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SORPTION OF ATRAZINE AND METOLACHLOR BY EARTHWORM SURFACE CASTINGS AND SOIL

Key Words: Herbicide, sorption, desorption, earthworm castings, crop leaf residues

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ABSTRACT

Atrazine and metolachlor were more strongly retained on earthworm *(Lumbricus terrestris* L.) castings than on soil, suggesting that earthworm castings at the surface or at depth can reduce herbicide movement in soil. Herbicide sorption by castings was related to the food source available to the earthworms. Both atrazine and metolachlor sorption increased with increasing organic carbon (C) content in castings, and Freundlich constants (K_f values) generally decreased in the order: soybean-fed > corn-fed > not-fed-earthworm-castings. The amount of atrazine or metolachlor sorbed per unit organic carbon (K_{OC} values) was significantly greater for corn-castings compared with other castings, or soil, suggesting that the composition of organic matter in castings is also an important factor in determining the retention of herbicides

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in soils. Herbicide desorption was dependent on both the initial herbicide concentration, and the type of absorbent. At small equilibrium herbicide concentrations, atrazine desorption was significantly greater from soil than from any of the three casting treatments. At large equilibrium herbicide concentrations, however, the greater organic C content in castings had no significant effect on atrazine desorption, relative to soil. For metolachlor, regardless of the equilibrium herbicide concentration, desorption from soybean- and corn-castings treatments was always less than desorption from soil and not-fed earthworm castings treatments. The results of this study indicate that, under field conditions, the extent of herbicide retention on earthworm castings will tend to be related to crop and crop residue management practices.

INTRODUCTION

The herbicides atrazine [2-chloro-4-ethylamino-6-isopropylamino-1,3,5- triazine] and metolachlor [2-chloro-N-(2-ethy1-6-methylpheny1)-N-(2-methoxy-1- methylethyl) acetamide] are often used in combination on corn fields to provide for a greater control of broadleaf weeds. Atrazine-metolachlor mixtures are more effective than either herbicide alone and require less total herbicide use (Solomon *et al.,* 1996). The residual activity of metolachlor is commonly ten to fourteen weeks. Atrazine may persist for more than one planting season (Struger and Fisher, 1989). Rotational crops such as soybeans may be grown the following spring when atrazine application in the previous season was low, that is less than 1.5 kg ha^{-1}. Current application rates of both herbicides are 1 to 4.5 kg ha^{-1}, depending on crop, weed pressure, soil properties and climatic conditions (Trotter et al., 1990, OCPC, 1996).

Earthworms have been shown to affect the fate of herbicides in soil. Earthworms *directly* influence the persistence of pesticides in soil by metabolizing a parent compound in their gut (Gilman and Vardanis, 1974, Stenersen *et al.*, 1974), by transporting herbicides to depth and increasing the soil-bound (non-extractable herbicides) fraction in soil (Farenhorst *et al.*, in press), or by absorbing herbicide residues in their tissue (Edwards and Lofty, 1977). Earthworms modify soil pesticide persistence *indirectly* by affecting the chemical, physical and biological properties in the soil that control herbicide transformation and sorption processes.

Earthworms transfer crop leaf residues from the surface into the soil, increasing organic decomposition rates and enhancing the amount of available nutrients (Lee, 1985). Earthworm burrow linings were enriched in organic carbon (C) and, for a range of herbicides, batch experiments in the laboratory showed that sorption partition coefficients were greater for burrow linings than for matrix soil (Stehouwer *et al.*, 1993, 1994). Others indicated that microbial activity and pesticide mineralization rates were greater in burrow linings than in the surrounding soil matrix (Mallawantantri *et al.*, 1996).

Earthworms can reduce the susceptibility to surface sealing by their egestion of castings at the soil surface (Kladivko *et al.*,1986). Sorption of herbicides by earthworm surface castings has been examined in a few studies. Akhouri *et al.* (1994) found that earthworm surface castings (middens) in zero-tilled fields sorbed more atrazine than soil, while no differences were observed for castings and soil obtained from conventional-tilled fields. In contrast, sorption partitioning coefficients for the herbicide imazaquin showed no significant differences between soil and castings collected from zero-tillage fields, but sorption was greater by soil than by castings in conventional-tilled sites.

It has been shown that the nature and amount of organic matter in earthworm surface castings is dependent on the food source available to the earthworms (Shipitalo *et al.*, 1988). Therefore, we expect that food source will also play an important role in influencing the sorption characteristics of castings, and the amount of herbicides retained. For example, atrazine sorbs on both inorganic and organic colloid surfaces, but preference is shown for organic matter over clay (Ma and Selim, 1996). Metolachlor sorption also increases with increasing organic matter content in the soil, specifically humic matter (Kent *et al.*, 1991). The objective of our study was to test the hypothesis that the type of crop residues at the soil surface determines the amount of organic C in earthworm castings, therefore influences the sorption of herbicides by earthworm egested materials.

MATERIAL AND METHODS

Soil

A loamy Ap horizon (0-15cm) of a Gobles soil (Gleyed Brunisolic Gray Brown Luvisol) at a field moisture content of 13 % was collected from a no-till corn field near Belmont, Ontario. Neither atrazine nor metolachlor residues were detected in the sampled soil (HPLC detection limit 25 ng g^{-1} soil). Key physical and chemical soil properties of the soil include the following: 29 % sand, 46 % silt, 24 % clay, 1.63 % organic carbon, pH 6.35, CEC 12.38 cmol kg^{-1}, and an exchangeable K, Ca, Mg and Na of 0.47, 5.62, 1.56 and 0.07 cmol kg^{-1} respectively. Soil texture was determined by the hydrometer method (Gee and Bauder, 1986), organic C by the modified Walkley-Black volumetric oxidation method (Nelson and Sommers, 1982), pH in a 1:1 soil to 0.01 M $CaCl_2$ solution, CEC by the NH_4OAC method (Chapman, 1965), and exchangeable K, Ca, Mg and Na according to Jackson (1958).

Chemicals and Analytical Methods

A commercially available atrazine-metolachlor liquid formulation, Primextra® (label content: 153 g L^{-1} atrazine, 364 g $L^{-'}$ metolachlor, and 10 g $L^{-'}$ unidentified other active triazines; Ciba-Geigy Co, Greensboro, NC) was used. Analytical standards (> 97 % purity) of atrazine and metolachlor were obtained from Ciba-Geigy Co, Greensboro, NC.

Equilibrium sorption solutions from Freundlich sorption isotherm determinations were quantified as follows. Aqueous herbicide concentrations were determined by HPLC with UV detector (Waters 486 Tunable Absorbance Detector, Waters Corporation, Milford, Massachusetts) and the following operating parameters: Column: reversed-phase, 15.0 cm H 3.9 mm (5 µm spherical particle C18 packing); Mobile phase: acetonitrile/water (40:60) at 0.9 mL min^{-1} for atrazine, and acetonitrile/water (60:40) at 0.9 mL min^{-1} for metolachlor; Detector wavelength: 220 nm for atrazine, and 200 nm for metolachlor. Herbicides were quantified using a Waters Millennium data management system. Samples were appropriately diluted in volumetric flasks with 50:50 methanol-H_2O to obtain concentrations in the optimal working range of the UV detector (20 ng mL^{-1} to 3 µg mL^{-1}). The minimum detectable concentration for atrazine was in the 5 to 15 ng mL^{-1} range, and for metolachlor, 20 to 30 ng mL^{-1}. The variation between repeat sample analyses was always less than 1 %.

Earthworms and Crop Leaf Residues

Corn and soybean leaves were obtained from a pesticide-free field plot at the Southern Crop Protection and Food Research Centre, London, Ontario. Wet leaves were held in plastic bags at room temperature for one month to decompose and stimulate food acceptance by earthworms (Edwards and Lofty, 1977). Further decomposition was delayed by storing leaves at 4°C. One week before using leaves in the experiment, leaves were left to dry at 12 °C and weighed. Leaves were pulverized into small pieces (2.5 - 7.5 mm^2) using a blender to produce a material more palatable for earthworms.

Mature earthworms *(Lumbricus terrestris L.)* were purchased locally and stored at 12 °C. Worm digestive tracts were cleared of previously ingested contents by incubating them in soil containing corn leaf residues for 5 days before they were used in the experiment.

Development of Earthworm Castings

Sieved soil (< 3mm) at 13 % (w/w) was brought to 25 % soil moisture content (w/w), re-sieved (< 3 mm) and compacted in 18 Acrylonitrile Butadiene Styrene (ABS) columns (30 cm high, 8.9 cm i.d.) to obtain a bulk density of 1300 kg m^{-3} and a 25 cm soil depth.

Earthworms were incubated in soil columns to produce surface castings using three different crop residue treatments: 1) corn leaf residues (6 replicated columns), 2) soybean leaf residues (6 replicated columns), and 3) no crop residues (6 replicated columns). All columns were conditioned for 135 days at 12°C with two mature *L. terrestris* (4 to 5 g) per column. During this time, leaf residues (2 g) were added every second week onto the soil surface of the crop residue-treated columns.

After incubation, surface castings were removed and weighed. For each crop residue treatment, three columns with a casting production of at least 30 g per column were selected. Surface castings from each column were air-dried separately, providing three replicates per crop residue treatment. In the no-residue treatment, only two columns generated more than 30 g surface castings, sufficient for two replicates, and for the third replicate, castings of two other columns were combined. Samples of castings, used in batch sorption experiments (see below), were analysed for organic C content by the modified Walkley-Black volumetric oxidation method (Nelson and Sommers, 1982). The remaining columns were preserved for other experiments, reported elsewhere (Farenhorst, 1998).

One additional column was prepared and incubated as described above without earthworms and without crop residues. After incubation of 135 days, this soil was analysed for organic C and used in the batch experiments as a control.

Freundlich Isotherms

Atrazine and metolachlor adsorption isotherms on soil were determined using the batch equilibrium procedure and 15 mL volumes. Herbicide solutions were prepared in 0.01 M $CaCl_2$ and initial concentrations were for metolachlor approximately 0.9, 1.8, 4.8, 12, 30 and 60 mg L^{-1} and for atrazine approximately 0.3, 0.6, 1.6, 4, 10 and 20 mg L^{-1}. The ratio of atrazine:metolachlor in Primextra® determined by HPLC was slightly different from that given on the product label (1 : 2.38).

Surface castings and soil (control) were sieved (2 mm). Each herbicide solution (15 mL) was added to 5 g of air-dried surface castings, or soil, in 30 mL glass COREX® centrifuge tubes in triplicate. Tubes were tumbled for 24 h at 21°C to reach equilibrium. Previous batch experiments have shown that atrazine and metolachlor sorption on soil occurred rapidly, with most of the herbicides being removed from solution within the first hour, and that a 24 h equilibrium period was sufficient to characterize the second phase of slow sorption (Seybold and Mersie, 1996). Tubes were then centrifuged for 45 min at 7,000 RPM (5900 x g) and 13 mL of supernatant was removed and sub-sampled to determine the concentration of herbicides remaining in solution by HPLC analysis. Amount of herbicides adsorbed on soil was determined by the difference between the initial and equilibrium herbicide concentration.

For the desorption procedure, supernatant was replaced by an equal amount of 0.01 M $CaC1_2$ solution (13 mL). Tubes were placed on a vortex shaker for 1 min to disperse soil pellets, and then tumbled and centrifuged as described for the adsorption isotherms. After centrifugation, the supernatant was sub-sampled to determine the herbicide concentration of the equilibrium solution after desorption by HPLC analysis. Desorption was calculated by the difference between the solutes adsorbed onto the soil at equilibrium after adsorption and that remaining at equilibrium after desorption.

Adsorption isotherms were fitted using the log transformation of the empirical Freundlich equation:

$$\mathrm{Log}\ (X/M) = \mathrm{Log}\ K_f + 1/n\ \mathrm{Log}\ C_e \qquad (1)$$

where X/M = amount of herbicide adsorbed [µmol] / amount of adsorbent [$Kg^{-1]}$,
K_f = Freundlich constant [$\mu mol^{(1-1/n)}\ L^{1/n}\ Kg^{-1}$], 1/n = dimensionless Freundlich constant, and C_e = herbicide concentration of equilibrium solution [$\mu mol\ L^{-1}$].

The organic C distribution coefficients, K_{oc}, [$\mu mol^{(1-1/n)}\ L^{1/n}\ Kg^{-1}$] was calculated by:

$$K_{OC} = K_f / f_{OC} \qquad (2)$$

where f_{OC} = the fraction of organic C in soil (dimensionless).

Statistical analysis included Analysis of Variance and Multiple Comparison (Student-Newman-Keuls-Test, $P < 0.05$ level) on casting production, soil organic matter content, soil pH, and herbicides K_f, K_{OC}, K_d, and n values, and on % of atrazine or metolachlor desorbed using SigmaStat® Windows Version 1.0 (Jandel Scientific). All statements reported in this study are at the $P < 0.05$ level.

RESULTS AND DISCUSSION

No significant differences were observed in casting production rates among earthworms fed different foods. Average casting production was highest for earthworms fed on corn (63 mg g^{-1} day^{-1}) and lowest when no food was offered (30 mg g^{-1} day^{-1}), but replicates within treatments showed also considerable differences (Table 1). Shipitalo *et al.* (1988) reported similar results for earthworms fed on corn and various other diets. Organic C in castings decreased in the order: soybean-fed > corn-fed > not-fed-earthworm-castings (Table 1). No-residue castings had the same organic C content as the original soil (1.63%). Organic C in corn and soybean-castings was within the range previously reported for *L. terrestris* castings developed under similar laboratory conditions (Shipitalo *et al.*, 1988) and for *L. terrestris* middens in soybean and corn fields (Akhouri *et al.*, 1996).

Freundlich nonlinear adsorption isotherms for the herbicides showed very good fit ($r^2 > 0.99$) to the measured data, for both soil and casting materials (Table 2). Slopes of isotherms ranged between 0.86 and 0.92, for both atrazine and metolachlor suggesting that herbicide sorption on soil was nonlinearly proportional to the equilibrium solution concentration. The degree of herbicide sorption on soil and castings was greater for initially low herbicide concentrations than for initially high herbicide concentrations, reflecting the saturation of the adsorption sites as the molecule concentration increased, and suggesting that sorption was an adsorption process rather than an absorption process (Seybold and Mersie, 1996, Businelli, 1997, Farenhorst and Bowman, 1998).

The K_f values for metolachlor were generally greater than that for atrazine. Since metolachlor was more strongly sorbed on soils than atrazine, it may have a lower mobility in soils (Bowman, 1989, Struger and Fisher, 1989, Bowman *et al.*, 1994b). K_f values of both atrazine and metolachlor generally increased with increasing organic matter content in castings, as might be expected. Both atrazine and metolachlor sorption were significantly greater on corn- and soybean-castings than on no-residue castings, or soil. Most other studies have indicated that herbicide sorption increased with increasing

TABLE 1: Earthworm Casting Activity at the Surface in Soils with Different Crop Residues.

Crop residue treatments	Casting activity [mg $^{-1}$ day^{-1}]		Organic C in castings [%]		pH of castings	
No-residues	30.36 ± 8.89 [1]	a [2]	1.63 ± 0.01 [3]	a [2]	6.37 ± 0.05 [3]	a [2]
Corn-residues	63.34 ± 3.26	a	2.60 ± 0.18	b	6.35 ± 0.06	a
Soybean- residues	47.02 ± 18.68	a	3.73 ± 0.09	c	6.33 ± 0.04	a

[1] Mean of six replicates followed by standard error.

[2] Means followed by same letters are not significantly different

[3] Mean of three replicates followed by standard error

TABLE 2: Best-Fit Parameters (K_f, 1/n) and Goodness of Fit (r^2) of the Freundlich Model to Describe Atrazine and Metolachlor Adsorption by Soil and Earthworm Surface Castings.

Treatments	K_f [µmol $^{(1-1/n)}$ L $^{1/n}$ Kg $^{-1}$]		1/n		r^2
Atrazine:					
Soil	1.096 ± 0.011 [1]	a [2]	0.870 ± 0.014 [1]	a [2]	0.994 ± 0.001
No-residue-castings	1.322 ± 0.020	a	0.886 ± 0.006	a	0.999 ± 0.000
Corn-castings	2.685 ± 0.210	b	0.865 ± 0.013	a	0.996 ± 0.002
Soybean-castings	3.009 ± 0.250	b	0.916 ± 0.011	a	0.998 ± 0.001
Metolachlor:					
Soil	2.315 ± 0.020 [1]	a [2]	0.867 ± 0.004 [1]	a [2]	0.997 ± 0.002
No-residue-castings	2.390 ± 0.029	a	0.877 ± 0.016	a	0.997 ± 0.002
Corn-castings	5.777 ± 0.351	b	0.874 ± 0.011	a	0.999 ± 0.000
Soybean-castings	6.786 ± 0.521	b	0.920 ± 0.081	b	0.996 ± 0.001

[1] Mean of three replicates followed by standard error

[2] Means followed by same letters are not significantly different

organic matter content in soils (Green and Karickhoff, 1990). Atrazine can form complexes with amide and carboxylic acid groups of organic matter surfaces through hydrogen-bonding (Welhouse and Bleam, 1993). Metolachlor adsorption has been correlated to hydrogen-bonds between the carbonyl oxygen of metolachlor and hydrogen from hydroxyl and carboxyl groups of organic matter (Chesters *et al.*, 1989).

Organic C content in soil and castings were similar for the no-residue treatment, but the K_f values for both atrazine and metolachlor on no-residue castings were somewhat greater (although not statistically significant) than that on soil. It is possible that mucilage secretion by earthworms might have increased the herbicide binding to soil exchange sites (Meharg, 1996).

Atrazine K_{OC} values ranged from 68 to 103 (Table 3) and are consistent with those previously reported by Gustafson (1989), Wauchope *et al.* (1992) and Seybold *et al.* (1994). Metolachlor K_{OC} values were always greater than 140 (Table 3) and were within the range of previously reported values that varied from 102 to 190 (Graham and Conn, 1992, Zheng *et al.*, 1993, Seybold and Mersie, 1996). Normalizing for differences in organic C decreased the variability in sorption among soil and casting treatments for both atrazine and metolachlor, but sorption per unit of C was significantly greater on corn-castings than on other castings, or soil. This indicated that the composition of organic matter in castings is also an important factor in determining the retention of herbicides in soils.

Percent desorbed from soil was 30% for metolachlor (averaged across all treatments and initial herbicide concentrations) and 43% for atrazine (averaged across all treatments and initial herbicide concentrations), revealing that a relatively larger proportion of metolachlor was retained by more energetic bonding mechanisms.

Metolachlor and atrazine desorption was dependent on the type of adsorbent. Analysis of variance revealed that the interaction "adsorbent material x initial herbicide concentration" was also statistically significant, indicating that the differential effect of adsorbent material depended on the initial solution concentration.

TABLE 3: Organic C Distribution Coefficients (K_{OC} Values) Averaged across all Initial Herbicide Concentrations to Describe Atrazine and Metolachlor Adsorption by Soil and Earthworm Surface Castings.

Treatments	K_{OC} [µmol $^{(1-1/n)}$ L $^{1/n}$ Kg C $^{-1}$]
Atrazine:	
Soil	68 ± 0.6[1] a[2]
No-residue-castings	81 ± 1.2 a
Corn-castings	103 ± 8.0 b
Soybean-castings	80 ± 6.7 a
Metolachlor:	
Soil	143 ± 1.2[1] a[2]
No-residue-castings	146 ± 1.7 a
Corn-castings	222 ± 13.5 b
Soybean-castings	182 ± 14.0 a

[1] Mean of three replicates followed by standard error.

[2] Means followed by same letters are not significantly different.

General trends were as follows: At small equilibrium herbicide concentrations, atrazine desorption was significantly greater from soil than from castings (Table 4), indicating that there was a greater availability of stronger (more energetic) sorption sites for herbicide sorption on castings than on soil. At greater equilibrium herbicide concentrations, however, the greater organic C content in soybean- and corn-castings had no significant effect on atrazine desorption when compared with soil. It is likely that the binding or sorption energy of solute molecules on the adsorption sites decreased with increasing solute loading, leading to less energetically-sorbed atrazine. Regardless of either the organic C content in the adsorbent or the equilibrium solution concentration, atrazine desorption was always favored from lower-energy sorption sites. For metolachlor, regardless of the initial herbicide concentration, desorption from soybean- and corn-

TABLE 4: The Percentage of Atrazine Desorption from Soil and Earthworm Surface Castings for Each Adsorbent x Initial Herbicide Concentration Combination.

Adsorbent	Concentration $[\mathrm{mg\ L^{-1}}]$	Atrazine desorbed as % of adsorbed	
Soil	0.9	51.83	a[1]
Soil	4.0	51.68	a
Soil	1.6	50.86	a
Soil	10	50.24	ab
Soil	0.3	47.81	abc
Corn-castings	20	47.61	abc
Soil	20	46.16	abcd
Corn-castings	10	44.83	abcd
No-residues-castings	1.6	44.38	abcd
No-residues-castings	0.9	43.46	abcd
Soybean-castings	20	43.09	abcd
Soybean-castings	4.0	42.59	abcd
No-residues-castings	20	42.38	abed
Soybean- casting	10	42.14	abcd
Corn-castings	4.0	40.89	bcd
No-residues-castings	0.3	40.25	cd
No-residues-castings	10	39.89	cd
Soybean-castings	0.9	39.39	cd
Soybean-castings	0.3	38.67	cd
Corn-castings	1.6	38.20	cd
Corn-castings	0.3	38.15	cd
Soybean-castings	1.6	38.09	cd
No-residues-castings	4.0	37.59	cd
Corn-castings	0.9	36.84	d

[1] Means followed by same letters are not significantly different.

TABLE 5: The Percentage of Metolachlor Desorption from Soil and Earthworm Surface Castings for Each Adsorbent x Initial Herbicide Concentration Combination.

Adsorbent	Concentration [mg L^{-1}]	Metolachlor desorbed as % of adsorbed	
No-residues-castings	60	57.70	a[1]
Soil	60	41.39	b
Soil	12	40.34	be
No-residues-castings	0.3	38.86	bcd
Soil	4.8	37.23	bcde
Soil	1.8	36.97	bcde
No-residues-castings	12	35.90	bcde
No-residues-castings	1.8	35.62	bcde
Soil	4.8	35.00	cde
No-residues-castings	4.8	33.91	de
Soil	0.3	33.23	def
Corn-castings	12	34.83	efg
No-residues-castings	4.8	31.76	efg
Corn-castings	60	31.55	efg
Soybean-castings	60	27.89	fgh
Corn-castings	4.8	27.67	fgh
Soybean-castings	30	27.30	gh
Soybean-castings	12	25.96	gh
Corn-castings	4.8	25.00	h
Corn-castings	1.8	23.23	h
Soybean-castings	4.8	23.01	h
Soybean-castings	1.8	22.89	h
Corn casings	0.9	22.12	h
Soybean-castings	0.9	21.57	h

[1] Means followed by same letters are not significantly different.

castings was less than metolachlor desorption from soil and no-residue castings (Table 5). This might be explained by the different types or strength of bonding involved in metolachlor sorption by organic C-rich adsorbents (soybean- and corn-castings) compared with adsorbents that contain a lower percentage of organic C (soil and no-residue castings).

CONCLUSION

Atrazine and metolachlor were more strongly retained on earthworm *(Lumbricus terrestris* L.) surface castings than on soil, suggesting that earthworm castings at the surface or at depth can reduce herbicide movement in soil. Herbicide sorption by castings was related to the organic carbon content in castings, and Freundlich constants (K_f values) for both atrazine and metolachlor on castings decreased in the order of soybean-fed- > corn-fed- > not-fed earthworms. The amount of herbicides sorbed per unit C, however, was significantly greater for corn-castings than for other castings, or soil, indicating that herbicide retention was also determined by the composition of organic matter in castings. Metolachlor desorption from soil and no-residue castings was greater than desorption from soybean- and corn-castings. For atrazine, at small equilibrium herbicide concentrations, desorption from soil was always less than desorption from soybean-fed-, corn-fed-, and not-fed-earthworm castings, but the greater organic C content in castings had no significant effect on atrazine desorption at large equilibrium herbicide concentrations, when compared to soil.

These results indicate that, under field conditions, the extent of herbicide retention on earthworm castings will be related to crop and crop residue management practices. Earthworm castings on the surface or at depth can increase the sorption potential for atrazine and metolachlor in field soils. Surface castings around earthworm burrows may also reduce herbicide leaching to groundwater by burrow flow by retaining atrazine and metolachlor before flow enters the burrows. Further research, quantifying earthworm cast production, characteristics, and distribution in soils under different cropping systems would help to assess the overall importance of earthworms in increasing herbicide retention in soil.

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