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Sorption−Desorption of Two "Aged" Sulfonylaminocarbonyltriazolinone Herbicide Metabolites in Soil

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Aging (herbicide−soil contact time) has been shown to significantly affect the sorption−desorption characteristics of many herbicides, which in turn can affect the availability of the herbicide for transport, plant uptake, and microbial degradation. In contrast, very little work in this area has been done on herbicide metabolites in soil. The objective of this study was to characterize the sorption−desorption of sulfonylaminocarbonyltriazolinone herbicide metabolites incubated in soils at different soil moisture potentials. A benzenesulfonamide metabolite and a triazolinone metabolite from sulfonylaminocarbonyltriazolinone herbicides were incubated in clay loam and loamy sand soils for up to 12 weeks 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 (solution and sorbed phase concentrations, respectively), and apparent sorption coefficients ($K_{d,app}$) were calculated. Sufficient metabolite remained during the incubation (>55% of applied) to allow determination of the coefficients. The initial aging period (2 weeks after application) significantly increased sorption as indicated by increased $K_{d,app}$ values for the chemical remaining, after which they remained relatively constant. After 12 weeks of incubation at −33 kPa, $K_{d,app}$ values for benzenesulfonamide and triazolinone increased by a factor of 3.5 in the clay loam soil and by a factor of 5.9 in the loamy sand as compared to freshly treated soils. There was no effect of moisture potential on aged apparent $K_{d,app}$ values. These data show the importance of characterization of sorption−desorption in aged herbicide residues, including metabolites, in soil, particularly in the case of prediction of herbicide residue transport in soil. In this case, potential transport of sulfonylaminocarbonyltriazolinone herbicide metabolites would be overpredicted if freshly treated soil K_d values were used to predict transport.

KEYWORDS: Sulfonylaminocarbonyltriazolinone; metabolites; benzenesulfonamide; triazolinone; sorption; desorption; aged residues

INTRODUCTION

Characterization of availability (particularly bioavailablity) of pesticides and toxic organic chemicals in aged soils continues to be of interest because this information is necessary for environmental risk assessment of these chemicals. The effect of aging, which is increased organic chemical−soil contact time, on bioavailability has been characterized by a variety of methods. For instance, significant amounts of soil-bound ^{14}C-labeled pesticide residues that were not extractable by exhaustive organic solvent extraction were taken up by earthworms (i.e., refs *1* and *2*) and crops plants (i.e., ref *3*). Bioavailability has also been characterized by comparing solvent extraction to earthworm uptake and microbial degradation (*4*, *5*) and by determining mineralization of aged pesticide in soil after inoculation of the aged residues with a specific pesticide-degrading microorganism (*6*). It is generally concluded that aging decreases the availability of the organic chemical for transport, plant uptake, and microbial degradation.

Effects of aging on availability are primarily through effects on sorption−desorption processes by a variety of mechanisms (*7*). Despite the multiple mechanisms involved, many transport and degradation models have traditionally characterized the availability of pesticides via a simplistic approach, 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. However, sorption−desorption processes are much more complex and cannot be

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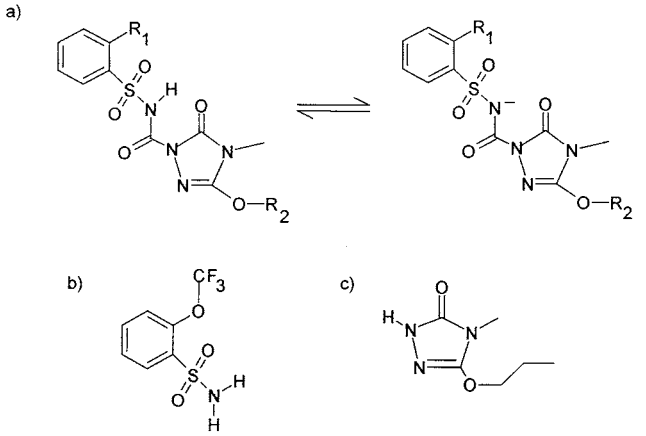

Figure 1. Sulfonylaminocarbonyltriazolinone ionization (a) and structures of benzenesulfonamide (b) and triazolinone (c) metabolites.

adequately characterized by a single value (*8*). 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, that is, a hysteresis effect.

For a number of pesticides [i.e., picloram (*9*), carbofuran (*10*), atrazine (*11*), metolachlor (*11*), imidacloprid (*12*), imazethapyr (*13*), and imazamox (*14*)] the effect of aging on sorption−desorption processes in soil has been characterized by the determination of apparent sorption coefficients, $K_{d,app,}$ for the chemical remaining after a given incubation period. In these studies, after each aging period, the parent chemical was first extracted from soil with aqueous $CaCl_2$ to give the solution phase concentration and then by organic solvents to give the sorbed phase concentration, from which $K_{d,app}$ values can be calculated as in traditional batch sorption studies. Increases in the sorption coefficient $K_{d,app}$ with incubation time have generally been observed using this method, similar to the effects observed in the bioavailability studies previously cited.

Whereas there is limited information on the sorption and degradation of aged pesticide residues, there is even less information on these processes for aged pesticide metabolites. Imidacloprid metabolites, although similar in structure to imidacloprid, have very different sorption characteristics (*15*). For instance, imidacloprid-urea is sorbed less than imidacloprid, whereas imidacloprid-guanidine is sorbed to a much greater extent than imidacloprid. However, in aged residue studies, sorption, as indicated by $K_{d,app}$ values, increased similarly for all three chemicals by a factor of 2.3−2.8 during an 8-week incubation (*15*, *16*).

The present study was conducted to determine the changes in distribution between sorbed and solution phases of the main metabolites of a new class of herbicide chemistry, sulfonylaminocarbonyltriazolinone, in aged soils. Sulfonylaminocarbonyltriazolinone herbicides are weak acids ($pK_a \approx 2$), in which the bridge N proton is ionized (**Figure 1a**). Sorption of these herbicides has recently been shown to increase with aging (*17*). These herbicides are also subject to hydrolysis, which would result in benzenesulfonamide and triazolinone metabolites. Aged sulfonylaminocarbonyltriazolinone metabolites, benzenesulfonamide residues from the herbicide flucarbazone [4,5-dihydro-3-methoxy-4-methyl-5-oxo-*N*-[[2-(trifluoromethoxy)phenyl]sulfonyl]-1*H*-1,2,4-triazol-1-carboxamide] and triazolinone residues from the herbicide propoxycarbazone [methyl 2-[[[(4,5-dihydro-4-methyl-5-oxo-3-propoxy-1*H*-1,2,4-triazol-1-yl)carbonyl]amino]sulfonyl]benzoate], were created by incubation of the chemicals in clay loam and loamy sand soils at different moisture potentials for up to 12 weeks.

MATERIALS AND METHODS

Chemicals and Soils. Pure analytical (chemical purity > 99%) and radiolabeled (radiochemical purity > 99%) 2,4-dihydro-5-propoxy-4-methyl-3*H*-1,2,4-triazol-3-one (5-^{14}C, specific activity = 2.157 GBq mmol^{-1}) (triazolinone) (**Figure 1c**) and 2-trifluoromethoxybenzenesulfonamide (*ring*-UL-^{14}C, specific activity = 2.653 GBq mmol^{-1}) (benzenesulfonamide) (**Figure 1b**) were supplied by Bayer Corp. Radiolabeled chemical was mixed with unlabeled material to give a final triazolinone or benzensulfonamide 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. Soil texture was determined by the hydrometer method. 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.

Soil Treatment. Duplicate 20-g soil samples in 250-mL flasks were treated with 500 μL of 4 mg L^{-1} [^{14}C]benzenesulfonamide or triazolinone solution, which was added dropwise using a microliter syringe. The final amount of chemical added to the soil was 0.1 mg kg^{-1}, which is near the normal field application rate of the parent herbicide assuming uniform distribution in the surface 1 cm of soil. The moisture content of the soil was adjusted, the water content corresponding to −33 kPa potential, 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 closed 250-mL glass flasks for up to 12 weeks. 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. At this time, the flasks were reweighed and soil water contents were adjusted to the original moisture content by adding distilled water, if necessary. To determine $^{14}CO_2$, a 1-mL aliquot of NaOH solution was mixed with 6 mL of EcoLite scintillation cocktail. After the samples had been in the dark for 24−48 h, the amount of radioactivity, corrected for quenching, was determined by liquid scintillation counting (LSC) for 5 min in a 1500 Tri-Carb Packard liquid scintillation analyzer. No chemiluminescence was observed.

Soil Extraction and Analysis. At each sampling time, all of the soil in each flask (20 g) was transferred from the flasks to Teflon centrifuge tubes with 40 mL of 0.01 M $CaCl_2$ and shaken for 1 h. The samples were allowed to sit overnight (∼20−24 h), then 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 had been 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 was determined by LSC. The remaining supernatant was saved to later determine the amounts of benzenesulfonamide and triazolinone metabolites in the extracted ^{14}C (see below).

Soil was then extracted twice with 48−50 mL of 4:1 (v/v) acetonitrile (ACN)/0.2 M ammonium acetate (NH_4OAc) (1% HCl) in the same manner as with the 0.01 N $CaCl_2$ extraction. The remaining soil was filtered and washed with 25 mL of 4:1 (v/v) ACN/0.2 M NH_4OAc (1% HCl). ACN was removed from the combined filtrates by evaporation at 40 °C using a Zymark Turbovap. One-milliliter aliquots of the remaining aqueous solution were removed and mixed with 6 mL of scintillation cocktail, and the total amount of radioactivity was determined by LSC, as described earlier. The remaining supernatant was saved to later determine the amounts of benzenesulfonamide and triazolinone metabolites in the extracted ^{14}C (see below).

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 was a gradient of ACN and filtered distilled water with 0.1% v/v orthophosphoric acid (85%). 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

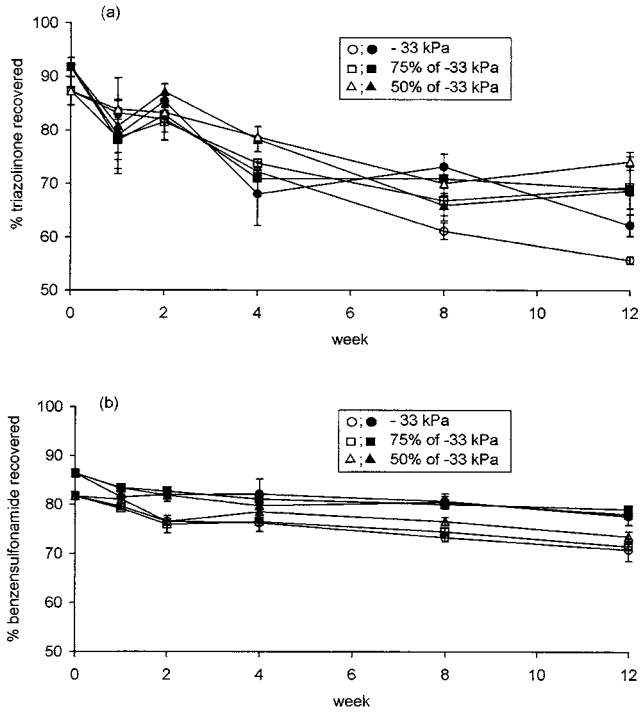

Figure 2. Recovery of triazolinone (a) and benzenesulfonamide (b) metabolites at three moisture potentials.

ACN from 90 to 30% from 24 to 25 min. The flow rate was 0.75 mL min^{-1}, and the injection volume was 100 μL. Detection of both chemicals was determined at 200 nm. According to the retention times of triazolinone (2.8 min) and benzensulfonamide (12.7 min), obtained by injecting the pure analytical standards, HPLC fractions corresponding to the benzenesulfonamide and triazolinone metabolites were collected and mixed with liquid scintillation cocktail, and ^{14}C was quantified by LSC. Fractions containing ^{14}C more and less mobile than the benzenesulfonamide and triazolinone metabolites were also collected and quantified. The percentages of the total ^{14}C that was benzenesulfonamide and triazolinone metabolites in the supernatant were calculated and used to determine total benzenesulfonamide and triazolinone metabolites in each supernatant solution.

Soil Sorption—Desorption Calculations. To calculate apparent sorption coefficients, $K_{d,app}$, as a function of incubation time, the amounts of benzenesulfonamide and triazolinone metabolites recovered from aged soil when soil was sequentially extracted first by 0.01 N $CaCl_2$ and then by ACN/0.2 M NH_4OAc (1% HCl) were determined. Parent benzenesulfonamide and triazolinone metabolites extracted by ACN/0.2 M NH_4OAc (1% HCl) corresponded to the sorbed phase concentration in the batch method, and the $CaCl_2$ extractable corresponded to the solution phase concentration in the batch method. $K_{d,app}$ was then calculated at each incubation time by

$$K_{d,app} = [\text{amount of parent chemical extractable by ACN/0.2 M } NH_4OAc\ (1\%\ HCl)]\ g^{-1} \div [\text{amount of parent chemical extractable by } CaCl_2]\ mL^{-1}$$

RESULTS

Benzenesulfonamide and Triazolinone Dissipation. Under the conditions of the incubation, triazolinone and benzensulfonamide metabolite dissipation was relatively slow (**Figure 2**; **Table 1**). Depending on soil moisture content, 68−90% of triazolinone metabolite extractable at time 0 was extractable after the 12-week incubation, with slower dissipation in drier soils. In the case of the benzenesulfonamide metabolite, 85% of the amount of chemical extractable at time 0 was extractable after the 12-week incubation, with no effect of soil moisture on dissipation.

Table 1. Amount of Benzenesulfonamide and Triazolinone Metabolites Recovered after 12 Weeks

		soil moisture[a]		
chemical	soil	−33 kPa (%)[b]	75% of −33 kPa (%)	50% of −33 kPa (%)
benzenesulfonamide	clay loam	70.8 ± 2.4	71.5 ± 0.5	73.5 ± 1.1
	loamy sand	77.7 ± 1.8	79.1 ± 0.6	78.0 ± 0.05
triazolinone	clay loam	55.6 ± 0.7	69.3 ± 6.6	74.2 ± 1.0
	loamy sand	62.2 ± 2.0	68.9 ± 3.6	68.7 ± 0.8

[a] Soil moisture = −33 kPa, or 50 or 75% of the moisture content of the water content at −33 kPa. [b] Percent of metabolite recovered after 12 weeks of incubation ± standard deviation.

The decreased recovery of the sulfonylaminocarbonyltriazolinone herbicide metabolites during the incubation was due to formation of bound, unextractable residues and degradation. HPLC fractionation of the extracts resulted in very small amounts of unidentifiable metabolites. There was negligible mineralization of both chemicals in both soils at the three matric potentials, <0.8% of applied in all cases. The mass balance for the ^{14}C in the experiments was >93%.

Benzenesulfonamide and Triazolinone Sorption—Desorption. $K_{d,app}$ values without previous incubation, calculated from aqueous $CaCl_2$ extractable amounts of benzenesulfonamide metabolite (solution phase) and ACN/0.2 M NH_4OAc (1% HCl) extractable amounts (sorbed phase) at time 0, were 1.79 mL g^{-1} for the clay loam and 0.18 mL g^{-1} for the loamy sand (**Table 2**). These values were similar to those obtained by batch equilibration with similar initial concentration ranges (Koskinen et al., unpublished results). $K_{d,app}$ values increased during the first week of incubation and then were relatively constant during the rest of the incubation (**Figure 3**). For instance, values of $K_{d,app}$ after the 12-week incubation at −33 kPa were 6.18 mL g^{-1} for the clay loam and 0.98 mL g^{-1} for the loamy sand, increases in $K_{d,app}$ by factors of 3.5 for the clay loam and 5.4 for the loamy sand, as compared to those determined in freshly treated soil, similar to increase factors after a 2-week incubation (**Table 2**). $K_{oc,app}$ increased from 56 to 195 mL g^{-1} for the clay loam and from 69 to 377 for the loam sand during the 12-week incubation. There were no significant differences in $K_{d,app}$ values as a result of differences in soil matric potentials during incubation.

Triazolinone metabolite $K_{d,app}$ values also increased during aging, with the majority of the increase occurring during the first 2 weeks of incubation. At the end of the 12-week incubation at −33 kPa, values of $K_{d,app}$ were 9.20 mL g^{-1} for the clay loam and 1.36 mL g^{-1} for the loamy sand, increases in K_d by factor of 3.7 for the clay loam and 6.5 for the loamy sand, as compared to those determined in freshly treated soil (**Table 2**). $K_{oc,app}$ increased from 79 to 290 mL g^{-1} for the clay loam and from 81 to 523 for the loam sand during the 12-week incubation. As in the case of the benzenesulfonamide metabolite, there were no differences in triazolinone metabolite $K_{d,app}$ values as a result of differences in soil water potential during incubation (**Figure 3**).

DISCUSSION

Although more research is needed to determine the kinetics and mechanisms of sulfonylaminocarbonyltriazolinone herbicide metabolite degradation, this research was not designed to determine degradation kinetics and mechanisms. At this time we do not know the mechanism of degradation, whether it is chemical, microbial, or a combination of the two processes. In

Table 2. Determination of K_d As Affected by Incubation Time

chemical	soil	moisture[a] (kPa)	K_d time 0[b]	K_d week 2[b]	IF-1[c]	K_d week 12[b]	IF-2[d]
benzenesulfonamide	clay loam	–33	1.79 ± 0.08	5.40 ± 0.33	3.02	6.18 ± 0.48	3.45
	loamy sand	–33	0.18 ± 0.01	1.00 ± 0.02	5.56	0.98 ± 0.10	5.44
triazolinone	clay loam	–33	2.51 ± 0.07	6.88 ± 0.76	2.74	9.20 ± 0.88	3.67
	loamy sand	–33	0.21 ± 0.01	1.23 ± 0.01	5.86	1.36 ± 0.39	6.48

[a] Soil moisture = –33 kPa, or 50 or 75% of the moisture content of the water content at –33 kPa. [b] Time of incubation at which K_d was calculated. [c] Increase factor 1 = K_d week 2/K_d time 0. [d] Increase factor 2 = K_d week 12/K_d time 0.

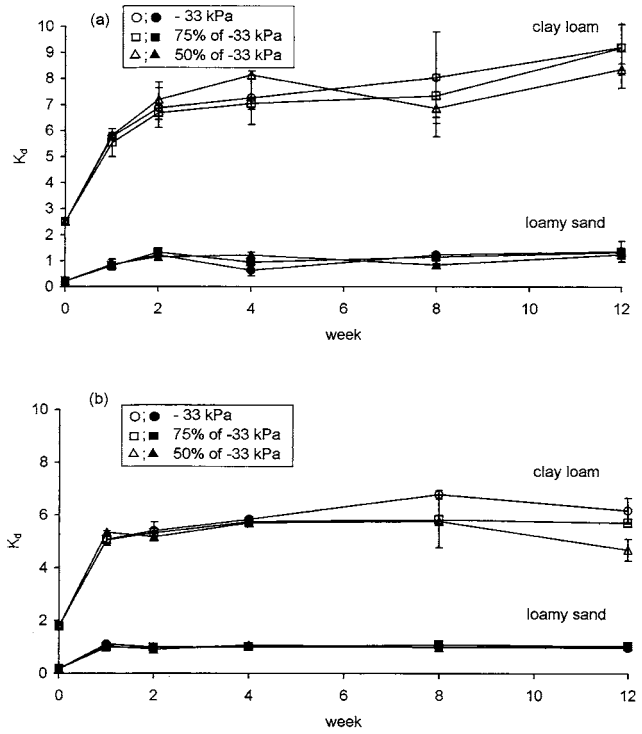

Figure 3. Sorption–desorption of triazolinone (a) and benzenesulfonamide (b) metabolites incubated for varying times at three moisture potentials. Open symbols are for clay loam soil and solid symbols for loamy sand soil.

this research, we wanted to ensure sufficient metabolite remained by the end of the incubation period to be able to determine the distribution between sorbed and solution phases of the amount of sulfonylaminocarbonyltriazolinone metabolites remaining at different times during incubation at different initial moisture contents, which would allow the effect of the aging process on sorption−desorption to be determined. After the 12-week incubation, a minimum of 56% of applied benzenesulfonamide and triazolinone metabolites remained, sufficient to determine $K_{d,app}$ values.

The increase in calculated $K_{d,app}$ values resulted from a decrease in the amount of applied chemical that was labile or readily available ($CaCl_2$ extractable) with incubation time and an increase in amount sorbed (solvent extractable), the ratio of which depended on soil type. In the clay loam, the largest change was in the $CaCl_2$ extractable over the 12-week incubation, whereas in the loamy sand the largest change was in the solvent extractable. In the clay loam, there was 3.7 times more $CaCl_2$ extractable (solution phase) and 1.2 times less solvent extractable (sorbed phase) sulfonylaminocarbonyltriazolinone metabolites at time 0 as compared to week 12 for both triazolinone and benzenesulfonamide metabolites, averaged over the three moisture potentials. The nonextractable fraction increased by a factor of 2.0 over the 12-week incubation. In the loamy sand, there was 1.8 times more $CaCl_2$ extractable and 3.3 times less solvent extractable sulfonylaminocarbonyltriazolinone metabolite at time 0 as compared to week 12 for both benzesulfonamide and triazolinone metabolites, averaged over the three moisture potentials. The nonextractable fraction increased by a factor of 1.1 over the 12-week incubation.

The increase in calculated sorption coefficients for both sulfonylaminocarbonyltriazolinone metabolites with increasing incubation time can be attributed to a rate of degradation in solution and on labile sites that is faster than the rate of desorption from soil (*7*, *10*). Degradation of labile chemical would leave more strongly sorbed sulfonylaminocarbonyltriazolinone metabolite on the soil surface, resulting in a net increase in $K_{d,app}$ values. The increase in calculated sorption coefficients can also be attributed to diffusion of the chemicals, particularly the anion, to less accessible sorption sites or "stronger" binding sites. If diffusion processes were coupled to degradation of readily available chemical, it would also result in the net effect observed, decreased solution phase and increased sorbed phase concentrations.

It was hoped that incubating these chemicals in soil at different soil moisture potentials would help to distinguish the two possible mechanisms. Decreasing levels of soil moisture have consistently been observed to decrease microbial degradation on pesticides (i.e., ref *10*) and diffusion into soil particles (i.e., ref *7*). However, in this study there was generally no identifiable effect of soil moisture on degradation or diffusion. Also, there was no consistent effect of increased sorbed and decreased solution concentrations as a function of aging between soils. More research into these processes is necessary.

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 sorption coefficients determined on aged residues were used. In the case of these triazolinone and benzensulfonamide metabolites, the mobility classification would change to less mobile, similar to what was observed for their parent sulfonylaminocarbonyltriazolinone herbicides.

Similar to the case of effect of aging on sorption−desorption of imidacloprid and its main metabolites (*15*, *16*), based on $K_{d,app}$ values, it is difficult to predict the effect of aging on sorption−desorption of sulfonylaminocarbonyltriazolinone herbicides and the triazolinone and benzensulfonamide metabolites. For instance, in freshly treated soils, $K_{d,app}$ values for propoxycarbazone and the triazolinone and benzensulfonamide metabolites were similar, whereas the $K_{d,app}$ values for flucarbazone were significantly lower (*17*). However, in aged soils, $K_{d,app}$ values increased by similar factors.

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, for both parent chemical and main metabolites. Use of simplistic equilibrium partitioning coefficients based on freshly treated samples under slurry conditions is inadequate.

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