The Kinetics of Sorption by Retarded Diffusion into Soil Aggregate Pores

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This study investigates time-dependent sorption of pesticides in soil aggregates. We tested if the sorption kinetics of pesticides in soil aggregates can be described by modeling diffusion into aggregates for a range of soils and pesticides. Our hypothesis is that the rate of sorption is negatively related to sorption strength due to retardated diffusion. Natural aggregates of 3–5 mm diameter were separated from three soils: a clay, a silty clay loam, and a clay loam. The aggregates were stabilized with alginate gel, and adsorption of azoxystrobin, chlorotoluron, and atrazine was measured in batch experiments with eight equilibration times up to 28 days. Equilibrium sorption appeared to be reached within the 28-day period for each pesticide. An intra-aggregate diffusion model was employed to describe the increase of sorption with time. The model describes diffusion of the dissolved pesticides through the pore space inside the aggregates and sorption on internal surfaces. Sorption could be described by pore diffusion into the aggregates with diffusion coefficients between 0.5×10^{-10} and 1.5×10^{-10} m² s⁻¹. The model fits support the theory that pore diffusion is the rate-limiting process for sorption of pesticides in aggregates, although the diffusion coefficients were a factor 3–10 smaller than the theoretical diffusion coefficient for diffusion in water. Comparing the results from the different pesticide–soil combinations showed that the extent of nonequilibrium increased with increasing sorption strength. This confirmed that sorption takes longer to reach equilibrium for pesticides and soils with stronger sorption. The differences between the different pesticides and soils were fully accounted for in the model by stronger retardation of the more strongly sorbed pesticides. The results imply that diffusion into aggregates may be the major time-limiting process for sorption of pesticides in structured soils. Commonly performed sorption experiments with sieved soil fail to account for this process.

Introduction

Sorption of organic contaminants to soil is an important control on their mobility and availability in the environment. Conceptual representations of sorption are often simplified by assuming the establishment of instantaneous equilibrium. However data deviating from this assumption have been widely reported, challenging the validity of the simplification (e.g., refs *1–3*).

Nonideal or time-dependent sorption behavior has been attributed to several factors, including diffusive mass-transfer resistances, rate-limited sorption reactions, nonlinearity in sorption isotherms, and sorption–desorption nonsingularity (*4*). Sorption nonequilibrium resulting from physical nonequilibrium and intraorganic matter diffusion have been suggested to be the two predominant factors responsible for the nonideal sorption of nonionic or hydrophobic compounds (*5–7*). Any increase in strength of sorption with time directly affects the availability of chemicals for transport to ground or surface waters. Several authors working at a range of scales have reported how concentrations of pesticide and other chemicals in leachate or groundwater decrease more rapidly than expected based solely on loss of chemical by degradation (*8–13*).

Most sorption studies are performed on sieved soils and the number of studies of pesticide sorption to intact soil aggregates is limited. Studies on sieved soil do not necessarily represent sorption behavior in structured soils. Working with natural aggregates poses the practical difficulty that many aggregates would disintegrate when used in batch sorption studies. Sorption studies on aggregates have been conducted by batch equilibration with pesticide solution (*14*) and by extracting available water from aggregates at different times after application of pesticide (*15, 16*). While application on moist aggregates is more realistic in relation to application in the field, batch studies have the advantage that experimental conditions are more controlled and therefore give the opportunity to differentiate between the multiple causes of time-dependent sorption.

In previous work a method was developed to study sorption on natural aggregates in batch systems (*17*). Aggregates from a clay loam soil were stabilized by coating with Hydro-gel. Hence it was possible to use the aggregates in gently shaken batch sorption studies without disintegration of the aggregates. An intra-aggregate diffusion model was developed to describe the increase of sorption with time (model C (*17*)). The model describes diffusion of the dissolved pesticides through the pore space inside the aggregates and sorption on internal surfaces. This work supports the assumption that diffusion into aggregates is rate limiting for the retention of nonionic pesticides.

According to the diffusion model it takes longer for a pesticide that is more strongly sorbed to attain equilibrium sorption than for one that is more weakly sorbed. Diffusion coefficients for pesticides are expected to vary little between compounds as pesticide molecules tend to have similar size and molecular weight. The model showed that even if the diffusion coefficient is identical for two pesticides studied in a single soil, it will take longer until equilibrium is achieved for the more strongly sorbing compound (*17*). Similarly, for a single pesticide studied in two soils, it is predicted that sorption equilibrium will be attained later in the soil with stronger capacity for sorption. This corresponds to the theory that transport of pesticide into the interior of soil aggregates is retarded by sorption. In moist soil, pesticides will move into aggregates by diffusion though the water-filled internal pores (pore diffusion). If a pesticide is sorbed, only a small part of the pesticide will be in solution and able to move by diffusion (*18*) and this will slow down the movement of pesticides into the aggregate. The delay can be calculated and is often referred to as the retardation factor (*19*). The extent of retardation is proportional to the sorption strength.

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TABLE 1. Soil Properties

soil series	textural classification	pH(H2O)	CaCO3[a](%)	OC[a](%)	CEC(cmol kg^{-1})	clay(%)	silt(%)	sand(%)
Evesham	clay	7.9	11.1	3.40	25.5	59.2	33.5	7.3
Brockhurst	silty clayloam	6.7	<0.1	2.47	19.4	36.4	52.8	10.8
Ragdale	clayloam	7.0	0.188	2.55	15.9	33.7	44.5	21.8

[a] According to the Metson method, ref 21.

The present paper sets out to evaluate the hypothesis that the extent of nonequilibrium sorption in soil aggregates is related to strength of sorption. Assuming that the diffusion coefficient is similar for different pesticides and soils, the diffusion model will be used to describe time-dependent sorption on aggregates using a single diffusion coefficient irrespective of sorption strength. The diffusion model reported by van Beinum et al. (17, 20) is applied systematically to several pesticide−soil combinations. The capability of the model to match sorption for all pesticide-soil combinations using a single diffusion coefficient is assessed to evaluate the model assumption that time to sorption equilibrium is determined only by the strength of sorption. A negative outcome would imply that either the model assumption is incorrect and that a further process is implicated in controlling sorption kinetics or that effective diffusion coefficients vary more markedly than expected between the soils and pesticides.

Materials and Methods

Soils, Pesticides and Analysis. The main properties and textural classification of the selected soils are shown in Table 1. The main properties and textural classification of the selected soils are shown in Table 1. Soil analysis were performed on air-dry soil sieved at 2 mm (Laboratoire d'Analyses des Sols d'Arras, INRA). Organic carbon and CaCO3 were analyzed according to ISO 10694. CEC was determined according to the Metson method (21).

Soils were sampled from the top 15 cm of agricultural fields in different locations in the UK. Moist soil aggregates between 3 and 5 mm were isolated by sieving. Spherical aggregates of similar size were selected manually with the aim of obtaining homogeneous batches. The porosity and density of the soil aggregates were estimated using the paraffin coating method reported by Black et al. (22). 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}. Values obtained are given in Table 2. The average radius of the aggregates was calculated from the dry weight and bulk density of the aggregates.

Pesticides investigated were the strongly sorbing fungicide azoxystrobin [methyl (E)-2-{2[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate], and two moderately sorbing herbicides, chlorotoluron [3-(3-chloro-p-tolyl)-1,1-dimethylurea], and atrazine 6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine. The commercial formulations used were Amistar, 250 g/L, 23.1% w/w azoxystrobin suspension concentrate (SC); Alpha chlorotoluron 500 g/L, 43.9% w/w SC; and Atrazol atrazine 500 g/L, 40% w/w SC. Interaction between the three pesticides was tested in a preliminary sorption experiment (soil/solution ratio 1:2, 24 h of shaking) with a starting concentration of 1 mg L^{-1} for each pesticide. No difference in adsorption was observed when three pesticides were applied together compared to when individual pesticides were applied to different soil samples.

Pesticide concentrations were measured on an Agilent 1100 series HPLC equipped with a PDA photodiode array detector and a Discovery C-18 column (Supelco, Bellefonte, PA). The mobile phase was 40% acetonitrile and 60% aqueous

TABLE 2. Input Parameters for the Intra-Aggregate Diffusion Model

	aggregate parameters		
	Evesham	**Brockhurst**	**Ragdale**
radius (mm)	2.41	2.43	2.54
dry bulk density (kg dm^{-3})	1.70	1.65	1.45
porosity	0.34	0.36	0.44
tortuosity factor	0.70	0.71	0.76

	freundlich Sorption Parameters Kf (mg$^{(1-n)}$L^{n}kg^{-1}) and n (−)					
	Kf	n	Kf	n	Kf	n
azoxystrobin	25.29	0.8	25.05	0.82	20.04	0.84
chlorotoluron	14.61	0.55	6.44	0.69	5.05	0.68
atrazine	4.16	0.73	2.87	0.75	2.62	0.70

	pesticide degradation rates (d^{-1})		
azoxystrobin	$7.67 \cdot 10^{-3}$	0	$1.28 \cdot 10^{-3}$
chlorotoluron	6.27×10^{-3}	2.64×10^{-3}	2.68×10^{-3}
atrazine	2.83×10^{-3}	0	2.72×10^{-3}

	fitted diffusion coefficients (D$_w$ in m^2 s^{-1})		
azoxystrobin	1.0×10^{-10}	1.0×10^{-10}	0.5×10^{-10}
chlorotoluron	1.0×10^{-10}	1.5×10^{-10}	1.5×10^{-10}
atrazine	1.0×10^{-10}	1.0×10^{-10}	1.0×10^{-10}

solution of phosphoric acid (0.04% H3PO4 by volume) with a flow rate of 1 mL min^{-1}. Detection was by UV absorbance at 210 nm. The limits of quantification were 150 μg L^{-1} for azoxystrobin, 50 μg L^{-1} for chlorotoluron, and 60 μg L^{-1} for atrazine.

Preparation of Coated Aggregates. For each replicate, 10 aggregates were selected with a total weight of 1 g (moist soil). The aggregates were stabilized by coating them with alginate gel following the method in Van Beinum et al. (17). Alginate solution was prepared by adding 7.5 g of sodium alginate from brown algae (Sigma) to 1500 mL distilled water. The solution was stirred thoroughly and left overnight to allow air bubbles to release. This gel was selected because it has an open structure that allows small molecules to diffuse through the gel at a similar rate as diffusion in water (23, 24). Individual oven-dry aggregates were initially placed in a desiccator connected to a vacuum pump (−80 kPa) with the aim of removing the air from the aggregate pores. Under vacuum, the aggregates were dipped in alginate solution. A thin layer of alginate solidified immediately upon contact with the aggregate, therefore we assume that the alginate did not diffuse into the aggregate pores during the coating process but remained on the outside of the aggregates The coated aggregates were transferred into a 0.1 M CaCl2 solution to complete cross-linking of the alginate gel. Aggregates then underwent the same process three times. The final coated aggregates were washed and equilibrated another three times with a diluted CaCl2 solution (5 mM). The sets of coated aggregates were weighed to calculate the amount of water

associated with the aggregates and gel, assuming a water content of approximately 1 mL g^{-1} gel (17).

Time-Dependent Sorption Experiments. Sorption experiments were performed under conditions of gentle shaking. Ten coated soil aggregates (~1 g dry weight) were placed in a 20 mL glass vial, and 4 mL of pesticide solution was added to each vial. Three replicates were prepared for each time-point and for each pesticide concentration. Four different concentrations were used for each added pesticide solution. The concentrations were approximately 4, 8, 12, and 16 mg L^{-1} for chlorotoluron and atrazine. The concentrations of azoxystrobin were approximately 0.5, 1, 3, and 6 mg L^{-1} for application to the Evesham soil, and 1, 2, 5, and 10 mg L^{-1} for application to the Brockhurst and Ragdale soils. The solutions of azoxystrobin were prepared at a smaller concentration because of its low hydrosolubility. All solutions were prepared in 0.01 M CaCl$_2$.

After 1, 3, 9 h and 1, 3, 7, 14, and 28 days, three replicates were taken for each pesticide concentration and the supernatant was taken off with a pipet and retained for analysis. Then the sampled aggregates were crushed with a glass rod to break the alginate coating; the pesticide was extracted from the crushed aggregates with 6 mL acetonitrile in a wrist-action shaker for 2 h. The recoveries obtained at the beginning of the experiment were 95−110% of the added pesticide mass. Degradation of the pesticides during the 28 days of shaking was limited (residue recovered was 88−110% of the initial mass). Degradation rates were derived by fitting first-order kinetics to total residue concentrations. Adsorption in coated aggregates was calculated from the solution concentration in the samples and corrected for degradation. The solution volume used in the calculations included the water inside the aggregate pores and in the gel coating, so redistribution of pesticide between the external and internal solution was not counted as adsorption. The solution volume in the aggregates and gel was calculated from the difference in weight of the coated aggregates and the soil dry-weight.

Diffusion Modeling. An intra-aggregate diffusion model was used to describe diffusion and adsorption of pesticide in natural clay loam soil aggregates (17). The model describes pesticide migration into a spherical aggregate via diffusion through the aggregate pores followed by adsorption on the solid phase inside the aggregate. Local instantaneous equilibrium is assumed between the concentration in the pore solution and the locally adsorbed concentration. Local adsorption is described by the Freundlich equation

$$S = K_F C^n \tag{1}$$

where S is the locally adsorbed concentration (mg kg^{-1}), C is the local concentration in the pore solution (mg L^{-1}), K_F is the Freundlich coefficient (mg$^{(1-n)}$L^n kg^{-1}) and n is the Freundlich exponent (−). Degradation of the compounds during diffusion and sorption was calculated assuming first-order degradation and equal degradation rates for the dissolved and adsorbed fractions.

The soil aggregates were assumed to be homogeneous and spherical with an identical radius. Diffusion across the gel coating is fast relative to diffusion inside the aggregates and was not taken into account in the model. Diffusion inside the aggregate is described by

$$\theta\frac{\partial C}{\partial t} + \rho\frac{\partial S}{\partial t} = -\theta\tau D_w\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) - k(\theta C + \rho S) \tag{2}$$

where C is the local concentration in the pore solution (mg m^{-3}), S is the locally adsorbed concentration (mg kg^{-1}), D_w is the diffusion coefficient in water (m^2 d^{-1}), τ is the correction factor for tortuosity (−), ρ is the bulk density of the aggregate (kg m^{-3}), θ is the water-filled porosity of the aggregate (−),

and k is the first-order degradation rate (d^{-1}). The equations were solved numerically for an ideally mixed external solution with a finite volume. The model was implemented in ORCHESTRA, a modeling framework for chemical speciation and transport calculations developed by Meeussen (25).

The input parameters for the diffusion model are summarized in Table 2. The theoretical tortuosity factor in the pores was calculated from the water-filled porosity as $\theta^{1/3}$ (26). The Freundlich parameters for local sorption are the same as the sorption parameters that would be found after prolonged equilibration in a batch experiment. The sorption parameters in the model were set to the experimental sorption parameters that were measured after 28 days, assuming that equilibrium in the experiment was reached within 28 days. The diffusion coefficient in water (D_w) depends on the hydrated molecular volume of the compounds. For molecules with a molecular weight around 300 g mol^{-1} the diffusion coefficient in water is expected to be around 5×10^{-10} m^{2}s^{-1} (27). The diffusion coefficients were initially set to 1×10^{-10} m^{2}s^{-1} for all soils and compounds. The calculations were repeated with an adjusted diffusion coefficient where necessary to quantify the magnitude of change required to obtain an acceptable fit to the measured data.

Results and Discussion

Time Dependent Sorption Experiments. Results for adsorption of the three pesticides on natural soil aggregates up to 28 days are shown in Figure 1 (symbols). The solid lines in Figure 1 show the results of the model simulations, which will be discussed later. In all cases, the measured pesticide adsorption isotherms were well described by the Freundlich equation (see the Supporting Information). On the whole, the isotherms were "L" type (concave initial curvature) according to the classification of Giles et al. (28). The extent of sorption linearity decreased with increasing contact time for atrazine and chlorotoluron. For example, the Freundlich exponent for atrazine in the Evesham soil decreased from 1.02 after 1 h to 0.75 after 28 days. Freundlich exponents for azoxystrobin did not show a consistent trend. This decrease of sorption linearity is consistent with previous findings in the literature (15, 29, 30). The phenomenon may be partly due to increased retardation at smaller concentrations. Retardation is proportional to the sorption strength (K_d) and is therefore greater for smaller concentrations than larger concentrations when sorption is nonlinear. The sorption curve may therefore appear more linear at smaller equilibration times, because the smaller concentrations are further from equilibrium than the larger concentrations.

The results suggest that equilibrium sorption was reached during the 28-day experiment for all pesticide−soil combination. The amount of sorption increased rapidly during the first three days. The curves started to overlap at later time points, indicating that the amount of sorption was no longer increasing. For some soil-pesticide combinations this was more obvious than for others due to the variability between measurements. For example the curves for azoxystrobin sorption to the Ragdale soil were almost overlapping for the 3-day and 7-day measurements, but then sorption increased again between 7 and 14 days. Overall, sorption seemed to reach equilibrium sooner for atrazine and chlorotoluron than for azoxystrobin.

To investigate the extent of nonequilibrium for each soil−pesticide combination we calculated K_d-values for each of the measurements after 1 day and after 28 days. The K_d (L kg^{-1}) was calculated as the ratio between the amount adsorbed (mg kg^{-1}) and the concentration in the external solution (mg L^{-1}). Figure 2 shows the extent of nonequilibrium (expressed as 1-day K_d as a percentage of 28-day K_d) plotted against the K_d at equilibrium (taken as that at 28 days). All values are the average of three replicates. If sorption was far
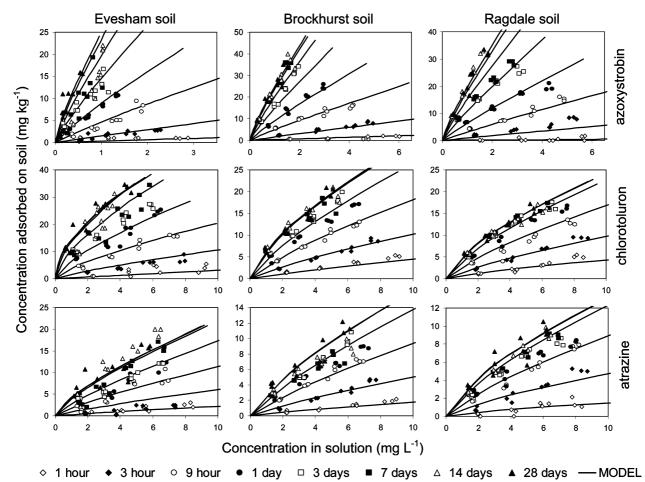
FIGURE 1. Adsorption of azoxystrobin, chlorotoluron, and atrazine on coated soil aggregates after different equilibration times, measured (symbols) and simulated with the intra-aggregate diffusion model (solid lines).
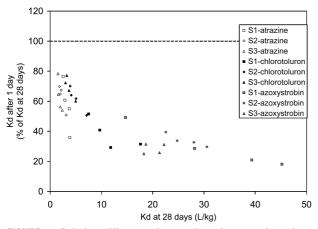

FIGURE 2. Relative difference in sorption after 1 and 28 days for different combinations of soil and pesticide.

from equilibrium after 1 day, this would give a small value on the *y*-axis. The results show that sorption is closer to equilibrium after 1 day for soil-pesticide combinations with lower K_d. The 1-day measurements were generally closer to equilibrium for atrazine samples and some of the chlorotoluron samples. The measurements were furthest from equilibrium for the azoxystrobin samples and for the chlorotoluron in the Evesham soil. A clear inverse relationship between the speed of approach to sorption equilibrium and the strength of sorption was confirmed. Sorption was further from equilibrium after 1 day for those pesticides and soils that had stronger sorption after 28 days.

Diffusion Modeling. Diffusion and sorption in the aggregates was simulated with the intra-aggregate diffusion model using the model parameters in Table 2. Solid lines in Figure 1 give the results of the model simulations. Initially a diffusion coefficient (D_w) of 1.0×10^{-10} m^2 s^{-1} was used to describe pore diffusion for each soil−pesticide combination. This value gave a good description of most of the soil-pesticide combinations. However, the rate at which equilibrium was reached was overestimated for azoxystrobin in the Ragdale soil and underestimated for chlorotoluron in the Brockhurst and Ragdale soils. Better fits were obtained with $D_w = 0.5 \times 10^{-10}$ m^2 s^{-1} for azoxystrobin in the Ragdale soil and with 1.5×10^{-10} m^2 s^{-1} for chlorotoluron in the Brockhurst and Ragdale soils. Figure 3 illustrates the effect of the diffusion coefficient for sorption of azoxystrobin in the Ragdale soil. With the adjusted diffusion coefficients (Table 2), the model gave a good description of most curves. In cases where the data are not well described by the model this is often due to large variations in the measurements. For example, the 3 h sorption curve for atrazine in the Evesham soil could not be described because there was no sorption increase between the 1 and 3 h data and a large increase between the 3 and 9 h data.

Most of the data sets (six out of nine) could be described with the same diffusion coefficient which supports the theory that time-dependent sorption in the aggregates is controlled by pore diffusion. Each of the three pesticides was described despite strength of sorption differing between the pesticides by up to a factor of 10. This suggests that the model describes the retardation caused by sorption correctly. Not all the sorption data could be described with the same diffusion coefficient. The diffusion coefficient had to be halved for one data set and increased by 50% for two data sets. There
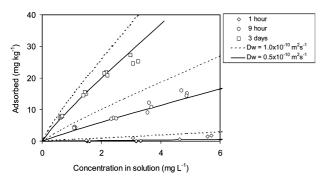
FIGURE 3. Influence of the diffusion coefficient on the model description of azoxystrobin sorption by aggregates from Ragdale soil. Dotted and solid lines show the results from model simulations with a Dw of 1.0×10^{-10} m^{2}s^{-1} and 0.5×10^{-10} m^{2}s^{-1}, respectively.

is, however, no obvious trend that shows that certain soils or pesticides deviate from the theory.

The fitted diffusion coefficients are a factor of 3−10 smaller than the diffusion coefficient expected for diffusion of pesticides in water, which is around 5×10^{-10} m^2 s^{-1} (*27*). The diffusion coefficient in water should be applicable to diffusion in aggregate pores based on the assumption that diffusion is not restricted by the size of the pores, and that all reactive surfaces are directly in contact with the pore solution. The size of the hydrated pesticide molecules is expected to be small in comparison to the majority of the pores. However, it is possible that part of the reactive surfaces are not in direct contact with the larger pores and that sorption on these surfaces is slowed down by diffusion into denser regions inside the aggregates. Similar diffusion coefficients were found in previous studies. Van Beinum, et al. (*17*) fitted diffusion coefficients of 7×10^{-11}, 1×10^{-10}, and 5×10^{-11} m^{2}s^{-1}, for sorption of azoxystrobin, chlorotoluron, and cyanazine, respectively, in aggregates from a clay loam soil. These values were a factor of 5−10 smaller than expected from the diffusion coefficient for diffusion in water. Renaud et al. (*31*) found comparable results for pesticide diffusion in artificial clay aggregates from two clay soils. They found diffusion coefficients that were between 1.1 and 4.4 times smaller than the values they calculated based on the diffusion coefficients in water.

The model description is based on the assumption that diffusion through the pores of the aggregates is the only rate-limiting process. The successful fitting of the sorption curves supports this assumption; however, it does not necessarily exclude alternative diffusion mechanisms. Alternatively, the sorption rate could be governed by diffusion into organic soil particles inside the aggregates. In previous work (*17*) sorption by coated aggregates was compared to sorption onto soil particles in a suspension of the same soil. Sorption onto soil particles was characterized by a fast initial sorption during the first hour followed by a slower increase in sorption during the following period. Coupling diffusion into the aggregate with diffusion into the internal particles in a two-dimensional diffusion model did not aid the description of sorption in aggregates. The gradual approach of equilibrium within 28 days does not give support for a second diffusion step to occur. It may be that retarded sorption in the organic particles could not be observed, either because the process is fast relative to retarded diffusion into the aggregates or because the process is too slow to observe an additional increase in sorption after 28 days. It was concluded that diffusion into the particles did not contribute to time-dependent sorption in aggregates at the observed time scale.

The results in Figure 2 confirmed that there is an inverse relationship between the speed of approach to sorption equilibrium and the strength of sorption. Sorption measured

after 24 h was further from equilibrium for those pesticides and soils that showed stronger sorption. It is not certain whether sorption on disturbed soil will show the same relationship. Some studies on sieved soil have shown an opposite relationship, i.e., that the extent of nonequilibrium sorption is greater for less strongly sorbed pesticides. Mamy and Barriuso (*32*) studied increases in apparent K_d with time by extracting incubated soil with calcium chloride solution at intervals. They demonstrated greater increases in the apparent sorption coefficient (K_d) with time for more weakly sorbed pesticides. However, they explained that this was partly due to nonextractable residues and to nonlinear sorption and degradation. Gaillardon (*2*) also found a greater increase of the partition coefficient for isoprotoron than for the more strongly bound pesticide diuron in sterile soils. Kah and Brown (*33*) measured adsorption of six pesticides in nine soils after 1 day and after 7 days. They expressed the extent of nonequilibrium as the increase of K_d between 1 and 7 days and found no correlation with sorption strength. More research is required into discrepancies between sorption kinetics in sieved soil (<2 mm) and intact aggregates (>3 mm). The fact that studies with sieved soil to not show the correspondence between extent of nonequilibrium and strength of sorption that has been demonstrated here is indirect evidence that transport through intra-aggregate pores influences the kinetics of sorption. Sorption experiments are commonly performed with sieved soil and fail to account for this process.

Acknowledgments

Supporting Information Available

Freundlich parameters were derived for the adsorption curves measured after 1, 3, 9, and 24 h, and after 3, 7, 14, and 28 days. The Freundlich parameters are presented in Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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