JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Degradation and Sorption of Pirimiphos-methyl in Two Nigerian Soils†

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This research is a continuation of a study on the behavior of hydrophobic organic compounds in the environment and describes the simultaneous abiotic degradation and sorption of pirimiphos-methyl (*O*-2-diethylamino-6-methylpyrimidin-4-yl *O*,*O*-dimethylphosphorothioate) under controlled conditions in soil/water slurries. A microfiltration−HPLC technique was employed to follow these processes in two well-characterized soils from the Middle Belt region of Nigeria. Rapid sorption of the pesticide occurs during the first 10 min of equilibration and accounted for 37% of the original pirimiphos-methyl in the Rhodic Kandiustalf soil and for 41% of the original concentration in Aquic Ustropept soil. Subsequent slow processes were followed during the remaining 30 days of the experiment. During this time, first-order rate constants for disappearance from solution of pirimiphos-methyl were found to have values of 6.1×10^{-7} and 9.8×10^{-7} s^{-1} for the Rhodic and Aquic soils, respectively. Similarly, rate constants for production of the product, pyrimidinol, were calculated to be 6.0×10^{-7} and 9.4×10^{-7} s^{-1} for the Rhodic and Aquic soils, respectively, giving pesticide degradation half-lives of 13 and 8.5 days. Disappearance of the pesticide is discussed in terms of a scheme involving both sorptive uptake by the soil and degradation by hydrolysis in the presence of the soil matrix. The labile sorption capacities for pirimiphos-methyl in the Rhodic and Aquic soils were found to be 0.75 and 0.90 μmol g^{-1}, respectively.

KEYWORDS: Pirimiphos-methyl; degradation; hydrolysis; soil sorption; pesticide

INTRODUCTION

Pesticides are widely used in agriculture to protect seeds and crops, and therefore they can be of major benefit in food and fiber production systems. However, there are problems associated with the use of pesticides in terms of health to humans and other organisms living in the environment as a whole. Pesticides, and in some cases their degradation products, are generally toxic materials, and their toxic effects can also be played out on nontarget organisms. For this reason there is a considerable interest in the fate of pesticides as they interact with other components of the environment including target and nontarget organisms.

There are some 200 different organophosphorus insecticides available in the marketplace, representing ∼40% of global insecticide use and accounting for 30−45% of the registered pesticides in North America alone (*1*). The use of this class of pesticides is favored over that of their more persistent organochlorine counterparts because of their potency and their ability to degrade more readily in the environment. Despite being susceptible to relatively rapid degradation, organophosphorus insecticides have been found in varying concentrations in ground and surface waters, including that used for drinking. There is therefore an increasing environmental concern with regard to these compounds.

Pirimiphos-methyl is a powerful insecticide and acaricide with a range of activity toward many crop pests. Pirimiphos-methyl has been recommended (*2*) as a contact insecticide for preventive application on common beans, strawberry, and corn, provided the application ceases 2 weeks before harvest. It has also been recommended as a fumigant to be used against pests in stored products and for public health applications.

The present research continues a series of studies on the behavior of hydrophobic organic compounds in soil/water systems and involved examination of the interaction between pirimiphos-methyl and two Nigerian soils. The objectives of the research were to investigate the fate of pirimiphos-methyl including its abiotic degradation in soil/water slurries and the subsequent distribution of pesticide and degradation product between the soils and associated soil water. Kinetic experiments were designed to obtain rate information related to the disappearance of the pesticide from solution and to the simultaneous formation of its primary degradation product in solution. The studies were further designed to measure the sorption capacities of the soils for the pesticide and to test for intraparticle diffusion.

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† Part 8 in a series titled "Mechanisms of Abiotic Degradation and Soil−Water Interactions of Pesticides and Other Hydrophobic Organic Compounds".

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10.1021/jf0203747 CCC: $22.00
Published on Web 08/31/2002

Table 1. Properties of the Study Soils (Values Taken from Ref *4*)

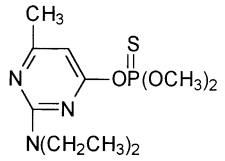
property	Rhodic Kandiustalf	Aquic Ustropept
pH in H_2O	4.89	6.20
pH in slurry	5.20	6.58
organic carbon (%)	0.35	0.84
clay content (%)	8.5	19.1
sand content (%)	90.4	72.6
silt content (%)	1.2	8.3
effective cation exchange capacity (CEC) [cmol (+) kg^{-1}]	3.05 (±0.02)	20.2 (±1.4)

MATERIALS AND METHODS

Liquid Chromatography (LC). Gamble and Khan (*3*) have devised a technique that allows one to determine the changing distribution of pesticide between water and soil in a slurry under controlled conditions in the laboratory. The method involves successive injections of filtrate from the slurry, as well as the unfiltered slurry, into an LC instrument. To allow direct injection of aliquots of well-dispersed slurries, it is necessary to modify a conventional LC instrument by incorporation of in-line microfilters (0.5 and 2 μm) upstream from the guard column. The filters trap the soil particles, and the flow of the mobile phase results in the removal of extractable pesticide from the retained soil. In the present study, a Varian LC instrument was used, consisting of a Varian Star 9002 solvent delivery system and a Varian 9050 variable-wavelength UV−visible detector. A Varian Star chromatography workstation version 4.02 was employed for peak integration. A Rheodyne model 7125 injector (20 μL loop) was used to load samples onto the column. The column was an Altech Platinium C-18 100 A, 5 μm particle size, with a diameter of 4.6 mm and 150 mm in length. A replaceable stainless steel guard column (10 μm, protein and peptide C-18 cartridge) was used to trap solids and protect the main analytical column. The guard column was itself protected by a 0.5 μm microfilter. The mobile phase as an acetonitrile/water (70/30%) solution with a flow rate of 1.0 mL min^{-1}. In a typical experiment, a 20 μL injection of slurry contains ~400 μg of soil particles, trapped on the in-line filters. Using the mobile phase flow rate of 1.0 mL min^{-1} and with a peak retention time of 5.8 min, the ratio of "extractant" to sample is 14.5 L g^{-1} of soil.

Soils. A sandy red soil from the Ankpa Plateau, Rhodic Kandiustalf, and a medium-fine, gray alluvial soil associated with the River Benue, Aquic Ustropept, were collected in Benue State (the Middle Belt) in Nigeria for investigations in this research. These represent two of the major agricultural soils in the area. Some of their important properties (*4*) are given in **Table 1**. To eliminate biological activity and prevent microbial degradation of the pesticide, the soils were γ-irradiated at Nordion International, Quebec.

Chemicals. The pirimiphos-methyl (*O*-2-diethylamino-6-methylpyrimidin-4-yl *O*,*O*-dimethylphosphorothioate, **1**) and one of its degradation products (2-dimethylamino-6-methylpyrimidin-4-ol, henceforth called pyrimidinol, **2**) were analytical grade chemicals of 99.5% purity. They were obtained from ChemService Inc. U.S.A. and used without further purification.



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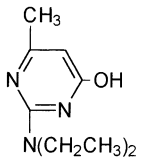

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Preparation of Stock Solution. A stock standard solution of pirimiphos-methyl (3.04×10^{-4} mol L^{-1}) was prepared in 10 mL of dry 1,4-dioxane and then diluted to 1 L with deionized distilled water (DDW). Analytical standards were prepared from this stock by serial dilution of aliquots to achieve the required concentration.

Sorption Kinetic Procedure. To ensure complete wetting of the soil surface, a 500 mg portion of the soil (particle size of <150 μm) was suspended with stirring in ~20 mL of deionized distilled water for 24 h in a 40-mL Pyrex sample vial with a Teflon/silicon rubber septum, housed in a constant-temperature jacket at 25 °C. Before the kinetic run, nitrogen gas was bubbled into the slurry for 10 min at 50 mL min^{-1} to establish anaerobic conditions. The kinetic run was initiated by the addition of 5.0 mL of the pirimiphos-methyl standard stock solution. Stirring with a Teflon-coated magnetic stir bar maintained a uniform suspension of particles throughout the course of analysis. Analysis of the spiked samples started 10 min after addition of the pesticide and was monitored by measuring areas of the peaks for pesticide and degradation product at programmed wavelengths of 220 nm (pyrimidinol, $t_R = 2.5$ min) and 248 nm (pirimiphos-methyl, $t_R = 5.8$ min). Identical spikes of pirimiphos-methyl and pyrimidinol in unbuffered DDW without soil were processed in the same way as the slurry and were used as external standards for the LC analysis. In soil-free solutions, peak areas for the pesticide remained constant (within experimental error) throughout the experimental period. This indicated that there were no or insignificant losses occurring as a result of adsorption onto container walls, volatilization, or uncatalyzed degradation.

Two types of samples were analyzed at measured times. The first involved preinjection centrifugation, for 10 min at 6200*g*, of an aliquot of the slurry. The clear supernatant containing residual pirimiphos-methyl was then injected into the LC for analysis. A sequence of such measurements at predetermined time intervals produced a kinetic curve for the solution phase concentration. The second type of analysis used a postinjection filtration. An aliquot of slurry was taken into a Hamilton syringe and injected directly into the injection loop. The on-line filters trapped the suspended particles, where they were washed by the mobile phase. The chromatographic peaks from the latter analysis measured the total of the pirimiphos-methyl in solution plus that removed from the solids by the mobile phase. This sequence of measurements produced a kinetic curve for the pirimiphos-methyl present in solution plus that sorbed in labile forms on the soil particles.

Labile Sorption Capacity (LSC). The LSC of the two soils was determined by equilibrating a 500-mg portion of the soil with pirimiphos-methyl solutions, ranging in concentration from 1.52×10^{-5} to 9.09×10^{-5} M, for 24 h with constant stirring to maintain a uniform suspension of soil particles. LC analysis of the filtrate and slurry gave equilibrium measurements of solution and solution plus labile sorbed pirimiphos-methyl, respectively. The labile sorbed (LS) pirimiphos-methyl was calculated as the difference between the slurry and filtrate analysis for each concentration. The LSC values of the soils for pirimiphos-methyl were determined from the plot of equilibrium sorbed concentration of pirimiphos-methyl against equilibrium solution phase concentration.

RESULTS AND DISCUSSION

Labile Sorption Capacity. Figure 1 shows the S-shaped sorption isotherms that were obtained for the interaction of pirimiphos-methyl with Rhodic Kandiustalf and Aquic Ustropept soils, respectively. Adsorption isotherms can have a variety of forms, and similar S-shaped isotherms have been reported for a number of systems involving various adsorbates and solids (*5*). The plateau of the sorption curves indicates saturation of the surface sites, and this was used to obtain the LSC with respect to each soil. The LSC values were calculated to be 0.75 μmol g^{-1} for the Rhodic Kandiustalf soil and 0.90 μmol g^{-1} for the Aquic Ustropept soil.

The somewhat higher sorption capacity of the Aquic soil may be attributed to its greater concentration of organic matter. However, other parameters such as the amount and nature of the clay minerals may also affect the extent of sorption of pirimiphos-methyl by the two soils.

There are no literature values reported for the LSC of pirimiphos-methyl on other soils. However, sorption capacities

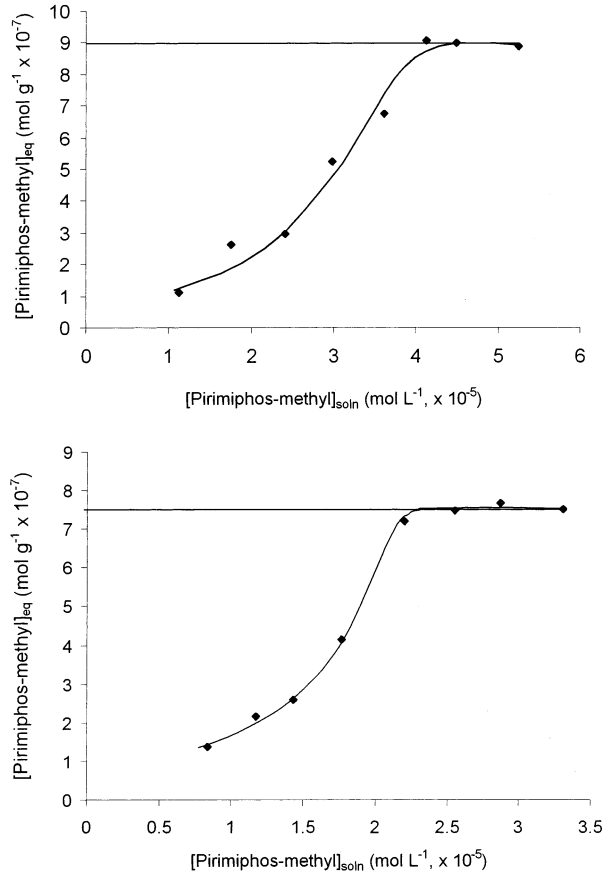


Figure 1. Measurement of labile sorption capacity (LSC) for Rhodic Kandiustalf (top) and Aquic Ustropept (bottom) soils with pirimiphos-methyl at 25.0 °C. The horizontal lines along the plateau give the LSC.

Table 2. Labile Sorption Capacities (LSC) (μmol g^{-1})

pesticide	Rhodic Kandiustalf	Aquic Ustropept	ref
pirimiphos-methyl	0.746	0.896	this work
atrazine	0.130	0.160	*5*
metribuzin	0.016	0.025	*5*

of atrazine and metribuzin for the same two Nigerian soils have been measured in our laboratory (*4*) and are included in **Table 2**. The higher value of pirimiphos-methyl (compared to the triazine herbicides) sorption capacity is not surprising because it is more hydrophobic than atrazine and metribuzin, as indicated by their K_{ow} values—16000 for pirimiphos-methyl compared to 219 for atrazine and 40 for metribuzin.

LC Microfiltration Data. The LC microfiltration experiments allowed us to study the distribution between water and soil of both pirimiphos-methyl and its pyrimidinol degradation product as a function of time. **Figures 2**−**5** show the kinetic curves obtained for analysis of slurries of the two soils over a 30-day period; points on the curves are average values for experiments done in triplicate. For a single injection, two chromatographic peaks were obtained corresponding to pirimiphos-methyl and pyrimidinol. The standard deviation for individual replicate points ranged from <1 to 18%, the average standard deviation for the data as a whole being 7.3%.

Using either slurry or filtered solution, the pirimiphos-methyl peak areas decreased with time (**Figures 2** and **3**), whereas the corresponding curves for the pyrimidinol (**Figures 4** and **5**) showed a continuous increase. The concentrations of LS pirimiphos-methyl and the pyrimidinol are shown on the same

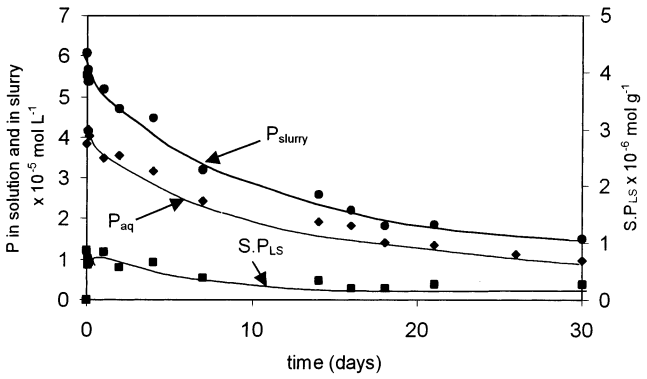


Figure 2. Concentration of pirimiphos-methyl species in solution and soil during equilibration with the Rhodic Kandiustalf soil at 25.0 °C over a period of 30 days. P_{aq}, dissolved pirimiphos-methyl; P_{slurry}, pirimiphos-methyl in the slurry; $S.P_{LS}$, labile sorbed pirimiphos-methyl.

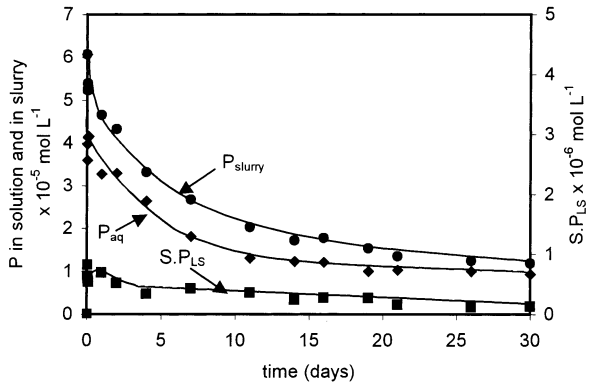


Figure 3. Concentration of pirimiphos-methyl species in solution and soil during equilibration with the Aquic Ustropept soil at 25.0 °C over a period of 30 days. P_{aq}, dissolved pirimiphos-methyl; P_{slurry}, pirimiphos-methyl in the slurry; $S.P_{LS}$, labile sorbed pirimiphos-methyl.

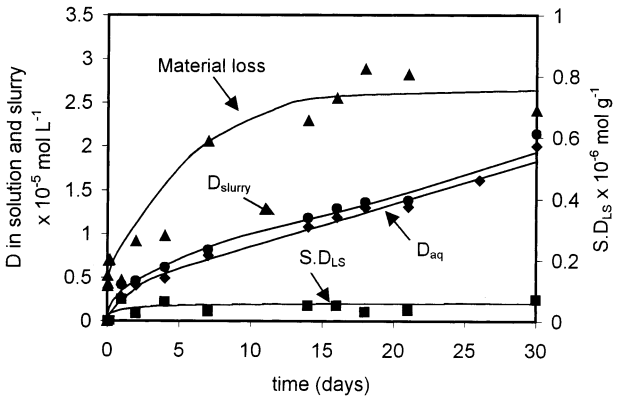


Figure 4. Concentration of pyrimidinol species in solution and soil during equilibration with the Rhodic Kandiustalf soil at 25.0 °C over a period of 30 days. In units of solution concentration are D_{aq}, dissolved pyridiminol; D_{slurry}, pyrimidinol in the slurry; and material loss. $S.D_{LS}$, labile sorbed pyridiminol, is given in units of concentration in the soil.

figures; these were determined by subtracting solution values from the corresponding slurry values. The material balance loss (**Figures 4** and **5**) was obtained as the difference between the initial concentration of pirimiphos-methyl and the sum of slurry concentrations of pirimiphos-methyl and the pyrimidinol. This loss combines both pesticide and degradation product that is irreversibly bound so that it could not be stripped from the soil during the course of slurry analysis. We refer to it as bound residue (BR).

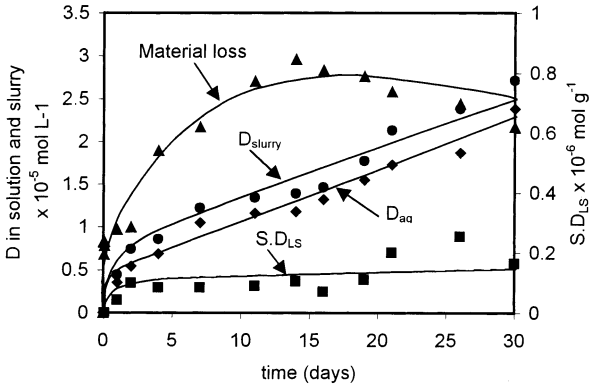


Figure 5. Concentration of pyrimidinol species in solution and soil during equilibration with the Aquic Ustropept soil at 25.0 °C over a period of 30 days. In units of solution concentration are D_{aq}, dissolved pyrimidinol, and D_{slurry}, pyrimidinol in the slurry. $S.D_{LS}$, labile sorbed pyrimidinol, is given in units of concentration in the soil.

As each experiment began, over a very short period of time (within the first 10 min of spiking), we found that there was a large drop in the initial concentration of pirimiphos-methyl in the solution, and there was no evidence of any degradation having occurred. The initial process accounted for removals of about 37% of the original pirimiphos-methyl concentration in the case of the Rhodic Kandiustalf soil and 41% of the original concentration in the case of the Aquic Ustropept soil. The greatest portion of pirimiphos-methyl taken up in the initial process was present as a labile-sorbed form, but smaller amounts (8.6 and 13.7% in the two soils, respectively) were in the BR fraction. The initial rapid loss of pirimiphos-methyl from solution was followed by a slower loss, due to both soil retention and hydrolytic degradation, that continued throughout the 30 days of the experiment.

In the natural environment, hydrolytic transformation of pirimiphos-methyl can occur via purely chemical reactions (abiotic processes) or it can be biologically mediated (biotic processes). In the present experiments, we assumed that the degradation processes occur through abiotic means alone, because the soil used had been sterilized by irradiation and the experiments were carried out under conditions that would prevent any microorganisms from entering the sample. Furthermore, the good reproducibility over extended periods of time is further evidence that microorganisms did not mediate this degradation. In other situations where unsterilized soils have been used, microbial degradation is evidenced by a sudden increase in the rate of disappearance of pesticide and by irreproducibility of replicate measurements.

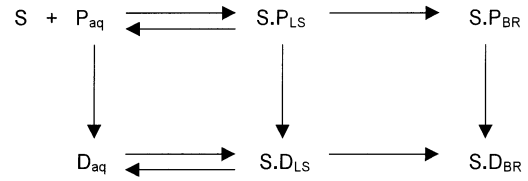
During the period of slow loss of pesticide from solution, the LS pirimiphos-methyl showed a gradual decrease in concentration (**Figures 2** and **3**); on the other hand, the LS pyrimidinol remained almost constant (**Figures 4** and **5**). The material balance loss increased until about 14−16 days, but beyond this time, it appears to have reached a plateau (**Figures 4** and **5**, expressed in terms of original solution concentration).

At the end of the experiment, the total concentrations of pirimiphos-methyl associated with the labile sorbed fraction were 0.28 and 0.13 μmol g^{-1} for the Rhodic Kandiustalf and Aquic Ustropept soils, respectively. As indicated above, for the two soils the LSC values are 0.75 and 0.90 μmol g^{-1}, respectively. Therefore, the fractions of sites occupied in a labile sorbed form by the pesticide were about 0.37 for Rhodic and 0.14 for Aquic soils.

Table 3. Percent Distribution of Pirimiphos-methyl and Pyrimidinol after 30 Days of Reaction at 25 °C

speciation	Rhodic Kandiustalf	Aquic Ustropept
filtrate pesticide	15.6	15.3
labile sorbed pesticide	9.3	4.2
filtrate metabolite	33.0	39.3
labile sorbed metabolite	2.3	5.5
material balance loss	39.8	35.7

Scheme 1. Proposed Sorption/Degradation[a]



[a] S, sorption sites; P_{aq}, dissolved pesticide; D_{aq}, dissolved degradation product; $S.P_{LS}$, labile-sorbed pesticide; $S.D_{LS}$, labile-sorbed degradation product; $S.P_{BR}$, bound residue pesticide; $S.D_{BR}$, bound residue degradation product.

Final Distribution of Pirimiphos-methyl/Pyrimidinol Species. After 30 days of reaction at 25.0 °C, the percent distribution of the pesticide in various fractions was determined and is given in **Table 3**. The distributions of solution-phase species of pirimiphos-methyl and its degradation product were found to be similar for the two soils. In both cases, the pyrimidinol product became a large proportion of the sample in solution, a factor of ~2 greater than pirimiphos-methyl. Interestingly, for the Rhodic soil about twice as much pesticide remained in the LS fraction compared with the Aquic soil. The Rhodic soil contained a higher proportion of iron and aluminum oxides than the gray-black Aquic soil. The oxide materials may have been responsible for retention of the phosphorothioate pesticide. On the other hand, a greater proportion of the hydrophobic pyrimidinol product was found in sorbed form in the Aquic soil, which contained a higher concentration of organic matter than the Rhodic soil.

The material balance loss represents the amount of pesticide (either as pirimiphos-methyl or as the pyrimidinol) that could not be observed in the slurry samples. The material loss is due to bound residue but, because it is determined by difference, it is not possible to indicate to what extent this fraction is in the form of original pesticide or its degradation product.

Sorption and Degradation Processes for Pirimiphos-methyl in Soil/Water Systems. On the basis of the experimental data reported here, the following scheme for the fate of pirimiphos-methyl in soil/water mixtures can be proposed. When pirimiphos-methyl is equilibrated over a period of time with soil, kept as a slurry in aqueous solution, a number of processes occur. The pirimiphos-methyl distributes itself between the solution phase and the solid phase, and in the latter phase may be present as labile sorbed or irreversibly bound (BR) forms. Simultaneously, degradation of the pesticide can take place in solution or in one of the phases associated with solid soil particles. Any product species formed in the degradation can then also distribute between the solution phase and the two (LS and BR) forms of association with the soil. Considering these processes together, a diagrammatic summary of the possible fate of pesticide during the course of the LC microfiltration experiment is shown in **Scheme 1**.

Kinetics of Pirimiphos-methyl Degradation in Soils. Following an initial rapid sorption of pesticide by the soil, the slower rate of loss from solution and slurry continued over the

Table 4. Kinetic Parameters for Degradation/Sorption of Pirimiphos-methyl in Soil Slurries at 25 °C

parameter	Rhodic Kandiustalf	Aquic Ustropept
k_{pm} (pirimiphos-methyl loss from solution) (s^{-1})	6.1×10^{-7}	9.8×10^{-7}
disappearance half-life (days)	13	8.2
k_{py} (pyrimidinol appearance in solution) (s^{-1})	6.0×10^{-7}	9.4×10^{-7}
degradation half-life (days)	13	8.5
labile sorption capacity (μmol g^{-1})	0.75	0.90
intraPD test statistic	0.30	0.25

1-month period of the experiment. This is in part due to degradation of pirimiphos-methyl, as it was observed (**Figures 4** and **5**) that the concentration of degradation product, the pyrimidinol, increased with time.

It is therefore logical to ask if it is possible to determine the rate constants that are associated with the various material loss processes. From the experiments, data for concentrations of five pesticide fractions are available. These are solution-phase reactant and product, LS reactant and product, and material balance loss equivalent to total BR formed. As a first approximation, it is possible to use the concentrations of solution-phase pesticide and degradation product to obtain rate constants, because these calculations involve the use of experimental results directly. We have plotted these data in the form of the integrated first-order kinetic equation

$$\ln C_t - \ln C_{\text{initial}} = -k_{\text{pm}} t$$

where k_{pm} is the rate constant for the disappearance from solution of pirimiphos-methyl with units of reciprocal of time and C is the aqueous concentration of pirimiphos-methyl in mol L^{-1}.

Using the pirimiphos-methyl solution data from **Figures 2** and **3**, plots of the integrated rate equation gave linear relationships ($R^2 = 0.954$ for Rhodic soil over the entire 30-day period and 0.912 for the Aquic soil covering the first 20 days of equilibration).

Plots of

$$\ln \frac{C_{\text{final}} - C_t}{C_{\text{final}}} = -k_{\text{py}} t$$

that followed the appearance of pyrimidinol in solution (data in **Figures 4** and **5**) were similarly linear ($R^2 = 0.985$ and 0.954 for the two soils). The R^2 values are in line with those obtained in other studies of pesticides in soil/water systems. Curvature in the final 10 days of the pesticide loss plot using the Aquic soil was evidence that loss was not a simple process. Rate constants, measured from the slopes of the plots, are reported in **Table 4**.

If pesticide loss from solution is due to degradation alone, the rate of its disappearance will be equal to that of the appearance of the degradation product. In the present case the two rates, over the 1-month period of the experiment, are very close. Nevertheless, it is clear from the material balance loss data that adsorption plays a significant role in augmenting the disappearance of the pesticide from solution. **Figures 2** and **3** indicate that adsorption of the pesticide occurs rapidly, mostly within the first few hours, and is essentially complete within 5 days.

Table 5. Rate Constants for Sorptive Uptake of Pesticides by Soil Materials, As Determined in Other Studies

pesticide	sorption rate constant (s^{-1})	soil material	ref
atrazine	9.62×10^{-6}	mineral soil (3.75% OM)[a]	*6*
	5.81×10^{-7}	peat soil (37.3% OM)	*3*
	8×10^{-4}	pure clay	*7*
	8.7×10^{-7}	Nigerian Aquic soil[b]	*4*
	1.1×10^{-6}	Nigerian Rhodic soil[b]	*4*
metribuzin	7.6×10^{-7}	Nigerian Aquic soil[b]	*4*
	1.1×10^{-6}	Nigerian Rhodic soil[b]	*4*
	5.4×10^{-9} to 2.1×10^{-7}	various pure soil separates	*8*
chlorthalonil	8.6×10^{-7}	quartz sand soil	*9*
carbaryl and parathion	$\sim 10^{-4}$	organic matter	*10*

[a] OM, organic matter. [b] Soils as used in the present study.

To quantify the adsorption and degradation processes, a more sophisticated treatment than that involving simple first-order kinetic is required; the experiments we have described here do not allow us to carry out these kinds of calculations. Nevertheless, the overall scheme and the approximate rate calculations go beyond what has been reported in the literature for any organophosphorus pesticides.

Gamble and Khan (*3*) have followed the simultaneous adsorption and hydrolytic degradation of atrazine in the presence of a Typic Mesisol peat soil and determined rate constants for the two processes of 5.8×10^{-7} and 1.7×10^{-6} s^{-1}, respectively. We are not aware of other rate constant values for pesticides in soil/water systems that distinguish between loss from solution due to sorptive uptake and degradation. Rate constants for sorption of some pesticides by soils and soil materials have been reported, and most are in the range (10^{-7}–10^{-6} s^{-1}) of the combined sorption/degradation loss values reported here (**Table 5**).

There are also relatively few kinetic rate constant values for the disappearance of pesticides that have been determined under controlled abiotic conditions. Babu et al. (*11*) reported rate constants of 6.2×10^{-7} and 5.3×10^{-7} s^{-1} for the disappearance of quinalphos, under aerobic conditions, in black cotton soil and red sandy clay loam soils, respectively. Charles et al. (*12*) reported 2.7×10^{-6} s^{-1} as the degradation rate constant for fenitrothion in forest soil under aerobic condition. Gajbhiye et al. (*13*) reported half-life values of 2.1−2.4 days, which represents rate constants of 3.8×10^{-6} to 3.4×10^{-6} s^{-1} for the degradative dissipation of quinalphos from soil and water. Again, these values related to degradation of other organophosphorus compounds are in the range of the ones reported here for production of the pyridimol degradation product.

Material Balance Loss. Whereas uptake of pesticides is assumed to occur initially by reversible sorption processes at the surface of soil particles, these chemicals may subsequently slowly diffuse into the interiors or become covalently bonded to the soil particles. Such processes, otherwise known as intraparticle diffusion or chemisorption, respectively, have been used to explain the material balance loss, due to the formation of bound residue species. Several workers (*4*, *6*, *7*, *9*) have used a diagnostic plot to test material balance loss data for behavior consistent with diffusion mechanism, by employing the Crank equation based on Fick's law. Diffusion of organic compounds into semi-infinite media from steady-state coverage is expressed in terms of Q_{BR}, the material balance loss of pesticide (mol g^{-1} of soil). Q_{BR} is then given by

$$Q_{BR} = [2(Q_{LS}/r)(D/\pi)^{1/2}]t^{1/2}$$

where Q_{LS} is the labile sorption capacity, D is the diffusion coefficient characterizing the pesticide movement into the particle, and r is a particle dimension appropriate to diffusion.

The derivative version of the equation is

$$\ln(Q_{BR}) = \ln(A) + 0.5 \ln(t)$$

where $A = 2(Q_{LS}/r)(D/\pi)^{1/2}$.

A plot of $\ln(Q_{BR})$ against $\ln(t)$ will therefore be linear with a slope of 0.5 if the material balance loss (bound residue) is associated with intraparticle diffusion.

Deviations from the slope can be attributed to factors such as (i) slower diffusion and higher uncertainty with regard to low surface saturation of the labile sorption sites, (ii) approach of the interior sites to sorption saturation, (iii) the rate of diffusion of pesticide molecules out of the particles being greater than the rate of diffusion into the particles, and (iv) irreversible surface sorption due to specific chemical reaction.

In the present study, the results of the diagnostic test (**Table 4**) for intraparticle diffusion gave slope values of 0.30 and 0.25 in Rhodic Kandiustalf and Aquic Ustropept soils, respectively. The BR fractions of the pesticide and product are therefore not solely associated with simple diffusion into the interior of particles. The values given here are similar to ones reported by Oketunde (*4*) for metribuzin and atrazine with the same Nigerian soils.

LITERATURE CITED

(1) Government of Canada. *Pesticides: Making the Right Choice for the Protection of Health and the Environment;* Report of the Standing Committee on Environment and Sustainable Development: Ottawa, ON, Canada, 2000.

(2) Worthing, C. R.; Hance, R. J. *The Pesticide Manual. A World Compendium*, 9th ed.; 1991; 1141 pp.

(3) Gamble, D. S.; Khan, S. U. Atrazine in organic soil: chemical speciation during heterogeneous catalysis. *J. Agric. Food Chem*. **1990**, *38*, 297.

(4) Oketunde, O. F. The adsorptive behaviour of two triazine herbicides in three Nigerian soils. M.Sc. Thesis, Queen's University, Kingston, ON, Canada, 1997; 186 pp.

(5) Giles, C. H.; MacEwan, T. H.; Nakhwa, S. N.; Smith, D. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *J. Chem. Soc*. **1960**, 3973.

(6) Li, J.; Langford, C. H.; Gamble, D. S. Atrazine sorption by a mineral soil: Processes of labile and nonlabile uptake. *J. Agric. Food Chem*. **1996**, *44*, 3672.

(7) Gilchrist, G. F. R.; Gamble, D. S.; Kodama, H.; Khan, S. U. Atrazine interactions with clay minerals: kinetics and equilibria of sorption. *J. Agric. Food Chem*. **1993**, *41*, 1748−1755.

(8) Sha'ato, R.; Buncel, E.; Gamble, D. S.; vanLoon, G. W. Kinetics and equilibria of metribuzin sorption on model soil components. *Can. J. Soil Sci*. **2000**, *80*, 301−306.

(9) Gamble, D. S.; Bruccoleri, E. L.; Langford, C. H. Chlorothalonil in a quartz sand soil: Speciation and kinetics. *Environ. Sci. Technol*. **2000**, *34*, 120−124.

(10) Leenheer, J. A.; Ahlrichs, J. L. A kinetic and equilibrium study of the adsorption of carbaryl and parathion upon soil organic matter surfaces. *Soil Sci. Soc. Am. Proc*. **1971**, *35*, 700.

(11) Babu, G. V. K.; Reddy, B. R.; Narasimha, G.; Sethunathan, N. Persistance of quinalphos and occurrence of its primary metabolite in soils. *Bull. Environ. Contam. Toxicol*. **1998**, *60*, 723−731.

(12) Charles, J. S., Jr.; DeBaun, J. R.; Menn, J. J. Degradation of fenitrothion in forest soil and effects on forest soil microbes. *J. Agric. Food Chem*. **1979**, *27*, 1054−1060.

(13) Gajbhiye, V. T.; Agnihotri, N. P.; Gupta, R. K. Effect of formulation on the dissipation of quinalphos from soil and water. *J. Entomol. Res*. **1995**, *19* (4), 295−300.

Received for review March 29, 2002. Revised manuscript received July 16, 2002. Accepted July 19, 2002.

JF0203747