

Lysimeter Experiment To Investigate the Potential Influence of Diffusion-Limited Sorption on Pesticide Availability for Leaching

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Pesticide leaching from soil has been shown to decrease with increasing time from application to irrigation. It is hypothesized that the availability of compounds for leaching decreases due to diffusion and sorption inside soil aggregates. Previous work showed that pesticide sorption inside soil aggregates increases significantly during the first days after application. The study presented here tested if diffusion into aggregates could explain the leaching of four aged pesticides from manually irrigated soil cores. Azoxystrobin, chlorotoluron, cyanazine, and bentazone were applied to 30 undisturbed cores (25 cm long, 23.7 cm diameter) from a clay loam soil. The soil cores were irrigated 1, 3, 7, 14, and 28 days after application. Leachate was collected and analyzed. The amount of pesticide found in leachate decreased rapidly with time from application. Pesticide losses in leachate declined 2.5–27 times faster than total residues in soil. The decline was 4–5 times faster for the more strongly sorbed pesticides (azoxystrobin, chlorotoluron, and cyanazine) than for bentazone. In previous work, we derived a model to describe sorption and diffusion of the pesticides in small aggregates from the same soil. The diffusion model was used here to describe sorption inside the large aggregates in the soil cores and extended to describe pesticide leaching by interaggregate flow. The model showed a significant decline in leaching with time from application, which supports the theory that diffusion-limited sorption in aggregates influences the availability for pesticide leaching, although it does not exclude alternative explanations for this decline. The model well described the decline in leaching for three out of four pesticides. The interaggregate transport model could, however, not account for the amount of preferential flow in the cores and underestimated the leaching of bentazone.

KEYWORDS: Lysimeter; pesticide; aging; sorption kinetics; time-dependent sorption; mobile–immobile transport; pesticide fate modeling; ORCHESTRA

INTRODUCTION

There is continued concern about the contamination of ground and surface waters by pesticides and other organic chemicals, and considerable emphasis is placed on our ability to predict the fate of these substances in the environment. Accurate predictions can only be made if all major physical, chemical, and biological processes that determine the fate are understood. A large number of studies have shown that the binding of organic compounds to soil organic material becomes stronger with increasing residence time in soil (1–4). This directly affects the availability for the transport of chemicals to ground or surface waters (5–9). In a study by Pignatello et al. (4), 75%

of freshly injected atrazine and 85% of metolachlor were eluted after 20 pore volumes passed through repacked soil columns in which microbial activity was inhibited. In contrast, only approximately 40% was eluted after 66 pore volumes when the same herbicides were aged for a period of 7 months. Renaud et al. (5) found that leaching of the moderately mobile, moderately persistent herbicides isoproturon and chlorotoluron from undisturbed lysimeters of four contrasting soil types decreased rapidly with increasing time from application to irrigation. The rapid decline of leached loads with time was faster than could be explained by degradation alone. In the same study, leaching of the weakly sorbed herbicide triasulfuron and a noninteractive bromide tracer decreased rapidly only in a clay soil. Similar results have been found at the field scale. Losses in drainflow of isoproturon from a cracking clay soil at Brimstone Farm (Oxfordshire, UK) decreased exponentially with increasing time from application to first drainflow (7). Again, the decline

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Table 1. Pesticides

compound	IUPAC name	formulated product ^a	application rate ^b (kg ha ⁻¹)	
			A	B
azoxystrobin	methyl(E)-2-[2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl]-3-methoxy acrylate	Amistar 250 g/L SC	1.05	1.04
chlorotoluron	3-(3-chloro- <i>p</i> -tolyl)-1,1-dimethylurea	Alpha 500 43.9% w/w SC	2.12	2.16
cyanazine	2-(4-chloro-6-ethylamino-1,3,5-triazin-2-ylamino)-2-methylpropionitrile	Fortrol 45.5% w/w SC	2.10	1.93
bentazone	3-isopropyl-(1 <i>H</i>)-2,1,3-benzothiadiazin-4(3 <i>H</i>)-one-2,2-dioxyde	Basagran 87% w/w SG	1.99	2.04

^a SC = suspension concentrate and SG = soluble granule. ^b Suspension A was applied to the lysimeters sampled after 1 and 3 days and suspension B to those sampled after 7, 14, and 28 days. Actual application rates were determined by analysis of the concentration of the application solution.

occurred faster than degradation. In contrast, the effect of aging on leaching of triasulfuron applied to the same soil was not significant. First-order dissipation coefficients for weighted mean concentrations of the herbicides simazine and diuron in runoff exceeded those for in-field herbicide degradation by a factor of 2–3 in a field experiment in France (8).

It is likely that the decline in pesticide bioavailability and potential for leaching to depth is caused by slow sorption kinetics and/or diffusion. In sorption experiments, equilibrium between the liquid and the solid phases of a soil is often only reached after periods ranging from several days to several months (3), and the partition coefficient between the two matrices can increase several fold with time of exposure (1–3). Rate-limited sorption can be partly due to molecular diffusion of the compounds from the solution surrounding the soil aggregates into the aggregates themselves (3, 10–11). Pignatello and Xing (3) identified three diffusion routes: across stagnant water films surrounding aggregates, through water-filled mesopores and micropores, and within the solid phase of the soil. The latter comprises intra-organic matter diffusion and retarded intraparticle diffusion (12). During these processes, organic molecules have the opportunity to interact with new sorption sites. Once diffusion has taken place, molecules may become unavailable for leaching as they are incorporated within sites that are largely unaffected by water flow in the soil (9) or are incorporated irreversibly into organic structures within the soil (3, 13).

To date, there is still no clear understanding of how slow sorption and diffusion influence availability for leaching in intact, structured soils. The present study is one of a set of experiments and model investigations that were undertaken at sequential levels of complexity to improve our knowledge in this area. First, lignin was used as a model compound for soil organic matter to gain insight into the mechanisms that control the kinetics of pesticide adsorption and desorption (14). Sorption of isoproturon on lignin immobilized in a matrix of alginate gel increased with time and reached equilibrium within 7–14 days. Desorption experiments showed strong hysteresis effects. A model was developed that described kinetic sorption as radial diffusion into spherical particles in combination with Freundlich sorption and first-order degradation inside the particles. The model fitted the data well, and the observed hysteresis of the sorption and desorption isotherms could be fully explained by the nonattainment of equilibrium due to slow diffusion into and out of the lignin particles. At the next level of complexity, adsorption–desorption experiments were undertaken with aggregates (5 mm diameter) of a clay loam soil and three pesticides (15). Results for isolated aggregates were very similar to those for sorption onto immobilized lignin. The model was modified for diffusion into and out of the aggregates. Again, the observed hysteresis could be fully explained by the nonattainment of equilibrium due to slow diffusion. Given the positive outcome at the scale of individual aggregates, the next phase of work

was to couple the diffusion model to a mechanistic leaching model and to evaluate the process description against pesticide losses from intact, structured soil columns. The soil and three of the four pesticides were the same as those previously investigated (15). The specific objectives of the research presented here were (i) to determine pesticide leaching patterns of four aged pesticides through undisturbed lysimeters, (ii) to compare the rates of decline in leached loads with rates of pesticide degradation, and (iii) to modify the model used in previous work and evaluate whether diffusion of the compounds within soil aggregates may be important in controlling their leaching behavior.

MATERIALS AND METHODS

Experimental Studies. Thirty undisturbed soil cores were taken in December 2003 from an agricultural field in Warwickshire, UK. The soil was a clay loam of the Salop series (USDA classification: Typic Endoaqualf, 25% clay, 2.3% organic carbon, pH [H₂O] 7.4). The lysimeters were collected in cylindrical PVC drainage pipes (0.35 m long, 0.237 m internal diameter). The inner surface of the pipes was roughened prior to collection of the lysimeters to ensure a good contact between the sleeves and the soil. A cutting ring was attached to the pipes. These were then driven vertically into the ground using the back actor of a JCB excavator. A 5 cm gap was left at the top of the sleeve to give a soil core 30 cm in length. The pipes were excavated by hand and closed at both ends with plastic caps for transport. The 5 cm gap was packed with molded polystyrene to prevent the core slipping within the sleeve before lysimeters were inverted and their base exposed. The bottom soil surface was picked back to remove any smearing caused during excavation, and a 5 cm layer of gravel was added to the base of the lysimeter to aid drainage. A galvanized steel base plate with an outlet was secured to the bottom of the lysimeter that was then returned to the upright position. The rim of the base plate was sealed with tape before irrigation.

The lysimeters were kept under outdoor conditions for 2 weeks. They were then transferred to a 15 °C room with a humidifier to maintain moist conditions. They were left for 3–5 weeks before pesticides were applied. One fungicide (azoxystrobin) and three herbicides (bentazone, chlorotoluron, and cyanazine) were applied in 5 mL of aqueous suspension made from formulated products (Table 1). The suspension was distributed manually across the soil surface with a Pasteur pipet followed by a 5 mL water rinse. The application volume (10 mL) was equivalent to 0.23 mm irrigation. The outer rim of the soil surface was avoided when applying the pesticide to avoid preferential flow via the edges. The target application dose corresponded to 1 kg ha⁻¹ active ingredient for azoxystrobin and 2 kg ha⁻¹ active ingredient for bentazone, chlorotoluron, and cyanazine. The application rates of bentazone, chlorotoluron, and cyanazine were similar to the approved application rates of the products (3.5, 2.1, and 1.44 kg of active ingredient ha⁻¹). The application rate of azoxystrobin was 4 times higher than the maximum approved rate (250 g of active ingredient ha⁻¹) to ensure concentrations above the quantification limit. Bromide (5 mL of a 42 g L⁻¹ KBr solution) was applied as a noninteractive tracer at a rate equivalent to 31.7 kg of Br ha⁻¹ just before irrigation.

The treated soil columns were stored in the controlled temperature room at 15 °C. Leaching of the pesticides was measured 1, 3, 7, 14,

and 28 days after application. On each date, four replicate lysimeters were taken and irrigated intermittently (twice per hour) at an intensity of 33 mm h^{-1} to give a total irrigation volume of 30 mm over a period of 5.5 h. Deionized water was sprayed from a nozzle at 2 bar pressure from 2 m above the soil columns. Leachate was collected every half an hour between 30 min and 6 h after starting the irrigation, giving a total of 12 fractions. The volume of the samples was determined, and subsamples were taken from each fraction for bromide analysis. The leachate fractions were then combined into five larger fractions with volumes ranging from 90 to 360 mL for analysis of the four pesticides. The samples were acidified with 0.1% H_3PO_4 (purity 80–85%, Fluka) and concentrated onto Supelco Supelclean Envi-18 solid-phase extraction (SPE) cartridges (1000 mg, 6 mL), which had been preconditioned with 5 mL of acetonitrile followed by 5 mL of water. Leachate was drawn through the cartridge at approximately 5 mL min^{-1} . The loaded cartridges were dried overnight in a desiccator before elution with acetonitrile and acidified water (2 mL, 75:25 by volume). The eluate was made up to 2 mL in a volumetric flask and stored at -20°C prior to analysis by HPLC as described next. The recovery rates of the SPE method were determined by comparing the concentrations after SPE with the concentrations in the raw leachate for three samples. Recovery rates were 88.2% (± 15.7) for azoxystrobin, 86.2% (± 2.0) for bentazone, 93.3% (± 4.3) for chlorotoluron, and 80.8% (± 3.2) for cyanazine (with the standard deviation in brackets). All concentrations measured after SPE were corrected accordingly.

Two additional soil cores were sampled destructively on each date to determine the moisture content and pesticide residues in the soil cores. Six samples were taken from the soil surface of each soil core using metal rings (5 cm depth \times 5.1 cm inner diameter). Two samples were oven-dried for 24 h to estimate the moisture content. The four remaining samples were extracted with acetonitrile. Each sample was divided into two subsamples to improve the extraction efficiency. The subsamples were shaken with 90 mL of acetonitrile on a wrist-action shaker for 1 h. They were allowed to settle for 1 h, and the clear supernatant was analyzed for pesticide residues by HPLC. The pesticide concentrations in the subsamples exceeded the dosed concentration by 13–36%, and the variation between the subsamples was large. Recovery rates on the first day after application were 127% (± 31) for azoxystrobin, 120% (± 28) for bentazone, 113% (± 31) for chlorotoluron, and 136% (± 29) for cyanazine (standard deviation in brackets). The variability was mainly due to variations across the soil surface. In a separate recovery test with sieved soil from the same plot, the recovery rates were 98.7% (± 0.5) for bentazone and 95.9% (± 0.3) for cyanazine 1 day after application.

Pesticide concentrations were measured on a DX600 (Dionex, Sunnyvale, CA) HPLC equipped with a PDA100 photodiode array detector and a Discovery C-18 column (Supelco, Bellefonte, PA). The mobile phase was 40% acetonitrile and 60% aqueous solution of phosphoric acid (0.04% H_3PO_4 by volume) with a flow rate of 1 mL min^{-1} . Detection was by UV absorbance at 200 nm. The limits of quantification were $190 \mu\text{g L}^{-1}$ for azoxystrobin, $300 \mu\text{g L}^{-1}$ for bentazone, $50 \mu\text{g L}^{-1}$ for chlorotoluron, and $60 \mu\text{g L}^{-1}$ for cyanazine in the concentrated samples. Bromide was analyzed in a 1:6 dilution of leachate analyzed with a Metrohm 790 Personal Ion Chromatograph (Herisau, Switzerland). All bromide concentrations were well above the limit of quantification (1 mg L^{-1}).

Model Description. Pesticide leaching from the soil cores at different times from application was simulated with a two-region transport model with diffusion into soil aggregates. The model is based on the intra-aggregate diffusion model that was developed in previous work (15). The model was first applied to describe adsorption and desorption of azoxystrobin, chlorotoluron, and cyanazine on stabilized aggregates sampled from the same field as the lysimeters. The model was extended further to simulate vertical transport within the undisturbed soil cores.

The extended model conceptualizes two soil regions: (i) an interaggregate region, the pore space in between the aggregates and (ii) an intra-aggregate region inside the aggregates. Pesticides are transported downward with the flowing water in the interaggregate region. Transport in the intra-aggregate region is controlled by diffusion, adsorption, and desorption. The simulations of the experimental data entail two stages. The first stage is the period between pesticide

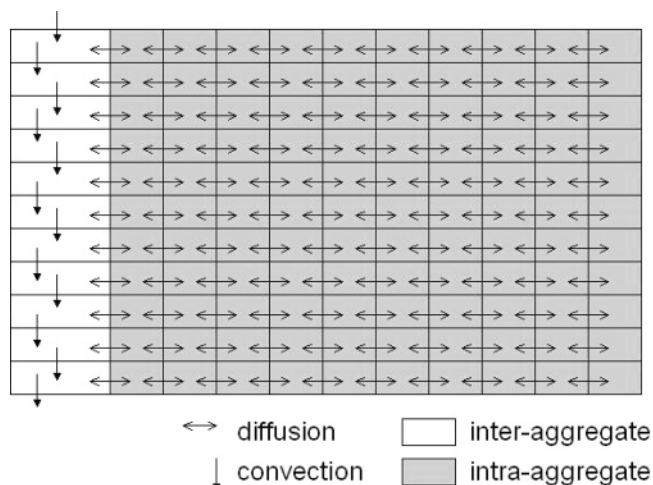


Figure 1. Diagram of the numerical calculation cells in the transport model describing radial diffusion into soil aggregates (horizontal arrows) and convection via interaggregate pores in the soil core (vertical arrows).

application and irrigation ranging from 1 to 28 days. During this stage, pesticides diffuse from the external solution around the aggregates into the pore solution inside the aggregates where they interact with associated sorption sites. The second stage is during the irrigation of the lysimeters when the pesticides are transported down the soil column with the water flowing through interaggregate pores. Pesticides are released from the aggregates by diffusion and desorption.

The model was implemented in ORCHESTRA (16), a computer program for chemical speciation and transport modeling. The soil aggregates or peds are assumed to be spherical and of identical size. Radial diffusion is simulated in the model by dividing a spherical aggregate into 10 concentric layers, represented by calculation cells. Diffusion fluxes between the cells are calculated as a function of the concentration gradient in the soil solution. Transport in the soil cores is solved numerically by dividing the 25 cm soil column into 10 layers of equal depth, each layer with an interaggregate pore region and an aggregate region (Figure 1). Diffusion into and out of the aggregates is calculated perpendicularly to the flow direction. The mass balance for radial diffusion, sorption, and degradation inside the aggregate is given by (15)

$$\theta_a \frac{\partial C}{\partial t} + \rho_a \frac{\partial S}{\partial t} = -\theta_a D_e \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) - k(\theta_a C + \rho_a S) \text{ for } r \leq a \quad (1)$$

where r is the distance from the aggregate center, a is the aggregate radius, C is the concentration in solution (mg m^{-3}), S is the adsorbed concentration (mg kg^{-1}), θ_a is the porosity ($\text{m}^3 \text{ m}^{-3}$), ρ_a is the bulk density of the aggregate (kg m^{-3}), and D_e is an effective diffusion coefficient ($\text{m}^2 \text{ h}^{-1}$) that accounts for tortuosity and the constricted movement of molecules through narrow pores. Degradation is calculated with a first-order degradation rate constant k (h^{-1}), assuming the same degradation rate for the adsorbed pesticide as for the pesticide in solution. The sorption sites are considered to be evenly distributed throughout the soil aggregates, and sorption is described by a Freundlich isotherm (17)

$$S = K_f C^n \quad (2)$$

where K_f is the Freundlich sorption coefficient and n is the Freundlich exponent.

Convection in the interaggregate pore region is described by (18)

$$\theta_m \frac{\partial C_m}{\partial t} = -\theta_m v_m \frac{\partial C_m}{\partial x} - k \theta_m C_m - J_{m \rightarrow a} \text{ for } r < a \quad (3)$$

where C_m is the concentration in interaggregate pore solution (mg m^{-3}), θ_m is the inter-aggregate porosity ($\text{m}^3 \text{ m}^{-3}$), v_m is the flow rate in the interaggregate pores (m h^{-1}), and $J_{m \rightarrow a}$ represents the loss caused by

Table 2. Generic Model Parameters

parameter	value	unit	source
external pore volume (interaggregate pores)	1.21	L	calculated (see text)
internal pore volume (inside aggregates)	4.62	L	calculated (see text)
aggregate weight	13.46	kg	calculated (see text)
density of aggregates	1.37	kg L ⁻¹	ref 15
porosity of aggregates	0.47		ref 15
aggregate radius (diffusion path length)	0.02	m	ref 20
aggregate pore saturation before irrigation	71.6%		estimated (see text)
aggregate pore saturation during irrigation	71.6%		estimated (see text)
interaggregate pore saturation before irrigation	30.4%		estimated (see text)
interaggregate pore saturation during irrigation	40.2%		estimated (see text)
flow rate	0.243	L h ⁻¹	set to irrigation rate

Table 3. Compound-Specific Model Parameters

	azoxystrobin	chlorotoluron	cyanazine	bentazone
Freundlich coefficient	11.2	7.02	2.89	0
K_F (L kg ⁻¹)				
Freundlich exponent n (-)	0.607	0.603	0.629	-
degradation rate constant k (h ⁻¹)	1.90×10^{-4}	9.76×10^{-4}	1.48×10^{-3}	7.02×10^{-4}
diffusion coefficient	2.52×10^{-7}	3.60×10^{-7}	1.80×10^{-7}	3.60×10^{-7}
D_0 (m ² h ⁻¹)				

diffusion into the aggregate (mg h⁻¹). Diffusion in the aggregates, convection in the interaggregate pore region, and degradation were calculated simultaneously. After each transport calculation, the new chemical sorption equilibrium was calculated by iteration. Sorption only takes place inside the soil aggregates, not at the interface between the interaggregate pore region and the aggregates. However, diffusion into the outer rim of the aggregates is fast due to the short diffusion path length. Sorption and desorption from the outer rim will, therefore, be relatively fast. The model includes hydrological dispersion indirectly by allowing numerical dispersion. The pesticides were applied to the interaggregate pore region of the uppermost layer in the model, which is the top 2.5 cm of soil.

Model Input Parameters. Tables 2 and 3 show the model input parameters with their values. The mass of soil in the lysimeter (13.5 kg oven-dry) was estimated based on the dimensions of the soil core (25 cm soil depth \times 23.7 cm inner diameter = 11.0 L) and a field bulk density of 1.22 kg dm⁻³ (19). The aggregates that were used in previous experiments had a porosity of 47% and density of 1.37 kg dm⁻³ (15). If we assume all soil in the cores is aggregated and that the aggregates have the same density for the aggregated soil in the undisturbed soil cores, then the volume of aggregates in the cores is 9.82 L (=1.22/1.37 \times 11.0), and the total interaggregate pore volume is 1.21 L. The pore volume inside the soil aggregates is 4.62 L. The total porosity of the cores is calculated to be 5.83 L or 52.9%. This is very similar to the mean porosity of the Salop soil series of 53.3% given by Hollis et al. (19).

The water content of the soil during incubation was estimated from the moisture content in the top 5 cm of the soil cores. This varied between 0.24 and 0.32 g g⁻¹ with an average of 0.273 g g⁻¹ water per dry weight soil, equating to 3.68 L of water per soil core. An arbitrary 10% of the water was assumed to be present in the interaggregate pore volume and the residual 90% in the internal pores of the aggregates. This distribution gives a 30.4% saturation of the interaggregate pores and 71.6% saturation of the intra-aggregate pores during the incubation period. The exact distribution of the water is not of major importance for the leaching because the distribution of the pesticides is mainly determined by the amount of adsorption inside the aggregates. It may, however, influence the leaching of the nonadsorbing bentazone to a small extent. After irrigation, the weight of the soil cores had increased by 118 g on average. Assuming that this is caused by additional water in the interaggregate pores, the saturation of the interaggregate pores would be 40.2% during and after irrigation. The effective diffusion

path length (aggregate radius) was derived using the relationships proposed by Jarvis et al. (20) from the size and shape of aggregates and degree of structural development according to the FAO classification (21). For a soil with blocky, medium-sized aggregates and a moderately developed structure, an effective diffusion path length of 20 mm is expected. The volumetric flow rate in the model was set to the irrigation rate of 243 mL h⁻¹.

Sorption parameters and effective diffusion coefficients for azoxystrobin, chlorotoluron, and cyanazine were measured previously (15). It was demonstrated that sorption of bentazone is negligible in this clay loam soil (22). Applying the pesticides together did not have any visible effect on the adsorption of the individual pesticides in an additional batch experiment (results not published). The diffusion coefficient of bentazone is expected to be very similar to that of chlorotoluron based on the sizes of the molecules. The degradation parameters for the four pesticides were derived by fitting first-order kinetics to the decline in pesticide residues measured in the soil columns. The degradation rate constant was assumed to be the same for dissolved and adsorbed pesticide and for intra- and interaggregate regions.

RESULTS AND DISCUSSION

Solute Leaching. Figure 2 shows concentrations of bromide and the four pesticides in leachate from the four replicate lysimeters that were irrigated 1 day after pesticide application. (Note that bromide was applied just before irrigation on all sampling dates.) Concentrations are plotted versus the cumulative volume of water leached. The amount of pesticide and bromide leaching was varied notably between the four replicate cores. This was probably due to heterogeneity in soil structure and differences in preferential flow between the soil cores. The solutes were detected at large concentrations in the first fraction of leachate (Figure 2). This suggests that part of the chemical added to the soil surface bypasses the soil matrix and moves rapidly to depth via preferential flow. Similar results were found for the later irrigation dates. The first leachate fraction that was analyzed for pesticides had a volume of approximately 200 mL, which is only about 6% of the total amount of water in the soil core (3.7 L). It is not possible that the chemicals have reached the bottom of the soil core yet by matrix flow. Therefore, any bromide or pesticide leaching is caused by preferential flow, although the extent of preferential flow differed somewhat between the replicate lysimeters. Attempts were made in this study to prevent any significant flow of water and solutes along the walls of the drainage pipes that held the soil cores. The inner surface of the pipes was roughened, and the cores were kept vertical during irrigation. However, side-wall flow cannot be fully excluded, and this may have contributed to the large concentrations found in the first fraction of leachate.

The total amount of pesticide leached from each lysimeter was plotted against the time between pesticide application and irrigation in Figure 3. To allow comparison between the lysimeters, we calculated the amount of pesticide in the first 1000 mL of leachate by linear interpolation. The percentage of pesticide in the leachate varied considerably between the four replicate lysimeters with coefficients of variation of up to 110%. Differences in sorption between the soil cores was small (results not shown), and the variation is most likely caused by differences in soil structure and thus in extent of preferential flow. Average pesticide loads declined strongly with increasing time from application. The rate in decline was largest for azoxystrobin, cyanazine, and chlorotoluron where the amount leached after 28 days was an order of magnitude smaller than that found after 1 day. The decline in leaching for the pesticides will partly arise from degradation. To differentiate this process, the soil residue data were analyzed, and the rate of degradation was compared with the decline in leaching losses.

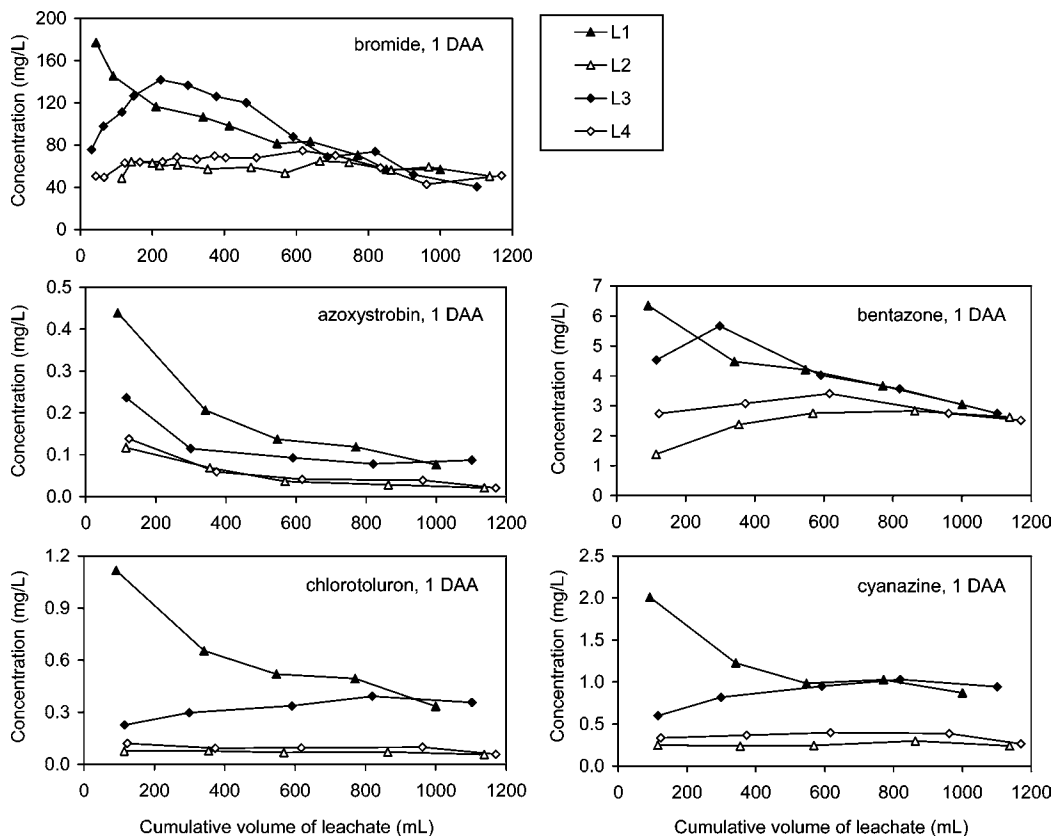


Figure 2. Concentrations in leachate plotted against the cumulative volume of leachate for the four replicate lysimeters (L1–4) that were irrigated 1 day after pesticide application (DAA). Note differences in scales.

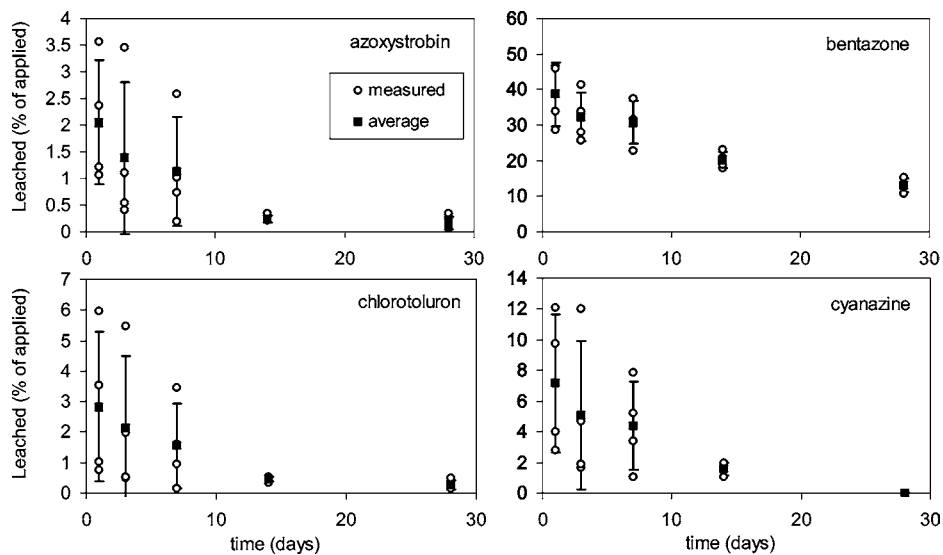


Figure 3. Pesticide loss by leaching (% of applied) in first 1000 mL of leachate plotted against the time between pesticide application and irrigation. The open symbols are the results for the individual replicates. The solid symbols are averages of the four replicates, and the bars are standard deviations.

Figure 4 shows pesticide residues measured on the different sampling dates. Means and standard deviation of four samples from two replicate soil cores (eight samples total) are presented. First-order degradation kinetics was fitted to the data by least-squares fitting. The variability in pesticide residues between the replicate samples was large. This is probably due to an uneven application. The presence of large soil aggregates (several centimeters in diameter), stones, and residues of the previous crop made it very difficult to distribute the pesticide solution evenly across the soil surface. The decline in extractable residue over 28 days was approximately 50% for chlorotoluron and cyanazine, 30% for bentazone, and negligible for azoxystrobin.

DT50 values (times for 50% decline of the initial amount) calculated from degradation rate constants were 152 days for azoxystrobin, 42 days for bentazone, 30 days for chlorotoluron, and 20 days for cyanazine.

First-order decline rate constants were fitted to the leaching data to allow comparison between the decline in leaching and the decline caused by degradation. **Figure 5** shows the first-order decline curves that were fitted to the leaching data by least-squares optimization. The fitted decline rate constants are shown in **Table 4** together with the degradation rate constant determined from the extractable pesticide residue in the soil cores and the net decline rate constants after correction

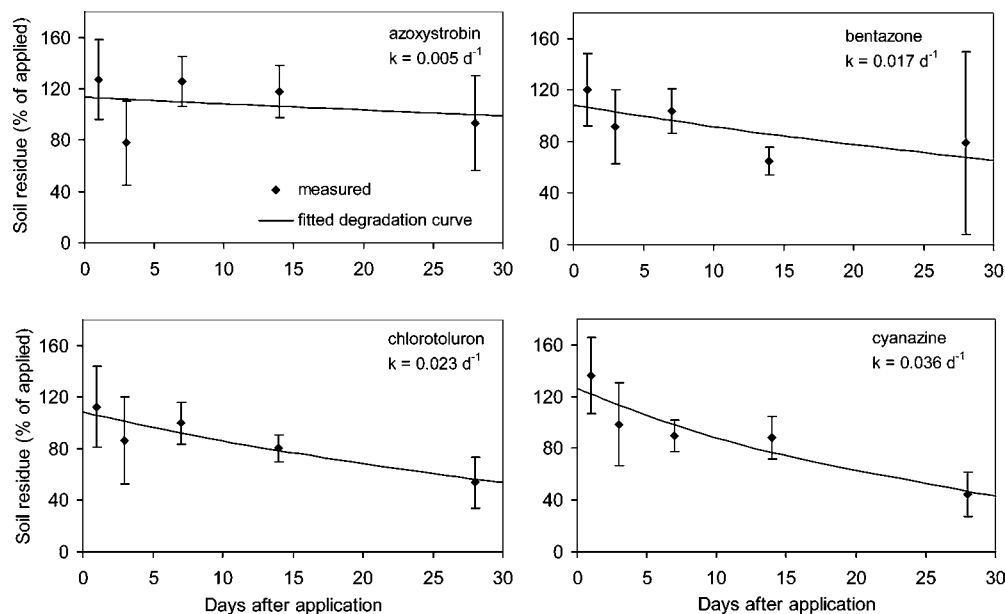


Figure 4. Total pesticide residues in the soil cores (% of applied). Means \pm standard deviations of eight samples are shown. The lines are first-order degradation curves, and k is the fitted degradation rate constant.

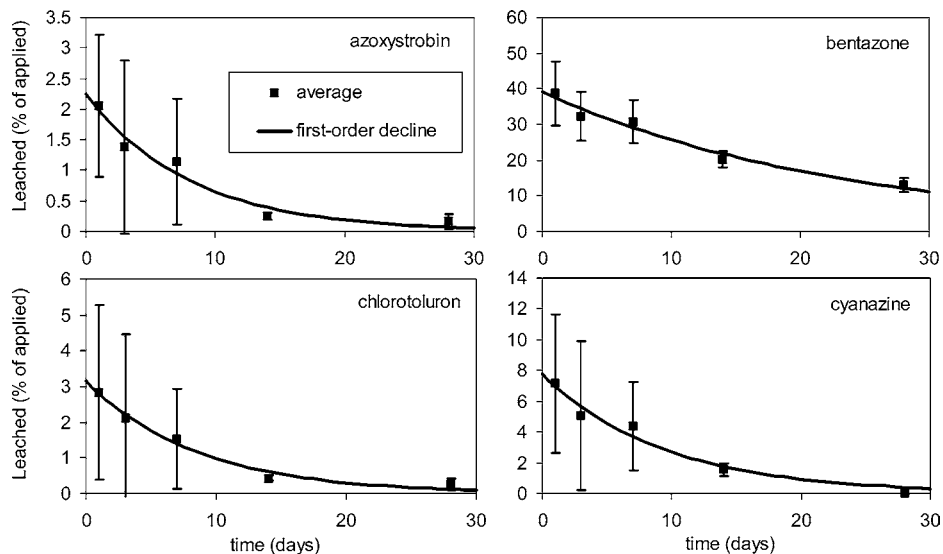


Figure 5. Pesticide loss by leaching (% of applied) in first 1000 mL of leachate plotted against the time between pesticide application and irrigation. The solid symbols are averages of the four replicates, and the bars are standard deviations. The solid lines are the fitted first-order decline curves.

Table 4. Fitted Decline Rate Constants for Pesticide Leaching after Aging and Net Decline Rate Constants after Correction for Decline Caused by Degradation

	azoxystrobin	chlorotoluron	cyanazine	bentazone
% leaching at time zero	2.25	3.15	7.77	39.01
decline rate constant (h^{-1})	5.18×10^{-3}	4.88×10^{-3}	4.42×10^{-3}	1.74×10^{-3}
degradation rate constant (h^{-1})	1.90×10^{-4}	9.76×10^{-4}	1.48×10^{-3}	7.02×10^{-4}
kinetic rate constant (h^{-1})	4.99×10^{-3}	3.91×10^{-3}	2.94×10^{-3}	1.04×10^{-3}

for degradation. The decline rate constants for leaching were 2.5–27 times larger than the degradation rate constants. Therefore, the decline in leaching cannot be explained by degradation alone. The net decline rate constants were 4–5 times larger for the sorbing pesticides azoxystrobin, cyanazine, and chlorotoluron than for bentazone, which did not interact with the soil. Apart from bentazone, the decline rate constants were

similar for the different pesticides despite the different sorption coefficients. We used the transport model to determine whether the decline in leaching can be explained by diffusion and sorption inside soil aggregates.

The model simulated a rapid decline in the amount of pesticide leached (**Figure 6**) and gave a good overall representation of the decline in leaching for azoxystrobin, chlorotoluron, and cyanazine. The simulated decline in leaching losses of chlorotoluron and cyanazine and particularly those of azoxystrobin was initially faster than the average of the observed losses. However, the variability between the replicate measurements was large, and the predicted losses were within the mean \pm standard deviation on most occasions. The amount of bentazone leached from the system was greater than that simulated despite assuming no bentazone sorption. The discrepancies are possibly due to the simplicity of the transport model. The high concentrations in the first leachate samples indicated the importance of preferential flow for leaching of bromide and pesticide. In the two-region model, preferential

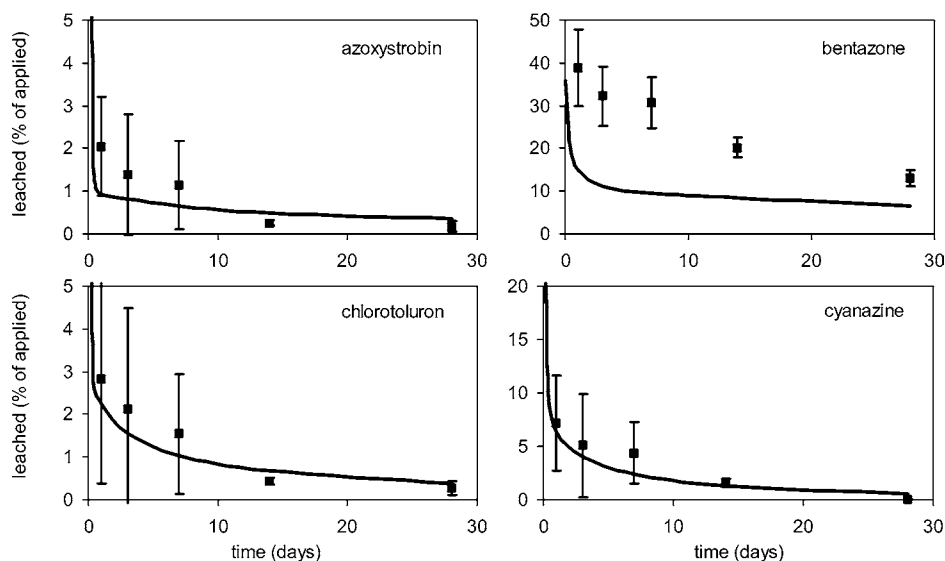


Figure 6. Pesticides leached (% of applied) from the lysimeters, plotted against time between application and irrigation. The thick solid line shows the results from two-region transport simulations with diffusion into aggregates. The solid symbols are averages of the four replicates, and the bars are standard deviations.

flow was simulated by interaggregate flow. Interaggregate flow is relatively fast in the model but not fast enough to correctly represent the rapid movement of water that occurred in the lysimeters. The longer residence time allows the pesticides to diffuse into the outer layers of the aggregates in the subsoil. Therefore, the model was not capable of simulating the large concentrations that were found in the first leachate fractions. A breakthrough of the pesticide concentrations only occurs in the model when the solution in the interaggregate pores (380 mL) has leached. To give a more accurate description of bromide and pesticide leaching, the model would have to describe preferential flow channels as well as interaggregate pores.

General Discussion and Conclusion. The model in this study described kinetic sorption as a diffusion-controlled process. This approach was successful for systems ranging from immobilized organic material to stabilized soil aggregates (14, 15). The ability of the model to also describe the leaching of three out of four pesticides from intact, structured soil cores is promising. The results suggest that the frequently observed decline in pesticide availability for leaching may be caused by diffusion, although alternative explanations for this decline cannot be excluded. Bentazone leaching was underestimated by the model, possibly due to the simplified way in which water flow was described by intra-aggregate flow. The model was not capable of simulating the extent of preferential flow that was observed in the lysimeters.

The model was based on a number of assumptions. The model described single-sized spherical aggregates, while in reality, the aggregates vary in size. Sorption and degradation were assumed constant throughout the soil, and dissolved pesticides as well as adsorbed pesticides were assumed to degrade. There is some evidence that small pores are not accessible for degrading microorganisms and that pesticide inside aggregates may be partly protected from degradation (23). However, in previous unpublished work, we did not find any differences between degradation of pesticides in intact and sieved, repacked soil systems. In an additional study, there was a tendency for slower degradation of cyanazine and bentazone in soil aggregates 3–5 mm in diameter than in soil sieved to 3 mm, but the differences were not significant for most datasets (22). Pesticide sorption inside the aggregates was considered to be instantaneous. Any additional time-dependent processes, such as diffusion into

organic particles or slow sorption reactions, were excluded from the model. These processes may also contribute to a decline in availability for leaching. Further work is required to evaluate the assumptions inherent in the model and to test the transferability of the results. The leaching behavior of the pesticides tested in this study was influenced by (i) the strength of sorption, (ii) the extent of degradation of bulk residues in soil, and (iii) a chemical-specific process reducing the relative availability for leaching over time. Sorption of pesticides to soil will clearly be an important influence on availability for leaching. The percentage of the applied pesticide that was leached increased with decreasing strength of sorption. The availability of pesticides for leaching over time was also influenced by the decline in total residues present due to degradation. In this study, pesticide losses in leachate declined 2.5–27 times faster than total residues in soil. The rate of decrease in leaching over and above that attributed to degradation was 4–5 times greater for the more strongly sorbed pesticides azoxystrobin, chlorotoluron, and cyanazine than for bentazone. These results are in line with those of Renaud et al. (5). The authors found that leached loads of isoproturon and chlorotoluron in soil decreased rapidly with time in four soils tested, whereas loads of the weakly sorbed triasulfuron and a bromide tracer were relatively constant over events in all but a clay soil. Very similar results were obtained by Jones et al. (7). The findings suggest that the extent of kinetic sorption may be larger for more strongly sorbed compounds. More pesticide is taken up by the aggregates if the pesticide is more strongly adsorbed inside the aggregate. The difference between initial sorption and equilibrium values is thus likely to be greater for the more strongly sorbed compounds.

The main application of the research will be to evaluate and improve models that are used to predict transport of pesticides and other contaminants to ground and surface water. These models have applications in regulatory risk assessment, and improved simulations will strengthen regulatory decision-making, allowing better protection of the environment and helping to ensure the sustainability of agricultural systems. Pesticide leaching models including MACRO5.0 (24) and PEARL (25) give the option to include time-dependent sorption. Time-dependent sorption is described as a first-order mass transfer between an instantaneous sorption pool and a slow sorption pool (i.e., kinetic sorption). First-order mass transfer can be used to simulate

diffusion-limited sorption in spherical aggregates or peds by estimating the mass transfer coefficient from the aggregate radius (26). However, the coefficient is time-dependent (27), and a different time-averaged coefficient will need to be derived to describe short periods (e.g., the first hours) or long periods (e.g., weeks). Additionally, the first-order model does not describe gradients inside the soil aggregates or peds, and it is thus uncertain whether the model would give a reasonable representation of repeated sorption–desorption as would occur in soils with intermittent leaching. The diffusion model reported here provides a more robust representation of time-dependent sorption caused by diffusion into aggregates. As with the derivation of the mass transfer coefficient, the aggregate or ped radius is required as a measure for the diffusion path length. It is a challenge for both modeling approaches to estimate a representative aggregate size in soils with variable aggregate sizes. The only disadvantage of the diffusion model over the first-order mass transfer model is that the former is more computationally intensive due to the increased number of numerical cells or compartments. Ten compartments were used to describe diffusion into a sphere, whereas the first-order approach only requires two compartments to represent the instantaneous and slow sorption pools. The diffusion model is expected to give a more realistic representation in systems where intermittent leaching and wetting and drying occurs and can describe sorption and desorption at very short intervals (e.g., hours) up to long intervals (e.g., days or weeks) with the same parameters. It should, however, be noted that there was a large variability in the observed behavior of the pesticides in this study. Any modeling approach that is based on a single set of input parameters cannot encompass this variability. Model applications should ideally take into account the heterogeneity of structured soils and give information on the likelihood of a leaching risk to occur.

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