

Measurement and modelling of glyphosate fate compared with that of herbicides replaced as a result of the introduction of glyphosate-resistant oilseed rape

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Abstract

BACKGROUND: Crops resistant to glyphosate may mitigate the increasing contamination of the environment by herbicides, since their weeding requires smaller amounts of herbicides and fewer active ingredients. However, there are few published data comparing the fate of glyphosate with that of substitute herbicides under similar soil and climatic conditions. The objectives of the work reported here were (i) to evaluate and compare the fate in soil in field conditions of glyphosate, as used on glyphosate-resistant oilseed rape, with that of two herbicides frequently used for weed control on the same crop, albeit non-resistant: trifluralin and metazachlor, and (ii) to compare field results with predictions of the pesticide root zone model (PRZM), parameterized with laboratory data. Dissipation and vertical distribution in the soil profile of glyphosate, trifluralin and metazachlor were monitored in an experimental site located in Eastern France for 1 year.

RESULTS: Herbicide persistence in the field increased as follows: metazachlor < glyphosate < trifluralin, contrary to laboratory results showing glyphosate to be least persistent. The main metabolite of glyphosate – aminomethylphosphonic acid (AMPA) – was more persistent than glyphosate. AMPA and trifluralin had the largest vertical mobility, followed by metazachlor and glyphosate. PRZM underestimated the dissipation rate of glyphosate in the field and the formation of AMPA, but its predictions for trifluralin and metazachlor were correct. The simulation of herbicides and AMPA distribution in the soil profile was satisfactory, but the mobility of trifluralin and metazachlor was slightly underestimated, probably because PRZM ignores preferential flow. In general, data from the laboratory allowed an acceptable parameterization of the model, as indicated by goodness-of-fit indices.

CONCLUSION: Because of the detection of AMPA in the deep soil layer, the replacement of both trifluralin and metazachlor with glyphosate might not contribute to decreasing environmental contamination by herbicides. PRZM may be used to evaluate and to compare other weed control strategies for herbicide-resistant as well as non-resistant crops.

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Keywords: AMPA; trifluralin; metazachlor; field dissipation; field mobility; PRZM

1 INTRODUCTION

Crops resistant to glyphosate [*N*-(phosphonomethyl) glycine], a broad-spectrum herbicide, may mitigate the increasing contamination of the environment by herbicides¹ since their weeding requires smaller amounts of herbicides and fewer active ingredients.² Many studies have been published on the economic, ethical and some of the ecological impacts of this technology, focusing on the diversity of weed population, weed resistance and gene dispersion.^{2–5} However, the impacts of the associated modifications

in herbicide use on soil and water quality have been comparatively little investigated.^{6,7}

In France, three glyphosate-resistant crops, which are already cultivated in many countries,⁸ may be introduced: oilseed rape, sugarbeet and maize. In previous studies, the authors compared in the laboratory the retention and the degradation properties – the major processes regulating the environmental fate of pesticides – of glyphosate in soils with those of herbicides currently used on non-resistant crops.^{9–11} For oilseed rape, the most widely

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used herbicides in France were selected, namely trifluralin (α,α,α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine) and metazachlor [2-chloro-*N*-(pyrazol-1-ylmethyl)acet-2',6'-xylidide]. Compared with these molecules, glyphosate generally appeared as the most adsorbed and least persistent herbicide, and was therefore ascribed the lowest risks of dispersion into the environment.^{9–11} However, in France, glyphosate and its main metabolite, aminomethylphosphonic acid (AMPA), are among the most frequently detected molecules in ground and surface water, followed by trifluralin to a lesser extent. On the other hand, metazachlor is not detected.¹ The results obtained under controlled conditions needed to be complemented by field experiments and modelling, which is the purpose of this paper. In the work reported here, the authors elected to focus on oilseed rape, comparing the fate of glyphosate with that of trifluralin and metazachlor.

The fate of these three herbicides under field conditions is relatively well documented: the persistence of glyphosate is generally short, with half-lives of less than 2 months, but they can reach up to 130 days.^{7,12,13} The degradation of glyphosate leads to the formation of AMPA, which is more persistent, with half-lives ranging from 76 to 240 days.¹³ In general, these two compounds are poorly mobile in soil (see, for example, Laitinen *et al.*,⁷ Roy *et al.*,¹⁴ Newton *et al.*¹⁵ and Giesy *et al.*¹⁶), but significant mobility has been observed in soils characterized by macropore flows and in forest soils.^{17,18} Trifluralin is generally more persistent than glyphosate, but its half-lives vary from 1.5 to 350 days depending on temperature and soil moisture conditions and on the extent of volatilization.^{19–22} Trifluralin is unlikely to leach to groundwater with matrix flow, but may be transported by preferential flow in soils prone to such mechanisms.^{21,23} Metazachlor is less persistent than trifluralin, with half-lives ranging from 19 to 82 days, and leaching in soil is generally restricted by the rapid rate of degradation.^{24–26} However, these results were obtained under different conditions of soil and climate, hampering a precise comparison of the behaviour of these three herbicides.

Field studies provide reliable information on the fate and mobility of pesticides, but have the disadvantage of being site specific, time consuming and expensive.²⁷ From that standpoint, biophysical models are more efficient tools for making predictions of the pesticide fate in the environment, integrating different environmental and hydrological conditions, pesticide chemical properties and management practices. Among these models, the pesticide root zone model (PRZM)²⁸ is widely used and has been shown to provide reliable results in a number of instances.^{29–33} This model uses a balanced and consistent approach to the range of processes determining the fate of pesticides in the environment, including sorption, degradation, volatilization, leaching, plant uptake, runoff, erosion

and plant washoff.²⁸ Furthermore, it is one of the models used in environmental risk assessment for pesticide registration in many countries (Europe, USA).

However, a prerequisite to the extrapolation of a model is an assessment of its performance by comparing its predictions with experimental data. This allows a quantification of model prediction accuracy.³⁴ The performance of PRZM has primarily been tested for US situations, but also in some European countries. Depending on pesticide types and locations, the dissipation rate of pesticides in the soil was found to be either over- or underestimated.^{29,31,32,35} Likewise, concentrations in the soil profile were over- or underestimated.^{29,30,32–34,36} These contrasting results show the importance of testing PRZM in situations similar to those being modelled. This is particularly necessary in France, for which few results exist.³¹

The objectives of this work were twofold: firstly, an evaluation and comparison of the fate of glyphosate in the soil under field conditions, as used on glyphosate-resistant oilseed rape, with that of trifluralin and metazachlor used on the same crop, albeit non-resistant; secondly, a comparison of field observations with the predictions of PRZM, as parameterized from laboratory data on pesticide properties.

2 MATERIALS AND METHODS

2.1 Field study

2.1.1 Experimental site

A 0.8 ha field experiment located near Dijon (Eastern France) with genetically modified (GM) crops cultivated since 1995 was used. The soil is a clay-loam calcareous Cambisol (Table 1). The field was cropped with glyphosate-resistant oilseed rape (*Brassica napus* L.), which was sown on 4 September 2003 and harvested on 27 July 2004. Daily temperature, precipitation, air moisture, wind speed and orientation were monitored using a meteorological station located in the middle of the field. The average temperature from 1 September 2003 to 30 April 2004 was 6.9 °C, and the total precipitation was 392.2 mm (Fig. 1). Total precipitation fell within the range of values over the past 5 years on the same site (from 331 to 491.6 mm), but the temperatures were lower than usual (from 7.2 to 7.6 °C). Some climatic data that were not recorded on site (evapotranspiration and solar radiation) were obtained from a station located 15 km away from the site.

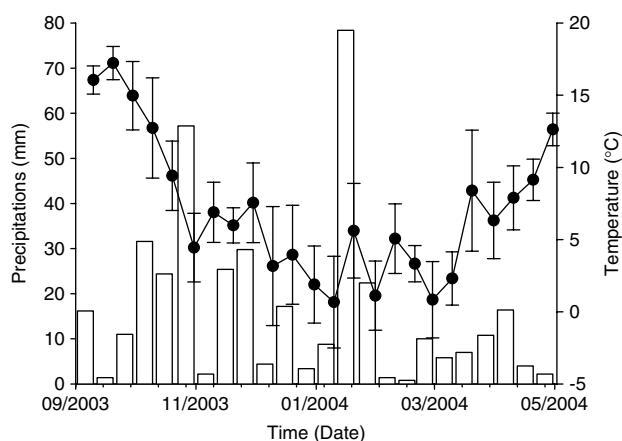
From 1995 to 2003, the site was treated each year with glyphosate, but only twice with trifluralin and once with metazachlor.

2.1.2 Herbicides

Commercial glyphosate 360 g AI L⁻¹ (Roundup Bioforce[®], Monsanto), trifluralin 480 g AI L⁻¹ (Treflan[®] EC, Dow AgroSciences) and metazachlor 500 g AI L⁻¹ (Butisan S[®], BASF Agro SAS) were applied once with a tractor coupled to a 12 m wide boom-sprayer at 720 g AI ha⁻¹ (five- to six-leaf stage

Table 1. Selected characteristics of the soil from the Dijon experimental site

Depth (cm)	Clay (g kg ⁻¹)	Silt (g kg ⁻¹)	Sand (g kg ⁻¹)	CaCO ₃ (g kg ⁻¹)	pH (water)	Organic carbon (g kg ⁻¹)	Water holding capacity (g kg ⁻¹)
0–10	400	386	214	167	8.2	16.3	261
10–20	405	391	204	144	8.2	14.8	270
20–30	436	372	192	113	8.3	9.5	286
30–60	483	351	166	88	8.4	7.7	317
60–90	346	462	192	416	8.6	6.9	218

**Figure 1.** Cumulative precipitations (bars) and average temperatures (●), with indication of minimum and maximum temperatures, for each 10 day interval from the Dijon experimental site.

of oilseed rape), 1200 g AI ha⁻¹ (before sowing) and 750 g AI ha⁻¹ (before the emergence of oilseed rape) respectively (Table 2). Trifluralin was immediately incorporated in the surface 8 cm of soil. Trifluralin and metazachlor were applied on one-half of the field, and glyphosate on the other half. For each herbicide, the rates actually reaching the soil surface were determined with ten glass microfibre filter traps (Whatman GF/B, 90 mm, Brentford, UK) placed in petri dishes randomly located in the field, and by soil sampling.

2.1.3 Soil sampling

For trifluralin, the soil surface (0–5 cm, see below for sampling method) was sampled on the day of application, before incorporation. Trifluralin and metazachlor were then analysed in the same soil samples. Soil samples and filters were put either in plastic bags (glyphosate) or glass jars (trifluralin and

metazachlor), immediately placed in a cooler and taken to the laboratory where they were frozen at –20 °C pending analysis. The dates (eight intervals) and depths (maximum of 90 cm) of soil sampling are summarized in Table 2 for the three herbicides.

The surface layer (0–5 cm) was sampled with steel rings (5 cm diameter, 5 cm height). For each sampling date, an average of ten soil surface samples were randomly collected per herbicide. Between the 5 cm and 60 cm depths, soil was sampled in 40 cm square pits, using copper rings (3 cm diameter, 2 cm height) inserted perpendicularly into the middle of each soil layer. For each time step and plot, the soil was sampled on each face of the four pits randomly located in the field. All replicates (at least 16) were pooled together. For the 60–90 cm layer, the soil was sampled with an auger, with six replicates randomly collected and subsequently pooled.

2.1.4 Chemical analysis

Filters from pesticide application and soil samples were analysed by two laboratories accredited by COFRAC (French Committee of Accreditation): Groupement Interrégional de Recherche sur les Produits Agropharmaceutiques (Beaucouzé, France) for glyphosate and AMPA, and the INRA Soil Analysis Laboratory (Arras, France) for trifluralin and metazachlor.

2.1.4.1 Glyphosate and AMPA. The analytical method for soil samples was adapted from Royer *et al.*³⁷ Ten grams of soil (previously 5 mm sieved) were mixed with 100 mL of 1 M ammonium hydroxide solution. The samples were homogenized for 30 min with a magnetic stirrer and centrifuged for 20 min. The supernatant was adjusted to 200 mL

Table 2. Soil sampling depths and dates for glyphosate, trifluralin and metazachlor

Sample	Depth of sampling (cm)	Date of sampling (days after application)		
		Glyphosate	Trifluralin	Metazachlor
Control	0–30; 30–60	1 September 2003	1 September 2003	1 September 2003
Application	0–5 + filters	17 October 2003	4 September 2003	15 September 2003
Autumn	0–5; 5–10; 10–20; 20–30	27 October 2003 (10)	16 September 2003 (12)	16 September 2003 (1)
		3 November 2003 (17)	25 September 2003 (21)	25 September 2003 (10)
		20 November 2003 (34)	13 October 2003 (39)	13 October 2003 (28)
		22 January 2004 (97)	22 January 2004 (140)	22 January 2004 (129)
Winter	0–5; 5–10; 10–20; 20–30; 30–60; 60–90	22 January 2004 (97)	22 January 2004 (140)	22 January 2004 (129)
		29 March 2004 (164)	29 March 2004 (207)	29 March 2004 (196)
Spring	0–5; 5–10; 10–20; 20–30; 30–60; 60–90	26 April 2004 (192)	26 April 2004 (235)	26 April 2004 (224)

with ultrapure water and brought to pH 2 (± 0.05) with 3–5 mL of 6 M hydrochloric acid. The extract was then purified by elution at 6 mL min⁻¹ through a Chelex[®]-100 resin column, and the column was rinsed with ultrapure water and 0.2 M hydrochloric acid at a high flowrate. All preceding fractions were discarded. Both glyphosate and AMPA were eluted with 6 M hydrochloric acid at a flowrate of 4 mL min⁻¹, and the elute was purified again with anion-exchange resin with 6 M hydrochloric acid rinse. The total elute was collected in a 100 mL round-bottom flask that had been silanized beforehand. The flask was evaporated to dryness, and the residue was dissolved in 12 M hydrochloric acid + methanol + water (1.3 + 78.9 + 19.7 by volume; 0.5 mL). Derivatization was subsequently carried out with 2,2,3,3,4,4,4-heptafluoro-1-butanol in trifluoroacetic anhydride (vials were placed for 1 h in a heating block maintained at 92–97 °C). The excess of derivatizing reagent and trifluoroacetic acid was evaporated under a stream of nitrogen, and the residue was dissolved in ethyl acetate containing 2.0 μ L citral mL⁻¹. The final extracts were analysed by gas chromatography on a capillary column and using a mass/mass spectrometer detector in electronic impact mode.

For the application filters, the same protocol was used but without extraction with ammonium hydroxide and with direct recuperation in the solution with derivative agent.

The limit of quantification was 10 μ g kg⁻¹ soil for glyphosate and AMPA. The range of tested concentrations was 50–500 μ g kg⁻¹, and the daily recovery efficiency ranged from 73 to 95% for glyphosate and from 71 to 92% for AMPA.

2.1.4.2 Trifluralin and metazachlor. The two herbicides were simultaneously analysed in soil samples. For each sample, soil was unfrozen and homogenized. A quantity of 150 mL of acetone was put on 50 g fresh soil, and the sample was then shaken for 12 h on a rotary shaker. Sodium chloride (30 g) and dichloromethane (50 mL) were then added to the soil and acetone, the mixture shaken again for 5 min and the liquid extract decanted. Anhydrous sodium sulphate (50 g) was added to the extract, and a second extraction was performed in the same way. The two extracts were mixed, shaken for 2 h, and hexadecane + hexane (1 + 99 by volume; 0.5 mL) was added to an aliquot (100 mL) of the extract, which was partially evaporated at 60 °C and 0.5 hPa under a rotary evaporator, then evaporated to dryness using nitrogen flux. The residue was dissolved in methanol (2 mL) for 30 min, and the resulting sample was analysed by HPLC with an UV diode-array detector.

Filters were extracted with 100 mL methanol in 250 mL glass jars closed with Teflon[®] joints. The sample was shaken for 16 h. Following decantation, an aliquot (92 μ L) was analysed by HPLC with an UV diode-array detector.

The limits of quantification of trifluralin and metazachlor were 30 and 4 μ g kg⁻¹ soil respectively. The average efficiency in filters was 97.9% for trifluralin and 99.7% for metazachlor. In the soil, it ranged from 40.7 to 68.8% for trifluralin and from 88.0 to 90.2% for metazachlor. The range of tested concentrations was 200–2000 μ g kg⁻¹. The results were corrected to take into account the recoveries.

2.1.5 Data analysis

Herbicide dissipation kinetics were fitted with single first-order kinetics (SFO):

$$C(t) = C_0 \exp(-kt)$$

where $C(t)$ is the amount of herbicide remaining in soil (kg ha⁻¹) at time t (day), C_0 is the initial amount of herbicide (kg ha⁻¹) and k is the first-order rate constant of dissipation (day⁻¹). The values of k were determined by non-linear regression (Marquardt–Levenberg algorithm, SigmaPlot; SPSS Inc., Chicago, USA) and were used to calculate the herbicide dissipation half-lives $T_{1/2}$ with the following equation:

$$T_{1/2} \text{ (day)} = \ln(2)/k$$

2.2 Modelling

2.2.1 Description of PRZM 3.12

The pesticide root zone model (PRZM) is a one-dimensional, dynamic, compartmental model used to simulate the movement of chemicals in unsaturated soil systems within and immediately below the plant root zone. The model has two major components: hydrology and chemical transport.²⁸ Water movement is determined with a capacity approach in which water in excess of field capacity percolates to deeper soil layer. Runoff is calculated by the Soil Conservation Service curve number technique, erosion is estimated using the universal soil loss equation and evapotranspiration (evaporation from crop interception and soil, and transpiration by the crop) is estimated by pan evaporation data or by an empirical formula. Irrigation can also be taken into account. The chemical component (for a parent substance and two metabolites at most) includes adsorption (instantaneous and reversible, or time dependent), degradation (first order or biphasic), volatilization, uptake by plants, leaching, runoff, erosion and foliar washoff. Solute transport is described by the advection–dispersion equation, and dispersion and diffusion in liquid and vapour phases are described by Fick's law. The transport equations can be solved using a finite-difference numerical solution or a method of characteristic algorithm (MOC) that reduces numerical dispersion.

2.2.2 Parameterization

Table 3 summarizes the input parameters of PRZM and their setting. The parameters relating to adsorption and degradation were previously determined in

Table 3. PRZM input parameters and setting (the parameters not included here were set to zero)

	Input parameters ^a	Values	
Herbicide	* Adsorption coefficients per horizon	See Table 4	
	* Dissolved and adsorbed phase degradation rates (<i>k</i>)	See Table 4	
	* Variation in <i>k</i> with depth	<i>k</i> for 0–30 cm, <i>k</i> × 0.5 for 30–60 cm, <i>k</i> × 0.3 for 60–90 cm (Ref. 39)	
	* Q ₁₀ factor (= <i>k</i> at 28 °C/ <i>k</i> at 18 °C), reference temperature	See Table 4, 28 °C	
	Dissolved and sorbed phase transformation fraction for glyphosate to AMPA	Soil: 0.093/oilseed rape: 0.027	
	* Hydrodynamic solute dispersion coefficient (only for glyphosate and AMPA)	34.08 cm ² day ⁻¹ (Ref. 44)	
	Henry's law constant/diffusion coefficient in the air (only for trifluralin)	6.7 × 10 ⁻³ Pa m ³ mol ⁻¹ /4300 m ² day ⁻¹ (Ref. 28)	
	Initial glyphosate/AMPA/trifluralin/metazachlor levels in 0–30 and 30–60 cm soil layers (µg kg ⁻¹)	5 and 5/21 and 12/75 and 15/11 and 2 (0 in 60–90 cm for all molecules)	
	Soil	Total depth of soil core, total number of horizons and thickness of the horizon	90 cm, 3 × 10 cm + 2 × 30 cm
		Thickness of compartments in the horizon: 0–10 cm/10–30 cm/30–90 cm	0.1 cm/0.1 cm; 5 cm (only for glyphosate)/5 cm (Ref. 28)
* Bulk density: 0–30 cm/30–60 cm/60–90 cm		1.45/1.50/1.40 (Ref. 40)	
Organic carbon, sand and clay contents		See Table 1	
Monthly values of soil surface albedo and reflectivity of soil surface to longwave radiation		0.25/0.97 (Ref. 28)	
* Field capacity (33 kPa)/wilting point (1500 kPa)		From Arrouays <i>et al.</i> ⁴¹ /Tessier <i>et al.</i> ⁴²	
Initial soil water content in the horizon		Field capacity (Refs 28 and 41)	
Initial temperature of the horizons: 0–10 cm/10–90 cm		20 °C/15 °C	
* Average monthly values of bottom boundary temperatures (January to December)		7–8–9–10–11–10–9–8–7–6–6–6 °C	
Application		Target application date and rate	See Section 2.1.2 and Table 2
	Chemical application method: glyphosate/trifluralin/metazachlor	2/6 (8 cm)/1	
	Application efficiency	100%	
	Condition for disposition of foliar herbicide after harvest (only for glyphosate)	Left alone	
	Foliar extraction coefficient for herbicide washoff per cm of rainfall (only for glyphosate)	0.1 (Ref. 28)	
	Crop	Crop emergence/maturation/harvest dates	16 September 2003/10 July 2004/27 July 2004
* Maximum rooting depth of the crop/maximum canopy height at maturation date		60 cm/140 cm	
Maximum areal coverage of the canopy		100%	
Surface conditions of the crop after harvest date		Residue	
Plant uptake factor: glyphosate and trifluralin/metazachlor		0/0.5 (See Section 2.2.2)	
Climate	Pan factor used to estimate daily evapotranspiration	1	
	Snowmelt factor	0.46 cm/°C (Ref. 28)	
	* Minimum depth of which evaporation is extracted	15 cm (Ref. 28)	
	Height of wind speed measurement above the soil surface	2 m	

^a The sensitivity of PRZM to the input parameters marked * was tested.

the laboratory for the parent herbicides and AMPA (Table 4).^{9,10,38} For all herbicides, the degradation rate in the dissolved phase was parameterized with the same value as that pertaining to the adsorbed phase as determined in the laboratory (Tables 3 and 4).³⁴ The plant uptake factor was set to zero for the strongly sorbed (poorly available) herbicides glyphosate and trifluralin and to 0.5 for the weakly sorbed herbicide metazachlor (Table 3).^{9,10} To model the fate of the foliar herbicide glyphosate, the authors assumed that 20% of the applied rate was intercepted by crops and weeds³⁹ and ran two simulations. The first one

involved the fraction of applied glyphosate that directly reached the soil surface (i.e. 80% of the total dose), and was based on the degradation rate measured in the laboratory in soils.¹⁰ The second simulation involved the remaining 20% of the total dose, which was intercepted by plants. The degradation rate measured by incubating plant residues containing glyphosate in soils was used.³⁸ All other input data were identical for the two simulations.

The input soil characteristics were measured (Table 1). However, bulk density had to be estimated according to the soil texture triangle of Jamagne

Table 4. Adsorption coefficients as a function of depth (K_d), degradation rates in soil (k_{soil}), degradation rates in soil after absorption by oilseed rape (k_{OR}) (only for glyphosate and AMPA) and Q_{10} factors of glyphosate, AMPA, trifluralin and metazachlor in Dijon soil

	Glyphosate	AMPA	Trifluralin	Metazachlor
<i>Adsorption</i>				
K_d (L kg ⁻¹)				
0–10 cm depth	42.8 ^a	32.0 ^b	46.8 ^a	1.06 ^a
10–20 cm depth	53.3 ^a	39.8 ^b	47.8 ^a	0.92 ^a
20–30 cm depth	54.3 ^a	40.6 ^b	34.5 ^a	0.70 ^a
30–60 cm depth	50.4 ^a	37.6 ^b	32.2 ^a	0.64 ^a
60–90 cm depth	56.2 ^a	42.0 ^b	20.7 ^a	0.37 ^a
<i>Degradation</i>				
k_{soil} (day ⁻¹) ^c	0.142	0.020	0.018	0.216
k_{OR} (day ⁻¹) ^b	0.042	0.006	–	–
Q_{10} factor ^b	2.3	–	2.1	1.7

^a From Mamy and Barriuso.⁹^b From Mamy.³⁸^c From Mamy *et al.*¹⁰

et al.,⁴⁰ and water contents at field capacity and wilting point were estimated using pedotransfer rules.^{41,42} For the bottom soil temperatures, an average of 8 °C, corresponding to the average air temperature, was used, furthermore assuming that the variations in temperature were much lower than those in air temperature.⁴³

The crops and technical programme data were provided by CETIOM (Centre Technique Interprofessionnel des Oléagineux Métropolitains).

The transport equations were solved using finite-difference numerical solutions for trifluralin and metazachlor, and with the MOC for glyphosate and AMPA. The hydrodynamic dispersion coefficients of these two molecules were parameterized with the mean value determined by Raturi *et al.* (Table 3),⁴⁴ as very few data are available in the literature.

2.2.3 Sensitivity analysis

A comprehensive sensitivity analysis of PRZM was beyond the scope of this work, and many such studies have already been published. The authors therefore only tested its sensitivity to those input parameters that had to be estimated or that are known to have an important impact on the results.^{45–47} They performed a one-at-a-time sensitivity analysis that involved varying input parameters independently one at a time, all others parameters being constant.⁴⁷

The base-case (nominal) scenario for this sensitivity study corresponded to the field experiment, and the variation range of input parameters corresponded to the spatial variability of the measurements (for the adsorption coefficients and degradation rates) or to the maximum realistic range of values according to measurements or literature (for all other parameters) (Table 5).

The sensitivity of PRZM was judged from two output variables: the simulated herbicide degradation rate and the maximum herbicide concentration in the liquid phase (Table 5). For herbicides, the simulated degradation rates were estimated according to a

single first-order (SFO) kinetic model, fitted with the Marquardt–Levenberg algorithm (SigmaPlot). For AMPA, the degradation rate was estimated using a three-compartment model fitted with ModelMaker 4.0 (FamilyGenetix Limited, Oxford, UK).

Quantifying the sensitivity of PRZM to one input parameter was done by calculating the ratio of variation ROV .⁴⁷

$$ROV = \frac{P - P_{BC}}{I - I_{BC}} \times \frac{I_{BC}}{P_{BC}}$$

where I is the value of the input parameter, I_{BC} is the value of the input parameter for the base-case scenario, P is the predicted value and P_{BC} is the predicted value for the base-case scenario. The ROV takes negative values if a decrease in an input parameter results in an increase in the predicted value or if an increase in an input parameter results in a decrease in the predicted value. The larger the ROV , the more influence a parameter has on model output.

2.2.4 Evaluation of PRZM performance

The performance of PRZM was evaluated by calculating four statistical indices:⁴⁸

- (i) the sample coefficient correlation r , which is a measure of the degree of association between simulation and measurement, and indicates whether the shape of the plotted simulation is similar to the measured data or not:

$$r = \frac{\sum_{i=1}^n (O_i - \bar{O}) \times (P_i - \bar{P})}{\left[\sum_{i=1}^n (O_i - \bar{O})^2 \right]^{1/2} \left[\sum_{i=1}^n (P_i - \bar{P})^2 \right]^{1/2}} \quad (1)$$

where O_i and P_i are the observed and predicted values respectively, \bar{O} and \bar{P} are the mean observed and predicted values respectively and n is the number of sampling dates.

If $r = +1$ (-1), then there is perfect positive (negative) correlation between simulated and measured values; if $r = 0$, then there is no correlation between simulations and measurements.

- (ii) the modelling efficiency EF indicates whether the simulated values correspond closely to measured values:

$$EF = \frac{\sum_{i=1}^n (O_i - \bar{O})^2 - \sum_{i=1}^n (P_i - O_i)^2}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad (2)$$

$EF = 1$ indicates a perfect correspondence.

- (iii) the root mean square error $RMSE$ provides a percentage term for the total difference between the predicted and the observed values:

$$RMSE = \frac{100}{\bar{O}} \sqrt{\frac{\sum_{i=1}^n (P_i - O_i)^2}{n}} \quad (3)$$

The lower limit for $RMSE$ is 0, in which case there is no difference between measured and simulated values.

- (iv) the coefficient of residual mass CRM gives an indication of the consistent errors in the distribution of all simulated values across all measurements with no consideration of the order of the measurements:

$$CRM = \frac{\sum_{i=1}^n O_i - \sum_{i=1}^n P_i}{\sum_{i=1}^n O_i} \quad (4)$$

A negative (positive) value indicates that the majority of predicted values are greater (less) than the measured values. A CRM value of 0 denotes no bias in the distribution of predicted values with respect to measured values.

3 RESULTS AND DISCUSSION

3.1 Fate of herbicides in field conditions

3.1.1 Herbicides on non-GM oilseed rape – trifluralin and metazachlor

The filter traps allowed a measurement of the actual herbicide application rate and its spatial variability. For trifluralin and metazachlor, $82.2 \pm 12.7\%$ and $80.6 \pm 26.4\%$ of the theoretical doses was recovered on filter traps respectively. Recoveries from the soil surface just after herbicide application were higher than those in the filters, being 108.7% and 115.4% for trifluralin and metazachlor respectively.

During the 235 days experiment, the herbicide concentration on the soil surface (0–5 cm) decreased following SFO kinetics, giving half-lives of 203.8 days (coefficient of determination $r^2 = 0.66$) for trifluralin and 11.6 days ($r^2 = 0.93$) for metazachlor (Fig. 2). These $T_{1/2}$ values are in agreement with those reported in the literature.^{19,20,24} Trifluralin was the most persistent herbicide: 235 days after application (DAA), 28% of the applied dose was still found in the 0–5 cm segment soil (Fig. 2). This high persistence is also shown by the initially high amounts of trifluralin in the 0–30 cm soil layer (Table 3), which resulted from a spraying of that herbicide 2 years prior to the present experiment. The dissipation of trifluralin was characterized by an initial phase of rapid dissipation (43% during the first 39 days), followed by a second phase of slower dissipation (29% during the next 197 days), in agreement with Laabs *et al.*²¹ The first phase was probably dominated by volatilization,²² and the second phase by chemical and biological degradation, and a decrease in the bioavailability of the substance was due to an increase in its adsorption over time.^{10,11,21} The decrease in the rate of degradation in the second phase may also be due to the lower temperatures during winter. The dissipation of metazachlor on the soil surface was very rapid (Fig. 2), resulting in negligible herbicide concentrations in the soil 129 DAA. In the laboratory, the main dissipation pathways were shown to be non-extractable residues formation and degradation to an unidentified main metabolite.¹⁰

The vertical mobility of trifluralin (Fig. 3) and metazachlor (Fig. 4) was high shortly after application. Trifluralin was incorporated to a depth of 8 cm, and was mainly concentrated in the 0–10 cm layer

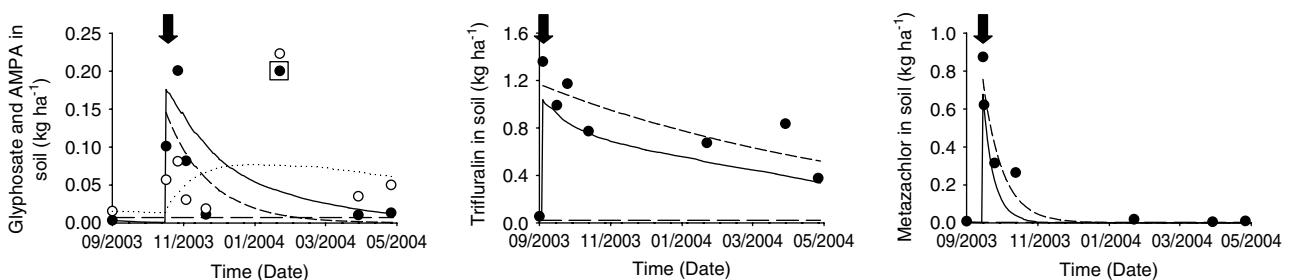


Figure 2. Observed (circles) and simulated (lines) dissipation kinetics of glyphosate, trifluralin, metazachlor (●, —) and AMPA (○, ·····) in the soil surface (0–5 cm). The long-dash lines show the limit of quantification, and the short-dash lines the adjustment with single first-order kinetics. The datum point marked with a box was disregarded in the adjustment. The arrows indicate the day of herbicide application.

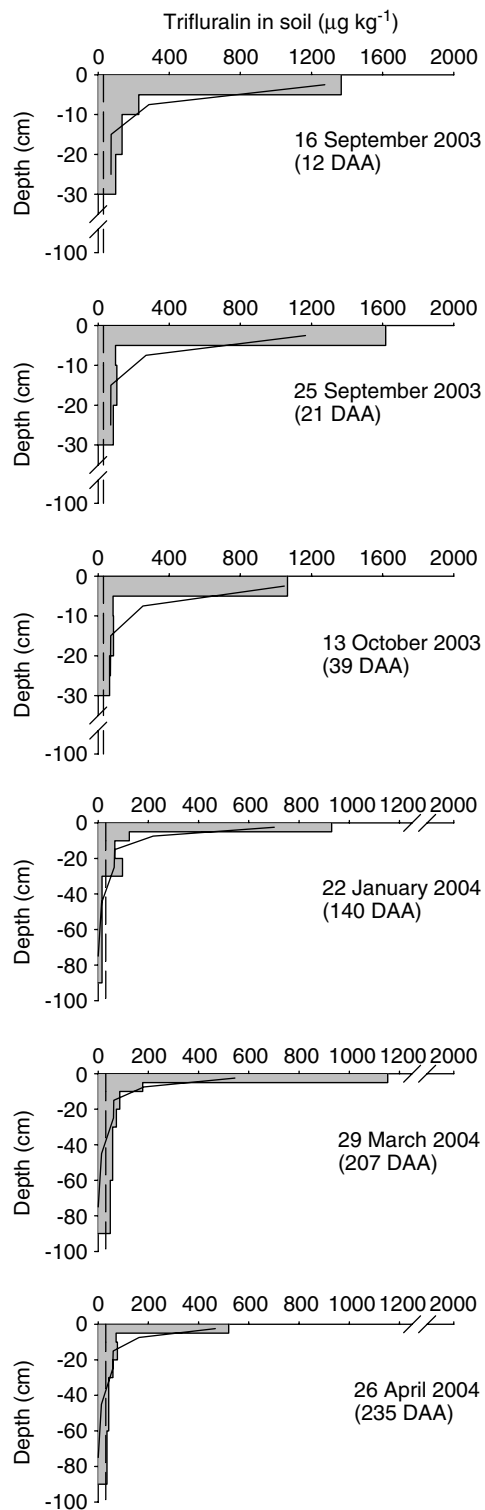


Figure 3. Observed (bars) and simulated (line) distribution of trifluralin as a function of time. Concentrations lower than LOQ are represented as equal to LOQ/2. The dashed line shows the limit of quantification. Initial amounts of trifluralin in soil were $75 \mu\text{g kg}^{-1}$ and $<\text{LOQ}$ in the 0–30 and 30–60 cm soil layers respectively.

of soil over the course of the experiment. Both herbicides were detected to a depth of 30 cm from 16 September to 13 October 2003 (Figs 3 and 4). More than 5 and 3% of the initial amounts of trifluralin and metazachlor, respectively, reached the 30 cm depth on 16 September, implying a transfer to

the deeper soil layers. The similar transport pattern of the two herbicides, in spite of great differences in their adsorption coefficients (Table 4), was probably the result of preferential flow. Several rainfall events occurred a few days after the application of trifluralin, from 7 to 8 September ($5.8\text{--}9.2 \text{ mm day}^{-1}$), which could explain the movement of trifluralin. The amounts of trifluralin in the 60–90 cm layer were high, representing 2.56 and 1.86% of the applied rates in March and April respectively. The presence of trifluralin in deeper soil layers has been observed by several authors and may result, in addition to preferential flow, from the adjuvants in the commercial formulation, from colloidal or particulate leaching or from vertical translocation in gaseous phase.^{21,23,49} In contrast to trifluralin, metazachlor was retained in the surface layer of soil throughout the period that it was detected, in agreement with Rouchaud *et al.*^{25,26} The mobility of a pesticide is the result of adsorption and degradation; the adsorption of metazachlor is low, but transport to a deeper soil layer is reduced because this molecule is rapidly degraded.

3.1.2 Herbicide on GM oilseed rape – glyphosate

The actual application dose of glyphosate was lower than planned. Only $28.0 \pm 7.5\%$ of the glyphosate theoretical dose was recovered in the filters, and only 27.8% in the surface soil sampled just after glyphosate application. Both estimations of the applied dose were consistent. The low recoveries of glyphosate may be due to an incomplete dilution of the substance in the spray solution, to crop or weed interception or to drift on the day of application. Regarding the latter point, wind speed averaged 0.9 m s^{-1} over the day of application, with a maximum of 5.5 m s^{-1} . Volatilization and photodegradation are usually negligible for this substance.^{7,10,16,50} The glyphosate dissipation on the soil surface (0–5 cm) was rapid: 34 DAA, less than 10% of applied glyphosate was detected (Fig. 2). It was described by SFO kinetics, giving a $T_{1/2}$ of 25.3 days ($r^2 = 0.55$), which is in agreement with the literature.^{7,12,14} In spite of the low-quality fitting of the SFO kinetics, it was used to be consistent with the other herbicides and with the assumptions of the numerical model. The glyphosate persistence in the field was higher than in the laboratory experiments.¹⁰ This may result from the interception of glyphosate by plants in the field, which may lead to a delayed release of glyphosate in soil following foliage senescence.^{18,38}

The dissipation of glyphosate was not due to transport in the deeper soil layers, since its concentration was always under the limit of quantification (LOQ) below the 5 cm depth (Fig. 5), except 10 DAA when a small amount was detected in the 20–30 cm soil layer. An unlikely high concentration was measured in the soil surface sample (0–5 cm) in January 2004 (Fig. 2). As no application of glyphosate had occurred in the meantime, this concentration could not be explained and the datum was discarded. Glyphosate

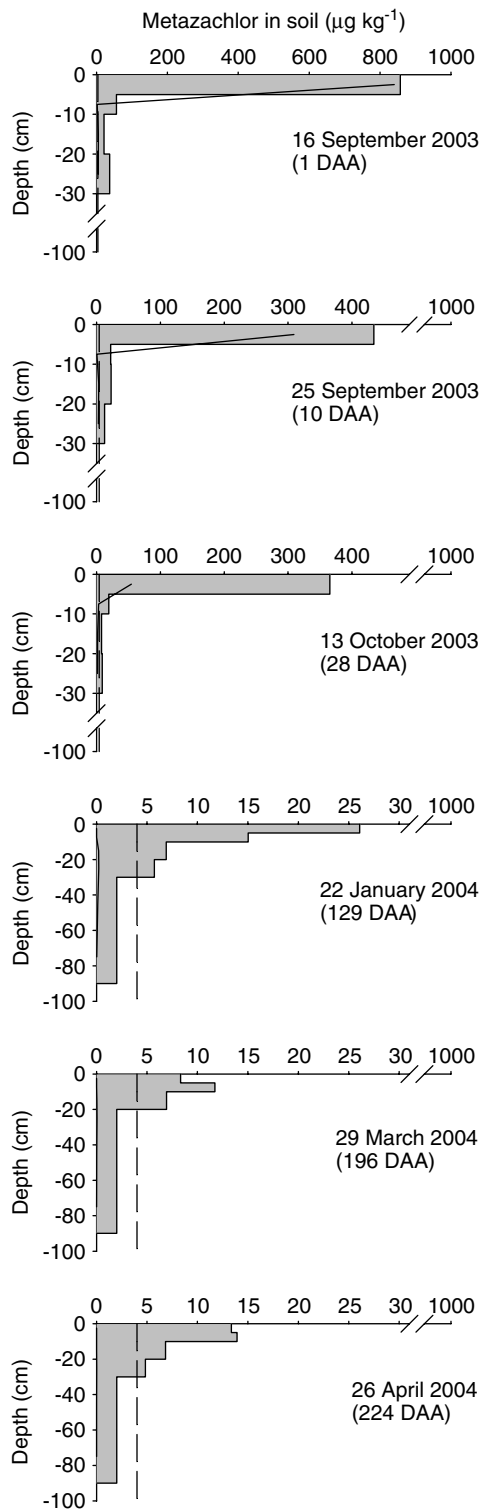


Figure 4. Observed (bars) and simulated (line) distribution of metazachlor as a function of time. Concentrations lower than LOQ are represented as equal to LOQ/2. The dashed line shows the limit of quantification. Initial amounts of metazachlor in soil were 11 µg kg⁻¹ and <LOQ in the 0–30 and 30–60 cm soil layers respectively.

is poorly mobile in soil because of its high adsorption and rapid degradation (Fig. 5).^{9,12,14,15,17} The detection of glyphosate in the 20–30 cm soil layer 10 DAA corresponded to the rainy period that occurred 2 DAA, from 19 to 23 October 2003 (Fig. 1), which could have been coupled with preferential flow.^{7,17}

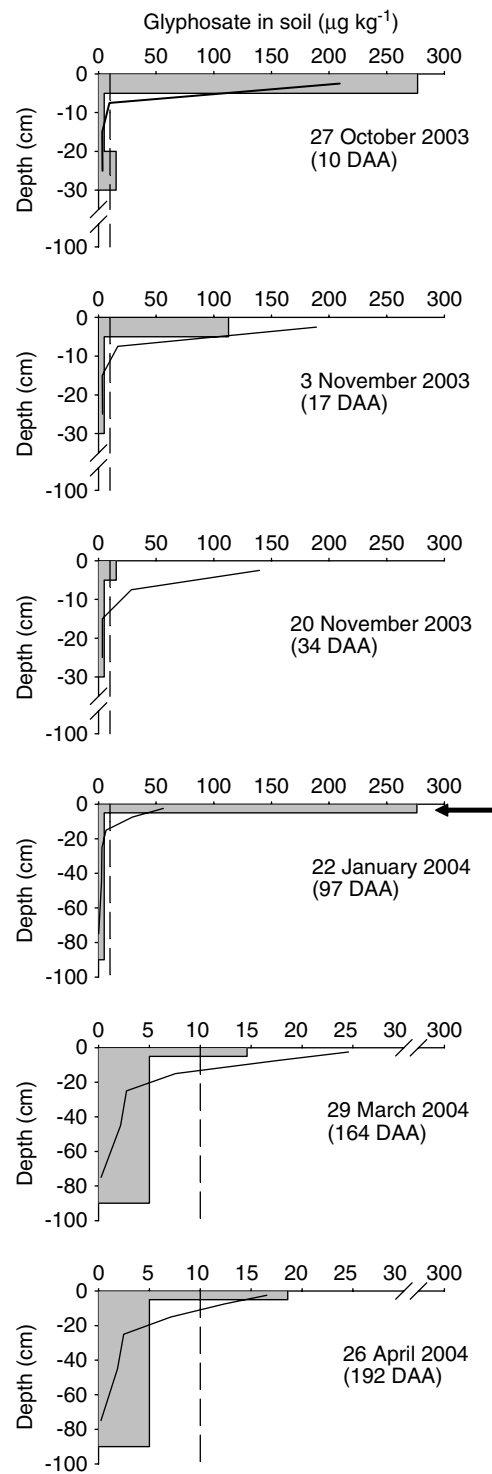


Figure 5. Observed (bars) and simulated (line) distribution of glyphosate as a function of time. Concentrations lower than LOQ are represented as equal to LOQ/2. The dashed line shows the limit of quantification. Initial amounts of glyphosate in soil were <LOQ in the 0–30 and 30–60 cm soil layers. The datum marked with an arrow was disregarded.

Glyphosate may also originate from root exudates of crops or weeds,¹⁸ or from root decomposition.⁷

Glyphosate is mainly degraded to AMPA and mineralized, but the formation of non-extractable residues may also contribute to its dissipation.¹⁰ AMPA was found to be more persistent than

glyphosate, as reported in the literature.^{7,12,14,16} Contrary to glyphosate, AMPA was detected in the control soil samples taken before the experiment (Table 3). Also, it was still detected in the soil 192 DAA (Fig. 2). The AMPA concentration was at its maximum in January (97 DAA) in the 0–5 cm soil layer. Its concentration was high but still consistent with the amount of glyphosate detected in the soil shortly after application.

The vertical mobility of AMPA is higher than that of glyphosate (Fig. 6): AMPA was detected at a depth of 30 cm in January 2004, and in the 60–90 cm soil layer in April 2004 (Fig. 6). This is in agreement with the results of Kjaer *et al.*¹⁷ and Veiga *et al.*¹⁸ As with glyphosate, the presence of AMPA in deep soil layers may result from root exudates or decomposition, or from transport by preferential flow. In April, the amount detected in the 60–90 cm layer made up 6.8% of the amount of glyphosate applied.

3.2 Modelling the fate of herbicides with PRZM

3.2.1 Sensitivity analysis

The dissipation kinetics predicted by PRZM for the three herbicides and AMPA were mostly influenced by: the temperature dependency factor (Q_{10}) > the degradation rate (k) > the hydrodynamic solute dispersion coefficient for glyphosate and AMPA > soil bulk density > field capacity and wilting point > the average monthly temperatures at the bottom of the soil profile > the adsorption coefficient (K_d) (Table 5). The predictions of herbicide leaching were mainly influenced by K_d > hydrodynamic solute dispersion coefficient for glyphosate and AMPA > Q_{10} > bulk density > k > field capacity and wilting point > average monthly bottom boundary temperatures (Table 5). On the other hand, the sensitivity of the model to the modification of the degradation rate with depth, the maximum rooting depth or the minimum depth of evaporation was marginal (Table 5). These results are in agreement with those reported in the literature,^{45–47} and show that the variables that were measured in the laboratory (k , Q_{10} , K_d) are those for which the sensitivity of PRZM was the most important. For glyphosate and AMPA, the prediction of dissipation and mobility was very sensitive to the value of the hydrodynamic solute dispersion coefficient which was estimated from literature data.

3.2.2 Prediction of the dissipation of herbicides

The best values of the statistical indices for PRZM dissipation predictions were obtained for metazachlor, followed by trifluralin, glyphosate and AMPA (Table 6). Except for AMPA, the shape of the dissipation kinetics was correctly described by PRZM, as shown by $r > 0.7$ (Fig. 2, Table 6). The values of EF and $RMSE$ were in agreement with those found by Baer and Calvet.³¹

The relative persistence of the herbicides was the same in the simulations as in the field observations, with the following ranking (simulated $T_{1/2}$

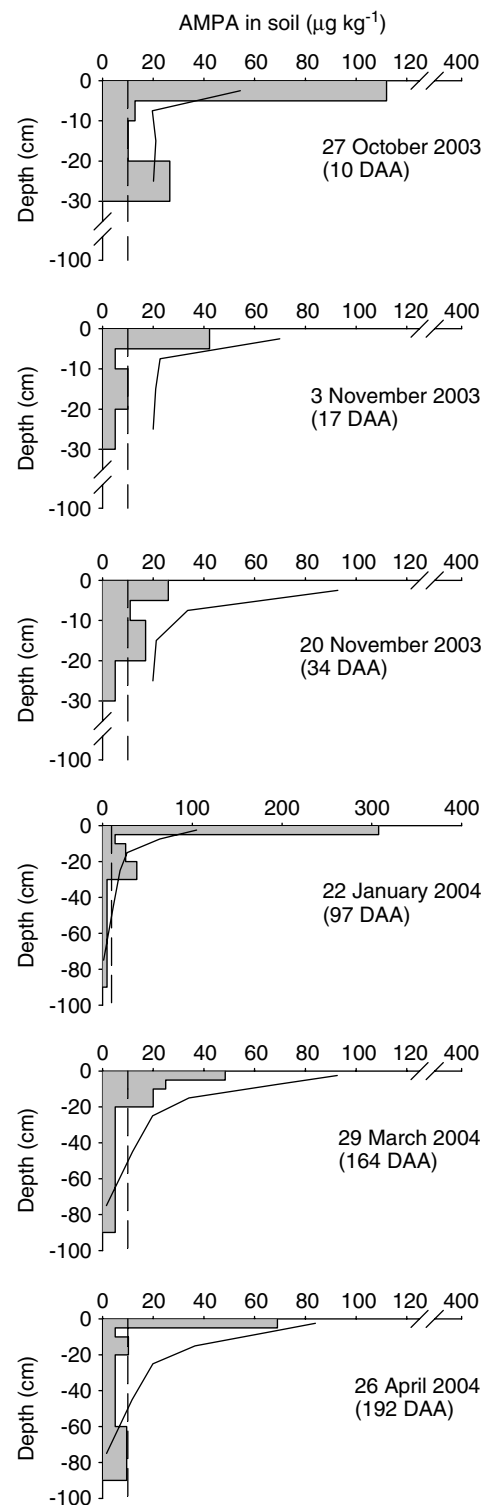


Figure 6. Observed (bars) and simulated (line) distribution of AMPA as a function of time. Concentrations lower than LOQ are represented as equal to LOQ/2. The dashed line shows the limit of quantification. Initial amounts of AMPA in soil were $21 \mu\text{g kg}^{-1}$ and $12 \mu\text{g kg}^{-1}$ in the 0–30 and 30–60 cm soil layers respectively.

in brackets): trifluralin (161.2 days) > glyphosate (45.9 days) > metazachlor (6.6 days). However, the simulated half-lives differed from those deduced from the observed dissipation kinetics. The prediction of dissipation kinetics was mostly sensitive to the Q_{10} factor and to the degradation rate (Table 5). Thus,

Table 5. Nominal values, variation range and ratio of variation (ROV) of the input parameters tested. ROVs are given as a function of output parameters: simulated first-order dissipation rates (k_s) and maximum concentrations in liquid phase (C_{liq})

Input parameter	Variation range ^a	Glyphosate		AMPA		Trifluralin		Metazachlor	
		k_s (day ⁻¹)	C_{liq} (µg L ⁻¹)	k_s (day ⁻¹)	C_{liq} (µg L ⁻¹)	k_s (day ⁻¹)	C_{liq} (µg L ⁻¹)	k_s (day ⁻¹)	C_{liq} (µg L ⁻¹)
<i>Herbicide</i>									
Adsorption coefficient K_d	$K_d - 10\% - K_d + 10\%^*$	0.11 ^c	-0.89 ^f	0.21 ^c	-0.82 ^c	0	-1.11	-0.01	-0.75
Degradation rate k	$k - 10\% - k + 10\%^*$	1.18 ^c	-0.33 ^f	1.37 ^c	0.60 ^c	1.00	-0.20	1.15	-1.99
k as a function of depth	k for the entire soil profile-FOCUS (Ref. 39)*	0	0	0	-0.03	0	0	0	0
	k (0-10 cm), $k/10$ (10-90 cm)-FOCUS (Ref. 39)*	0	0	0	0	0	0	0	0
Q ₁₀ factor	1.0-2.8*	-13.33	0.99	-21.21	-0.34	-10.62	0.49	-9.28	1.45
Hydrodynamic solute dispersion coefficient	20 cm ² day ⁻¹ -60 cm ² day ⁻¹ *	-0.20	-0.46	-0.35	-1.00	-	-	-	-
<i>Soil</i>									
Bulk density	1.35-1.55*	0.14	-0.85	0.21	-0.57	-0.59	-0.31	-0.06	-0.66
Field capacity, wilting point	Carsel <i>et al.</i> ²⁸ -Arrouays <i>et al.</i> ⁴¹ , Tessier <i>et al.</i> ⁴² *	-0.12	-0.25	-0.19	-0.48	-0.13	0.25	-0.02	0.01
Average monthly bottom boundary temperatures	5 °C-mean 8 °C ^{b*} 15 °C-mean 8 °C ^{b*}	0.09	-0.02	0.17	0.03	0.13	-0.02	0.09	-0.17
		0.27	-0.10	0.24	0.15	0.25	-0.02	0.30	-0.43
<i>Crop</i>									
Maximum rooting depth	60 cm-120 cm*	-0.02	-7.26 × 10 ⁻⁴	-0.16	-1.31 × 10 ⁻⁴	0	0	0	0
<i>Climate</i>									
Minimum depth of evaporation	1 cm-15 cm*	3.8 × 10 ⁻⁴	-3.7 × 10 ⁻³	-4.6 × 10 ⁻⁴	-1.0 × 10 ⁻³	0	-8.3 × 10 ⁻²	2.0 × 10 ⁻³	-4.1 × 10 ⁻²

^a Base values marked *.

^b Temperatures from January to December: 7-8-9-10-11-10-9-8-7-6-6-6 °C.

^c Variations in K_d of glyphosate and AMPA were tested separately, but variations in k_s were tested simultaneously.

Table 6. Goodness-of-fit statistics for PRZM predictions of dissipation and vertical distribution in the soil profile of glyphosate, AMPA, trifluralin and metazachlor

		Dissipation	Vertical distribution in soil profile
r^a	Glyphosate	0.770	0.837
	AMPA	0.401	0.660
	Trifluralin	0.922	0.953
	Metazachlor	0.965	0.946
EF^b	Glyphosate	0.402	0.653
	AMPA	0.102	0.336
	Trifluralin	0.644	0.874
	Metazachlor	0.870	0.871
$RMSE^c$	Glyphosate	86.78	157.6
	AMPA	94.03	155.1
	Trifluralin	30.08	53.9
	Metazachlor	41.85	94.8
CRM^d	Glyphosate	-0.417	-0.319
	AMPA	0.231	-0.227
	Trifluralin	0.221	0.146
	Metazachlor	0.264	0.384

^a Sample correlation coefficient.^b Modelling efficiency.^c Root mean square error.^d Coefficient of residual mass.

the differences between observed and simulated dissipation kinetics may be due to discrepancies between laboratory and field conditions leading to inadequate parameter assessment in the laboratory. They may also result from herbicide losses that were either not included or not well represented by the model (formation of non-extractable residues, photodegradation, volatilization or wind erosion occurring shortly after application), deviations from first-order kinetics, discrepancies between simulated and actual soil temperature and moisture and/or variability of half-lives.^{31,35,51}

The persistence of glyphosate was overestimated by the model, as evidenced by a negative CRM . Therefore, the concentrations of AMPA were underestimated, in particular the peak value in January 2004 (Fig. 2, Table 6). On the other hand, PRZM underestimated the persistence of trifluralin and metazachlor in the soil ($CRM > 0$) (Fig. 2, Table 6). On the last sampling date, PRZM provided good predictions of the residues of herbicides and AMPA in soil (Fig. 2), showing that the model can predict correctly the concentrations of pesticides and metabolites in the long term.

3.2.3 Prediction of the vertical distribution of herbicides in the soil profile

Some of the observed concentrations of herbicides in the soil profile were several times lower than the LOQ (Figs 3 to 6), and therefore three hypotheses were tested to calculate the goodness-of-fit indices, by setting these concentrations either at 0, LOQ or LOQ/2. The value of LOQ/2 was retained (Tables 3 and 6) as it can be considered as the most probable

value. Furthermore, it led to the best values for statistical indices, although the differences across the three LOQ values were not significant (data not shown).

The simulated vertical distribution in the soil profile was quite good for the four molecules. The best predictions were obtained for trifluralin, followed by metazachlor, glyphosate and AMPA (Figs 3 to 6, Table 6). Acceptable predictions of the shape of the vertical distribution in the soil profile were obtained, with $r > 0.66$ for all substances (Table 6). The modelling efficiencies were relatively good, particularly for trifluralin and metazachlor (Table 6). The values of statistical indices are in agreement with those obtained by Parrish *et al.*³⁴ and Walker *et al.*³⁶ using an earlier version of PRZM.

Because of the strong adsorption of glyphosate and AMPA, the MOC algorithm was used to simulate the presence in deep soil layers of the two substances. PRZM overestimated the concentrations of glyphosate and AMPA in the soil profile ($CRM < 0$), except in October for both molecules and in April for AMPA (Figs 5 and 6). This overestimation corresponded to the overestimation of glyphosate persistence by PRZM, but may also result from the model's assumption of reversible adsorption, although glyphosate desorption is reported as strongly hysteretic.^{11,30,35} The predictions of the maximum depth reached by the molecules were good for glyphosate, but underestimated for AMPA in April 2004, probably because the model does not consider preferential flow. The $RMSE$ values were relatively high for glyphosate and AMPA (Table 6), but were mostly due to the extremely low range of concentrations occurring several months after application: low concentrations result in high $RMSE$ s, even when absolute deviations between modelled and measured data are acceptable.

The predictions of the vertical distribution of trifluralin and metazachlor in the soil profile as a function of time were satisfactory (Figs 3 and 4, Table 6). The model slightly underestimated the concentrations of trifluralin throughout the experiment ($CRM > 0$), which corresponded to the overestimation of dissipation. The presence of trifluralin in the 30–90 cm layer in March and April was not simulated by PRZM, probably because it ignores preferential flow pathways. The concentrations of metazachlor in the soil profile were correctly predicted 1 and 10 DAA, although slightly underestimated, probably because non-equilibrium adsorption/transport and preferential flow are not included in the model.³⁵ From 28 DAA, metazachlor concentrations were strongly underestimated owing to an overestimation by the model of the very rapid dissipation of metazachlor. However, from January onwards, the concentrations of metazachlor were low in the 0–30 cm layer ($< 30 \mu\text{g kg}^{-1}$) and under the LOQ in the deeper layers.

Overall, the parameterization of PRZM from laboratory data provided satisfactory predictions

of the behaviour of glyphosate, AMPA, trifluralin and metazachlor in the soil, since no calibration was performed. This shows that the estimation of parameters that were not measured was correct, and that it was relevant to take into account the modification of glyphosate degradation following its absorption by plants. The performance of PRZM was acceptable considering, in addition, that some processes are not taken into account (preferential flow for example). The model may thus be reasonably used to simulate other pesticides and field conditions.

4 CONCLUSION

The fate of herbicides glyphosate, trifluralin and metazachlor in the soil was compared for use under field conditions representative of agronomic practices in France. Glyphosate was more persistent than metazachlor but less than trifluralin, and was degraded to AMPA, a far more persistent compound. AMPA and trifluralin were detected in the deeper layers of soil. On the other hand, glyphosate and metazachlor remained in the soil surface. The risk of environmental contamination by accumulation in soil and/or vertical transport by trifluralin and AMPA appeared rather high, whereas metazachlor was least persistent and mobile and therefore ascribed with the lowest contamination potential. Because of the presence of AMPA in the deeper soil layers, the replacement of both trifluralin and metazachlor with low doses of glyphosate would not decrease the risks of environmental contamination. In fact, this metabolite is being increasingly detected in water bodies in France.¹

These results made it possible to compare the fate of all these herbicides under similar environmental conditions, but it should be noted that glyphosate was applied 40 days later than trifluralin and metazachlor, since it is a foliar herbicide. Extrapolation to other situations is difficult because of the specific conditions of any one field study. We therefore used the experimental data to test the adequacy of PRZM to simulate the behaviour of the various herbicides. PRZM provided satisfactory predictions of dissipation and vertical distribution in the soil profile of the four substances. An overestimation of the persistence of glyphosate was nevertheless observed, as well as an underestimation of the concentration and persistence of AMPA, trifluralin and metazachlor. The mobility of glyphosate was correctly predicted, while those of AMPA, trifluralin and metazachlor were slightly underestimated, probably because the model ignores preferential flow. The prediction of the relative behaviour of the herbicides was satisfactory, and therefore the model can be used to compare other weed control strategies and, more widely, other pest management techniques in a range of pedoclimatic situations. These results also indicate that the PRZM provides accurate predictions when parameterized from independent laboratory data,

without requiring calibration on posterior field data. However, the underestimation of persistence and mobility of substances by PRZM should be considered for risk assessment.

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