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Glyphosate adsorption in soils compared to herbicides replaced with the introduction of glyphosate resistant crops

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Abstract

Use of glyphosate resistant crops was helpful in addressing observed increases in environmental contamination by herbicides. Glyphosate is a broad-spectrum herbicide, and its behaviour – as well as that of other herbicides – in soils is an important consideration for the overall environmental evaluation of genetically resistant crop introduction. However, few data have been published comparing glyphosate behaviour in soil to that of the herbicides that would be replaced by introduction of glyphosate resistant crops. This work compares glyphosate adsorption in soil with that of other herbicides frequently used in rape (trifluralin and metazachlor), sugarbeet (metamitron) and corn (sulcotrione). Herbicide adsorption was characterised in surface soils and in the complete soils profiles through kinetics and isotherms using batch equilibration methods. Pedological and molecular structure factors controlling the adsorption of all five herbicides were investigated. Glyphosate was the most strongly adsorbed herbicide, thus having the weakest potential for mobility in soils. Glyphosate adsorption was dependent on its ionisable structure in relation to soil pH, and on soil copper, amorphous iron and phosphate content. Trifluralin adsorption was almost equivalent to glyphosate adsorption, whereas metazachlor, metamitron

and sulcotrione adsorption were lower. Trifluralin, metazachlor and metamitron adsorption increased with soil organic carbon content. Sulcotrione was the least adsorbed herbicide in alkaline soils, but its adsorption increased when pH decreased. Ranking the adsorption properties among the five herbicides, glyphosate and trifluralin have the lowest availability and mobility in soils, but the former has the broadest spectrum for weed control.

Keywords: Genetically modified crops; Glyphosate; Trifluralin; Metazachlor; Metamitron; Sulcotrione

1. Introduction

Introduction of genetically modified (GM) plants resistant to glyphosate (a broad-spectrum herbicide), provides a technical approach to weed control constraints in various crops. In theory, this approach allows a reduction in the total amount of herbicide needed, from 20 to 85 % according to various scenarios (Méssean, 2000), with a related decrease in number of active ingredients applied. This can contribute positively when overall benefits/impacts balance of GM crops will be considered. Furthermore, glyphosate is believed to have a lesser ecotoxicological impact than other herbicides, especially in aquatic ecosystems (Giesy et al., 2000). Therefore, introduction of GM plants can be part of a strategy to protect water quality and to decrease water contamination by those herbicides often found in water monitoring. However, a concomitant increase of treated area may increase glyphosate content in vulnerable waters, aggravated by the development of non-agricultural uses for glyphosate. Furthermore, in a long run, glyphosate widespread use may result in weed resistance or alter biological functions of soils.

Soil plays a key role in the environmental fate of herbicides. A large proportion of applied herbicides reaches the soil, because of direct application and/or after foliage wash off (Torstensson, 1985). Dispersion of herbicides towards other media (water, plants and atmosphere) will strongly depend on their behaviour in soil, and particularly on their retention, which regulates their availability in soils.

The introduction of GM glyphosate resistant plants will replace the use of other herbicides depending on the crop. GM rape, sugarbeet and corn are candidates for introduction in France, and the most frequently used herbicides on these crops are trifluralin and metazachlor, metamitron and sulcotrione, respectively. Previous researchers have shown that metazachlor, metamitron, and sulcotrione adsorption in soils is low (Baer and Calvet, 1999; Madsen et al., 2000; Beulke and Malkomes, 2001): consequently, dispersion risk seems high, especially towards water because of the close relationship between herbicide leaching potential and its adsorption coefficient (Calvet, 1989). On the contrary, trifluralin adsorption in soils is very high (Peter and Weber, 1985; Tavares and

Rezende, 1998; Coquet and Barriuso, 2002); similarly, glyphosate adsorption in soils is typically high, therefore leaching risks are limited (Hance, 1976; Piccolo et al., 1994; de Jonge et al., 2001). However, these results are obtained in different experimental conditions and on different soils, and rigorous evaluation of environmental risks associated with the substitution of the weed control strategy with glyphosate resistant crop introduction is difficult.

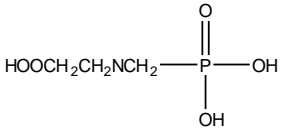
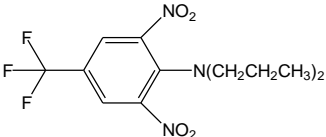
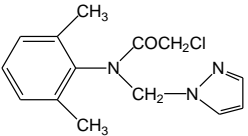
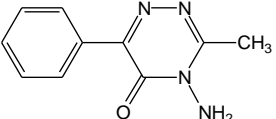
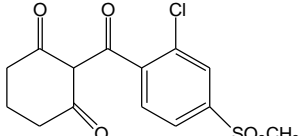
The aim of this work was to compare, on the same soils and with the same experimental conditions, glyphosate adsorption to that of trifluralin, metazachlor, metamitron and sulcotrione. Herbicides were chosen due to their general use on the three crops (rape, sugarbeet and corn) and their contrasting physico-chemical characteristics. Soils used were obtained from various experimental French inter-institutes platforms where GM crops have been cultivated since 1995. The contrasted physico-chemical properties of these soils and their distribution in various climatic regions are representative of typical situations in which these crops are cultivated. Herbicide adsorption in surface soils and in soil profiles was characterized with kinetics and equilibrium data. Results will allow evaluation of glyphosate leaching risks compared with that of other herbicides when introducing GM crops. They will also allow a better understanding of soil pedological factors and molecular structure factors controlling adsorption of the five herbicides.

2. Materials and methods

2.1. Herbicides

Herbicides used were the following (agronomically homologated doses in g a.i. ha⁻¹): glyphosate (1440 to 3060) used for GM crops, trifluralin (1200) and metazachlor (1250) used for rape, metamitron (2800) used for sugarbeet, and sulcotrione (450) used for corn (Table 1). [Methyl-¹⁴C]glyphosate was purchased from Sigma Chemicals (St Louis, USA; 122 MBq mmol⁻¹, 97.7 % radiopurity), [U-ring-¹⁴C]trifluralin from Amersham (Buckinghamshire, UK; 2960 MBq mmol⁻¹, 98.6 % radiopurity), [U-phenyl-¹⁴C]metazachlor from BASF (Limburgerhof, Germany, 1761 MBq mmol⁻¹, 95.5 % radiopurity), [U-phenyl-¹⁴C]metamitron from International Isotope (Munich, Germany; 477 MBq mmol⁻¹, 98.0 % radiopurity) and [U-phenyl-¹⁴C]sulcotrione from Izotop (Budapest, Hungary; 720 MBq mmol⁻¹, 91 % radiopurity). Solutions of ¹⁴C-labelled herbicides were prepared in 0.01M CaCl₂ by isotopic dilution with non-labelled herbicides (analytical standards, >99 % purity) at six different concentrations: 10, 5, 2, 1, 0.5, 0.2 mg L⁻¹ for glyphosate, metazachlor, metamitron and sulcotrione, and 0.16, 0.12, 0.08, 0.05, 0.03, 0.02 mg L⁻¹ for trifluralin because of its low solubility in water. Glyphosate solutions were also prepared in deionised water. Each solution contained 0.166 MBq L⁻¹.

Table 1. Some physicochemical properties^a of glyphosate, trifluralin, metazachlor, metamitron and sulcotrione with their parachor, dipole moment and the first-order connectivity index

Herbicide	Structural formula	pKa	Molecular mass (g mol ⁻¹)	Solubility in water (mg L ⁻¹)	logKow	Parachor P ^d (cm ³ g ^{1/4} s ^{-1/2} mol)	Dipole moment μ ^d (D)	First-order connectivity index ¹ χ ^d
Glyphosate		<2 – 2.6 – 5.6 – 10.6 ^b	169.1	12000	- 4.1	313	9.7 ^e	4.4
Trifluralin		-	335.3	0.22	5.07	635	2.3	10.8
Metazachlor		-	277.8	430	2.13	601	3.2	9.1
Metamitron		-	202.2	1700	0.83	432	2.5	7.2
Sulcotrione		3.1 ^c	328.8	165 ^c	< 0.75	633	3.7	9.7

^a Values are taken from Roberts (1998) except indications, ^b Sprankle *et al.* (1975), ^c Data obtained from Zeneca, ^d Calculated as indicated in the text, ^e Calculated for a pKa = 5.6

The first-order connectivity index (${}^1\chi$) of each herbicide was calculated as described by Baum (1998) and Sabljic (2001):

$${}^1\chi = \sum (\delta_i \delta_j)^{-0.5}$$

where δ_i is connectivity atom i value and is equal to the number of adjacent atoms other than hydrogen. For each pair of atoms i and j that are linked by chemical bonds, a product $\delta_i \delta_j$ is calculated.

Herbicide parachor (P) was calculated using McGowan's method as the sum of atomic parachors (Baum, 1998):

$$P = \sum n_i A_i - 19 N_{\text{bonds}} \quad (\text{cm}^3 \text{g}^{1/4} \text{s}^{-1/2} \text{mol})$$

where n_i is number of atoms of type i in the molecule, A_i is the contribution of atom i and N_{bonds} is the number of chemical bonds in molecule.

CHEM-3D molecular modelling software (CambridgeSoft) was used to build three-dimensional chemical structures to calculate herbicides dipole moment (μ). Like Reddy and Locke (1994), structures were energy-minimized in MOPAC using Austin Model parameterisation and ground electronic states were obtained as closed-shell molecular orbital wave functions in the restricted Hartree-Fock framework.

The calculated values of ${}^1\chi$, P and μ for the five herbicides are summarized in Table 1.

2.2. Soils

Samples of surface soils (0-10 cm) were collected from three French experimental GM platforms located at Champagne (Châlons), Bourgogne (Dijon) and Midi-Pyrénées (Toulouse). Châlons soil is a surface rendzina over limestone; Dijon soil is a clay-loam calcareous cambisol; and Toulouse soil is a desaturated silt-loam soil. Soil profiles were sampled at different depths, and samples were air-dried and passed through a 2-mm sieve prior to use. Soil profiles were characterized, and selected properties are reported in Table 2. Soil samples were collected in two ways: composite samples of surface soils (0-10 cm) from each of the three soil types, and discrete samples from specific depths in individual soil profiles.

Table 2. Principal soil characteristics of Châlons, Dijon and Toulouse sites

Soil site	Clay ^b	Water holding capacity	pH	Organic carbon	Fe Oxides ^c	Fe Amorphous ^d	Total Cu ^e	Total P ₂ O ₅	CaCO ₃	CEC ^f
Depth ^a (cm)	(g kg ⁻¹)	(g kg ⁻¹)	(water)	(g kg ⁻¹)	(g kg ⁻¹)	(g kg ⁻¹)	(mg kg ⁻¹)	(g kg ⁻¹)	(g kg ⁻¹)	(cmol kg ⁻¹)
Châlons										
<i>0-10</i>	88	286	8.4	18.6	1.82	0.69	6.3	3.59	824	6.4
0-10	93	271	8.2	20.0	1.90	0.68	5.7	2.72	819	7.1
10-20	95	251	8.3	17.8	1.87	0.69	5.8	2.69	826	6.2
20-30	91	224	8.5	13.2	1.57	0.48	4.1	1.93	851	4.6
Dijon										
<i>0-10</i>	376	263	8.3	13.5	13.95	1.25	13.3	2.49	221	17.8
0-10	377	261	8.2	16.9	12.96	2.00	16.0	2.76	167	20.6
10-20	327	270	8.2	14.8	13.02	2.05	16.3	2.46	144	27.0
20-30	363	286	8.3	9.5	12.44	2.53	15.7	1.70	113	28.6
30-60	396	317	8.4	7.7	13.28	2.43	13.6	1.04	88	31.7
60-90	307	218	8.6	6.9	9.82	1.08	7.8	0.77	416	21.8
Toulouse										
<i>0-10</i>	274	212	6.3	10.1	6.15	2.43	41.9	1.46	<10	16.4
0-10	235	190	7.6	9.6	4.92	2.08	15.1	1.31	<10	15.9
10-20	222	176	7.7	10.1	4.60	1.98	16.2	1.36	<10	15.3
20-30	221	192	7.7	9.4	5.00	1.97	14.9	1.33	<10	15.3
30-40	236	193	7.9	8.6	5.27	2.14	15.2	1.24	<10	14.9
40-50	245	216	8.2	6.8	5.31	2.04	15.3	1.08	11	15.0

^a Soil depths in soil profiles; italicized depths represent composite samples from surface soils, ^b Clay content after carbonate removal, ^c Subtraction of extracted iron by sodium dithionite-citrate and by acid ammonium oxalate, ^d Extracted iron by acid ammonium oxalate in darkness, ^e Dissolved by HF, ^f Cation exchange capacity at pH 7 (ammonium acetate)

2.3. Adsorption kinetics

Ten millilitres of 5 mg L⁻¹ herbicide solutions (0.08 mg L⁻¹ for trifluralin) were added to 2 g of dry soil in glass centrifuge tubes. Preliminary experiments were done to determine variation in adsorption according to different soil/solution ratios: 1/10, 1/5 and 1/2. Ratio 1/5 was chosen as a mean. Soil suspensions were shaken mechanically for 2, 4, 8, 16, 24, 48, 72, 96 h at 20 ± 2 °C in darkness and then centrifuged 15 min at 1800 × g. Blanks were prepared without soil. Only trifluralin adsorbed on tubes, and the average recovery in blank solutions was 83 % of the initial ¹⁴C-trifluralin. Two replicates were done for each soil, herbicide and time step.

Amounts of ¹⁴C-herbicides in supernatant were determined by liquid scintillation counting (Tri-Carb 2100 TR, Packard) using Ultima Gold XR (Packard) as the liquid scintillation cocktail. Amounts of adsorbed herbicide in soil were calculated as the difference between initial herbicide concentration in solution and centrifuged supernatant concentration. Supernatants recovered after 96 h shaking were analysed by HPLC with a Waters chromatography appliance (System controller 610, Autosampler 717) coupled with a radioactive flow detector (Flo-one A-500, Packard-Radiomatic). Glyphosate was analysed on a Sax Adsorbosphere column (Alltech, 5 µm, 250 × 4.6 mm), the mobile phase was KH₂PO₄ buffered at pH 2.1. The supernatant of others herbicides were analysed on a Novapak C18 column (Waters, 5 µm, 250 × 4.6 mm). Inverse phase chromatography with optimised gradient of water/methanol was used for analyses of trifluralin, metazachlor and metamitron. Ion pair chromatography was used for sulcotrione supernatants using water/methanol with 0.01M tetra-n-butylammoniumchloride. In all cases, mobile phase flow was 1.0 mL min⁻¹ and the injected volume 100 µL.

2.4. Adsorption isotherms

Ten millilitres of each herbicide solution at the six different concentrations were added to 2 g of dry soil in glass centrifuge tubes which were mechanically shaken for 24 h at 20 ± 2 °C in darkness and then centrifuged 15 min at 1800 × g. There were two replicates for each combination of soil, herbicide and herbicide concentration. Amount of adsorbed herbicide was calculated from difference between the radioactivity of the initial and supernatant solutions. Adsorption isotherms were described with Freundlich and/or linear models. The Freundlich model is defined as:

$$Q_s = K_f \times C_e^{n_f}$$

where Q_s (mg kg⁻¹) is amount of adsorbed herbicide in soil at equilibrium concentration, C_e (mg L⁻¹) is herbicide concentration in supernatant solution, and K_f and n_f are empirical adsorption coefficients.

The linear model is defined as:

$$Q_s = K_d \times C_e$$

where K_d ($L\ kg^{-1}$) is the herbicide distribution coefficient between soil and soil solution. For the adsorption in soil profile samples, K_d values were calculated only with an intermediary initial concentration of $5\ mg\ L^{-1}$ ($0.08\ mg\ L^{-1}$ for trifluralin).

K_{oc} ($L\ kg^{-1}$) coefficients were calculated as:

$$K_{oc} = (K_d \times 100) / C_{org}$$

where C_{org} is the percentage of organic carbon content in soils.

3. Results and discussion

3.1 Herbicides adsorption kinetics

Adsorption was generally very rapid for all herbicides and soils, with most adsorption occurring during the first two hours, corresponding to adsorption at the most accessible sites (Fig. 1). Then adsorption stabilised or increased slightly during the first 24 h depending on the soil and herbicide. The highest adsorptions found were for glyphosate and trifluralin at > 80 % of initial radioactivity, while adsorption of other herbicides was generally < 30 % of initial radioactivity. Beyond 24 h, different adsorption behaviour was observed: adsorption stabilisation, which denoted that equilibrium was reached; or a continuous slight increase, mainly for the least adsorbed herbicides (metamitron, metazachlor and sulcotrione) which can be explained by chemical non-equilibrium due to mass transfer by molecular diffusion within the micro-pores of mineral or organic soil constituents (Dao and Lavy, 1987; Brusseau et al., 1991; Celis et al., 1996; Tavares and Rezende, 1998; Beulke and Malkomes, 2001).

In the case of glyphosate, adsorption decreased after 24 h, probably due to glyphosate degradation to aminomethylphosphonic acid (AMPA): all radioactivity in the supernatant at 96 h corresponded to AMPA, except adsorption without $CaCl_2$ on Châlons soil, in which 25 % of the supernatant radioactivity was attributable to glyphosate. AMPA adsorption can be weaker than that of glyphosate (Gerritse et al., 1996). Thus, the degradation of glyphosate to AMPA seemed favoured in the adsorbed phase.

Only sulcotrione and metamitron were detected in the corresponding 96 h supernatant. In particular, adsorption kinetics for metamitron in Châlons soil showed that adsorption increased from 29 % of the initial radioactivity at 48 h to 63 % at 96 h. This adsorption increase may be attributed to complete adsorption of a likely metamitron metabolite. Metazachlor supernatants contained 7 to 11 % of the radioactivity as a single, unidentifiable metabolite. The 96 h supernatants from trifluralin adsorption contained 68 to 53 % trifluralin, with

the remaining radioactivity attributable to unidentifiable metabolites. The highest proportion of trifluralin metabolites was found in Dijon supernatants, corresponding to soil in which ^{14}C -trifluralin adsorption exhibited a slight decrease with time.

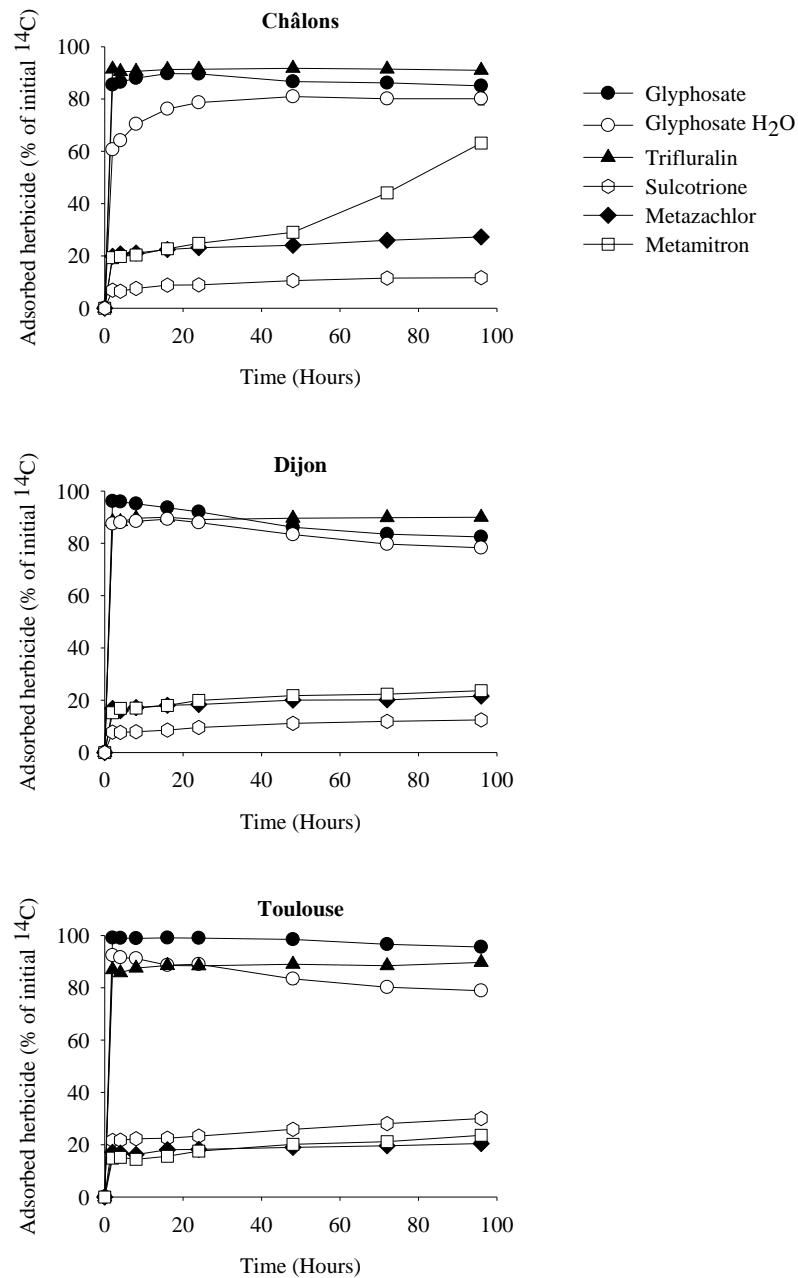


Fig. 1. Glyphosate, trifluralin, metazachlor, metamitron and sulcotrione adsorption kinetics on Châlons, Dijon and Toulouse soils (Standard deviations are shown only when larger than symbols).

After 24 h, most herbicides did not reach adsorption equilibrium. Nevertheless, it is customary to use 24 h adsorption values to determine adsorption isotherms, and at 24 h glyphosate, trifluralin and metamitron

degradation is likely limited. Occurrence of a non-equilibrium induced adsorption coefficients, smaller (metazachlor, metamiltron, sulcotrione) or greater (glyphosate and AMPA) than the true one, results in an overestimation or underestimation of herbicide mobility in soil (Streck et al., 1995).

3.2 Herbicide adsorption isotherms

Herbicide adsorption in Châlons and Dijon soils decreased as follows: glyphosate > trifluralin > metamiltron > metazachlor > sulcotrione, while in Toulouse soil the decrease is as follows: glyphosate > trifluralin > sulcotrione > metamiltron > metazachlor (Fig. 2, Table 3). Adsorption isotherms fit well to the Freundlich model ($r \geq 0.98$), and n_f values are lower than 1 (between 0.76 and 0.92). Furthermore, if $0.8 < n_f < 1.1$, linear isotherm approximation is acceptable (Baer and Calvet, 1999) allowing calculation of distribution coefficients K_d (Table 3). For glyphosate and metamiltron in Châlons and Toulouse soils, linear isotherms approximation is nevertheless critical ($0.76 < n_f < 0.79$) (Table 3).

Glyphosate is strongly adsorbed in the three soils. Its high adsorption coefficients K_f and K_d (Table 3) were consistent with others reported in literature (Hance, 1976; de Jonge et al., 2001). Glyphosate adsorption in different soils decreases as follows: Toulouse > Dijon > Châlons. Presence of CaCl_2 in solution increased glyphosate adsorption compared to glyphosate in deionized water, probably due to formation in solution of a Ca-glyphosate complex (Scalla and Gauvrit, 1991). As previously reported (Sprankle et al., 1975; Piccolo et al., 1994; Morillo et al., 2000; de Jonge et al., 2001), glyphosate adsorption in soils increased with lower pH, total copper content, and iron and aluminium oxides content, and it was negatively correlated to phosphate content, all corresponding to Toulouse soil properties in which glyphosate adsorption was highest. These results are validated below with data on glyphosate adsorption in soil profiles. Glyphosate K_{oc} variability in the three soils (1152 to 44630 L kg^{-1}) indicated that organic carbon content is not a major factor in glyphosate adsorption, in agreement with de Jonge et al. (2001).

Trifluralin adsorption in soils was comparable to that of glyphosate; values of adsorption coefficients (Table 3) correspond to values reported in literature (Peter and Weber, 1985; Tavares and Rezende, 1998). Trifluralin adsorption decreased as follows: Châlons > Dijon > Toulouse, which is directly correlated to soil organic carbon content (Tavares and Rezende, 1998; Coquet and Barriuso, 2002), and exhibits high and less variable K_{oc} values (2296 to 3398 L kg^{-1}).

Metazachlor, metamiltron and sulcotrione are weakly adsorbed on the three soils: K_f values were between 1.26 and 1.73 for metazachlor, 1.45 to 2.12 for metamiltron, and 0.40 to 1.66 for sulcotrione (Table 3). These values

were consistent with values reported elsewhere (Wilson and Foy, 1992; Baer and Calvet, 1999; Madsen et al., 2000; Beulke and Malkomes, 2001; Coquet and Barriuso, 2002). Metazachlor and met amitron adsorption decreased as follows: Châlons > Dijon > Toulouse. Metazachlor and met amitron K_{oc} values are almost similar: 66 to 103 and 64 to 94 $L\ kg^{-1}$ respectively, corroborating that soil organic carbon is a major factor contributing to their adsorption (Celis et al., 1996; Beulke and Malkomes, 2001). Sulcotrione adsorption decreased as follows: Toulouse > Dijon > Châlons. Sulcotrione adsorption increased when soil pH decreased (Rouchaud et al., 1998), but, contrary to results of Wilson and Foy (1992), adsorption seemed to be independent of soil organic carbon content, with K_{oc} values varying between 17 and 132 $L\ kg^{-1}$.

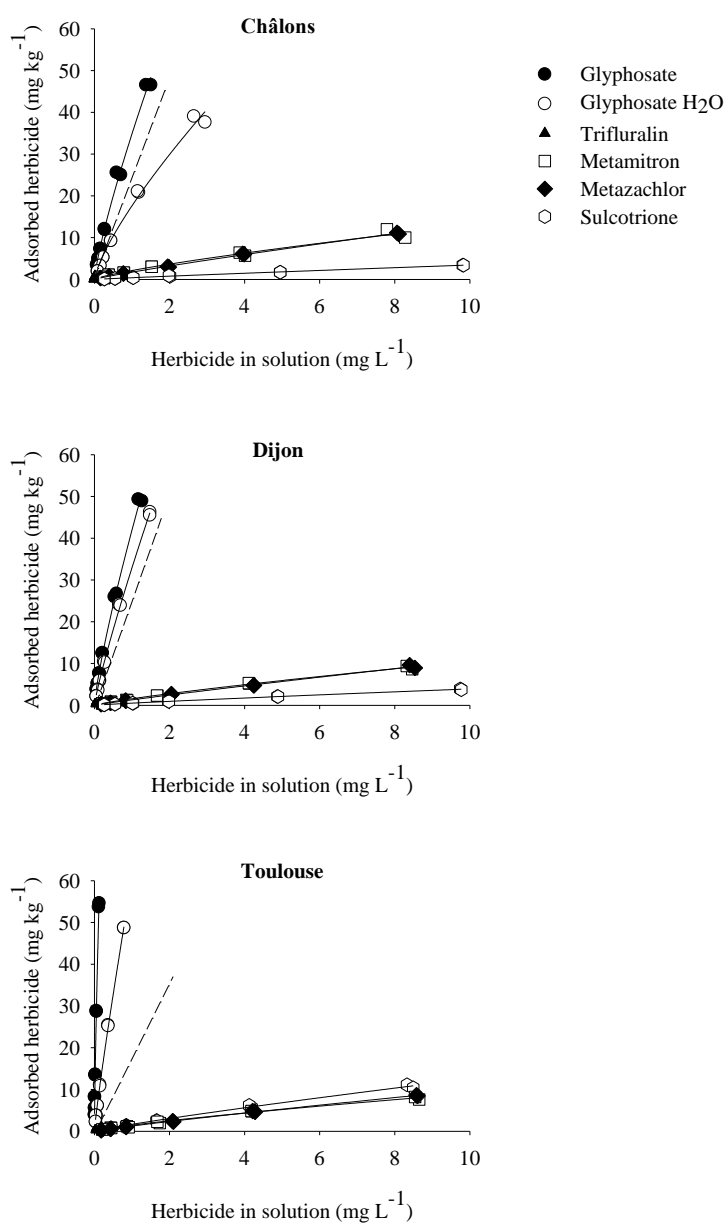


Fig. 2. Adsorption isotherms of glyphosate, trifluralin, met amitron, metazachlor and sulcotrione in Châlons, Dijon and Toulouse soils (Dotted lines are extrapolated trifluralin isotherms because of very low concentrations).

Table 3. Freundlich adsorption isotherm parameters and distribution coefficients (K_d and K_{oc}) of glyphosate, trifluralin, metazachlor, metamitron and sulcotrione in soil surface (0-10 cm) samples

Soil	Herbicide	Freundlich isotherms		Linear isotherms	
		K_f	n_f	K_d (L kg ⁻¹)	K_{oc} (L kg ⁻¹)
Châlons	Glyphosate ^a	17.6 ± 0.5	0.76 ± 0.03	13.2 ± 1.0	660 ± 51
	Glyphosate	34.8 ± 0.6	0.80 ± 0.02	31.1 ± 2.1	1552 ± 105
	Trifluralin	33.1 ± 5.6	0.91 ± 0.03	46.0 ± 2.3	2296 ± 114
	Metazachlor	1.73 ± 0.05	0.88 ± 0.01	1.35 ± 0.04	67 ± 2
	Metamitron	2.12 ± 0.22	0.78 ± 0.05	1.29 ± 0.10	64 ± 5
	Sulcotrione	0.40 ± 0.01	0.92 ± 0.02	0.34 ± 0.00	17 ± 0
Dijon	Glyphosate ^a	32.9 ± 0.2	0.86 ± 0.01	30.5 ± 1.2	1878 ± 73
	Glyphosate	41.9 ± 0.5	0.80 ± 0.02	38.7 ± 2.5	2375 ± 153
	Trifluralin	27.9 ± 2.7	0.91 ± 0.02	38.0 ± 1.6	2335 ± 97
	Metazachlor	1.29 ± 0.06	0.91 ± 0.02	1.07 ± 0.03	66 ± 2
	Metamitron	1.56 ± 0.08	0.82 ± 0.02	1.05 ± 0.05	64 ± 3
	Sulcotrione	0.51 ± 0.01	0.88 ± 0.01	0.38 ± 0.01	23 ± 0
Toulouse	Glyphosate ^a	60.5 ± 0.5	0.88 ± 0.01	61.3 ± 1.9	6406 ± 204
	Glyphosate	276 ± 13	0.77 ± 0.02	427 ± 31	44630 ± 3341
	Trifluralin	20.6 ± 2.2	0.87 ± 0.02	32.5 ± 2.0	3398 ± 210
	Metazachlor	1.26 ± 0.04	0.89 ± 0.01	0.99 ± 0.03	103 ± 3
	Metamitron	1.45 ± 0.09	0.79 ± 0.03	0.90 ± 0.06	94 ± 6
	Sulcotrione	1.66 ± 0.08	0.87 ± 0.02	1.26 ± 0.04	132 ± 5

^a Glyphosate in H₂O, without CaCl₂

Numerous studies have shown that solubility in water (S), Kow, parachor (P), the first-order molecular connectivity index ($^1\chi$) and dipole moment (μ) are strongly related to chemical adsorption strength (Meylan et al., 1992; Lohninger, 1994; Sabljic et al., 1995): when S and μ decrease and when Kow, P, $^1\chi$ increase, adsorption increases. Trifluralin which has a low μ and S, a high Kow, P and $^1\chi$ (Table 1), was more strongly adsorbed than metazachlor, metamitron and sulcotrione. These three herbicides, with higher aqueous solubility and polarity have stronger affinity for the aqueous phase which limits their adsorption to soil.

The high solubility in water, high polarity, and weak parachor of glyphosate should result in a weak adsorption to soil unlike obtained results. However, ionizable molecules and molecules with phospho-groups like glyphosate (Tao and Lu, 1999; Meylan et al., 1992) involve high-energy binding adsorption phenomena (ionic and coordination bindings, complex formation with metals in solution or at the solid-liquid interphase). Trifluralin adsorption was through hydrophobic exclusion mechanisms in addition to weak energy interactions, and metazachlor, metamitron and sulcotrione adsorption is likely the result of weak energy interactions (hydrogen bridges and Van der Waals interactions).

3.3. Herbicides adsorption through soils profiles

K_d values on soil profiles (Fig. 3) are almost comparable to those determined on surface soils, and adsorption decreased as follows: glyphosate > trifluralin > metamiltron > metazachlor > sulcotrione. Glyphosate retention in soil profiles showed an adsorption increase with depth in the three soils except in the 20-30 cm horizon of Toulouse soil. In contrast, adsorption of others herbicides decreased with depth.

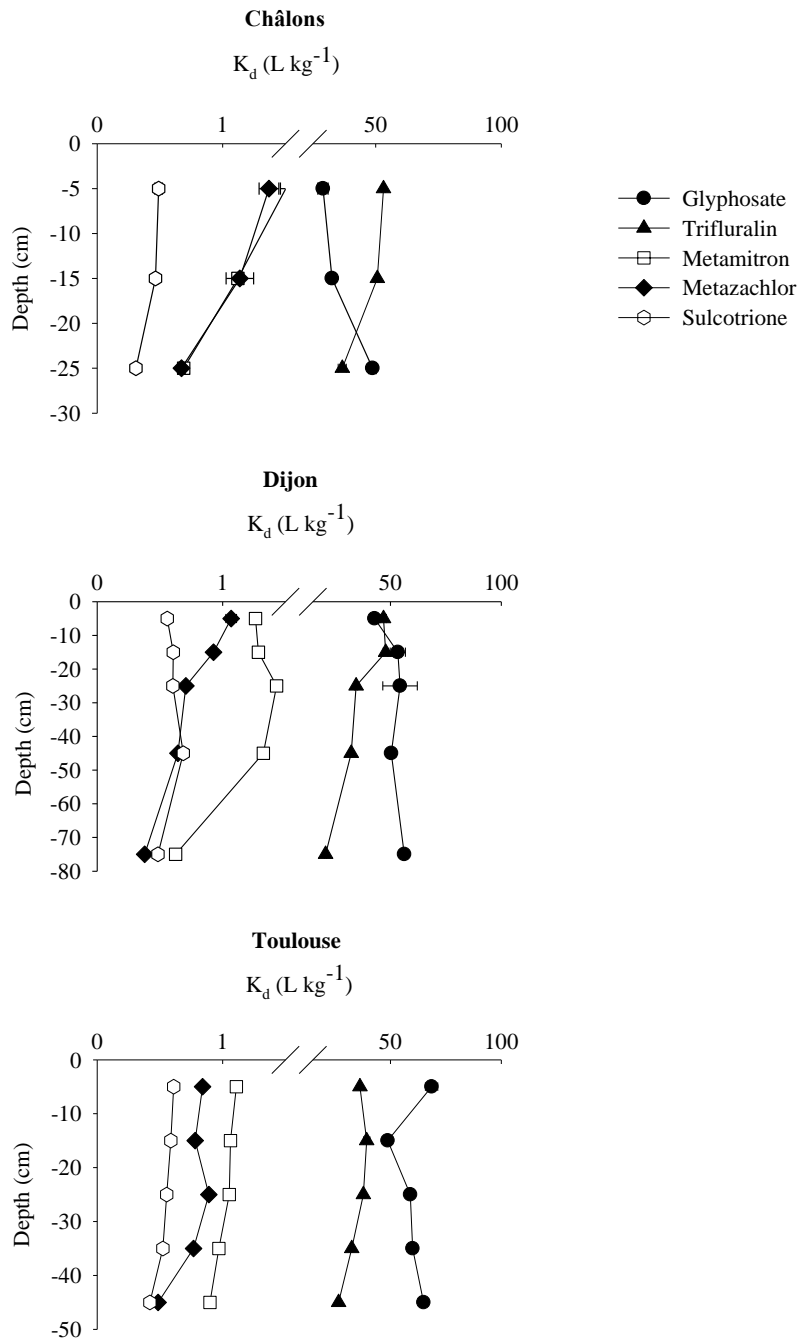


Fig. 3. Glyphosate, trifluralin, metamiltron, metazachlor, and sulcotrione sorption coefficient profiles (K_d) in Châlons, Dijon and Toulouse soils.

The primary correlations with glyphosate's K_d were as follows (linear correlation coefficient, r): total copper content (0.89), soil pH (-0.87), complexable Fe and Mn extracted with EDTA (0.96 and 0.86 respectively), total phosphate content (-0.82), amorphous iron (0.67). These correlations were in agreement with Sprankle et al. (1975), Piccolo et al. (1994), Morillo et al. (2000), and de Jonge et al. (2001). Copper content in soils enhances glyphosate retention because of surface complex and soluble complex formation favouring its adsorption (Morillo et al., 2000). Soil pH determines glyphosate ionisation and the surface charge of soil constituents: generally, adsorption increased when pH decreased (Sprankle et al., 1975; McConnell and Hossner, 1985). Glyphosate adsorption decreased with increasing phosphate content because of competition phenomena for adsorption sites; glyphosate is adsorbed on soil constituents mainly through its phosphonic moiety (Sprankle et al., 1975; de Jonge et al., 2001) and phosphate could exclude glyphosate from sorption sites (Gimsing and Borggaard, 2001). Amorphous iron enhanced glyphosate adsorption on soils by ligand exchange mechanisms (Sprankle et al., 1975; Piccolo et al., 1994). In contrast with Morillo et al. (2000) but in agreement with de Jonge et al. (2001), soil organic carbon content is not correlated to glyphosate adsorption ($r = -0.23$).

Trifluralin, metazachlor and metamitron adsorption on soils was correlated to soil organic carbon content ($r = 0.91, 0.88, 0.50$ respectively) in agreement with Peter and Weber (1985), Tavares and Rezende (1998), Beulke and Malkomes (2001), and Madsen et al. (2000).

Sulcotrione K_d was mainly inversely correlated with pH ($r = -0.85$) as reported by Rouchaud et al., (1998). A positive correlation with total copper content ($r = 0.91$) and the complexable metals Fe and Mn extracted by EDTA ($r = 0.90$ and 0.78 respectively) is evident, which may be due to formation of a transition metals-sulcotrione complex.

4. Conclusions

A study of herbicide retention in three soils demonstrated that glyphosate was the most adsorbed herbicide. Glyphosate adsorption was time-dependent and it degraded to AMPA, which was less adsorbed. Glyphosate adsorption depended on pedological factors: soil pH, copper, phosphate and amorphous iron content. Trifluralin was also strongly adsorbed, reaching equilibrium within 24 h. Its adsorption correlated positively with soil organic carbon content, and was explained by its low water solubility or high K_{ow} , large molecular volume and the high first-order connectivity index. In contrast, metazachlor, metamitron and sulcotrione adsorption in soils was low. Metazachlor and metamitron adsorption mainly depends on soil organic carbon content, while sulcotrione adsorption depends on pH. The low adsorption of these herbicides was also consistent with their moderate water

solubility, the low first-order connectivity index, molecular volume and polarity. Adsorption kinetics of these herbicides showed a time-dependency probably related to their capacity to diffuse into soil micro-pores. A consequence is that the measured adsorption coefficients at 24 h will likely be smaller than the true ones, resulting in the overestimation of their mobility in soil. The adsorption study on soil profiles demonstrated that glyphosate mobility in profiles decreased with depth, while for the four other herbicides potential mobility increased with profile depth. Furthermore, the potential mobility of herbicides as estimated from the adsorption coefficients must be complemented by the data on their persistence as well as the mobility of their metabolites. The effect of ageing on herbicide retention also must be considered to realistically evaluate pesticide mobility in soils.

GM crop introduction associated with glyphosate, made in part to decrease risks of environmental pollution (particularly toward groundwater), may help address observed increases in environmental contamination by herbicides. Glyphosate's foliar application and its ready adsorption to soils may reduce herbicide impacts on groundwater despite larger overall use rates. To illustrate this point, available herbicide concentration in the soil liquid phase was estimated from the adsorption K_d coefficients (Fig. 4). For this estimation, soil water content was set to the water holding capacity for each soil (Table 1), and the herbicide application rate was the maximum permissible in France (for glyphosate, a low and high level was used, and foliar interception was not considered). Even with the highest rate of glyphosate, its available concentration in the surface soil solution is one order lower than that of metamitron, metazachlor and sulcotrione. Glyphosate soil solution concentration was of the same order as trifluralin, which had the lowest overall concentration. However, trifluralin is a narrow-spectrum herbicides that can not be used alone, while glyphosate is a broad-spectrum herbicide and can replace most other herbicides when used with glyphosate-resistant GM crops.

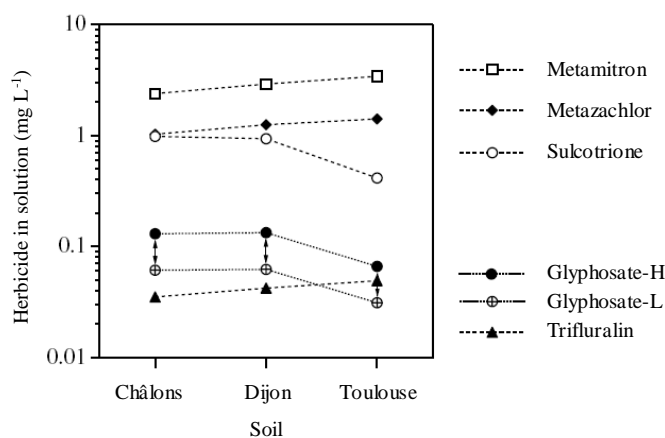


Fig. 4. Estimation of herbicide concentration in soil solution of three soils at 0-10 cm depth using measured K_d values and water contents corresponding to the field capacity of each soil. Herbicide application rate was the maximum permissible amount. For glyphosate, two levels were considered: H-high level of 3060 g ha⁻¹, and a L-low level of 1440 g ha⁻¹. The fraction of herbicide in solution is $1/(1+K_d/H)$, where H is the water content.

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