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MINI REVIEW

Predicting Pesticide Transport in Soil

G. SINGH, W. F. SPENCER[1], M. TH. VAN GENUCHTEN[2] and R. S. KOOKANA[3]
Department of Soil and Environmental Science,
University of California, Riverside, CA 92521, USA

Physical and chemical non-equilibrium processes affecting the fate and transport of surface-applied or soil-incorporated pesticides in the unsaturated (Vadose) zone between the soil surface and the groundwater table are discussed from an environmental pollution point of view. A review is also given of alternative mathematical models for predicting the movement of these chemicals under a given set of experimental conditions. While predictive models provide important tools in both research and management, comprehensive field data sets on pesticide transport and volatilization remain needed to accurately assess and improve the performance of these models. Improved technologies for measuring pesticide transport and degradation processes in heterogeneous field soil are also needed.

Surface-applied or soil-incorporated pesticides and other agricultural chemicals, after entering the agriculture system, may be translocated into plants, volatilized into the atmosphere, leached downward below the root zone, sorbed onto soil constituents, transported while being adsorbed on soil particles, or degraded to nontoxic molecules. They also may affect the next crop, as well as non-target species. The transport of pesticides in soil, and their rate of disappearance from soil, is of considerable importance, yet so complex that the composite behaviour of pesticides in the sub-surface is almost impossible to determine accurately. Although individual modes of disappearance have been extensively studies in isolation, it is of particular importance to develop predictive capabilities of their overall behaviour. This may be done with the help of mathematical models which consider the basic physico-chemical properties of a soil and the pesticide, along with pertinent micro- meteorological parameters. This paper gives a brief account of the potential use of models for predicting pesticide transport in the sub-surface.

The various transport phenomena, viz., leaching in soil, volatilization to the atmosphere and runoff to untreated fields, are important factors determining both the efficacy of a pesticide at the target site and its potential contamination of nearby surface and groundwater. Initial studies of the relative mobility of pesticides in soil involved mostly soil thin layer chromatography [1, 2] and displacement experiments through relatively short repacked soil column [3-7]. While such studies were helpful in understanding the underlying transport phenomena, they did not always provide results useful for field conditions. On the

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[1] USDA, ARS, Soils Dept., Univ. of California, Riverside, CA 92521, USA

[2] U. S. Salinity laboratory, USDA, 4500 Glenwood Dr., Riverside, CA 92521, USA

[3] CRC for Soil and Land Management, Waite Road, Urbane, SA 5064, Australia.

other hand, there are also a large number of experimental studies on the movement of pesticides which are of limited value mainly because of the site specificity of these experiments. Solute transport models can provide a better understanding of pesticide-soil interactions determining pesticide mobility. The complex phenomenon of pesticide transport in the sub-surface is made easier to understand by using computers which are capable of handling large amounts of data. Also, computer models provide a tool for integrating the many simultaneous and often interactive physical, chemical and biological processes know to affect pesticide behaviour.

A large number of mathematical models for the transport of non-reactive and reactive solutes (like pesticides) under steady and variably-saturated flow conditions have been developed over the past few decades. Recent reviews of these models are given by different scientists [8-14]. Most process-based models employ the classical convection-dispersion equation, or various modifications thereof. Mathematical models based on stochastic representations of the flow and transport properties in field soil have also been developed [15-17]. While useful for describing transport processes in naturally heterogeneous field soil profiles, most stochastic approaches currently in use provide limited understanding of the underlying physical and chemical mechanisms affecting pesticides behaviour in soils. Considerably more research in this area should be expected in the immediate future. This paper is limited to a discussion of alternative deterministic approaches of predicting pesticide transport in soils.

TRANSPORT MODELS BASED ON THE CONVECTION-DISPERSION EQUATION

According to miscible displacement theory, the total mass flux of solute is the result of the combined effects of diffusion, hydrodynamic dispersion and convective transport with flowing water. Mass of solute transported by convection is given by the product of the fluid flux density, q, and the concentration of the solute, C, while the mass of solute transported by diffusion through the bulk soil is governed by Fick's law. Macroscopically, hydrodynamic dispersion is thought to act in the same way as diffusion.

Mass conservation of a substance in a one-dimensional soil system is given by the continuity equation as follows

$$\frac{\partial C_t}{\partial t} = -\frac{\partial J_s}{\partial z} - R_t \qquad (1)$$

where C_t is the total concentration per unit bulk soil (kg m^{-3}), J_s is the total mass flux of solute per unit cross-sectional area (kg m^{-2} d^{-1}), z is distance (m) and R_t is the rate of transformation or degradation of the solute in soil (kg m^{-3} d^{-1}).

Representing the total mass flux by convection and diffusion plus dispersion, and considering sorption of the pesticide onto the soil solid phase, Eq. (1) takes the form

$$\frac{\partial(\theta C + \rho S)}{\partial t} = \frac{\partial}{\partial z}[\theta D(v, \theta)\frac{\partial C}{\partial z}] - \frac{\partial(qc)}{\partial z} - R_t \qquad (2)$$

where the total concentration (C_t) is partitioned into a liquid phase concentration (C) and a soil phase concentration (S) as follows

$$C_t = \theta C + \rho S \qquad (3)$$

in which θ is the volumetric water content, ρ is the dry bulk density of the soil system (kg m^{-3}), and S is the sorbed solute concentration (kg Mg^{-1}). Also v in Eq. (2) is the average pore- water velocity (m d^{-1}), approximated by q/θ, while D represents the combined effects of diffusion and dispersion. For short-term experiments which result in residence times of a solute in soil on the order of hours, and for persistent solutes, the term representing transformations can be neglected. Equation (2) now becomes

$$\frac{\partial(\theta C+\rho S)}{\partial t}=\frac{\partial}{\partial z}[\theta D(v,\theta)\frac{\partial C}{\partial z}]-\frac{\partial(qc)}{\partial z} \quad (4)$$

For transport during steady-state water flows in a homogeneous soil such that the pore water velocity and the water content do not change versus time and distance (e.g., a repacked laboratory soil column), Eq. (4) further reduces to

$$\frac{\partial C}{\partial t}+\frac{\rho}{\theta}\frac{\partial S}{\partial t}=D\frac{\partial^2 C}{\partial z^2}-v\frac{\partial c}{\partial z} \quad (5)$$

To solve Eq. (5) for given initial and boundary conditions, a sorption isotherm specifying the functional relationships between the concentrations of solute in the solution (C) and the solid phase (S) is required. When the sorption reaction is instantaneous, equilibrium between the solution and solid phase concentrations exists, in which case the relationship between the two concentrations is given immediately by the sorption isotherm. The transport process may then be described with an equilibrium model. However, when the sorption process is time-dependent, a suitable rate function describing the time dependency of the sorption process needs to be incorporated into the solute transport model.

TRANSPORT MODELS BASED ON THE NATURE OF THE SORPTION PROCESS

Solute transport models either assume sorption equilibrium during flow, or describe the presumed time-dependent sorption process with the help of one or more rate laws. Although equilibrium models have often been found unsatisfactory in predicting pesticide transport, they still can be very useful by providing comparative evaluations of pesticide mobility in the subsurface. Equilibrium models are also helpful for management purposes[10].

General numerical models based on the classical Richards equation for unsaturated water flow and the Fickian based convection- dispersion equation for solute transport have remained the most popular, especially in research. However, some simpler formulations based on equilibrium sorption and first-order degradation can also provide valuable information about the potential behaviour and mobility of pesticides in soil [18-20]. In this paper we discuss several types of models currently in use. Models based on the nature of the reaction processes may be conveniently grouped into equilibrium and non-equilibrium transport models.

TRANSPORT MODELS WITH EQUILIBRIUM SORPTION

Equilibrium models assume instantaneous sorption such that the sorbed phase concentration is always uniquely related to the solution phase concentration, while ignoring the effects of a stagnant phase[21]. Equilibrium models have been found acceptable in describing sorption behaviour of solutes in many cases[22,23].

For a linear sorption isotherm ($S=K\,C$), Eq. (5) can be restated as

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} \qquad (6)$$

where

$$R = 1 + \frac{\rho K}{\theta} \qquad (7)$$

The parameter R in Eq. (7) is often referred to as the retardation factor[24]. The distribution or soil water partitioning coefficient K in Eq. (7) depends strongly on the soil organic carbon fraction[25], and is usually measured using the batch equilibration method.

Defining $D^* = D/R$ and $v^* = v/R$, Eq. [6] yields

$$\frac{\partial C}{\partial t} = D^*\frac{\partial^2 C}{\partial z^2} - v^*\frac{\partial c}{\partial z} \qquad (8)$$

For a non-linear sorption isotherm ($S=KC^n$), the retardation function R(C) becomes concentration dependent and follows

$$R = 1 + \frac{\rho n K C^{n-1}}{\theta} \qquad (9)$$

Models described by Eqs. (6) through (9) assume that the sorption process is reversible and single-valued. In reality, the isotherms are not always single-valued, but may exhibit hysteresis[26-28]. Thus, parameters representing the adsorption and desorption isotherms may be different, and if so, should be incorporated in Eq. (8).

TRANSPORT MODELS WITH NON-EQUILIBRIUM SORPTION

Non-equilibrium models are those which use one-site and two-site type kinetic formulations for the sorption process. Closely related to the two-site model is the two-region (mobile-immobile) non-equilibrium model which assumes that physical rather than chemical processes are causing apparent non-equilibrium during pesticide transport in soils. While different in concept, the two-region physical process models are mathematically very similar to the two-site chemical-process models, and hence will be discussed within the same framework as the two-site models.

One-site kinetic models. One-site kinetic non-equilibrium models assume that the sorption reactions on all sites in the soil are controlled by a single kinetic rate law[29]. A first-order reversible kinetic equation has been used by many scientists[2,27,29]. Assuming a linear sorption isotherm, this kinetic equation is given by

$$\frac{\partial S}{\partial t} = \alpha\,(KC - S) \qquad (10)$$

where α is a kinetic rate coefficient. For equilibrium sorption when $\alpha \to \infty$, the equation reduces to the previous equilibrium relationship, i.e.,

$$S = KC \qquad (11)$$

Equation (10) can be rewritten in the form

$$\frac{\partial S}{\partial t} = k_a C - k_d S \qquad (12)$$

in which k_a and k_d are the forward and backward rate coefficients, respectively, Note from Eqs. (10) and (12) $K=k_a/k_d$, and $\alpha = k_d$.

Non-equilibrium models incorporating the one-site kinetic sorption equation have generally not resulted in accurate descriptions of pesticide transport data in soils [8, 27, 30], except possibly at relatively low flow rates when the sorption process is close to equilibrium anyway. This failure of the one- site model has led researchers to introduce the concept of two-site chemical-kinetic [31, 32] and two-region (mobile-immobile) type physical non-equilibrium models. The two-site and two-region models have been shown to more accurately describe solute movement in soil [30, 33-36]. While two-site chemical-process models assume that non-equilibriurn is a consequence of the time-dependent nature of the actual sorption reactions at soil surfaces, two-region physical-process models consider the sorption reactions to be instantaneous. Instead of invoking a kinetic rate process, physical non-equilibrium models assume that sorption is governed by the rate of physical transport of the pesticide to and from the reaction sites (e. g., by diffusion through immobile water).

Two-site chemical-process models: Two-site chemical non- equilibrium models proposed by Selim et al.[31] and Cameron and Klute[32] assume the presence of two types of sites (type-1 and type-2) for sorption reactions in soils. While type-1 sites are assumed to achieve sorption instantaneously and hence are equilibrium sites, sorption on type-2 sites is described with a first-order reversible kinetic reaction. The sites can be different in terms of their chemical composition (organic and inorganic surfaces), and/or their accessibility to solutes. Sites where the sorption is diffusion-controlled may be lumped with the type-2 sites[32].

At equilibrium, sorption on both sites is described by linear sorption isotherms, i.e.,

$$S_1 = fKC \tag{13}$$

$$S_2 = (1-f)\,KC \tag{14}$$

$$S = S_1 + S_2 \tag{15}$$

where the subscripts 1 and 2 refer to type-1 equilibrium and type-2 non-equilibrium sorption sites, respectively; and where is the fraction of sites occupied by the type-1. Since type-1 sites are always in equilibrium, Eq. (13) may be differentiated with respect to time to give

$$\frac{\partial S_1}{\partial t} = fK\frac{\partial C_1}{\partial t} \tag{16}$$

However, sorption on type-2 sites is governed by the following linear and reversible first-order kinetic reaction.

$$\frac{\partial S_2}{\partial t} = \alpha\,[\,(1-f)\,KC - S_2] \tag{17}$$

Using Eqs. (13) through (16), transport equation (5) now takes the form

$$(1 + \frac{\rho f K}{\theta})\,\frac{\partial C}{\partial t} + \frac{\rho}{\theta}\,\frac{\partial S_2}{\partial t} = D\,\frac{\partial^2 C}{\partial z^2} - v\,\frac{\partial c}{\partial z} \tag{18}$$

which must be solved in conjugation with rate equation (17) for the type-2 sites. Transport equations for the two-site kinetic model assuming a nonlinear sorption isotherm can be similarly developed.

Two-region physical process model. These types of models assume that the liquid phase in the soil can be divided into 'mobile' (macroporosity) and 'immobile' (microporosity) regions[21]. Solute transport in the mobile region is assumed to take place through convection and hydrodynamic dispersion as before, while transport in the immobile regions is considered to be controlled diffusion through the immobile liquid. The rate of diffusion depends on the concentration gradient between the two regions. Adsorption and desorption in both regions are assumed to be instantaneous and linear. The diffusion-controlled physical non-equilibrium processes are applicable to both sorbing and non-sorbing solutes.

According to this model, the transport equations for linear sorption can be stated as

$$\phi R_1 \frac{\partial C_1}{\partial t} + (1-\phi) R_2 \frac{\partial C_2}{\partial t} = \phi D \frac{\partial^2 C}{\partial z^2} - \phi v \frac{\partial c}{\partial z} \tag{19}$$

$$\theta_2 R_2 \frac{\partial C_2}{\partial t} = \alpha \, (C_1 - C_2) \tag{20}$$

$$R_1 = 1 + \frac{\rho f_1 K}{\theta_1} \tag{21}$$

$$R_2 = 1 + \frac{\rho \, (1 - f_1) \, K}{\theta_2} \tag{22}$$

$$\phi = \frac{\theta_1}{\theta} ; \qquad \theta = \theta_1 + \theta_2 \tag{23}$$

$$v_1 = \frac{v}{\phi} = \frac{\grave{q}}{\theta_1} \tag{24}$$

where the subscripts 1 and 2 denote mobile and immobile regions, respectively; α is a mass transfer coefficient for solute exchange between the mobile and immobile regions; ϕ is fraction of soil water in the mobile region, and f_1 is the fraction of sorption sites in the mobile region.

Despite the many assumptions, the two-site and two-region models appear to be promising for describing the transport of a variety of reactive as well as non reactive solutes[28, 30, 35-40]

TRANSPORT MODELS INCORPORATING DEGRADATION OF PESTICIDES

In addition to the excellent work of Allan Walker[41] on pesticide degradation modelling, a limited number of workers have tried to define this term theoretically[9, 42-44]. Also, some of the models predicting leaching have incorporated terms accounting for degradation[12, 44, 45]. The validity of these models under field situations is yet to be established.

LIMITATIONS OF EXISTING MODELS AND AREAS OF FUTURE RESEARCH

A major constraint in the development of the different transport models discussed in this overview is their validation on the basis of field observations. Except for a few studies[46-48], reliable information on pesticide leaching in field situations is relatively scarce.

Also, most current models describing the transport and fate of organic chemicals in soil do not account for volatilization[49], which is an important and independent process affecting pesticide behaviour in agricultural soils. Glotfelty et al.[50], Spencer et al.[51], Taylor and Spencer[52] and several others have shown significant contribution of volatilization to pesticide disappearance from soils. Volatilization has been given due representation in a screening/behaviour assessment model described by Jury et al.[20]. This assessment model has provided valuable approximations of pesticide behaviour in soils. Attempts have also been made to account for volatilization in the more general LEACHM and PRZM numerical models while studying the soil fumigant EDB[53] and DBCP[48] during unsaturated flow. The results have only been marginally successful. Additional work is especially needed to accurately model near-soil surface processes affecting volatilization, and to gather comprehensive laboratory and field data sets for validating combined volatilization and transport models. Potential volatilization of organic chemicals can be estimated through laboratory experiments[51-54-56], wetted wall column techniques[57], closed tube method[58], or through such indirect techniques as QSAR[59]. Still, field level quantification of volatilization processes remains essential for most modelling exercises[60].

CONCLUSIONS

The above discussion indicates that many models and modelling approaches are currently available to predict pesticide problems in the sub-surface environment. The deterministic models have provided valuable conceptual theories of solute transport mechanisms, although the applicability of these models to naturally variable field conditions has been questioned. Nevertheless, deterministic models remain helpful tools in both research and management. By comparison, stochastic approaches are useful for estimating solute transport from heterogeneous field soil. The stochastic and conceptual approaches eventually must be combined into a more unified theory to effectively deal with field-scale transport processes. Whatever modelling approach is followed, carefully executed field experiments are needed to determine their validity at the field-scale. Good experimental field data may actually become the critical factor for determining the accuracy of current methods. Novel instrumental methods and technologies for measurement of the different transport parameters and processes are also required to keep pace with our understanding of complex field situations.

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