

Sorption–desorption of flucarbazone and propoxycarbazono and their benzenesulfonamide and triazolinone metabolites in two soils[†]

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Abstract: 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. While sorption–desorption of many herbicides has been characterised, very little work in this area has been done on herbicide metabolites. The objective of this study was to characterise sorption–desorption of two sulfonylaminocarbonyltriazolinone herbicides, flucarbazone and propoxycarbazono, and their benzenesulfonamide and triazolinone metabolites in two soils with different physical and chemical properties. K_f values for all four chemicals were greater in clay loam soil, which had higher organic carbon and clay contents than loamy sand. K_{f-oc} ranged from 29 to 119 for the herbicides and from 42 to 84 for the metabolites. Desorption was hysteretic in every case. Lower desorption in the more sorptive system might indicate that hysteresis can be attributed to irreversible binding of the molecules to soil surfaces. These data show the importance of characterisation of both sorption and desorption of herbicide residues in soil, particularly in the case of prediction of herbicide residue transport. In this case, potential transport of sulfonylaminocarbonyltriazolinone herbicide metabolites would be overpredicted if parent chemical soil sorption values were used to predict transport.

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Keywords: flucarbazone; propoxycarbazono; sulfonylaminocarbonyltriazolinone; metabolites; benzenesulfonamide; triazolinone; sorption; desorption; aged residues

1 INTRODUCTION

Sorption–desorption interactions of pesticides with soil determine the availability of pesticides in soil for transport and microbial degradation. A variety of studies have suggested that only a pesticide in solution, or that is readily desorbable from soil, is available for transport or degradation. A pesticide that is sorbed to soil particles is not instantaneously available but must first desorb from the soil into solution. Therefore availability would be directly related to the pesticide's ability to be desorbed from soil.

Multiple mechanisms are involved in sorption–desorption of pesticides in soils, and different mechanisms may be operable for sorption as compared with desorption processes.¹ Sorption–desorption processes being complex, they cannot be adequately characterised by a single process. 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, i.e. a hysteresis effect. For an excellent review of deviations in simple sorption behaviour, see Ref. 2.

While there is information on sorption and degradation of pesticides in soils, there is less information on these processes for pesticide metabolites. The lack of data on metabolites results in modellers using data of a parent chemical as representative of those of a metabolite, an assumption that may or may not be acceptable. For instance, imidacloprid metabolites, although similar in structure to imidacloprid, have very different sorption characteristics; imidacloprid-urea is sorbed less than imidacloprid, whereas imidacloprid-guanidine is sorbed to a much greater extent than imidacloprid.³

The present study was conducted to determine the distribution between sorbed and solution phases of both the parent chemical and main metabolites of a new class of herbicide chemistry, sulfonylaminocarbonyltriazolinone, in soils. Sulfonylaminocarbonyltriazolinone herbicides are weak acids ($pK_a \approx 2$) in which the bridge N proton is ionised (Fig. 1(a)). Little research has been reported on soil processes affecting these herbicides. Sorption of the herbicides has recently been shown to increase with aging.⁴ These herbicides, such as flucarbazone (Fig. 1(b))

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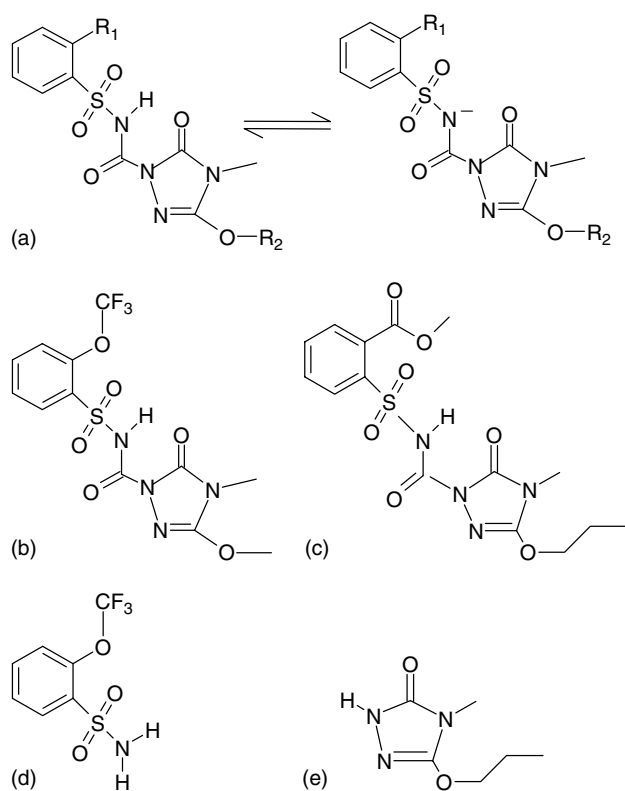


Figure 1. (a) Sulfonylaminocarbonyltriazolinone ionisation and structures of (b) flucarbazone, (c) propoxycarbazone and their (d) benzenesulfonamide and (e) triazolinone metabolites.

and propoxycarbazone (Fig. 1(c)), are also subject to hydrolysis, which would result in benzenesulfonamide (Fig. 1(d)) and triazolinone (Fig. 1(e)) metabolites. Sorption of benzenesulfonamide and triazolinone metabolites has also been shown to increase in soil with aging.⁵ In a heavier textured soil, sorption of the parent chemical was lower than that of its main metabolite, whereas there was no difference in a sandy soil. Sorption of a principal metabolite has been shown to be greater than or equal to that of the parent herbicide in a variety of organoclays.⁶

The only other published research on processes in soils and water for these chemicals was on flucarbazone dissipation, which was reported to be more rapid in wetter soils with higher organic carbon content.⁷ There is also little published research on related aryltriazolinone herbicides such as carfentrazone-ethyl.^{8,9}

Transport and degradation models have traditionally characterised the availability of pesticides using a simplistic characterisation of sorption–desorption through the incorporation of a single sorption coefficient (K_d) or Freundlich sorption–desorption isotherm coefficients (K_f and $1/n$), as determined using batch slurry techniques. There have been no reports of characterisation of soil sorption–desorption of sulfonylaminocarbonyltriazolinone herbicides or benzenesulfonamide and triazolinone metabolites using the batch equilibration method that would result in sorption–desorption values, which could be used in transport and

degradation models. In the present study we report the characterisation of sorption–desorption of flucarbazone [4,5-dihydro-3-methoxy-4-methyl-5-oxo-*N*-(2-trifluoromethoxyphenylsulfonyl)-1*H*-1,2,4-triazole-1-carboxamide] ($pK_a = 1.9$), its benzenesulfonamide metabolite 2-trifluoromethoxybenzenesulfonamide, propoxycarbazone (methyl 2-[[[(4,5-dihydro-4-methyl-5-oxo-3-propoxy-1*H*-1,2,4-triazol-1-yl)carbonyl]amino]sulfonyl]benzoate) ($pK_a = 2.1$) and its triazolinone metabolite 2,4-dihydro-5-propoxy-4-methyl-3*H*-1,2,4-triazol-3-one on two diverse soils, a clay loam and a loamy sand.

2 MATERIALS AND METHODS

2.1 Chemicals and soils

Pure analytical (chemical purity >99%) and radiochemical (radiochemical purity >99%) propoxycarbazone (triazole-3-¹⁴C, specific activity 2.157 GBq mmol⁻¹), triazolinone metabolite (5-¹⁴C, specific activity 2.157 GBq mmol⁻¹), flucarbazone (phenyl-U-¹⁴C, specific activity 2.653 GBq mmol⁻¹) and benzenesulfonamide metabolite (ring-U-¹⁴C, specific activity 2.653 GBq mmol⁻¹) were supplied by Bayer Corporation (Stilwell, KS, USA). Their structures are shown in Fig. 1.

Fresh soils from 0–15 cm depth of a Gardena clay loam from North Dakota (coarse-silty mixed Pachic Udic Haploborolls; pH 6.2, silt 42.2%, clay 30.8%, organic carbon 3.17%) and a Quincy loamy fine sand from Washington (mixed, mesic Xeric Torripsamments; pH 6.7, silt 7.0%, clay 5.3%, organic carbon 0.26%) were collected, passed through a 2 mm diameter sieve and stored at 4 °C until used (<4 weeks after collection). Soil texture was determined by the hydrometer method.¹⁰ Soil pH was measured in a 1:2 (w/w) soil/deionised water mixture. The organic carbon content of the soil samples was determined by dichromate oxidation.¹¹

2.2 Sorption–desorption

Sorption was characterised by the batch equilibration technique using triplicate 5 g soil samples equilibrated with aqueous calcium chloride (0.01 M, 10 ml) containing one of four concentration levels (1.0, 0.3, 0.1 or 0.03 g ml⁻¹) of a particular chemical. Each sample also contained 121–233 Bq of that chemical. Samples were equilibrated by shaking mechanically at 21 ± 2 °C in 30 ml glass centrifuge tubes (closed with Teflon-lined caps) for 24 h. Kinetic studies for both parent herbicide and metabolite chemicals using the same technique with 1.0 g ml⁻¹ initial solution concentration indicated that equilibrium was reached within 16 h and that no changes in concentration occurred after shaking for 48 h. Figure 2 shows kinetic studies for flucarbazone and the phenylsulfonamide metabolite. Previous research had shown that no degradation occurred within this period.^{4,5} Soils were then centrifuged (4300 × *g*, 20 min) and 5 ml of each supernatant was removed for analysis.

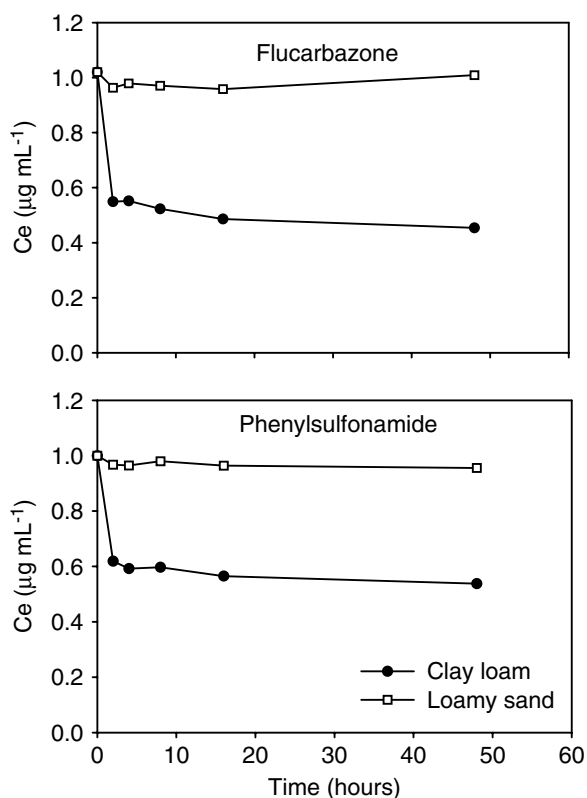


Figure 2. Sorption kinetic study of flucarbazone and its phenylsulfonamide metabolite in two soils.

Desorption experiments were conducted immediately after the sorption experiment using the soils from the 0.3 and 0.03 g mL^{-1} initial concentrations. After centrifugation in the sorption experiment and removal of 5 ml of supernatant for analysis, aqueous calcium chloride (0.01 M, 5 ml) without chemical was added to the soil. Soils were resuspended in a vortex action shaker and shaken for 24 h. Soil suspensions were centrifuged and 5 ml of each supernatant was removed for analysis. This desorption cycle was repeated four times for each sample. Previous research had shown that no degradation occurred within this period.^{4,5}

Aliquots (1 ml) of the clear supernatants were mixed with 10 ml of EcoLite scintillation cocktail,

and the amount of radioactivity was determined by liquid scintillation counting (LSC) for 10 min in a Packard (Meriden, CT, USA) 1500 TRI-CARB liquid scintillation analyser. The amount of chemical in solution was calculated considering the specific activity of the chemical. The amount of chemical sorbed to the soil after equilibration was calculated from the difference between the amount initially added and the equilibrium solution concentration. No chemiluminescence was observed.

Sorption and desorption isotherms were calculated using the linearised form of the Freundlich equation:

$$\log C_s = \log K_f + (1/n_f) \log C_e$$

where C_s is the amount of chemical sorbed (g g^{-1} soil), C_e is the equilibrium concentration (g mL^{-1} solution) and K_f and $1/n_f$ are empirical sorption–desorption coefficients. Sorption–desorption coefficients were calculated by the least squares technique on the mean of the replicates of the log-transformed equilibrium data. K_f and $1/n_f$ standard errors were calculated. Sorption coefficients were also calculated as a function of organic carbon (OC):

$$K_{f-oc} = (K_f/\%OC) \times 100$$

3 RESULTS AND DISCUSSION

All sorption data for both herbicides and metabolites fitted the Freundlich equation ($r^2 > 0.97$), except where there was extremely low sorption, i.e. $K_f \leq 0.11$ (Table 1). Figure 2 shows representative Freundlich sorption isotherms for flucarbazone and the phenylsulfonamide metabolite in the two soils. Sorption isotherm coefficients of both herbicides and metabolites in the two soils studied are given in Table 1. Sorption isotherms showed minimal curvature with slopes $1/n_f \geq 0.90$ (Table 1). Slopes of phenylsulfonamide sorption isotherms ($1/n_f < 1$) indicate that sorption was dependent on initial solution concentration, i.e. the amount of chemical in the system, with

Table 1. Sorption–desorption of flucarbazone, propoxycarbazine and their benzenesulfonamide and triazolinone metabolites in two soils

Chemical	Soil ^a	K_f^b	K_{f-oc}	$1/n_f^c$	r^2	$1/n_{fd0.3}^{c,d}$	$1/n_{fd0.03}^{c,e}$
Propoxycarbazine	CL	1.84 (1.77–1.92)	58.2	0.96 (± 0.02)	1.00	0.76 (± 0.02)	0.61 (± 0.03)
	LS	0.00 ^f		0.00	0.00	0.00	0.00
Triazolinone	CL	2.65 (1.93–3.62)	83.6	1.02 (± 0.07)	0.98	0.37 (± 0.06)	0.44 (± 0.02)
	LS	0.11 (0.07–0.17)	42.3	0.90 (± 0.18)	0.90	–0.07 (± 0.02)	–0.07 (± 0.01)
Flucarbazone	CL	0.91 (0.84–0.98)	28.7	0.97 (± 0.05)	1.00	0.11 (± 0.02)	0.13 (± 0.01)
	LS	0.31 (0.28–0.34)	119.2	0.99 (± 0.04)	0.99	–0.06 (± 0.01)	–0.07 (± 0.01)
Phenylsulfonamide	CL	1.59 (1.43–1.76)	50.2	0.90 (± 0.03)	0.99	0.49 (± 0.02)	0.39 (± 0.04)
	LS	0.13 (0.11–0.15)	50.0	0.92 (± 0.05)	0.99	–0.12 (± 0.01)	0.05 (± 0.03)

^a CL, clay loam; LS, loamy sand.

^b Number in parentheses is the standard error calculated from antilog of $\log K_f \pm$ standard error of $\log K_f$.

^c Mean (\pm standard error).

^d Desorption isotherm from initial solution concentration 0.3 g mL^{-1} .

^e Desorption isotherm from initial solution concentration 0.03 g mL^{-1} .

^f Using soil/solution ratio of 1:1 instead of 1:2; $K_d = 0.12$, $K_{d-oc} = 44.8$.

greater sorption for the lower initial solution concentrations. There were no significant differences between $1/n_f$ values for all the chemicals, therefore K_f values could be compared and contrasted.

The sorption mechanism for sulfonylaminocarbonyltriazolinone herbicides and their main metabolites on soil is complex, but it appears that organic matter and clay contents are principle factors controlling the degree of the interactions between soil and chemical. K_f values for all four chemicals were greater in the clay loam soil, which had higher organic carbon and clay contents than the loamy sand (Table 1). Expressing sorption as a function of soil organic carbon content (K_{f-oc}) reduced variability between soils;¹² K_{f-oc} ranged from 29 to 119 for the herbicides and from 42 to 84 for the metabolites. These values are similar to those previously observed in a ‘sorption–aging study’,^{4,5} in which soils were treated with the chemical and then desorbed to attain equilibrium, as opposed to the batch equilibration method. From a study of the sorption of these chemicals on smectites and organosmectites, it appears that polar interactions seem more relevant for propoxycarbazone and triazolinone metabolite, whereas hydrophobic interactions may be more important for flucarbazone and phenylsulfonamide metabolite.⁶ The sorption space between exchangeable organocations and the basal spacing of organoclays also impact sorption.

In the case of sulfonylaminocarbonyltriazolinone herbicides, pH could also directly affect sorption. At the pH of the soils, although these chemicals would primarily exist as anions, which are generally not sorbed by temperate soils, some degree of sorption would be expected. Even at the pH levels of these soils, there would be a small amount of neutral species, which would be subject to sorption processes, particularly in the clay loam soil. As the molecular species is sorbed, more anion would be protonated to re-establish the equilibrium. The flucarbazone and propoxycarbazone K_f values, however, were greater than expected, particularly in the clay loam soil. For instance, these K_f values were significantly greater than K_f values for metsulfuron-methyl,¹³ a sulfonylurea herbicide that is similarly ionised ($pK_a = 3.3$), in soils with pH levels and organic matter and clay contents similar to those in the present study. Therefore there were additional factors contributing to the magnitude of sulfonylaminocarbonyltriazolinone herbicide sorption.

The greater than expected sorption is presumably due to interactions between the soil particle surfaces and the benzenesulfonamide and triazolinone groups of the herbicides. In the clay loam soil, sorption of the individual benzenesulfonamide and triazolinone metabolites was greater than that of the corresponding sulfonylaminocarbonyltriazolinone herbicide itself. It would be interesting to see whether these chemicals behaved similarly in variable charge soils such as oxisols, which exhibit significant sorption by anion exchange mechanisms.^{14–16}

Regardless of the mechanisms involved, sorption K_f and K_{f-oc} values have been used in a variety of solute transport models. For instance, the leachability index model ‘groundwater ubiquity score’ (GUS)¹⁷

$$GUS = \log_{10}(t_{1/2\text{-soil}}) \times [4 - \log_{10}(K_{f-oc})]$$

classifies a chemical’s potential to leach to groundwater according to the combined effect of degradation and sorption processes, where $t_{1/2\text{-soil}}$ is the soil degradation half-life assuming first-order kinetics. According to this model, a chemical would be classified as a ‘leacher’ if $GUS > 2.8$, a ‘non-leacher’ if $GUS < 1.8$ and ‘transitional’ if $1.8 < GUS < 2.8$. Considering a K_{oc} value of 29, a chemical would be considered a ‘leacher’ when $t_{1/2} > 13$ days, whereas, considering a K_{oc} value of 119, a chemical would be considered a ‘leacher’ when $t_{1/2} > 29$ days. Therefore the two sulfonylaminocarbonyltriazolinone herbicides and their main metabolites considered here would all be considered ‘leachers’ under the GUS system if $t_{1/2} > 30$ days.

Classifying a chemical’s potential to leach to groundwater may be misleading, however, if the desorption process is not characterised. Freundlich desorption coefficients are given in Table 1. Figure 3 shows representative Freundlich desorption isotherms of flucarbazone and the phenylsulfonamide metabolite in the two soils. As can be seen in Fig. 3 and Table 1, $1/n_f \gg 1/n_{fd}$, indicating that a significant amount of the sorbed chemical is very difficult to

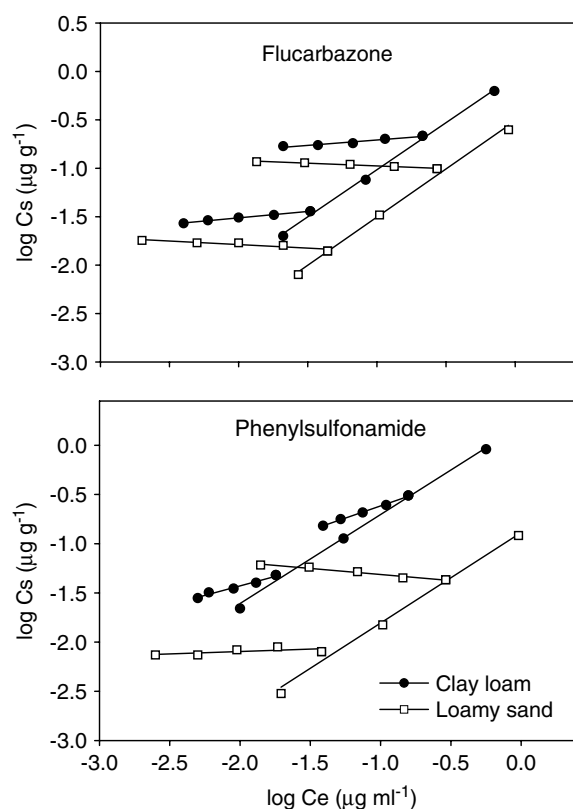


Figure 3. Sorption–desorption of flucarbazone and its phenylsulfonamide metabolite in two soils.

desorb and that desorption cannot be predicted from sorption isotherms. There was no effect of chemical concentration on desorption slopes, i.e. $1/n_{fd0.03} = 1/n_{fd0.3}$. Although the clay loam had a much higher sorption capacity than the loamy sand, greater absolute amounts of chemical could be desorbed; none of the small amounts of sorbed chemicals could be desorbed from the loamy sand, i.e. $1/n_{fd} = 0$ (negative desorption isotherm slopes for the loamy sand are an artefact of the low sorption and calculations of mass balance of the chemicals during desorption steps).

Desorption hysteresis has been reported for a large number of soil/organic compound systems, and several explanations, such as chemical or biological transformation, non-equilibrium conditions, kinetic effects and high-energy bonding, have been proposed; for examples see Ref. 2 and references cited therein. In our case the extended kinetic study did not indicate that degradation was taking place during desorption experiments, and further studies would be needed to understand this hysteresis phenomenon.

4 CONCLUSIONS

Sorption–desorption of sulfonylaminocarbonyltriazolinone herbicides and their principle metabolites is affected by soil properties, being greater in soils with higher soil organic carbon and clay contents. Desorption was hysteretic in every case. Lower desorption in the more sorptive system might indicate that hysteresis can be attributed to irreversible binding of the molecules to soil surfaces. Regardless of the sorption–desorption mechanisms, in the case of sulfonylaminocarbonyltriazolinone herbicides and their main metabolites it appears that characterisation of sorption alone is insufficient to classify their potential to leach to groundwater. In the case of the more sorptive clay loam soil, hysteresis was generally lower than that for the loamy sand. These very low hysteresis coefficients observed in the most sorptive system seem to indicate that irreversibility of strongly bound chemical to soil colloidal components, especially soil organic matter surfaces, can be the reason for the hysteresis phenomenon, although further investigation is required.

REFERENCES

- Koskinen WC and Harper SS, The retention process: mechanisms, in *Pesticides in the Soil Environment: Processes, Impacts and Modeling*, ed. by Cheng HH. Soil Science Society of America, Madison, WI, pp. 51–77 (1990).
- Wauchope RD, Yeh S, Linders JBHJ, Kloskowski R, Tanaka K, Rubin B, *et al.*, Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. *Pest Manag Sci* **58**:419–445 (2002).
- Cox L, Koskinen WC and Yen PY, Sorption–desorption of imidacloprid and its metabolites in soils. *J Agric Food Chem* **45**:1468–1472 (1997).
- Koskinen WC, Rice PJ, Anhalt JA, Sakaliene O, Moorman TB and Arthur EL, Sorption–desorption of ‘aged’ sulfonylaminocarbonyltriazolinone herbicide in soil. *J Agric Food Chem* **50**:5368–5372 (2002).
- Koskinen WC, Anhalt JA, Sakaliene O, Rice PJ, Moorman TB and Arthur EL, Sorption–desorption of ‘aged’ sulfonylaminocarbonyltriazolinone herbicide metabolites in soil. *J Agric Food Chem* **51**:3406–3608 (2003).
- Cox L, Koskinen WC, Hermosin MC, Cornejo J and Arthur EL, Sorption of two new sulfonylaminocarbonyltriazolinone herbicides and their metabolites on organic and inorganic exchanged smectites. *Int Environ Anal Chem* **82**:553–560 (2002).
- Eliaon R, Schoenan JJ, Szmigielski AM and Laverty WM, Phytotoxicity and persistence of flucarbazone-sodium in soil. *Weed Sci* **52**:857–862 (2004).
- Elmarakby SA, Supplee D and Cook R, Degradation of [14 C] carfentrazone-ethyl under aerobic aquatic conditions. *J Agric Food Chem* **49**:5285–5293 (2001).
- Ngim KK and Crosby DG, Fate and kinetics of carfentrazone-ethyl herbicide in California, USA flooded rice fields. *Environ Toxicol Chem* **20**:485–490 (2001).
- Gee GW and Bauder JW, Particle-size analysis, in *Methods of Soil Analysis – Part 1 (Agronomy Monograph 9)* (2nd edn), ed. by Klute A. American Society of Agronomy, Madison, WI, pp. 383–409 (1986).
- Nelson DW and Sommers LE, Total carbon, organic carbon and organic matter, in *Methods of Soil Analysis – Part 2 (Agronomy Monograph 9)* (2nd edn), ed. by Page AL. American Society of Agronomy, Madison, WI, pp. 539–579 (1982).
- Green RE and Karickhoff SW, Sorption estimates for modeling, in *Pesticides in the Soil Environment: Processes, Impacts and Modeling*, ed. by Cheng HH. Soil Science Society of America, Madison, WI, pp. 79–101 (1990).
- Berglof T, Koskinen WC, Duffy MJ, Norberg KA and Kylin H, Metsulfuron methyl sorption–desorption in field-moist soils. *J Agric Food Chem* **51**:3598–3603 (2003).
- Spadotto CA and Hornsby AG, Soil sorption of acidic pesticides: modeling pH effects. *J Environ Qual* **32**:949–956 (2003).
- Spadotto CA, Hornsby AG and Gomes MAF, Sorption and leaching potential of acidic herbicides in Brazilian soils. *J Environ Sci Health B* **40**:29–37 (2005).
- Hyun S and Lee LS, Quantifying the contribution of different sorption mechanisms for 2,4-dichlorophenoxyacetic acid sorption by several variable-charge soils. *Environ Sci Technol* **39**:2522–2528 (2005).
- Gustafson DI, Groundwater ubiquity score: a simple method for assessing pesticide leachability. *Environ Toxicol Chem* **8**:339–357 (1989).