JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Sorption−Desorption of "Aged" Sulfonylaminocarbonyltriazolinone Herbicides in Soil

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Sorption−desorption interactions of pesticides with soil determine the availability of pesticides in soil for transport, plant uptake, and microbial degradation. These interactions are affected by the physical and chemical properties of the pesticide and soil, and for some pesticides, their residence time in the soil. The objective of this study was to characterize sorption−desorption of two sulfonylaminocarbonyltriazolinone herbicides incubated in soils at different soil moisture potentials. The chemicals were incubated in clay loam and loamy sand soils for up to 12 wks at −33 kPa and at water contents equivalent to 50 and 75% of that at −33 kPa. Chemicals were extracted sequentially with 0.01 N $CaCl_2$ and aqueous acetonitrile, and sorption coefficients were calculated. Sufficient sulfonylaminocarbonyltriazolinone herbicides remained (>40% of that applied) during incubation to allow calculation of sorption coefficients. Aging significantly increased sorption as indicated by increased sorption coefficients. For instance, for sulfonylaminocarbonyltriazolinone remaining after a 12-wk incubation at −33 kPa, K_d increased by a factor of 4.5 in the clay loam soils and by 6.6 in the loamy sand as compared to freshly treated soils. There was no effect of moisture potential on sorption K_d values. These data show the importance of characterization of sorption−desorption in aged herbicide residues in soil, particularly in the case of prediction of herbicide transport in soil. In this case, potential transport of sulfonylaminocarbonyltriazolinone herbicides would be over-predicted if freshly treated soil K_d values were used to predict transport.

KEYWORDS: Sulfonylaminocarbonyltriazolinone; sorption; desorption; aged residues

INTRODUCTION

Sorption−desorption interactions of pesticides with soil determine the availability of the pesticides in soil for transport and microbial degradation. A variety of studies have suggested that only pesticide in solution, or that is readily desorbable from soil, is available for transport or for degradation. A pesticide that is sorbed to soil particles is not instantaneously available, it must first desorb from the soil into solution. Availability would be directly related to the pesticide's ability to be desorbed from soil; weakly sorbed and easily desorbed pesticides would be readily available, whereas pesticides that are strongly sorbed and hysteretic during desorption would be slowly available over time, and extremely strongly sorbed pesticides, i.e., bound residues, would be unavailable.

Models have traditionally characterized the availability of pesticides for transport and degradation through the incorporation of a sorption coefficient (K_d), which is the ratio of the amount of chemical sorbed to that in solution, as determined using batch slurry techniques. Although sorption−desorption processes are affected by the physical and chemical properties of the pesticide and soil, in many cases it is a much more complex process and cannot be adequately characterized by a single number (*1*). For instance, desorption of many pesticides cannot be predicted from their sorption isotherms; less chemical is desorbed than would be predicted by the sorption isotherm. Also, it appears that sorption may be affected by the residence time, or aging, in the soil. Increases in the sorption coefficient K_d with incubation time have been observed for a variety of classes of pesticides such as triazines (*2*, *3*), pyridine carboxylic acids (*4*), amides (*5*), carbofuran (*6*), substituted ureas (*3*, *5*, *7*, *8*), nitroguanidines (*9*, *10*) and imidazolinones (*11*, *12*).

The present study was conducted to determine the changes in distribution between sorbed and solution phases of a new class of herbicides chemistry, sulfonylaminocarbonyltriazolinone, in aged soils. The aged herbicides residues were created by incubation of two of these herbicides in clay loam and loamy sand soils at different moisture potentials for up to 12 wks.

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10.1021/jf0201733 CCC: $22.00
Published on Web 08/08/2002

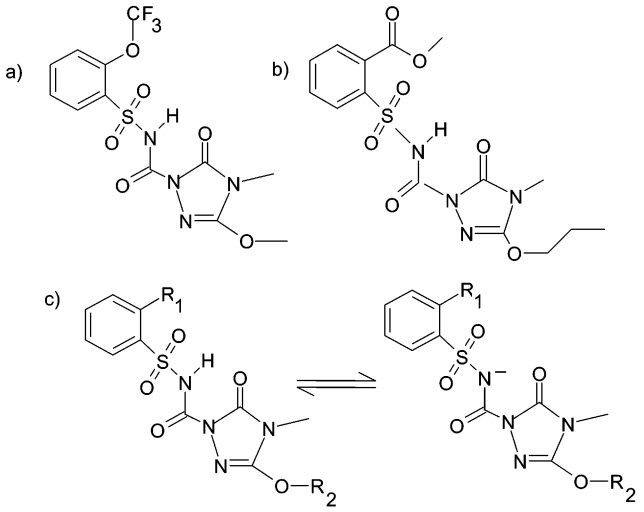

Figure 1. Structures of sulfonylaminocarbonyltriazolinones MKH 6562 (a) and MKH 6561 (b) and sulfonylaminocarbonyltriazolinone ionization (c).

MATERIALS AND METHODS

Chemicals and Soils. Pure analytical (chemical purity > 99%) and radiochemical (radiochemical purity > 99%)) methyl 2-[[[(4,5-dihydro-4-methyl-5-oxo-3-propoxy-1H-1,2,4-triazol-1-yl)carbonyl]amino]sulfonyl]benzoate (MKH 6561) and 4,5-dihydro-3-methoxy-4-methyl-5-oxo-*N*-[[2-(trifluoromethoxy)phenyl]sulfonyl]-1H-1,2,4-triazol-1-carboxamide (MKH 6562) were supplied by Bayer Corporation. Structures are shown in **Figure 1a** and **b**. Sulfonylaminocarbonyltriazolinone herbicides are weak acids (MKH 6561 pK_a = 2.1; MKH 6562, pK_a = 1.9), which can lose the bridge N proton (**Figure 1c**). Triazole-3-^{14}C-MKH 6561 (specific activity 2.157 GBq mmol^{-1}) and phenyl-UL-^{14}C-MKH 6562 (specific activity 2.653 GBq mmol^{-1}) was mixed with unlabeled material to give a final solution concentration of 4.0 mg kg^{-1} containing 3.7 MBq L^{-1}.

Fresh soils from the 0−15 cm depth of a Gardena clay loam from North Dakota (coarse-silty mixed Pachic Udic Haploborolls), pH 6.2, 42.2% silt, 30.8% clay, and 3.17% OC, and a Quincy loamy fine sand from Washington (mixed, mesic Xeric Torripsamments), pH 6.7, 7.0% silt, 5.3% clay, and 0.26% OC, were collected, passed through a 2-mm diameter sieve, and stored at 4 °C until used (<4 wks after collection) Soil texture was determined by the hydrometer method (*13*). Soil pH was measured in a 1:2 (w/w) soil/deionized water mixture. The organic carbon content of the soil samples was determined by dichromate oxidation (*14*).

Soil Treatment. Duplicate 20-g soil samples in 250-mL flasks were treated with 500 μL of 4 mg L^{-1} ^{14}C-MKH-6561 or MKH-6562. The solution was added dropwise using a μL-syringe. The soil was thoroughly mixed during and after application. The final amount of chemical added to the soils was 0.1 mg kg^{-1}, which is near normal field application rate, assuming uniform distribution in the surface 1 cm of soil. Moisture content of the soil was adjusted to −33 kPa, 75% of the water content at −33 kPa, and 50% of the water content at −33 kPa.

Incubation Study. Soils were incubated at 25 °C in the dark in closed 250-mL glass flasks for up to 12 wks. To monitor mineralization ($^{14}CO_2$ evolution), biometer flasks containing 10 mL of 1 N NaOH were used. NaOH was replaced weekly, thereby also aerating the flasks. To determine $^{14}CO_2$, a 1-mL aliquot of NaOH solution was mixed with 6 mL of EcoLite scintillation cocktail, and the amount of radioactivity was determined by liquid scintillation counting (LSC) for 5 min in a 1500 TRI-CARB Packard liquid scintillation analyzer.

Soil Extraction and Analysis. At each sampling time, all the soil in each flask (20 g) was transferred from the flask to Teflon centrifuge tubes with 40 mL of 0.01 M $CaCl_2$ and shaken for 1 h. The samples were then allowed to sit overnight (~20 to 24 h), shaken for 10 min, and the suspensions were then centrifuged at 2500 rpm for 5 min. The supernatant was transferred to preweighed glass vials. After any remaining material was allowed to settle out overnight, triplicate 1-mL aliquots were removed and mixed with 6 mL of EcoLite scintillation cocktail, and the total amount of radioactivity in the supernatant was determined by LSC. The remaining supernatant was saved to later determine the amount of parent herbicide in the extracted ^{14}C (see below).

Soil was then extracted twice with 48−50 mL of 4:1 acetonitrile/0.2 M ammonium acetate (1% HCl) in the same manner as with the 0.01 M $CaCl_2$ extraction. The remaining soil was filtered and washed with 25 mL of 4:1 acetonitrile/0.2 M ammonium acetate (1% HCl). Acetonitrile was removed from the combined filtrates by evaporation at 40 °C using a Zymark Turbovap. Aliquots (1 mL) of the remaining aqueous solution were removed and mixed with 6 mL of scintillation cocktail, and the total amount of radioactivity in the supernatant was determined by LSC. The remaining supernatant was saved to later determine the amount of parent herbicide in the extracted ^{14}C (see below).

The extraction efficiency of the combined 0.01 M $CaCl_2$ and acetonitrile/0.2 M ammonium acetate (1% HCl) extractions for freshly treated soils (i.e., day 0) was 88−94%. The extraction efficiency using the 1-hr shake, 20-hr static equilibration, 10-min shake procedure was the same as using an overnight (~18 h) shaking.

The aqueous extracts were analyzed by HPLC on a 1090 Hewlett-Packard high performance liquid chromatograph using a 250 mm × 4.6 mm i.d. Alltech Inertsil ODS-2 (5 μm) column operating at room temperature (~25 °C). The mobile phase for both MKH 6561 and MKH 6562 was a gradient of acetonitrile (ACN) and filtered distilled water with 0.1% v/v *o*-phosphoric acid (85%). For MKH 6561 the gradient started at 70% acidified water, increased ACN from 30 to 90% from 5 to 15 min, held ACN at 90% from 15 to 24 min, and decreased ACN from 90 to 30% from 24 to 25 min. The mobile phase gradient for MKH 6562 started at 90% acidified water, increased ACN from 10 to 70% from 1 to 25 min, increased ACN from 70 to 100% from 25 to 35 min, decreased ACN from 100 to 50% from 35 to 37 min, decreased ACN from 50 to 10% from 37 to 39 min, and held ACN at 10% from 39 to 44 min. The flow rate for MKH 6561 and MKH 6562 analyses was 0.75 mL min^{-1}. Injection volumes were 100 μL. Detection of MKH 6561 and MKH 6562 was determined at 200 nm. Based on retention times of MKH 6561 (15.2 min) and MKH 6562 (24.6 min), obtained by injecting the pure analytical standards, HPLC fractions corresponding to parent chemical were collected, mixed with liquid scintillation cocktail, and ^{14}C in each fraction was quantified by LSC. Fractions containing ^{14}C more and less mobile than parent chemicals were also collected and quantified. The percentage of the ^{14}C that was parent herbicide in the supernatant was calculated and used to determine total parent chemical in each supernatant solution.

Soil Sorption−Desorption Calculation. To calculate sorption coefficients, K_d, as a function of incubation time, the amounts of recovered parent sulfonylaminocarbonyltriazolinone herbicide in $CaCl_2$ and acetonitrile/0.2 M ammonium acetate (1% HCl) in the different soils incubated for up to 12 wks at different moisture potentials were determined. Aqueous ACN extractable corresponded to the sorbed concentration in the batch method, and the $CaCl_2$ extractable corresponded to the solution concentration: K_d = [amount parent herbicide extractable by acetonitrile/0.2 M ammonium acetate (1% HCl)] g^{-1}/(amount parent herbicide extractable by $CaCl_2$) mL^{-1}.

RESULTS AND DISCUSSION

Sulfonylaminocarbonyltriazolinone Recovery in Aged Soils. In general, more MKH 6561 was recovered throughout the incubation than MKH 6562, and the recovery was greater in the loamy sand than in the clay loam (**Figure 2**, **Table 1**). At 12 wks, when averaged over soil moistures, ~1.3 times more MKH 6561 was recovered in clay loam soil and ~1.2 times more in loamy sand than MKH 6562. For MKH 6561, averaged over soil moistures, 1.3 times more was recovered during 12 wks in loamy sand than in clay loam; whereas for MKH 6562, 1.5 times more was recovered in loamy sand than in clay loam. Soil moisture had little effect on recovery from either soil. Recovery for both herbicides in both soils was generally less

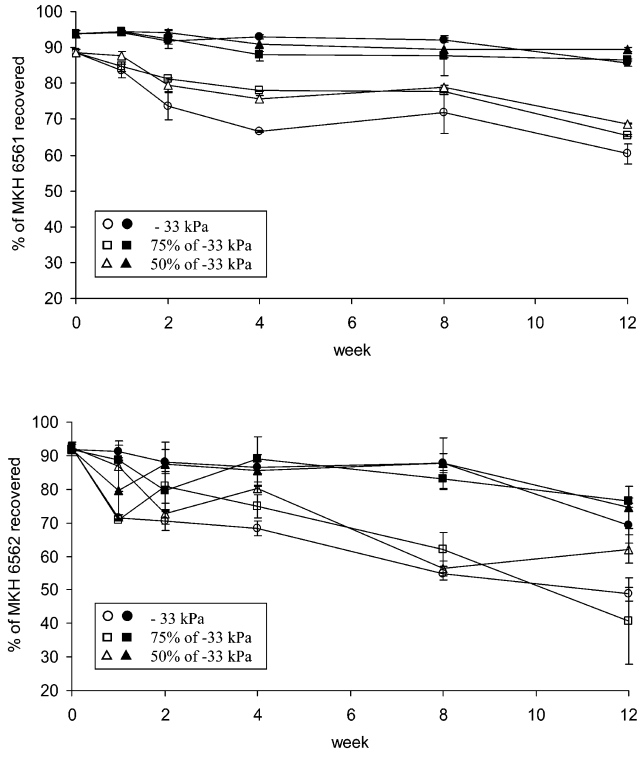

Figure 2. Recovery of MKH 6561 and MKH 6562 in soils at three moisture potentials during a 12-wk incubation. Open symbols are for clay loam soil and closed symbols are for loamy sand soil.

Table 1. Amount of Sulfonylaminocarbonyltriazolinone Herbicide Recovered after 12 Weeks

		soil moisture[a]		
chemical	soil	–33 kPa (%)[b]	75% of –33 kPa (%)	50% of –33 kPa (%)
MKH 6562	clay loam	48.7 ± 2.0	40.7 ± 13.0	62.1 ± 4.2
	loamy sand	69.2 ± 5.2	76.5 ± 0.7	74.7 ± 6.3
MKH 6561	clay loam	60.3 ± 2.9	65.5 ± 0.2	68.8 ± 0.2
	loamy sand	85.5 ± 0.7	86.5 ± 0.3	89.4 ± 0.6

[a] Soil moisture = –33 kPa, or 50% or 75% of the moisture content of the water content at –33 kPa. [b] Difference in % of parent chemical recovered between incubation times of 0 and 12 wks ± standard deviation.

in soils incubated at −33 kPa than in drier soils (i.e., water content of 50% of that at −33 kPa).

The decreased recovery of the sulfonylaminocarbonyltriazolinone herbicides during incubation was due to formation of bound, unextractable residues and degradation. Although we do not know the mechanism of degradation, it appears that there was hydrolysis at the $-SO_2-NH-CO-$ bridge. During MKH 6562 incubation, the only identifiable ^{14}C-labeled metabolite was the benzenesulfonamide metabolite (based on retention time of analytical standard (RT = 12.6 min). After 12 wks of incubation of MKH 6562, averaged over the 3 moisture contents, we found 12.3% of the applied ^{14}C was the benzenesulfonamide metabolite in the loamy sand and 20.2% in the clay loam. Although there was no effect of moisture potential on formation of the benzenesulfonamide metabolite in the loamy sand, twice as much metabolite was formed in the clay loam at −33 kPa (25.5%) than at 50% of −33 kPa (11.9%).

In the case of MKH 6561, the only identifiable ^{14}C-labeled metabolite was the triazolinone metabolite (based on retention time of analytical standard (RT = 2.9 min.) After 12 wks of incubation, we found 3.6% of applied ^{14}C was triazolinone metabolite in the loamy sand and there was no effect of moisture potential on metabolite formation. In the clay loam averaged over the 3 moisture contents, 7.9% of applied ^{14}C was triazolinone metabolite, with four times more metabolite at −33 kPa (13.3%) than at 50% of −33 kPa (3.1%).

The mass balance for ^{14}C in the experiments ranged from 94 to 100%. There was negligible mineralization of both chemicals in both soils at the three matric potentials: <0.8% of applied in all cases. The remaining ^{14}C was unidentified ^{14}C-labeled chemicals and bound, unextractable residues.

More research is needed to determine the kinetics and mechanism of sulfonylaminocarbonyltriazolinone herbicide degradation, particularly as a function of soil pH; this study was not designed to determine either kinetics or mechanism of degradation. There was, however, sufficient herbicide remaining in the soil at each sampling time (>40% of applied) to determine the distribution between sorbed and solution phases of the remaining amount of sulfonylaminocarbonyltriazolinone, thereby allowing the effect of the aging process on sorption−desorption to be determined.

Sorption−Desorption. MKH 6562 K_d values calculated from $CaCl_2$ and acetonitrile/0.2 M ammonium acetate (1% HCl) extractable amounts without previous incubation were 0.65 mL g^{-1} for the clay loam and 0.11 mL g^{-1} for the loamy sand (**Table 2**). These values were similar to those obtained by batch equilibration with similar initial concentration ranges. K_d values increased with incubation time (**Figure 3**), with the greatest increase occurring during the first two weeks of incubation. For instance, values of K_d after a 2-wk incubation at −33 kPa increased to 2.07 mL g^{-1} for the clay loam and 0.90 mL g^{-1} for the loamy sand. Values of K_d after the 12-wk incubation at −33 kPa were 2.59 mL g^{-1} for the clay loam and 0.75 mL g^{-1} for the loamy sand, an increase in K_d by a factor of 4.0 for the clay loam and 6.8 for the loamy sand, as compared to those determined in freshly treated soil (**Table 2**). K_{oc} increased from 21 to 82 mL g^{-1} for the clay loam, and from 42 to 288 for the loamy sand during the 12-wk incubation. There was no difference in K_d values as a result of differences in soil potential during incubation.

MKH 6561 K_d values also increased during aging, with the greatest effect occurring during the first two weeks. For instance, values of K_d after a 2-wk incubation at −33 kPa were 5.96 mL g^{-1} for the clay loam and 1.31 mL g^{-1} for the loamy sand.

Table 2. Determination of K_d as Affected by Incubation Time

chemical	soil	moisture[a] (kPa)	K_d[b] (wk 0)	K_d (wk 2)	IF 1[c]	K_d (wk 12)	IF 2[d]
MKH 6562	clay loam	–33	0.65 ± 0.08	2.07 ± 0.24	3.18	2.59 ± 0.18	3.98
	loamy sand	–33	0.11 ± 0.15	0.90 ± 0.16	8.18	0.75 ± 0.19	6.82
MKH 6561	clay loam	–33	2.16 ± 0.10	5.96 ± 0.50	2.76	10.74 ± 1.13	4.97
	loamy sand	–33	0.23 ± 0.04	1.31 ± 0.06	5.70	1.40 ± 0.07	6.09

[a] Soil moisture = –33 kPa. [b] Time of incubation at which K_d was calculated. [c] Increase factor: IF 1 = K_d week 2/ K_d week 0. [d] Increase factor: IF 2 = K_d week 12/ K_d week 0.

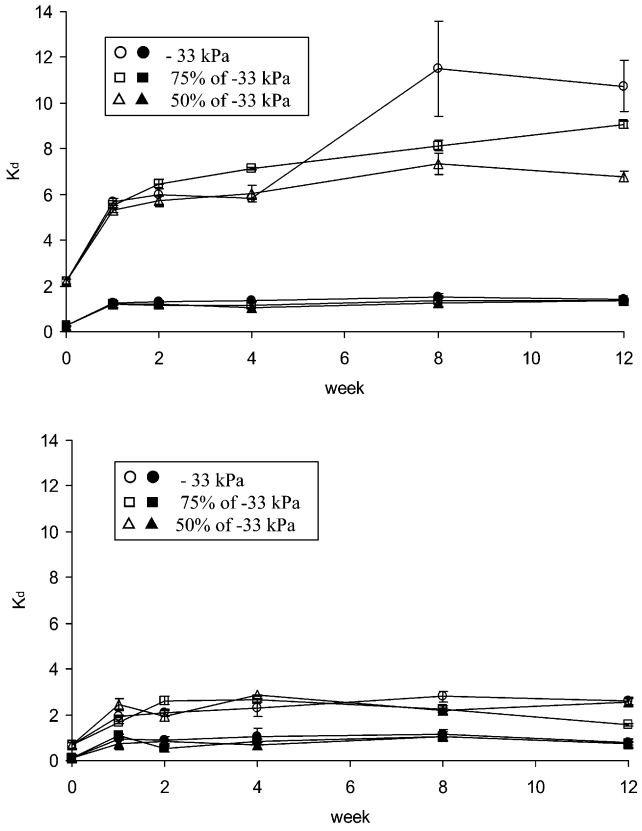

Figure 3. Sorption–desorption of MKH 6561 and MKH 6562 incubated in soils for varying times at three moisture potentials. Open symbols are for clay loam soil and closed symbols are for loamy sand soil.

Values of K_d after the 12-wk incubation at −33 kPa were 10.7 mL g^{-1} for the clay loam and 1.40 mL g^{-1} for the loamy sand, an increase in K_d by a factor of 5.0 for the clay loam and 6.1 for the loamy sand, as compared to those determined in freshly treated soil (**Table 2**). K_{oc} increased from 68 to 339 mL g^{-1} for the clay loam, and from 88 to 538 for the loamy sand during the 12-wk incubation. There was also no difference in K_d values as a result of differences in soil potential during incubation.

The increase in calculated K_d values resulted from a decrease in the herbicide solution concentration ($CaCl_2$ extractable) with incubation time and an increase in the amount of herbicide sorbed (solvent extractable). In the clay loam, the largest change was in the $CaCl_2$ extractable over the 12-wk incubation, whereas in the loamy sand the largest change was in the solvent extractable. In the loamy sand, there was 1.6 times more $CaCl_2$-extractable and 4.0 times less solvent-extractable sulfonylaminocarbonyltriazolinone at day 0 than at wk 12 for both MKH 6561 and MKH 6562, averaged over the three moisture potentials. Nonextractable increased by a factor of 1.1 over the 12-wk incubation. In slight contrast, in the clay loam, there was 3.2 times more $CaCl_2$-extractable and 1.1 times less solvent-extractable sulfonylaminocarbonyltriazolinone at day 0 than at wk 12 for both MKH 6561 and MKH 6562, averaged over the three moisture potentials. Nonextractable increased by a factor of 2.5 over the 12-wk incubation.

The mechanism for increased sorption with aging is not known. Sulfonylaminocarbonyltriazolinone herbicides are weak acids. In most agricultural soils, these herbicides exist predominantly as anions. However, depending on soil pH, a varying proportion of the chemical is the molecular species, which is strongly sorbed and does not appear to readily desorb using the traditional batch equilibration method (unpublished data). Therefore, the increase in calculated sorption coefficients for both sulfonylaminocarbonyltriazolinones with increasing incubation time can be attributed to a rate of hydrolysis in solution that is faster than the rate of desorption from soil. However, hydrolysis was greater in loamy sand than clay loam, but the increase in K_d was greater in loamy sand than in clay loam. Also, there was greater hydrolysis of MKH 6562 than MKH 6561, but there was no significant difference in the increase in sorption.

The increase in sorption with aging can also be attributed to diffusion of the chemicals, particularly the anion, to less accessible sorption sites, coupled to hydrolysis of readily available chemical, leaving more strongly sorbed sulfonylaminocarbonyltriazolinone. It is difficult to distinguish between the two possible mechanisms; the net result is probably a combination of the two mechanisms occurring, particularly during the first two weeks of incubation.

Regardless of the mechanism of the increase in sorption, the net effect would be that use of simplistic equilibrium partitioning coefficients based on freshly treated samples under slurry conditions would predict much greater movement of these chemicals than if we used the sorption coefficients determined on aged residues. In the case of these two chemicals, the mobility classification would change to less mobile.

If we are to improve models describing pesticide availability for transport and biodegradation in soil, we need to better understand the complex interactions of the sorption−desorption and degradation processes, particularly for aged herbicide residues. Use of simplistic equilibrium partitioning coefficients based on freshly treated samples under slurry conditions is inadequate.

ACKNOWLEDGMENT

We thank Bayer Corporation for kindly supplying the analytical and radioactive materials.

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Received for review February 8, 2002. Revised manuscript received May 7, 2002. Accepted May 29, 2002. Mention of a company name or trade name is for information only and does not imply recommendation by USDA-ARS or the Lithuanian Institute of Agriculture.

JF0201733