

Pesticide Sorption and Diffusion in Natural Clay Loam Aggregates

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Pesticide sorption in soils is controlled by time-dependent processes such as diffusion into soil aggregates and microscopic sorbent particles. This study examines the rate-controlling step for time-dependent sorption in clay loam aggregates. Aggregates (5 mm) were stabilized with alginate, and adsorption of azoxystrobin, chlorotoluron, and cyanazine was measured in batch systems equilibrated for periods between 1 h and 7 days. Stepwise desorption was measured at 1- or 3-day intervals following 1 or 7 days of adsorption. Time-dependent adsorption was also measured on dispersed soil. Results were interpreted using process-based modeling. Adsorption on dispersed soil was described by intraparticle sorption and diffusion. Adsorption in the aggregates was much less than in suspension, suggesting that part of the sorption capacity of the dispersed soil was not available within the aggregates (~50%). Adsorption and desorption were reversible and could be described by pore diffusion into the aggregate with effective diffusion coefficients between 0.5×10^{-10} and $1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, a factor 3–6 slower than estimated theoretically. Intraparticle diffusion did not seem to contribute to sorption in the aggregates at this time scale. Apparent hysteresis was explained by nonattainment of equilibrium during the adsorption and desorption steps.

KEYWORDS: Herbicides; time-dependent sorption; hysteresis; diffusion model; ORCHESTRA

INTRODUCTION

The fate of pesticides after application onto a field is highly controlled by the extent of interaction with the soil. Sorption onto the soil matrix controls the availability of the compound for transport to surface waters and groundwater. Sorption of organic compounds is known to be time-dependent (e.g., refs 1–4), and the extent of sorption in the field increases with time from application. As a result, the amount of pesticide available for transport decreases with the time between application and rainfall event, which was shown for runoff (5), leaching in the field (6), and leaching in lysimeters (7, 8).

Diffusion processes in soil are known to be a cause of time-dependent sorption (1, 3, 9). After application, pesticides redistribute within the soil matrix through intra-aggregate pores and by diffusion and sorption in soil aggregates. A slow increase in sorption may also be caused by diffusion and sorption inside small sorbent particles such as organic matter or mineral particles (intraparticle diffusion). Most likely a combination of processes will take place. In some cases irreversible sorption is observed, when sorption and desorption follow different mechanistic pathways. Lu and Pignatello (10) showed that irreversible

sorption can occur when a sorbate causes structural changes in the sorbent that enhance the sorption strength.

It is not possible to elucidate the relative importance of the individual processes from macroscale observations, but valuable insight can be gained from well-defined, controlled experiments. In previous work, time-dependent sorption of the herbicide isoproturon on lignin was examined (11). Lignin is a major component in wood and soil organic matter and was used as a model compound for organic matter. The results implied that sorption of isoproturon on lignin is diffusion-controlled and fully reversible and that sorption and desorption could be described with an intraparticle diffusion model with one set of model parameters. The study presented here investigates whether these findings can be extrapolated to natural soil aggregates. Controlled adsorption and desorption experiments using dispersed soil and intact, stabilized soil aggregates were combined with modeling to evaluate the hypotheses that (i) adsorption on dispersed soil is time-dependent and can be modeled as intraparticle diffusion, (ii) adsorption in intact soil aggregates is the result of diffusion into the aggregates followed by intraparticle diffusion and can be predicted from sorption on dispersed soil, and (iii) adsorption and desorption in intact aggregates can be described by the same mechanism with the same rate constants.

MATERIALS AND METHODS

Soil, Pesticides, and Analyses. Clay loam soil of the Salop series (Typic Endoaqualf; 24% clay, 2.3% organic carbon, and pH-H₂O 7.4)

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was sampled from the top 15 cm of an agricultural field in Warwickshire, U.K. The soil was air-dried, and aggregates between 3 and 5 mm diameter were isolated by sieving. The porosity and density of the soil aggregates were estimated using the paraffin coating method reported by Black et al. (12). The density of the aggregates was estimated from the weight and volume of 10 oven-dry aggregates. The aggregate porosity was calculated by assuming a particle density of 2.6 g cm^{-3} . The estimated dry density of the aggregates was $1.37 \pm 0.16 \text{ g cm}^{-3}$ and the porosity 0.47 ± 0.16 .

The pesticides selected for the experiments are the strongly sorbing fungicide azoxystrobin [methyl (*E*)-2-{2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate], the moderately sorbing herbicide chlorotoluron [3-(3-chloro-*p*-tolyl)-1,1-dimethylurea], and the weakly sorbing herbicide cyanazine [2-(4-chloro-6-(ethylamino)-1,3,5-triazin-2-ylamino)-2-methylpropionitrile]. The commercial formulations Amistar, 250 g/L azoxystrobin suspension concentrate (SC); Alpha Chlorotoluron 500, 43.9% w/w SC; and Fortol, 45.5% w/w cyanazine SC, were used. Mixed pesticide solutions in 5 mM CaCl_2 were prepared at concentrations of 6 mg L^{-1} azoxystrobin, 16 mg L^{-1} chlorotoluron, and 19 mg L^{-1} cyanazine and diluted 3:4, 2:4, and 1:4. Bromide (61 mg L^{-1}) was added as a nonreactive tracer. Interaction between the three pesticides was tested in a preliminary sorption experiment (soil/solution ratio 1:2, 24 h of shaking). There was no difference in adsorption when all three pesticides were applied together compared to when individual pesticides were applied to different soil samples.

Samples were stored in a freezer between sampling and analysis. 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, $50 \mu\text{g L}^{-1}$ for chlorotoluron, and $60 \mu\text{g L}^{-1}$ for cyanazine. Bromide and chloride concentrations were analyzed by ion chromatography after dilution 1:5.

Preparation of Coated Aggregates. For each replicate, 11 large aggregates were selected with a total weight of 1 g (air-dry). The aggregates were stabilized by coating them with alginate gel. Alginate has the advantage that it has an open structure that allows small molecules to diffuse through the gel with similar rates as diffusion in water (13, 14). The hydrated gel is elastic and does not inhibit any swelling of the aggregates. Individual aggregates were impregnated by immersing them in alginate solution (0.5% w/w sodium alginate) in a vacuum (-80 kPa) to avoid entrapped air, followed by immersing in a 0.1 M CaCl_2 solution to cross-link the alginate gel. They were then immersed in alginate and CaCl_2 baths three more times to form a gel coating around the aggregates. The aggregates were kept in 0.1 M CaCl_2 overnight to ensure complete cross-linkage. The final coated aggregates were washed and equilibrated several times with 5 mM CaCl_2 solution.

Time-Dependent Sorption Experiments. Sorption experiments were carried out in standard shaken systems with dispersed soil and with intact aggregates stabilized with alginate gel. For the experiments with dispersed soil, noncoated aggregates (1 g) were weighed into 30 mL glass vials, and 4 mL of pesticide solution was added to each vial. The aggregates fell apart as soon as the solution was added, but the vials were shaken briefly by hand to disperse the soil fully. The soil was kept in suspension subsequently by gentle rotation on an orbital shaker (in the dark at 20°C). After 1, 3, 9, and 24 h and after 3, 7, and 14 days, two replicate glass vials for each pesticide concentration were centrifuged at $3500g$ for 30 min, and the supernatant was decanted and frozen until analysis. The remaining soil was shaken vigorously with 6 mL of acetonitrile for 1 h and centrifuged to recover pesticide residues. The extracts were frozen until analysis, and the weight of the soil was determined after drying at 105°C . Degradation rates were derived by fitting first-order kinetics to total residue concentrations. These degradation rates were then used in the adsorption calculations. The amount of adsorption was calculated from the solution concentration after different equilibration times, the added amount of pesticide corrected for degradation, and the soil/solution ratio in the samples.

The coated aggregates were transferred to 30-mL glass vials and weighed after careful removal of any excess solution. Pesticide solution

was added (4 mL), and the vials were closed with polyethylene caps. Duplicate vials for each pesticide concentration were swirled continuously on an orbital shaker in the dark at 20°C for different time intervals between 1 h and 7 days. On each sampling date, solution was removed and frozen until analysis. The sampled aggregates were crushed with a glass rod to break the alginate coating and then shaken vigorously with 6 mL of acetonitrile for 1 h to extract pesticide residues. The extracts were frozen until analysis, and the weight of the soil was determined after drying at 105°C .

Adsorption on coated aggregates was calculated from the solution concentration in the samples. The solution volume included the water inside the aggregate pores and the gel coating, so redistribution of pesticide between the external and internal solution is not counted as adsorption. The solution volume in the gel and pores was calculated from the difference in weight of the coated aggregates and the oven-dry soil. Bromide concentrations were determined in the external solutions to check the redistribution of nonreactive tracer between the external solution and the solution in the gel and aggregate pores. There was good agreement between the internal solution volumes calculated from the bromide concentrations and those determined by weight, which suggests that there was no ion exclusion from any significant part of the solution volume inside the gel-coated aggregates.

Pesticide desorption from aggregates was measured in a parallel experiment. The aggregates were first incubated with pesticide solution on the orbital shaker for 1 or 7 days to allow pesticide adsorption. Then part of the pesticide solution (3.5 mL) was replaced by pesticide-free solution (5 mM CaCl_2), and the vials were returned to the orbital shaker for 1 or 3 days. This desorption step was repeated five times in total. The concentration of the pesticides in the sampled solution was measured after each adsorption and desorption step.

Diffusion Modeling. An intraparticle diffusion model was developed in previous work (4) and was successfully applied to describe adsorption and desorption of the herbicide isoproturon on lignin. The present study investigated whether the same model (referred to as model A in this study) could be used to describe sorption in more complex systems. First, the parameters of the intraparticle diffusion model were adjusted to provide a good fit to the data on adsorption in dispersed soil systems. Then, adsorption in intact soil aggregates was simulated on the basis of adsorption in dispersed soil. A combined model was used (model B) that simulates diffusion into the aggregates followed by intraparticle diffusion. Parameters for intraparticle diffusion were set to those for the dispersed system, and parameters describing diffusion into the aggregates were determined independently. A third modeling study investigated whether adsorption and desorption on intact aggregates can be described by an identical set of process descriptions and model parameters. An scaled up version of model A was used (model C) whereby the radius of the spherical particles was set to the size of the aggregates. The three models are described in more detail below.

Intraparticle Diffusion Model (Model A). Time-dependent sorption on dispersed soil was described with the intraparticle diffusion model previously used for adsorption on lignin (4). It was assumed that pesticides adsorb on the organic matter fraction of the soil only. Part of the adsorption in the model is instantaneous. The remaining part is controlled by diffusion and sorption in organic particles. The particles are assumed to be spherical with identical radius. The mass balance for radial diffusion, sorption, and degradation is given by

$$\theta \frac{\partial C}{\partial t} + \rho \frac{\partial S}{\partial t} = \theta D_e \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) - k(\theta C + \rho S) \quad (1)$$

where C is the concentration in solution (mg m^{-3}), S is the adsorbed concentration (mg kg^{-1}), θ is the porosity ($\text{m}^3 \text{ m}^{-3}$), ρ is the bulk density of the particle (kg m^{-3}), and D_e is an effective diffusion coefficient ($\text{m}^2 \text{ s}^{-1}$) that accounts for tortuosity and the constricted movement of molecules through the narrow particle pores. Degradation is calculated with a first-order degradation rate, k (s^{-1}), assuming the same degradation rate for the adsorbed pesticide as for the pesticide in solution. Sorption is described by the Freundlich equation

$$S = K_{\text{OM}}^F C^n \quad (2)$$

Table 1. Input Parameters for the Intraparticle, Combined, and Intra-aggregate Diffusion Models

model parameter	model A, intra- particle	model B, combined	model C, intra- aggregate
external solution vol (mL)	5.0	5.0	5.0
soil wt per sample (g)	1.0	1.0	1.0
organic matter content (%)	4.0	4.0	
organic particle radius (a) (μm)	10	10	
organic particle density (ρ) (kg dm^{-3})	1.4	1.4	
organic particle porosity (θ)	0.5	0.5	
instantaneous fraction (f)	0.35	0.0	
diffusion coeff (D_e) in particle pores ^a ($\text{m}^2 \text{s}^{-1}$)	1×10^{-15}	1×10^{-15}	
aggregate radius (a) (mm)		2.5	2.5
aggregate dry bulk density (ρ) (kg dm^{-3})		1.37	1.37
aggregate porosity (θ)		0.47	0.47
aggregate tortuosity (τ^{-2})		0.78	0.78

pesticide	diffusion coefficients (D_e) in aggregate pores					
	model A, intraparticle	model B, combined	model C, intra-aggregate			
azoxystrobin		$3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$	$7 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$			
chlorotoluron		$3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$	$1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$			
cyanazine		$3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$	$5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$			

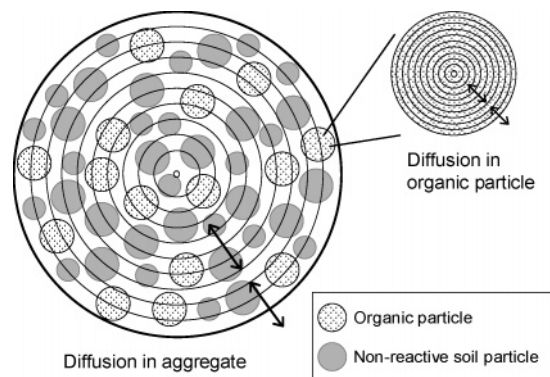
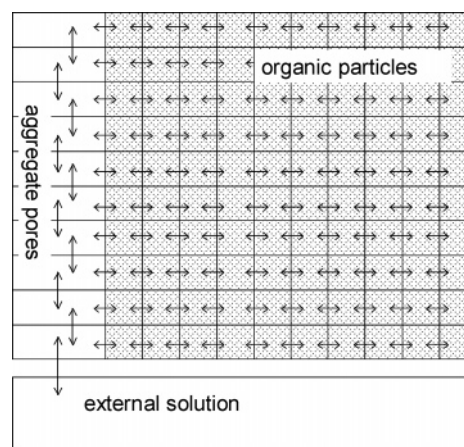
pesticide	Freundlich sorption parameters					
	K_F^b	n	K_F^b	n	K_F^b	n
azoxystrobin	27.0 ^c	0.62	27.0 ^c	0.62	11.2	0.61
chlorotoluron	15.9	0.65	15.9	0.65	7.0	0.60
cyanazine	5.8	0.75	5.8	0.75	2.9	0.61

pesticide	degradation rates (k)		
	model A, intraparticle	model B, combined	model C, intra-aggregate
azoxystrobin	0.005 day^{-1}	0.007 day^{-1}	0.007 day^{-1}
chlorotoluron	0.013 day^{-1}	0.028 day^{-1}	0.028 day^{-1}
cyanazine	0.014 day^{-1}	0.026 day^{-1}	0.026 day^{-1}

^a The same intraparticle diffusion coefficient was used for all pesticides. ^b $K_F = K_{OM}^F \times \text{organic matter fraction}$. ^c K_F for azoxystrobin was adjusted to improve fit.

where K_{OM}^F is the Freundlich coefficient for sorption on organic matter and n is the Freundlich exponent. The equations were solved numerically for an ideally mixed external solution with a finite volume (4). The model was implemented in ORCHESTRA, a modeling framework for chemical speciation and transport calculations developed by Meeussen (15). The model parameters are summarized in Table 1. The percentage organic matter fraction was calculated by multiplying the organic carbon content by a factor of 1.724 (16). The sorption parameters, instantaneous fraction, and effective diffusion coefficient were adjusted to fit the adsorption data, assuming the same fraction and diffusion coefficient for all pesticides. The particle size and porosity are unknown and therefore estimated. The degradation rates were measured.

Combined Diffusion Model (Model B). To describe sorption in aggregates, the intraparticle diffusion model was extended with diffusion into a porous soil aggregate. In this model, diffusion into the aggregate pores is followed by diffusion and sorption in particles inside the aggregates (Figure 1). In the numerical solution, 10 cells represent the 10 concentric aggregate layers, each connected to 10 cells that represent the organic particles in that aggregate layer (Figure 2). Diffusion into the aggregate layers and from there into the particles layers is calculated simultaneously. The model was used to predict sorption in aggregates based on adsorption that was measured on dispersed soil. The input parameters are listed in Table 1. The degradation rates were taken from the aggregate adsorption experiment.

**Figure 1.** Schematic representation of the combined diffusion model, in which diffusion into the aggregate pores is followed by diffusion and adsorption in organic particles.**Figure 2.** Numerical scheme for the combined diffusion model. Diffusion is calculated between the external solution (large cell) and 10 vertically connected cells that represent the aggregate pore solution. Each vertical cell is connected to 10 horizontal cells that represent the reactive particles inside the aggregate. The arrows show the diffusion directions. Each cell represents a concentric layer of a sphere, with its representative volume and surface area.

The aggregate radius (2.5 mm) was estimated from the total weight of the aggregates and the measured aggregate density. The effective diffusion coefficient in the aggregate pores was estimated from the diffusion coefficient in water and the theoretical tortuosity according to the equation of Millington and Quirk (17)

$$D_e = \tau^{-2} D_w = \theta^{1/3} D_w \quad (3)$$

in which D_e is the effective pore diffusion coefficient, D_w is the diffusion coefficient in water, τ^{-2} is the tortuosity correction, and θ is the aggregate porosity. The diffusion coefficient in water was estimated to be $4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ on the basis of the diffusion rate measured in pure alginate (see supporting measurements).

Intra-aggregate Diffusion Model (Model C). To investigate whether adsorption and desorption in soil aggregates can be simulated by radial diffusion and with identical model parameters, the intraparticle diffusion model (A) was scaled up to describe intra-aggregate sorption and diffusion. The soil aggregates are assumed to be homogeneous and spherical with an identical radius a . All soil particles are associated with aggregates, so all sorption is controlled by diffusion into the aggregates, and there is no instantaneous fraction. Diffusion across the gel coating is not taken into account in the model, as diffusion through the gel is fast compared to the time scale of diffusion and sorption in the aggregates. The input parameters are summarized in Table 1. The sorption parameters and the effective diffusion rate for each pesticide were adjusted to fit the adsorption data. The same model was then used (with identical parameters) to simulate desorption.

Supporting Experiments. Two additional experiments were performed and interpreted by diffusion modeling to test (i) pesticide diffusion through alginate gel and (ii) nonreactive diffusion in the coated aggregates. Diffusion of the three pesticides through alginate gel was investigated with spherical beads from pure alginate gel. The beads were prepared as described by Van Beinum et al. (14). One hundred gel beads (1.2 mL) were equilibrated with chlorotoluron (41 mg L⁻¹) and cyanazine (340 mg L⁻¹) in 5 mM CaCl₂ and then added to a beaker with 100 mL of CaCl₂ (5 mM) on a magnetic stirrer. Samples were taken at 10 selected time intervals to measure the diffusion rate of pesticides out of the beads, and three additional samples were taken after 2.5 h to estimate the total release. Azoxystrobin has a much lower solubility (~6 mg L⁻¹) than the other two pesticides, and diffusion was therefore measured in a separate experiment after equilibration with 3.7 mg L⁻¹ azoxystrobin. Separate replicates were used for the 10 sampling times, with a small external solution volume (1.6 mL of gel beads in 4.0 mL of external solution). The small volume of external solution was necessary to ensure that sample concentrations were above the quantification limit.

The diffusion rates of the pesticides in alginate gel were obtained by model fitting with a diffusion model adjusted for nonreactive diffusion in a homogeneous sphere. The release of azoxystrobin, chlorotoluron, and cyanazine was well described by the effective diffusion coefficients 3.5×10^{-10} ($R^2 = 0.971$), 3.5×10^{-10} ($R^2 = 0.995$), and 4.0×10^{-10} m² s⁻¹ ($R^2 = 0.996$), respectively. These values are similar to the diffusion rate expected for diffusion in pure water, which is $\sim 5 \times 10^{-10}$ m² s⁻¹ at 25 °C for organic molecules with a molecular mass of ~ 300 g mol⁻¹ (18).

Diffusion of chloride from the soil aggregates was measured to determine diffusion of a nonreactive tracer in the aggregates. The release of chloride from 22 aggregates (2 g) into 100 mL of 0.05 M CaBr₂ solution was measured after equilibration in 0.05 M CaCl₂. The solution was stirred on an orbital shaker, and 22 solution samples were taken at selected time intervals to measure the diffusion rate; an additional three samples were taken after 2.5 h to measure the total release. The diffusion coefficient for chloride was obtained by model fitting. The diffusion model for pore diffusion in aggregates was extended to describe diffusion in the aggregates as well as in the gel coating. The latter was disregarded in the model for pesticides because diffusion in the gel is much faster than diffusion and sorption in the aggregate interior. For nonreactive solutes, however, diffusion in the aggregate pores is in theory almost as fast as diffusion in the gel, so both processes need to be considered. The theoretical diffusion coefficients for chloride are 1.8×10^{-9} and 1.4×10^{-9} m² s⁻¹ for diffusion in gel and in pores, respectively (eq 3). However, the release curve was dominated by chloride release from the gel coating (~80%) and gave less precise information about diffusion in the pores. Chloride release from the aggregates was well described with a value of 1.4×10^{-9} m² s⁻¹ for diffusion in the gel and in the pores ($R^2 = 0.989$). Although the diffusion rate in the pores could not be determined precisely, the measured rate agreed well with the theoretical value. The results indicate that diffusion of small solutes in the aggregates can be described by pore diffusion with a theoretical tortuosity. The diffusion coefficient for pesticides in the aggregate pores could be predicted in similar manner from eq 3. However, this approach is valid only if there is no additional constrictivity caused by the molecular size of the pesticides.

RESULTS AND DISCUSSION

Time-Dependent Adsorption. The results for adsorption on dispersed soil are shown in Figure 3 (symbols). Adsorption of the three pesticides clearly increased during the 14-day period and showed no indication of attaining equilibrium. Freundlich sorption isotherms were fitted to the data (results not shown). The extent of sorption linearity decreased with contact time. For example, the Freundlich exponent for azoxystrobin decreased from 0.79 to 0.45 between 1 h and 14 days after addition. The lines in Figure 3 are model calculations that will be discussed later.

Adsorption studies in the literature often report that adsorption equilibrium in batch-slurry studies is reached in a relatively short

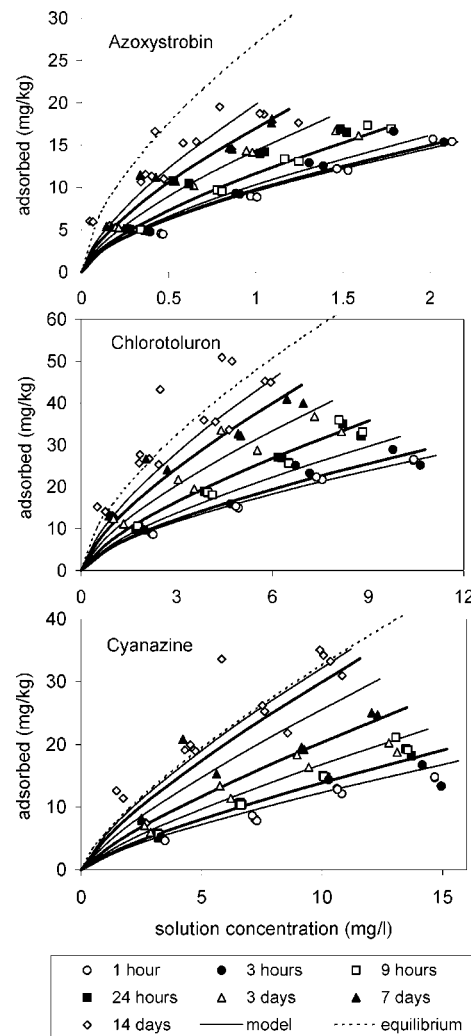


Figure 3. Adsorption of azoxystrobin, chlorotoluron, and cyanazine on dispersed soil after different equilibration times, measured (symbols) and simulated with the intraparticle diffusion model (model A; solid lines). The dotted lines describe the simulated equilibrium–sorption curves.

time, typically within 24 h (e.g., refs 19–21). However, other studies reported that adsorption increases over days, weeks, or even months (e.g., refs 22–24). Wauchope et al. (4) suggest that there are at least three time scales involved in adsorption: an initially rapid adsorption during the first minutes is followed by a slower adsorption step for hours up to days and very slow aging for weeks to years. Therefore, any observed equilibrium at shorter time scales is most likely only an “apparent” equilibrium. Karickhoff and Morris (25) showed that the rate of sorption is negatively correlated with the sorption coefficient K_d and that this can explain very slow sorption kinetics for strongly adsorbing compounds. Another explanation for slow sorption kinetics in batch studies is the disintegration of soil particles during the experiment. Adsorption can increase when particles are broken up by the friction caused by stirring or shaking. The samples in this study were shaken briefly by hand to disperse the soil, followed by gentle mixing on an orbital shaker to keep the particles in suspension, which would prevent particles from breaking up over time.

Time-dependent sorption on coated aggregates is shown in Figure 4. Adsorption of chlorotoluron strongly increased over the first 24 h but did not increase significantly during the following days. This suggests that the system is close to equilibrium after 24 h. Azoxystrobin adsorption increased with

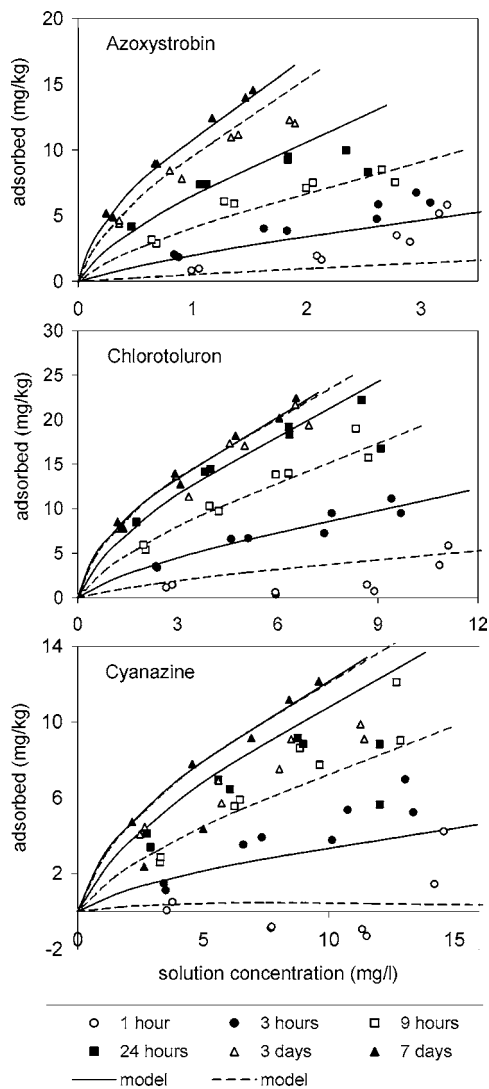


Figure 4. Adsorption of azoxystrobin, chlorotoluron, and cyanazine on coated soil aggregates after different equilibration times, measured (symbols) and simulated with the aggregate diffusion model (model C; solid and dashed lines).

time and did not appear to reach equilibrium during the experiment. It is not clear whether cyanazine adsorption reached equilibrium. The data up to 3 days suggest that adsorption equilibrium was reached within 24 h, but this is inconsistent with the additional increase in adsorption between 3 and 7 days. The latter could be due to the large variation in the adsorption measurements for cyanazine.

The amount of adsorption is much greater in the dispersed system than in the aggregates (Figures 3 and 4). When the 7-day adsorption data were compared, chlorotoluron and cyanazine sorption on dispersed soil is more than double the amount of sorption by aggregates. Even for chlorotoluron, which appeared to reach equilibrium sorption on aggregates, there is considerably more sorption on dispersed soil. The results indicate that part of the sorptive material inside the aggregates was not accessible for pesticide adsorption within a week. It seems that dispersing the soil aggregates released additional sorption capacity that was not accessible in the aggregates. Sorptive materials such as organic matter and clay particles may be associated in sub-aggregates, which could reduce their accessibility for pesticides. As expected, adsorption on aggregates changed over time to a greater extent than adsorption on dispersed soil. Adsorption on

aggregates was clearly slower, presumably because of the additional diffusion step into the aggregates. Sorption approached equilibrium in the aggregate samples, but not in the dispersed soil samples, probably because the very slow additional sorption was unavailable in the aggregates or because this component was too slow to notice at this time scale.

Desorption from Aggregates. Stepwise desorption was measured after one adsorption step and successive desorption steps. The results for azoxystrobin are shown in Figure 5. The top four graphs in Figure 5 show desorption after 7 days of initial adsorption, so the first measurements (at the highest concentration) coincide with the 7-day adsorption curve (dashed line). The bottom four figures show desorption after 1 day of initial adsorption and therefore start off at the 1-day adsorption curve (dotted line). The thick black lines show the results of model simulations that will be discussed later. The discrepancy between the first measurements and the Freundlich curves are mainly caused by variation in sorption between the samples. The sample sizes are small considering the heterogeneity of the soil. During the desorption steps, the concentrations decrease and the measurements describe a desorption curve. The azoxystrobin data clearly show signs of hysteresis (when adsorption and desorption curves do not overlay). The incongruity between the adsorption and desorption curves is particularly clear at smaller adsorption and desorption times (e.g., 1 day).

Hysteresis effects were also observed for cyanazine and chlorotoluron (Figure 6), although differences between the two curves are smaller than for azoxystrobin. The data for these two pesticides also showed more variability. Figure 6 shows only selected results for which the initial adsorption matched with the fitted adsorption curves. The 1-day adsorption data shown for chlorotoluron in the left-hand figures match the 1-day adsorption curve (dotted line). During the desorption steps, the data approach the 7-day adsorption line (dashed line). Cyanazine sorption after 7 days (right-hand figures) matches the 7-day adsorption curve. The desorption data show hysteresis only for the 1-day desorption intervals, not for the 3-day desorption intervals. This suggests that it takes between 1 and 3 days for desorption to approach equilibrium.

Modeling Results. Intraparticle Diffusion Model (Model A). One of our aims was to test whether time-dependent sorption on dispersed soil particles could be simulated with an intraparticle diffusion model (model A). The sorption and diffusion parameters in the model were adjusted to describe the adsorption data. Results from the model are shown in Figure 3. The sorption parameters in the model were taken from the Freundlich curves that were fitted to the 14-day adsorption data (dotted lines in Figure 3). It is possible that sorption equilibrium was not reached within 14 days, but no measurements were made over longer times. It was possible to describe time-dependent sorption of chlorotoluron and cyanazine by assuming equilibrium after 14 days. However, sorption of azoxystrobin was still far from equilibrium, and it was not possible to model the adsorption data by assuming equilibrium after 14 days. The equilibrium Freundlich coefficient (K_F) was adjusted to 1.4 times the coefficient for 14-day adsorption, to give a better description of the sorption data for the different adsorption times. A single diffusion rate was used for all three pesticides. The diffusion rate and the fraction of instantaneous sorption were fitted visually to provide the best description of the sorption data for all pesticides and every sorption interval, resulting in 35% instantaneous sorption and an effective diffusion coefficient of $1 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$. The optimized parameters are shown in Table 1. The model gave a good description for chlorotoluron and

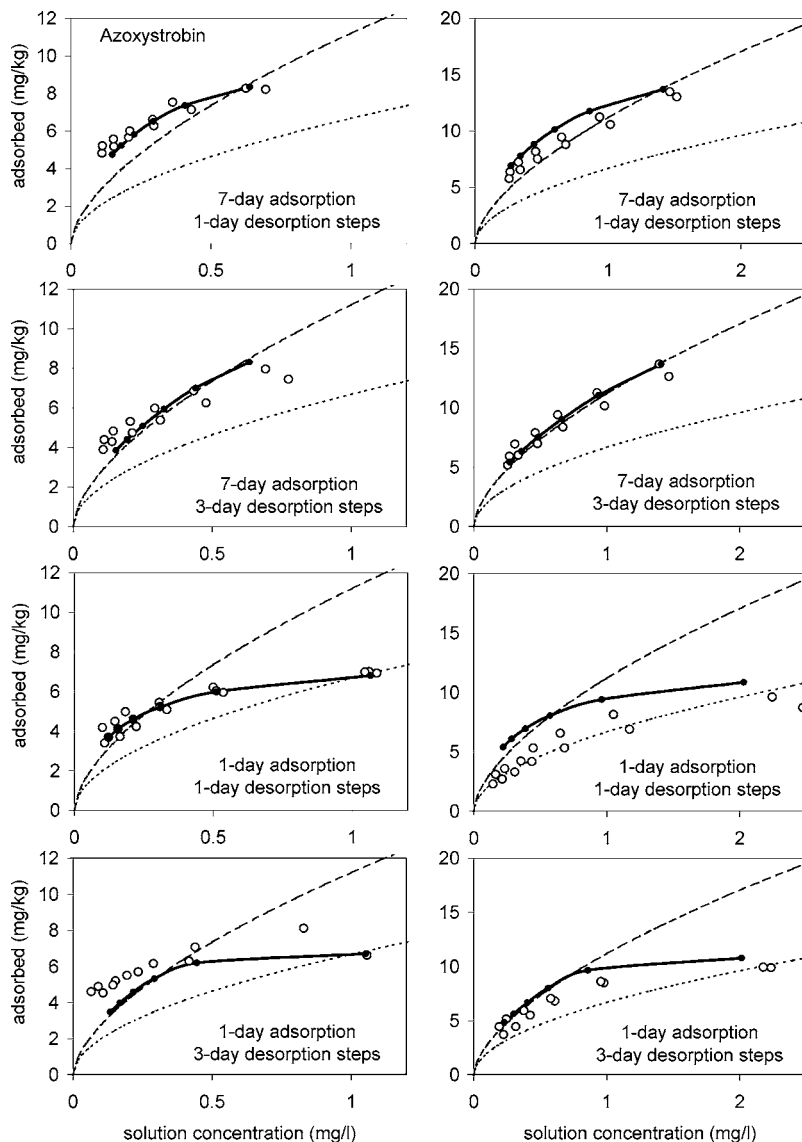


Figure 5. Azoxystrobin sorption measured during the stepwise desorption experiment (open spheres). Dotted and dashed lines are Freundlich curves for 1-day and 7-day adsorption, respectively. The solid spheres connected by the solid line are the model simulations for desorption (model C).

most of the azoxystrobin data. The cyanazine data are difficult to describe because of the sudden increase in sorption for the 7- and 14-day intervals.

The parameters are very similar to the ones that were found in the previous study for sorption of isoproturon on lignin (11). There we found 25% instantaneous sorption and a diffusion coefficient of $2.8 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ for 10- μm particles. The diffusion rate in the model is partly determined by the ratio of the diffusion coefficient and square of the particle radius (D_c/a^2). This value is very similar between the two studies, which means that the time scales for diffusion-limited sorption are very similar in both systems. The fitted diffusion coefficient for dispersed soil in itself does not have any quantitative meaning because the true sizes of the sorptive particles are unknown. We could only suggest that the diffusion rate for natural organic matter and for lignin were similar if particle sizes were similar.

Combined Diffusion Model (Model B). Model B was used to test whether sorption in the aggregates could be predicted theoretically, on the basis of aggregate properties and sorption on dispersed soil. The hypothesis was that sorption in intact soil aggregates is the result of diffusion into the aggregates followed by intraparticle diffusion. The model for diffusion into

organic particles was incorporated into a combined model with diffusion into aggregates and sorption and diffusion in particles inside the aggregate (model B). The particles in the dispersed system showed a large fraction of instantaneous sorption (35%). This was possibly due to fragments that had broken off from the organic matter particles during shaking. This would not have happened to the particles inside the coated aggregates, so no instantaneous sorption was assumed and all sorption sites were associated with particles. The additional parameters needed to describe diffusion into the aggregate pores before the particles were reached were estimated independently.

Figure 7 compares the simulated adsorption curves with the measured adsorption data (symbols). The amount of adsorption was highly overestimated by the model. Sorption in the dispersed system, on which the model was based, was much greater than sorption on the aggregates. Retardation due to diffusion into the aggregate was not enough to explain lesser sorption in the aggregates than on the dispersed soil. Adjusting the diffusion rate in the model did not improve the description. Adsorption of chlorotoluron in the aggregates clearly approached equilibrium as sorption increased less between the measurements at longer times. The same was observed to some extent for azoxystrobin. It would not be possible to reproduce this with

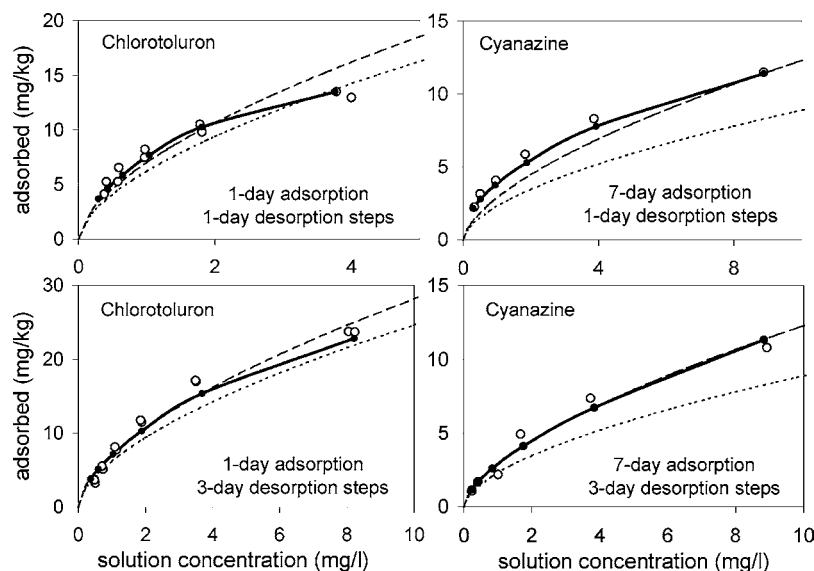


Figure 6. Chlorotoluron and cyanazine sorption measured during the stepwise desorption experiment (open spheres). Dotted and dashed lines are Freundlich curves for 1-day and 7-day adsorption, respectively. The solid spheres connected by the solid line are the model simulations for desorption (model C).

the large amount of sorption that was measured on the dispersed soil. It appears that the sorption capacity is not fully available in the aggregates, at least not at the time scale of the experiments. The combined diffusion model is based on a bimodal structure, in which the reactive particles are mixed evenly through the aggregate and all particles are directly in contact with the pore solution in the aggregate. In reality there will be a continuous distribution of different sized pores in the aggregates, and some of the particles will be clustered in subaggregates. The sorption behavior in the aggregates may have resulted from fast diffusion into larger pores, followed by sorption and diffusion into denser subaggregates and reaction only with particles that were directly in contact with the pore solution. In our system, it was not possible to predict sorption in aggregates from sorption on dispersed soil without a better knowledge of the aggregate structure.

Intra-aggregate Diffusion Model (Model C). To test whether sorption kinetics on aggregates could be explained by a reversible diffusion process, sorption and desorption were simulated with the model for diffusion in aggregates (model C). First, adsorption was modeled by adjusting the maximum sorption and diffusion rate in the model, and then the same parameters were used to simulate desorption from the aggregates. **Figure 4** shows the measured adsorption curves (symbols) with the simulated curves (dashed and solid lines). The Freundlich sorption parameters in the model were fitted to the 7-day sorption curve (solid triangles). It is not certain whether a sorption equilibrium was reached for azoxystrobin and cyanazine, but in the absence of data for longer sorption times, the 7-day sorption curve is the best estimate of equilibrium sorption. The diffusion coefficient was adjusted for each compound to fit the measured curves: $7 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for azoxystrobin, $1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for chlorotoluron, and $5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for cyanazine (**Table 1**). The diffusion model described the sorption data very well for azoxystrobin and chlorotoluron. It was not possible to find a good fit for the cyanazine data because of the sudden increase in sorption between 3 and 7 days. The fitted diffusion coefficients for the pesticides are a factor 3–6 lower than would be expected. The effective diffusion coefficient expected from the diffusion coefficients in water and the theoretical tortuosity in the

aggregates is $\sim 3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. The theoretical diffusion rate is based on the assumption that diffusion of the pesticide molecules is not constricted by their size and that all reactive particles are directly in contact with the pore solution. However, if pores are small, pesticide diffusion could be restricted to the larger pores and it would take longer to reach equilibrium. Renaud et al. (26) found comparable results for pesticide diffusion in artificial clay aggregates. They found effective diffusion rates that were up to 4 times smaller than the expected diffusion rates.

The desorption process was simulated with the same model with the parameters that were fitted to the adsorption curves. In the model, an initial adsorption step was simulated followed by stepwise desorption. The thick black lines in **Figures 5** and **6** show the simulated desorption curves. The model predicted the desorption curves reasonably well. The hysteresis effect that was observed for azoxystrobin (**Figure 5**) was matched well by the model. The observed hysteresis effect was less significant for cyanazine and chlorotoluron (**Figure 6**). The difference is caused by the difference in sorption strength between the three compounds: azoxystrobin adsorbs more strongly, and therefore the sorption and diffusion process takes longer to reach equilibrium. As the system is further from equilibrium, the hysteresis effect is more apparent. The results support the hypothesis that sorption in aggregates is diffusion controlled and reversible and that adsorption and desorption can be described by the same sorption and diffusion parameters. Apparent hysteresis in the adsorption and desorption measurements is probably caused by nonattainment of equilibrium. The results suggest that intraparticle diffusion was not relevant for sorption in our aggregates at the time scale tested.

Conclusions. Time-dependent sorption on soil was investigated for three pesticides with dispersed soil and with intact soil aggregates. The rate-controlling step in the sorption process was examined using process-based diffusion modeling. Significantly more sorption was measured on dispersed soil than on intact aggregates. It seemed that dispersion of the soil creates additional sorption capacity that was not available within the aggregates. Sorption was time-dependent in both systems, but the increase of sorption with time was much greater in the aggregated system than in the dispersed system. Time-dependent

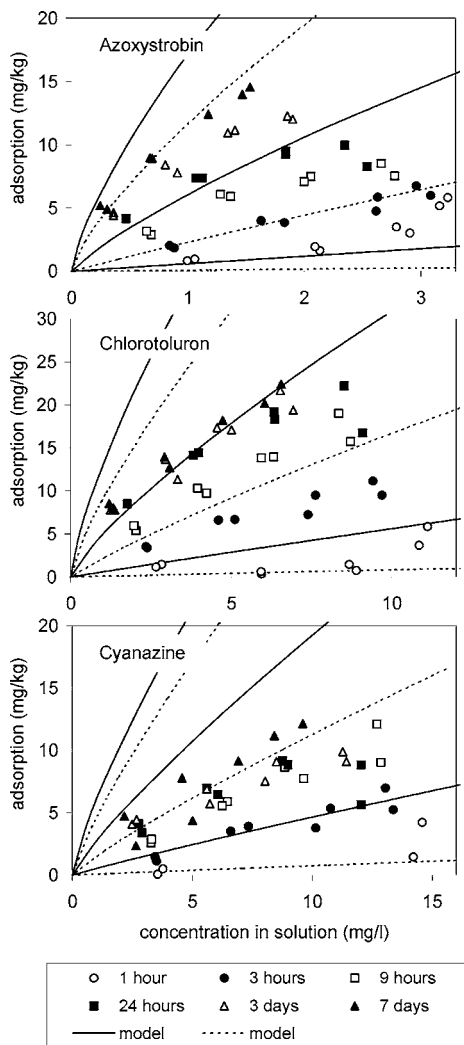


Figure 7. Pesticide adsorption on aggregates measured after different equilibration times (symbols) and simulated with the combined model that describes diffusion into aggregates followed by diffusion and sorption in organic particles inside the aggregates (model B; solid and dotted lines).

sorption in the dispersed system could be described with an intraparticle diffusion model developed previously for sorption on lignin particles (11). It was not possible to simulate the time dependence of sorption on intact aggregates from sorption in a dispersed system. A combined model that takes both intra-aggregate and intraparticle diffusion into account overestimated the rate and the amount of adsorption in aggregates.

Time-dependent sorption on intact soil aggregates could be described by a diffusion model that considers only diffusion into the aggregate followed by instantaneous sorption. No influence of intraparticle diffusion was observed during the 7-day experiments. Adsorption and desorption on soil aggregates were well described by diffusion, although with a diffusion coefficient that was 3–6 times lower rate than expected from the aggregate size and theoretical tortuosity. The results suggest that pesticide sorption and desorption on our clay loam aggregates was mainly controlled by diffusion into and out of the aggregates at the time scale of a week. Sorption was shown to be reversible at the time scale and concentrations tested in these experiments, and adsorption and desorption could be described with the same diffusion parameters. Differences between adsorption and desorption curves were explained by nonequilibrium in the adsorption and desorption steps.

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