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A Field Test of Root Zone Water Quality Model—Pesticide and Bromide Behavior

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Abstract: The Root Zone Water Quality Model (RZWQM) is a process-based model developed recently by USDA-ARS scientists. The model integrates physical, chemical and biological processes to simulate the fate and movement of water and agrochemicals over and through the root zone at a representative point in a field with various management practices. The model was evaluated using field data for the movement of water and bromide, and the transformation and transport of cyanazine and metribuzin in the soil profile. The model reasonably simulated soil water and bromide movement. Pesticide persistence was predicted reasonably well using a two-site sorption model that assumes a rate-limited (i.e. long-term) adsorption–desorption process with the additional assumption of negligible degradation of inter-aggregate adsorbed pesticides.

Key words: modelling, cranazine, metribuzin, soil water

1 INTRODUCTION

The desire for increased profit and the need to minimize adverse environmental consequences require more intensive management of the soil, water and agrochemicals in agricultural systems. Models such as Root Zone Water Quality Model (RZWQM, Agricultural Research Service, GPSR Technical Report No. 2)[1] which describe mathematically the important processes in an agricultural production system can be used to: (1) quickly and efficiently evaluate the relative effects of alternative management practices on water quantity and quality, (2) aid in identifying knowledge gaps for future research and (3) facilitate transfer of management technologies to other sites with limited expense and timely measurements. Assessment of RZWQM performance under a wide range of soil, crop and climatic conditions and management practices is needed to gauge model usefulness.

The main objective of this study was to evaluate the ability of RZWQM to simulate the movement and distribution of bromide and dissipation and transport of soil-adsorbed pesticides in the top-soil profile. Presently, the source code of the model has been verified and the model components are being tested extensively against experimental data from different sources. Herein, data collected from a field study in the Netherlands involving bromide and two herbicides were used with the above objective.

2 EXPERIMENTAL

2.1 Root Zone Water Quality Model (RZWQM)

RZWQM is a process-based simulation model of an agricultural cropping system. Specifically, it integrates important physical, biological and chemical processes to simulate the fate and movement of water, nutrients and pesticides in the soil-plant-atmosphere environment, and the effects of agricultural management practices on soil water and solute movement that may cause surface and ground water quality problems. A brief description of the model is given below. Interested readers may refer to RZWQM Technical Documentation (GPSR Technical Report No. 2)[1] and Ahuja *et al.*[2] for more detailed information on infiltration, water and chemical transport, and other processes.

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Physical processes simulate soil matrix infiltration, macropore flow (not considered herein), surface run-off, heat flow, evapotranspiration and soil water redistribution. Water infiltration in a homogeneous or layered soil is calculated based on the Green–Ampt equation. The soil profile is divided into 1-cm depth increments down to the bottom of the profile. Excess rainfall or overland flow is calculated as the difference between the rainfall and infiltration in each computational time step. Chemical transport within the soil matrix is calculated using a sequential partial displacement and mixing approach in 1-cm increments during infiltration. For chemical transport, the soil matrix porosity is divided into meso- and micropore regions. Initially and during the first wetting of a 1-cm depth increment, soil water and chemical in meso- and micropores are assumed in equilibrium. During the successive infiltration steps, the displacement of solution in the saturated soil layers occurs only in mesopore regions in the manner of piston displacement, but diffusion is allowed between meso- and micropore regions. Mixing is also allowed to occur within all mesopores of an increment after each displacement step. For a soil-adsorbed chemical, such as a pesticide, either a linear isotherm and instantaneous equilibrium adsorption or a first-order reversible kinetic adsorption-desorption is assumed to occur between the solution and adsorbed phases in both meso- and micropore regions. At the end of an infiltration event, the meso- and micropore regions are allowed to equilibrate.

Chemicals in the top two 1-cm soil layers are subject to non-uniform mixing by raindrops during precipitation and transfer to surface runoff. The degree of mixing (B) between rainwater and soil solution is assumed to be complete (equal to unity) at the soil surface ($z = 0$) and to decrease with depth as described by Ahuja:[3]

$$B = e^{-bz} \tag{1}$$

where b is a parameter that depends somewhat on the soil type, surface roughness and cover conditions, and z is depth below the soil surface. The value of b was found to be close to 4·3 for a number of soils and conditions when integrated over 1-cm increments.[3]

Pesticide processes simulate transformation and metabolism of a pesticide in different compartments of the soil-water-plant environment. Pesticides applied on plant and plant residues are subject to degradation and wash-off. Pesticide degradation in the soil matrix is generally assumed to follow the first order dissipation equation:

$$\frac{dC}{dt} = -kC \tag{2}$$

where C is pesticide concentration, k is a rate constant, and t is the time elapsed since pesticide application. This equation generally applies to initial degradation, but often not to later stages of degradation; the rate constant k may decrease in later stages. RZWQM provides four options for pesticide degradation modeling. These include: lumped dissipation, consisting of one-compartment model (i.e. eqn (2)) and two-compartment model (two k values); individual dissipation; and the daughter product(s) dissipation. The effects of temperature, rainfall, relative humidity, wind speed, pesticide chemical composition, soil physical and hydraulic properties, plant leaf and surface residue characteristics and soil surface water and oxygen content on pesticide dissipation are quantitatively described (Nash and Ma[4]).

Two methods are allowed for simulating pesticide sorption processes: (1) equilibrium sorption, and (2) two-site (kinetic) sorption. Equilibrium sorption is assumed linear and instantaneous, described by:

$$C_s = K_d C_l \tag{3}$$

where C_s and C_l are pesticide concentration in the solid and solution phases, respectively, and K_d is the overall pesticide equilibrium sorption constant. The K_d parameter is estimated from a pesticide sorption constant on soil organic carbon (K_{oc}) by:

$$K_d = K_{oc} f_{oc} \tag{4}$$

where f_{oc} is the fractional soil organic carbon content. Equation (4) implicitly assumes that pesticide sorption on other soil constituents of silt, sand and clay is negligible.

The two-site sorption model is based on the assumption that the adsorbed pesticide can be attributed to two different solid-phase sites. The adsorbed pesticide on one site is assumed to be continuously in equilibrium with pesticide in solution and thus described by eqn (3). Pesticide adsorption on the second site (i.e. the kinetic sites) is, however, a rate-limited process. For instance, it may take weeks or months to reach equilibrium depending upon the pesticide and soil properties. In other words, pesticide sorbed on kinetic sites (mainly represented by inter-aggregate porosity) is assumed to be strongly held. The kinetic process describes the long-term behavior of the sorbed pesticide and is different from the kinetic process encountered in soil column leaching experiments in which the whole processes may only last a few hours. This process may better be described by a kinetic equation as follows:

$$\frac{dC_a}{dt} = RK_2(EK_2 C_l - C_a) \tag{5}$$

where C_a is pesticide concentration on kinetic sorption sites, EK_2 is equilibrium partition coefficient and RK_2 is adsorption/desorption kinetic rate constant.

2.2 Field study

The field study was conducted in Creil in the North-East Polder of the former Zuyder Zee in the Netherlands. An experimental plot (12 × 30 m) of bare soil was first plowed and slightly tilled with a cultivator harrow, and then tilled manually with a harrow before pesticide and bromide applications. Two herbicides, cyanazine [2-(4-chloro-6-ethylamino-1,3,5-triazin-2-ylamino-2-methylpropionitrile; 'Bladex' 500 g kg^{-1} WP, Shell] and metribuzin (4-amino-6-*tert*-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-5-one; 'Sencor' 700 g kg^{-1} WP, Bayer) and bromide (sodium bromide solution) were sprayed on at rates of 164, 99 and 9900 mg AI m^{-2}, respectively. Soil profile samples were taken randomly from five locations on 1, 14, 34, 56 and 121 days after herbicide application. The maximum depth of soil sampling was 0·2 m for herbicide, and 0·4 m for bromide, based on the previous year's field experiments.

There were drain lines at 0·9 m depth in the field, with the water table remaining at about 1·2 m below the soil surface. The soil was classified as a loamy sand with an organic matter content of 1·8% and clay and silt contents of 30 and 20%, respectively. The soil pH was 7·4 and soil bulk density increased from 1·2 g cm^{-3} at the surface to 1·4 g cm^{-3} at 0·1 m and lower depths.

2.3 Laboratory experiments

Laboratory experiments were used to determine some of the pesticide parameters. These included pesticide short-term sorption isotherms, kinetic sorption and long-term kinetic sorption experiments. All laboratory experiments were conducted at 19°C using soil samples collected from the field plot the day prior to herbicide and bromide applications. A detailed description of the experiments is given by Boesten *et al.*[5]

2.4 Model parameter estimation

Most of the model input parameter values were obtained from field and laboratory experiments. The degradation half-life values for cyanazine and metribuzin were found to be 21 and 22 days, respectively. They were determined by fitting field-measured degradation data with the first-order decay equation (eqn (2)).

The two-site sorption model requires three input parameters to describe pesticide adsorption-desorption processes: an instantaneous equilibrium adsorption rate constant for the equilibrium sites, equilibrium partition coefficient (EK_2) and adsorption/desorption kinetic rate constant (RK_2). The former pesticide equilibrium adsorption rate constant was estimated from the short-term sorption isotherms (24 h) experiment at a reference concentration that corresponds to the average field measured pesticide concentration. The constants EK_2 and RK_2 were estimated from long-term laboratory sorption experiments using a curve-fitting technique.[5] The estimated values were $0{\cdot}2 \times 10^3$ and $0{\cdot}07 \times 10^3$ m^3 kg^{-1} for EK_2, and 0·02 and 0·01 day^{-1} for RK_2 for cyanazine and metribuzin, respectively. The pesticide diffusion coefficient in soil water for each compound was estimated from the pesticide diffusion coefficient in free water in conjunction with soil water content, soil bulk density and pesticide distribution constant.[4] Pesticide diffusion coefficients in free water were estimated using the method of Othmer and Thakar, as described by Reid and Sherwood[6] being 0·36 cm^2 day^{-1} for cyanazine and 0·39 cm^2 day^{-1} for metribuzin. Bromide was assumed to be conservative with no solid-phase interactions; its diffusion coefficient was 1·30 cm^2 day^{-1}.

RZWQM provides the user with various optional approaches as how to estimate unknown soil hydraulic parameters. One method, as utilized in this study, is based on the extended similar-media scaling technique[7] where the water content-matric suction relation is first estimated for each soil horizon, given bulk density, 1/3 or 1/10 bar water content and fractions of soil constituents. In this study, we used soil water content at 0·08 bar in place of unknown 1/10 bar values. RZWQM is capable of estimating soil evaporation using a Penman-Monteith-type evaporation model, given known daily climatic data. As utilized in this study, RZWQM can also estimate bare soil evaporation using measured pan evaporation data.

3 RESULTS

3.1 Soil water and bromide distributions

Figure 1 gives cumulative rainfall during the experimental period. Figure 2 shows two typical examples of the measured and simulated soil water distributions at 14

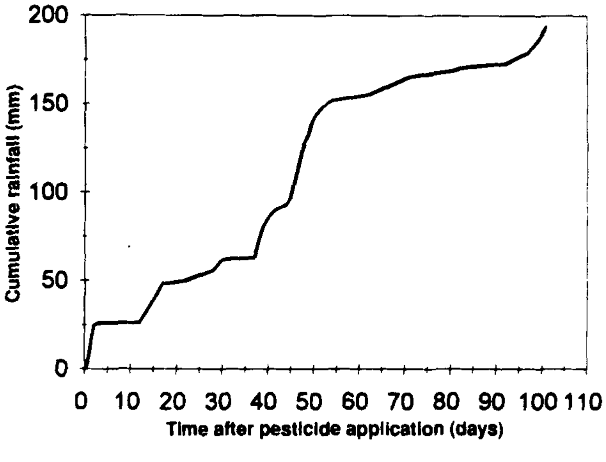

Fig. 1. Measured cumulative rainfall during the study period.

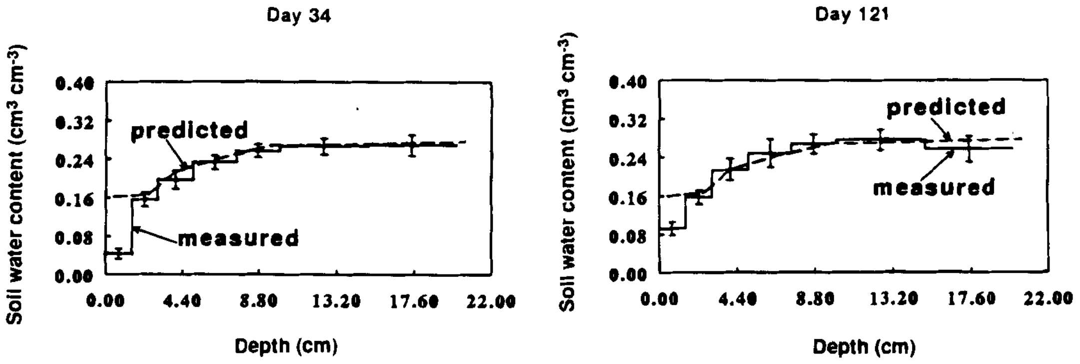

Fig. 2. Measured and predicted soil water distributions (with error bars) for 34 and 121 days after treatment.

and 121 days. The simulated curves match well with those measured except at the soil surface (0–3 cm). Comparisons of soil water distribution on other dates are similar. The simulated and measured bromide distributions (Fig. 3) also show reasonable agreements on most days. Except on 14 and 34 days after bromide application, the model over-predicted bromide concentration at the soil surface and thus under-estimated con-

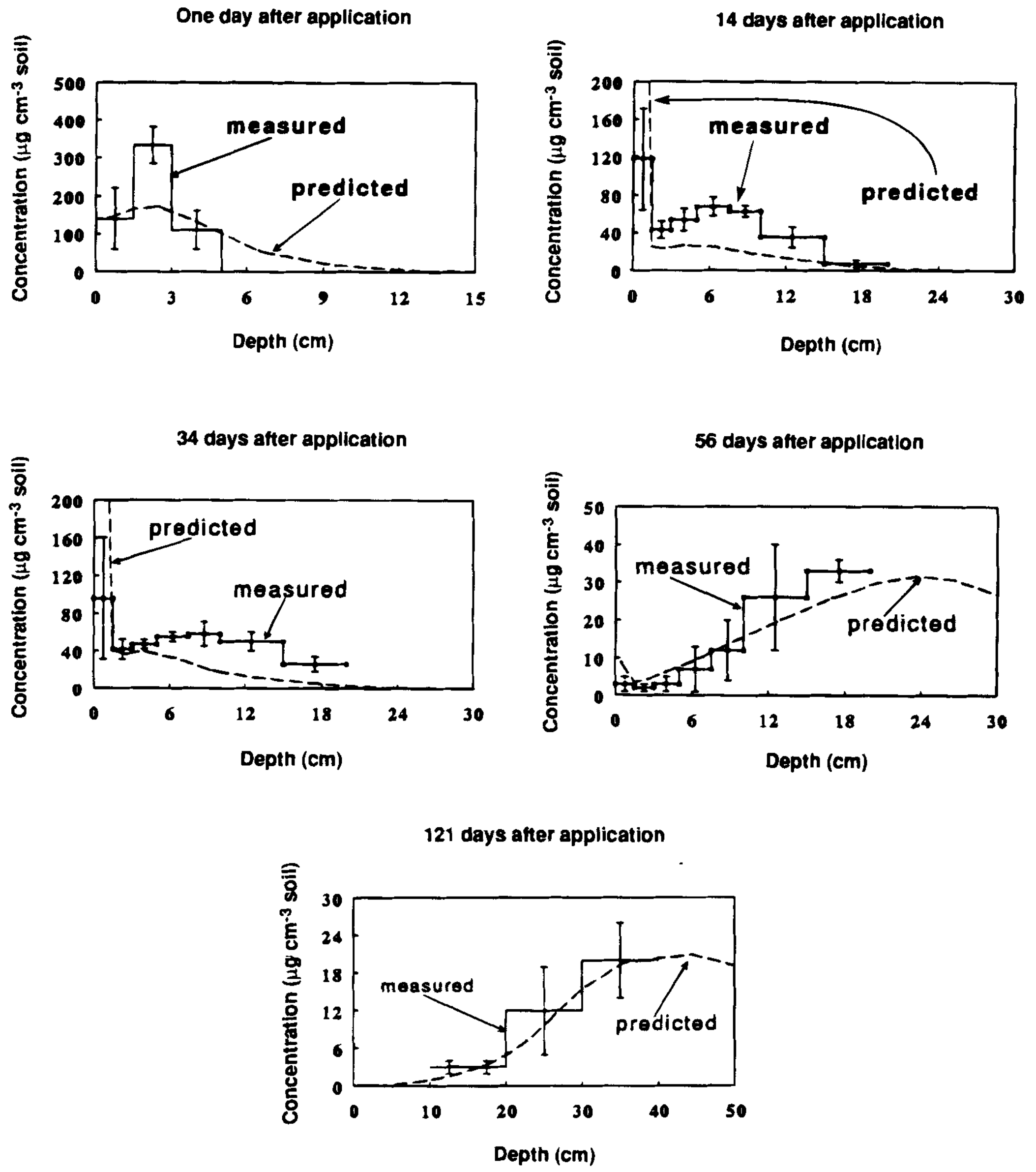

Fig. 3. Measured (with error bars) and predicted soil profile bromide concentrations for all measurement days.

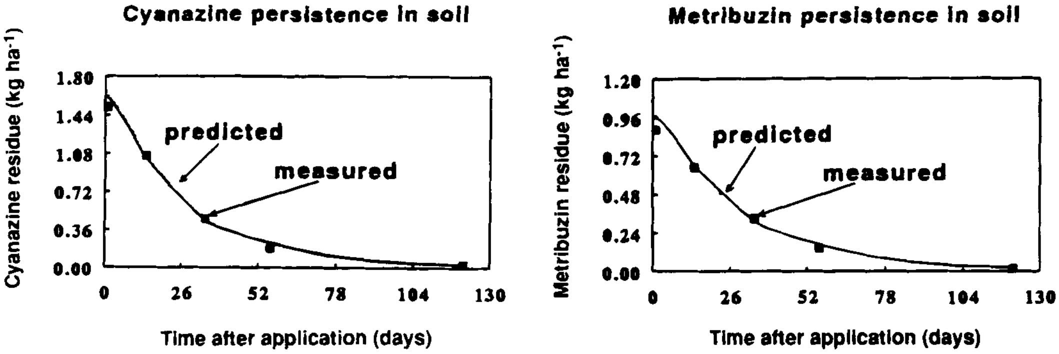

Fig. 4. Measured and predicted cyanazine and metribuzin persistence in the soil profile.

centrations in the lower soil layers. This is most likely caused by overprediction of actual soil water evaporation from the solution of the Richards' equation that leads to chemical movement to soil layers near to the soil surface.

3.2 Herbicide persistence in soil

Figure 4 shows the measured and the predicted cyanazine and metribuzin residues in the soil profile. In using the two-site sorption model, two assumptions

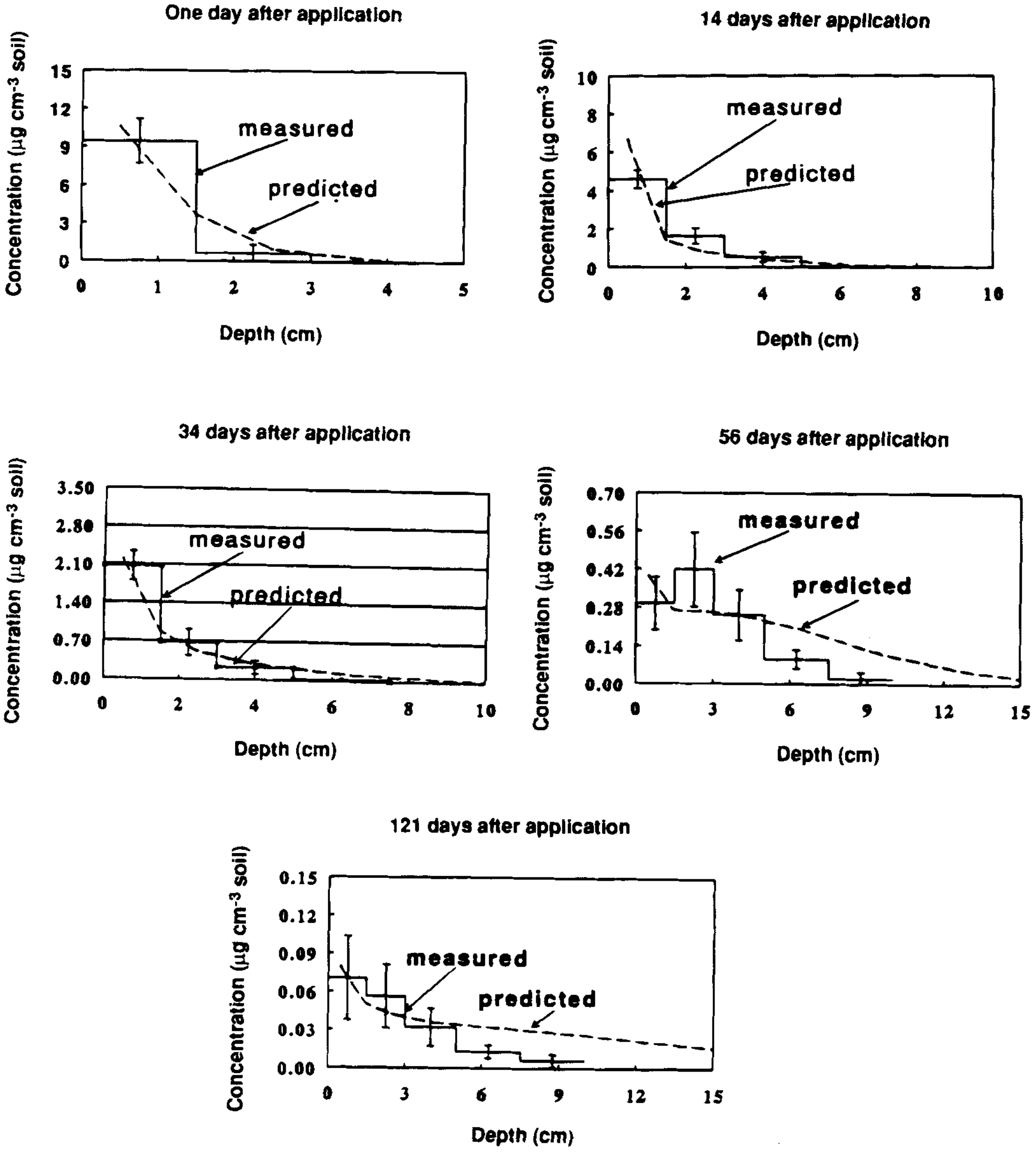

Fig. 5. Measured (with error bars) and predicted cyanazine movement in the soil profile.

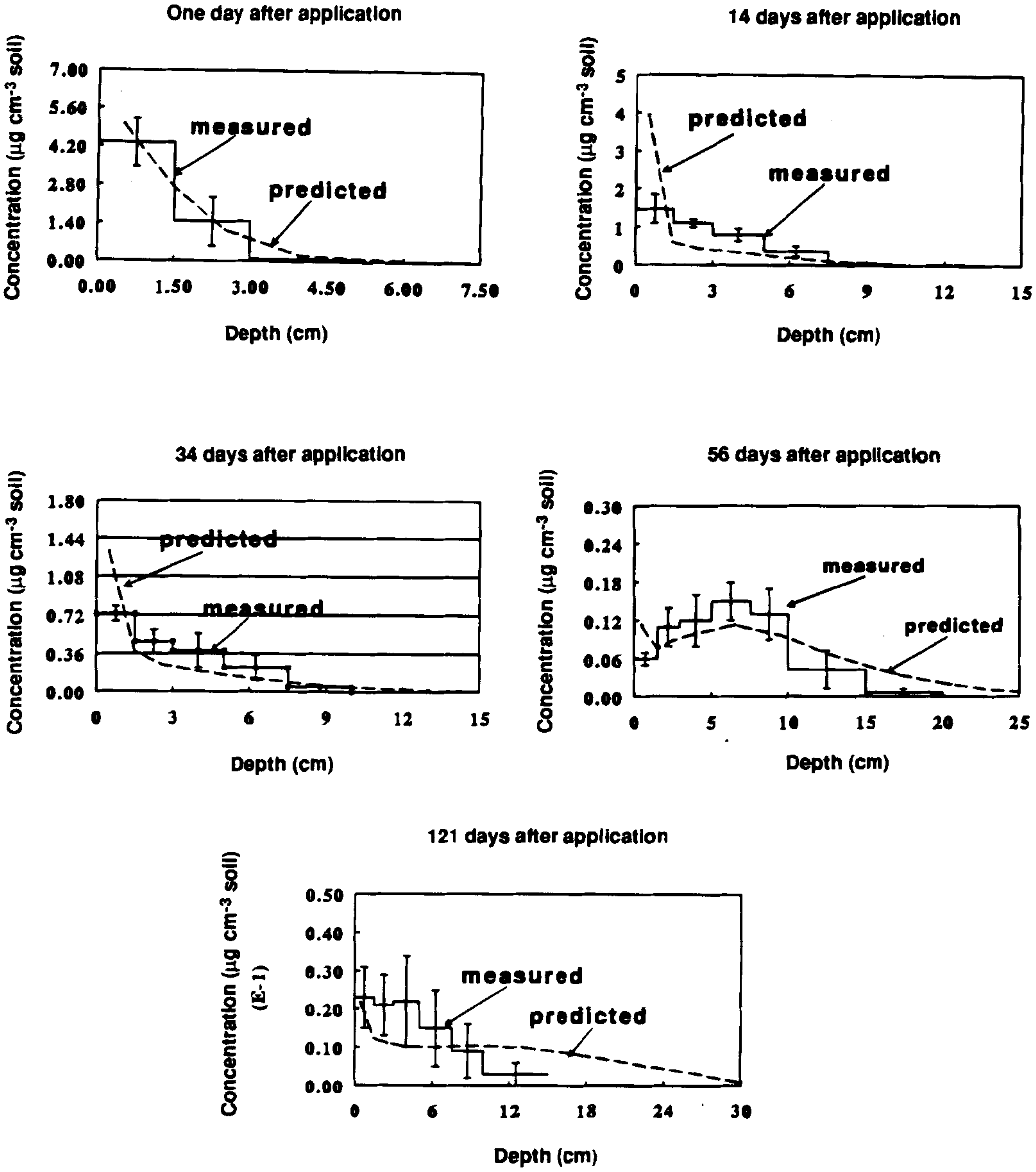

Fig. 6. Measured (with error bars) and predicted metribuzin movement in the soil profile.

were tested in simulating pesticide transformation processes. The first assumption was that pesticide sorbed on kinetic sites was transformed at the same rate as pesticide in soil solution. The model under-predicted pesticide persistence and over-predicted pesticide movement under this assumption (these are not shown herein). The second assumption was that pesticide sorbed on kinetic sites was not subject to transformation, but would desorb to soil solution controlled by RK_2. Under this assumption, both the predicted persistence and distribution of cyanazine and metribuzin were improved (given in Fig. 4), especially for the long-term period. Therefore we discarded the first assumption because it was not consistent with the observed data. We accepted the second assumption because it could describe both pesticide movement and dissipation reasonably. It seems reasonable to assume that pesticide sorbed on kinetic sites, located inside the soil aggregates, is not subject to biological degradation (usually biodegradation dominates pesticide dissipation inside the soil profile), although some chemical degradation may occur.

It is noted that the degradation rate constant was obtained from fitting field measured data. Hence, a good agreement (as shown in Fig. 4) was expected, suggesting that the persistence of these two herbicides could be well described by eqn (2)).

Figure 5 illustrates the measured and predicted distributions of cyanazine for the measurement days. The model reasonably simulated the distributions of cyanazine in the soil profile. The predicted distribution on 121 days after pesticide application indicated deeper movement than that measured. Perhaps the kinetic sorption process contributed more in determining pesticide movement. That will be discussed later.

Figure 6 shows the observed and the simulated dis-

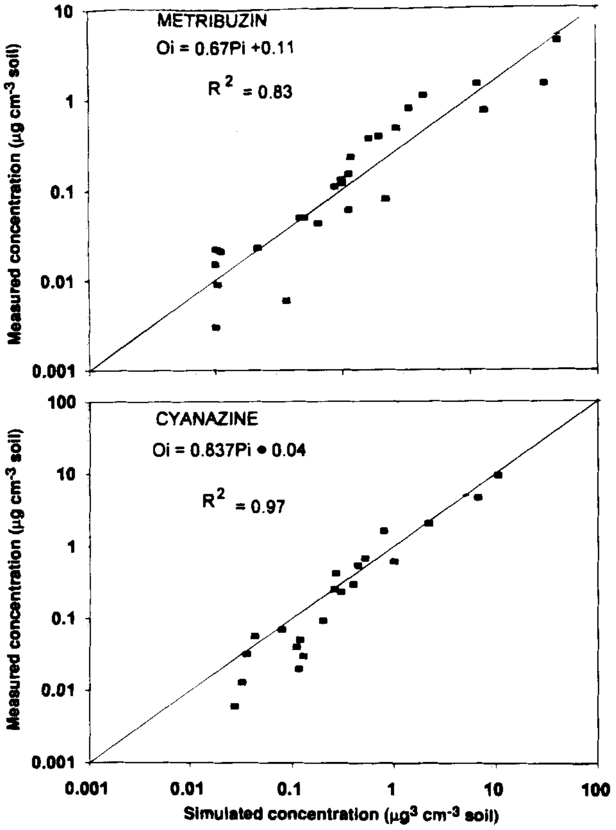

Fig. 7. Measured versus predicted cyanazine and metribuzin in the soil profile.

tributions of metribuzin for the measurement days. As for those for cyanazine, the model reasonably predicted the distributions of metribuzin in the soil profile.

To quantify the accuracy and variability of the model simulated values, we used least square linear regression fits of modelled versus predicted values as shown in Fig. 7 for all depths on all the sampling days. The line of perfect agreement (1 : 1 line) is also shown. The greater discrepancies with lower concentration between measured and predicted results were expected because the measurement errors were higher at lower concentration (close to detection limit).

4 DISCUSSION

The results presented in this report are from the application of a two-site sorption model in RZWQM. For the soil and conditions in this study, the RZWQM model is found to predict the movement of non-adsorbed bromide and adsorbed pesticides (cyanazine and metribuzin) reasonably well. Comparisons have shown that the two-site sorption model described pesticide distribution and movement in the soil profile better than that of the equilibrium adsorption model. Sensitivity analysis (not shown herein) indicated that pesticide movement and distribution were very sensitive to the second site adsorption and desorption rate constants, that is non-equilibrium sorption rate constants, especially the desorption one.

Walker[8] found that pesticide adsorptivity increased with time. Leonard and Wauchope[9] stated that '(pesticide) apparent K_d based on observed partitioning in runoff from experimental watersheds differs from the laboratory determined values and increases throughout the observation period.' Boesten[10] also found that pesticide (cyanazine and metribuzin) sorption coefficients after 121 days from application were five to 10 times higher than those derived from 24-h sorption experiments. Observations showed that a long-term sorption process existed for aged pesticide residue, emphasizing the need to introduce a long-term kinetic sorption process into pesticide fate models. The existence of long-term kinetic sorption processes for adsorbed pesticides long after pesticide application may partially account for the 'long-tail' in the measured pesticide concentration distribution, which cannot be simulated by the equilibrium sorption model. Adsorption-desorption hysteresis may also cause overprediction of adsorbed chemical movement when the model assumes adsorption-desorption singularity (as in RZWQM).

There is no *a priori* evidence whether or not sorbed pesticide is subject to degradation, since both retardation and acceleration effects have been observed on sorbed sites.[11,12] In most cases, sorption appears to reduce degradation rate. The assumption that pesticide sorbed on kinetic sites is not subject to degradation is only based on our observation and model simulation that without pesticide degradation on kinetic sites gives a better match with the field observed data for both the predicted pesticide persistence and distribution.

Further efforts should focus on the effects of pesticide non-equilibrium (kinetic) sorption processes, especially on the changes of pesticide sorptivity with time.

Problems encountered in evaluating a chemical fate model, such as RZWQM, are related to the paucity of available measured data. On most occasions, only part of the model input parameter values are available from measurements or field records (i.e. site-specific parameter values), others must be estimated from literature. As the behavior of a pesticide is strongly related to the environment in which it exists, site- and condition-specific parameters are needed to adequately predict pesticide field behavior.

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