{\partial x} - j_{\mathrm{a1}} - j_{\mathrm{a2}} - \theta \mu_1 c$$

j_s

j_{a1}

solid phase

$j_{\mathrm{a2}} = \alpha \rho [(1-f) k_{\mathrm{c}} - S_2]$

type-1 sites   type-2 sites

$$\rho \frac{\partial s_1}{\partial t} = \rho f k \frac{\partial c}{\partial t} \qquad\qquad \rho \frac{\partial s_2}{\partial t} = j_{\mathrm{a2}} - \rho \mu_{s2} s_2$$
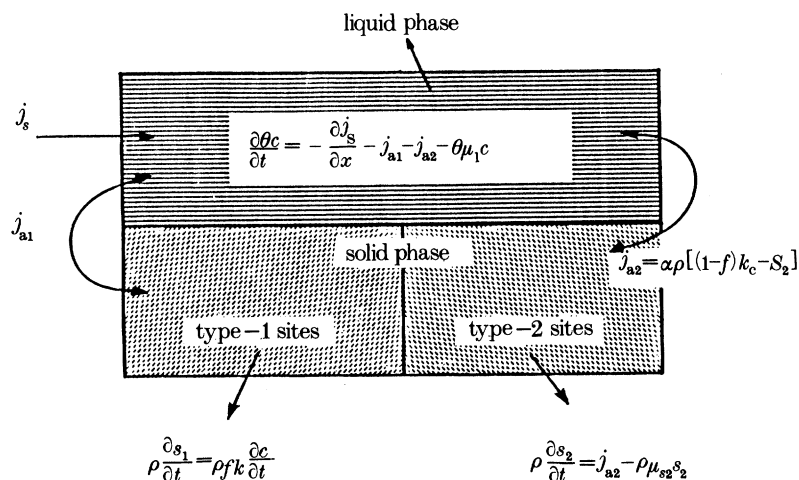
Figure 1. Conceptualization of the two-site partial equilibrium, partial kinetic sorption and transport model, with degradation (from van Genuchten & Wagenet 1989).

laboratory experiments, and then used in dynamic models of leaching. Although this assumption may be adequate for weakly sorbed organics, it does not appear adequate for description of a number of organics that interact with the soil surface to any appreciable degree.

A better conceptualization in these latter cases is the two-site model, first presented in part by Lapidus & Amundsen (1952), and developed further by several authors (van Genuchten & Wierenga 1976; Cameron & Klute 1977; van Genuchten 1981), in which sorption is characterized by simultaneous equilibrium and kinetic processes (figure 1). The soil's sorption capacity is divided into type–1 (equilibrium) 'sites' and type–2 (kinetic) 'sites'. Assuming equation (17) for equilibrium sorption, and assuming also that leaching occurs in a homogeneous media where dispersion and convection are the primary transport processes, van Genuchten (1981) derived the following for steady-state water flow conditions:

$$\left(1 + \frac{\rho f k_{\mathrm{D}}}{\theta}\right) \frac{\partial c_{\mathrm{L}}}{\partial t} = D \frac{\partial^2 c_{\mathrm{L}}}{\partial z^2} - v \frac{\partial c_{\mathrm{L}}}{\partial z} - \frac{\alpha \rho}{\theta} [(1-f) k_{\mathrm{D}} c_{\mathrm{L}} - c_{\mathrm{S2}}], \tag{19}$$

$$\frac{\partial c_{\mathrm{S2}}}{\partial t} = \alpha [(1-f) k_{\mathrm{D}} c_{\mathrm{L}} - c_{\mathrm{S2}}], \tag{20}$$

where f is now the fraction of type-1 sites, α is now a first-order kinetic rate coefficient, and c_{S2} is the sorbed-phase concentration at type-2 sites. Equations (19) and (20) are of the same general form as (15) and (16), which has provided the opportunity to distinguish non-equilibrium physical processes (mobile-immobile water) from non-equilibrium chemical processes (sorption) through the analysis of soil column data obtained using sorbing and non-sorbing solutes. Extensions of these solutions (van Genuchten & Wagenet 1989) also allow simultaneous consideration of degradation, and are intended for use in pesticide studies. Such approaches, which recognize the importance of non-equilibrium, will become increasingly important

in furthering the understanding of basic leaching processes and may be the basis for a new generation of deterministic leaching models useful in the field.

The author appreciates his interactions with Dr J. L. Hutson and the influence he had on this paper.

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DISCUSSION

P. H. Nye (*Department of Plant Sciences, University of Oxford, U.K.*). In all the solute continuity equations used in cation leaching models, it is assumed that the cation is mobile in solution, but immobile when adsorbed as an exchangeable cation (Staunton & Nye, 1987). We now know that cations, particularly the weakly bound monovalent ones such as sodium, have considerable surface mobility. I think it is necessary to include this effect in estimating their diffusion coefficients, particularly when percolation is very slow so that the diffusion term in the continuity equation becomes significant.

R. J. Wagenet. It is unclear as to consequence of this observation. In any leaching situation in which there is measurable water flux, the convective transport of solutes is orders of magnitude more important than is diffusive transport. In those relatively infrequent cases where convective fluxes approach zero, diffusion will be the principal transport pathway. However, the total flux in such cases will be very small, leading me to wonder what the net effect of self-diffusion will be. Although we have not included cation surface mobility in leaching models, reasonable descriptions of transient inorganic solute concentractions have in fact been achieved in a number of cases. However, I will grant you that these are all cases in which the water flux is high enough that diffusive transport is a minor component anyway.

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John Nowland (*CABI International, Wallingford, Oxfordshire, U.K.*). Would you comment on the need to consider bound residues of pesticides (and their slow release in response to a little known environmental trigger) in the modelling you describe? They can amount to 20–40% of the total applied.

R. J. Wagenet. Bound residues are generally not considered in soil leaching models. In those cases where 20–40% of the applied pesticide can be bound, it may well be an important compartment to consider. However, in my opinion, there is at this time insufficient information, from either field or laboratory experiments, to assess the relative importance of the slow release of bound residues as a factor in the long-term mass balance of pesticides in soil-water systems.

I. G. Burns (*AFRC Institute of Horticultural Research, Wellesbourne, Warwick, CV35 9EF, U.K.*). There is a major difficulty in providing accurate predictions of leaching of solutes in heterogeneous soils that have a wide range of pore sizes. To what extent will the newer generation of models be able to simulate leaching in practical agricultural situations where the soil is frequently cultivated?

R. J. Wagenet. Inadequate consideration of the effects of tillage upon soil leaching processes is often cited as a weakness in contemporary leaching models. It is doubtful that development of purely stochastic models will provide much positive contribution in this area, as these models do not include enough description of basic process in response to an external variable (e.g. tillage). However, deterministic models based upon the Richards' equation can incorporate the effect of tillage upon soil hydraulic properties, such as the relation between hydraulic conductivity, water content and matric potential. Similarly, capacity-type deterministic models can be modified to represent tillage effects on water holding capacity and infiltration rates. There are several research programs currently incorporating such effects into deterministic models.

T. M. Addiscott (*IACR, Rothamsted Exp. Stn. Harpenden, AL5 2JQ, U.K.*). Following on from what Professor Wagenet has just said, I should like to mention that my model has been used with the inputs presented as distributions. I think that it is also worth mentioning that any success that the simple models have had is because they each have a capacity parameter. It may be that we need models with both rate and capacity parameters, and I am currently developing such a model.

R. J. Wagenet. I have always followed Dr Addiscott's work with interest. I look forward to learning more of his 'new' model.

I. J. Graham-Bryce (*Shell Internationale Petroleum Maatschappij B.V. The Hague, Netherlands*). I believe we would all support Professor Wagenet's view that some of the greatest challenges in soil modelling are associated with heterogeneity in the field. This must apply particularly to some of the events that are becoming of greatest interest, for example, contamination of groundwater. The EEC Drinking Water Directive serves to illustrate the point. This requires that levels of contamination should be below 0.1 ppb for any single pesticide or similar product. Such very low levels might easily be achieved by transport events at the extremes of heterogeneity or probability. It may well be that such events will never be well represented in traditional convection-dispersion-diffusion models, however far they are refined by including kinetics of adsorption or desorption and so on. If so, is the way ahead to adopt simpler semi-empirical compartmental models or some other probabilistic or stochastic approach?

R. J. Wagenet. The degree of model complexity is not directly correlated with the model's ability to accurately predict very low chemical concentrations. Given field heterogeneity and our incomplete understanding of basic process in the field, it is unlikely that any one modelling approach will be universally appropriate. One of the most promising approaches is to use either complex mechanistic or compartmental models in an ad hoc stochastic manner. These models of soil leaching processes, repeatedly executed in such a way as to consider the extremes of variation present in the field, may provide the opportunity to assess the statistical likelihood of extreme events producing an impact upon groundwater. The alteratives you imply, such as the use of a compartmental model without considering soil variability, or the use of a purely stochastic model which usually does not directly represent important physico-chemical-biological processes, are approaches that probably will be unsatisfactory.

D. J. Greenwood (*AFRC Institute of Horticultural Research, Wellesbourne, Warwick, CV35 9EF, U.K.*). I wonder whether under certain circumstances an entirely different approach to modelling leaching might not be worthwhile? Could, for instance, the simple computer simulation programs be useful that have been found to give excellent descriptions of diverse physical phenomena, including fingering, when water is pumped to displace oil in sand, of diffusion-limited aggregation and of fractals in general? I believe all these phenomena can be simulated roughly in the following way. A particle is placed at a fixed position. Then another particle is released some distance away and allowed to take one random step after another until it approaches within the particle diameter of the first particle, where it sticks. Another particle is then released and moves randomly until it too sticks. Perhaps this approach could mimic the flow instability and variability that sometimes occurs in soil.

R. J. Wagenet. The suggested approach would certainly be possible as a means of describing solute movement in soil. However, it would suffer some of the same shortcomings as were experienced in early applications of chromatographic theory to soil leaching processes. That is, under the current state of the art, the application of purely statistical (or probabilistic) techniques does not result in the development of a comprehensive mechanistic description of multiple interacting processes in soil. This prevents easy extrapolation of the results of one study to a new situation; the incorporation into such models of the basic process information gained in the laboratory for the purpose of describing field leaching; and a straightforward use of models as a method of interpreting or estimating the magnitude and intensity of processes in the field. Therefore, as the suggested approach is possible, I believe it would probably be rather intellectually unsatisfying.

D. J. Greenwood (*AFRC Institute of Horticultural Research, Wellesbourne, Warwick, CV35 9EF, U.K.*). The modelling approaches to leaching that have been used

in western Europe seem to be based on capacity-type models, whereas those in the U.S.A. are almost entirely derived from Darcy's law of water flow. I noted that the saturated hydraulic conductivities to which you referred were very low by our standards. Could it be that the very different approaches used in the two continents result at least in part from the very different rates at which water percolates through the soils?

R. J. WAGENET. I believe the reason for differences in approach to quantifying leaching is because of the differences in the type of scientists in Europe and the U.S. who have focused on leaching. In the U.S., much of the leaching theory evolved from soil physicists who initially treated irrigation and inorganic salt transport in relatively deep, well-drained soils. Application of basic physics was their forte, and hence the focus on potential energy gradients, hydraulic conductivity and rate equations. In Europe, soil leaching has been most often modelled in relatively shallow soils by individuals who are primarily more interested in the biology and chemistry of the system (e.g. nitrogen cycling, pesticide degradation). Relatively few individuals, usually not soil physicists, have focused on chemical leaching. The description of leaching has therefore often been simplified to layer-type, capacity-driven models. I do not think that differences in soil hydraulic properties was a main reason for the evolution of these different approaches, but it is true that the resulting capacity-based models widely used in Europe are in fact very useful in many parts of the world where there are shallow soils that drain rapidly.