Science of the Total Environment 717 (2020) 137019

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Modelling herbicides mobility in amended soils: Calibration and test of PRZM and MACRO

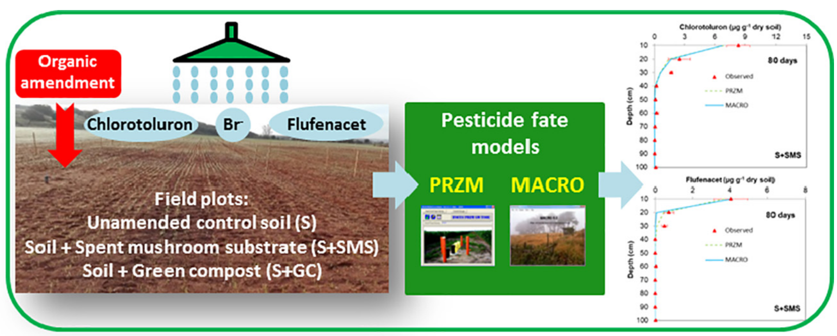
Jesús M. Marín-Benito [a,*], Laure Mamy [b], María J. Carpio [a], María J. Sánchez-Martín [a], M. Sonia Rodríguez-Cruz [a]

[a] Institute of Natural Resources and Agrobiology of Salamanca (IRNASA-CSIC), Cordel de Merinas 40-52, 37008 Salamanca, Spain
[b] Université Paris-Saclay, INRAE, AgroParisTech, UMR ECOSYS, 78850 Thiverval-Grignon, France

HIGHLIGHTS

- PRZM and MACRO performance to assess herbicides fate in amended soils was tested.
- MACRO simulated water contents in control and amended soils better than PRZM.
- Both models predicted well herbicide distributions in the amended soil profiles after a calibration step.
- The calibration of K_d and DT_{50} was different for each soil treatment, herbicide and model.
- The calibration of K_d and DT_{50} in the amended soils was based on their dissolved organic carbon content.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 December 2019
Received in revised form 28 January 2020
Accepted 29 January 2020
Available online 30 January 2020

Editor: Damia Barcelo

Keywords:
Pesticide fate model
Mobility
Herbicide
Bromide tracer
Soil amendment
Dissolved organic carbon

ABSTRACT

Addition of organic residues to soil is a current farming practice but it is not considered in the modelling studies for pesticide risk assessment at regulatory level despite its potential impact on the pesticide dynamics in soil. Thus, the objective of this work was to examine and to compare the ability of PRZM and MACRO pesticide fate models to simulate soil water content, and bromide (Br^-, tracer), chlorotoluron and flufenacet concentrations in the soil profiles (0–100 cm) of one agricultural soil, unamended (control soil, S), amended with spent mushroom substrate (S + SMS) or amended with green compost (S + GC). Based on a two-year field-scale dataset, the models were first calibrated against measurements of water and solutes contents in the soil profiles (first year) and then tested without any further model calibration by comparison with the field observations of the second year. In general, the performance of MACRO to simulate the whole dataset in the three soil treatments was higher than that of PRZM. MACRO simulated satisfactorily the water dynamics along the soil profiles whereas it was poorly described by the capacity model PRZM. Both models predicted very well the Br^- mobility in control and amended soils after dispersion parameters were fitted to observations. No calibration was necessary to reproduce correctly herbicides vertical distribution in the control soil profile. In the amended soils, MACRO simulations were highly correlated to the observed vertical distribution of flufenacet and chlorotoluron, but calibration of the K_d of chlorotoluron was needed. On the contrary, modelling with PRZM required calibration of K_d and DT_{50} of both herbicides to obtain an acceptable agreement between observations and predictions in the amended soils. K_d and DT_{50} calibration was based on the initial dissolved organic carbon contents (DOC) of amended soils. It allowed to take into account the processes that decrease the herbicides sorption on the soil and enhance their bioavailability, but that are not described in PRZM and MACRO (such as the formation of herbicide-DOC mobile complexes). This work showed that models such as PRZM and MACRO are able to simulate

* Corresponding author at: Institute of Natural Resources and Agrobiology of Salamanca (IRNASA-CSIC), Cordel de Merinas 40-52, 37008 Salamanca, Spain.
E-mail address: jesusm.marin@irnasa.csic.es (J.M. Marín-Benito).

https://doi.org/10.1016/j.scitotenv.2020.137019

the fate of pesticides in amended soils. However, before using these models as predictive tools in large amended soil conditions, and especially in the regulatory context, further modelling studies should focus on other pedoclimatic-pesticides-organic residues combinations, and on longer periods.

1. Introduction

Preserving the quality and sustainability of soils and waters represents a great challenge in the modern agriculture. This agriculture is mainly based on the use of pesticides for crop protection, and on the application of fertilizers such as organic wastes to increase soil organic matter (OM) content and fertility, and consequently crop yields (Chen et al., 2018). The dynamic of pesticides in the soil can be modified by the solid and dissolved OM of the organic wastes, leading to environmental consequences such as groundwater contamination by pesticides (Barriuso et al., 2011; Briceño et al., 2008; López-Piñeiro et al., 2013; Marín-Benito et al., 2014a; Song et al., 2008; Thevenot et al., 2009). However, studies tackling the influence of organic amendments on the fate of pesticides under real field conditions have been rarely conducted (Boesten and Van der Pas, 2000; Herrero-Hernández et al., 2011; Marín-Benito et al., 2018), and even less its modelling at this scale (Filipović et al., 2014; Ghirardello et al., 2010; Hughes et al., 2008; Jarvis et al., 2000).

Numerical models have become essential tools to study pesticide transport processes through soil profile, not only at research level but also for registration purposes. A large number of models has been developed to evaluate the fate of pesticides in the environment (Siimes and Kämäri, 2003). Among these models, four of them are recommended by the FOCUS (FOrum for Co-ordination of pesticide fate models and their USe) group for risk assessment for pesticide registration at the European level (FOCUS, 2000): MACRO (Larsbo and Jarvis, 2003), PEARL (Leistra et al., 2001), PELMO (Klein, 1995) and PRZM (Carsel et al., 2005). These models take into account the main processes affecting the dynamics of pesticides in soil (sorption, degradation, leaching, volatilization, absorption by plants, erosion, and/or runoff), and numerous studies showed they provided reliable simulations of the environmental fate of these compounds (Giannouli and Antonopoulos, 2015; Gottesbüren et al., 2000; Mamy et al., 2008; Marín-Benito et al., 2015; Vanclooster and Boesten, 2000). From a regulatory point of view, 125 groundwater scenarios (based on 9 pedoclimatic scenarios with 12 to 16 crops each) have been defined to collectively represent agriculture conditions in the European Union to assess the leaching of active substances (FOCUS, 2000, 2009) but the addition of organic amendments is not considered. Despite the nine pedoclimatic scenarios comprise soils having a wide range of OM contents, from 1.3% to 7.0% (FOCUS, 2000), the behavior of pesticides in soils with endogenous OM is different from their behavior in soils with exogenous OM added through organic amendments (Houot et al., 2014). It is therefore necessary to test the ability of numerical models to simulate the fate of pesticides in amended soils. In addition, this will help to improve risk assessment in the regulatory context.

Thus, the objectives of this work were: (i) to simulate, using PRZM and MACRO, the mobility of two herbicides widely used in wheat crops and having contrasting mobility (PPDB, 2019), chlorotoluron and flufenacet, in unamended (control soil, S) and amended (with spent mushroom substrate, S + SMS, or green compost, S + GC) agricultural soils, (ii) to assess and to compare their performances to be used as predictive tool in amended soils. Modelling was based on a two-year field dataset including water, Br^-, chlorotoluron and flufenacet contents in control and amended soil profiles cropped with winter wheat (Carpio et al., 2020).

2. Materials and methods

2.1. Pesticide fate models

The two one-dimensional PRZM 3.21 and MACRO 5.2 models were selected because they differ in their description of water and solute transport. A detailed description of PRZM and MACRO can be found in Carsel et al. (2005) and Larsbo and Jarvis (2003), respectively, and a comparative description of how both models simulate the main processes involved in the fate of pesticides in the environment is provided in Marín-Benito et al. (2014b). Briefly, PRZM describes the water movement in the soil profile with a capacity-based approach. Solute transport is described by convection, and numerical dispersion. MACRO considers non-steady state flows of water and solute for a variably-saturated layered soil profile. It is a dual-permeability model which divides the total soil porosity into two separate flow regions (micropores and macropores), each characterized by their own flow rates and solute concentrations. A soil water pressure head close to saturation and its associated water content and hydraulic conductivity define the boundary between the two regions. Soil water flow is described by the Richards equation in the micropores, and it is gravity driven in the macropore region. For the solute transport simulation, MACRO implements the convection–dispersion equation in the micropores, while it is assumed to be solely convective in the macropores. Exchange between the two domains is calculated according to physically based expressions using an effective aggregate half-width.

2.2. Experimental site, soil treatments and measurements

Simulations were based on a two-year (2016–2018) field experiment set up at the Muñovela experimental farm belonging to the Spanish Institute of Natural Resources and Agrobiology of Salamanca (40°54′15″N latitude and 5°46′26″W longitude). A detailed description of the Muñovela dataset is given by Carpio et al. (2020), therefore, only a short overview of the experimental site, soil treatments, and measurements is given here. Nine plots of 81 m^2 were treated as follows (three replicate plots per treatment): unamended control soil (S), soil amended with 140 t ha^{-1} (dry weight basis) of spent mushroom substrate (S + SMS), and soil amended with 85 t ha^{-1} (dry weight basis) of green compost (S + GC). The soil is an Eutric-Chromic Cambisol (IUSS Working Group WRB, 2015) with a predominant sandy-loam texture down to 1 m depth (Table 1). Organic amendments were incorporated into the top 20 cm using a rototiller in November 2016. Then each plot was equipped with one PVC pipe (120 cm length × 5.2 cm Ø) to monitor soil water content every 20 cm down to 1 m depth using a portable dielectric probe. From 29 November 2016 to 30 November 2018, 38 soil water content measurements at 20, 40, 60, 80 and 100 cm depth were recorded per plot. Winter wheat was annually sown in November in all plots (Table 2). After harvest, a bare soil was maintained during the fallow period.

The 9 plots were sprayed once a year with chlorotoluron and flufenacet herbicides at 15 and 5 kg a.i. ha^{-1} as Erturon® (Cheminova Agro S.A.) and Herold® (Bayer Crop Science S.L.) formulation, respectively, and with Br^- tracer at 53 kg a.i. ha^{-1}. The three compounds were jointly applied in pre-emergence on 1 December 2016, and on 13 November 2017 (346 days after the first application). Soil samples were taken on 17 sampling dates over the whole experiment (at 1, 17, 33, 60, 80, 151, 229 and 339 days after the first application, and at 1,

Table 1
Main physicochemical and hydraulic characteristics of unamended control (S), SMS- and GC-amended (S + SMS and S + GC) soil profiles.

Treatment	S					S + SMS		S + GC	
Parameter/soil layer (cm)	0–10	11–30	31–55	56–90	91–160	0–10	11–30	0–10	11–30
Sand (%)	80.4	79.7	77.4	72.9	68.3	76.7	78.8	78.7	79.2
Silt (%)	4.7	4.9	6.0	7.4	9.7	5.8	5.0	4.7	4.7
Clay (%)	14.9	15.4	16.6	19.7	22.0	16.5	16.2	16.6	16.1
pH	6.34	6.62	7.13	7.36	7.74	7.11	7.15	6.99	6.70
Bulk density (g cm^{-3})	1.48	1.45	1.54	1.61	1.60	1.23	1.45	1.34	1.45
OC (%)	0.77	0.91	0.51	0.27	0.29	2.64	0.95	1.69	0.94
DOC (mg g^{-1})	0.12	0.13	0.09	0.04	0.03	0.50	0.39	0.38	0.27
$\theta_{initial}$ (m^3 m^{-3})[a,b]	0.183	0.199	0.147	0.141	0.192	0.279	0.238	0.244	0.239
θ_{FC} (m^3 m^{-3})[c]	0.225	0.235	0.239	0.259	0.275	0.290	0.244	0.264	0.242
θ_{WP} (m^3 m^{-3})[c]	0.072	0.075	0.076	0.094	0.108	0.090	0.077	0.081	0.077
θ_r (m^3 m^{-3})[d]	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
θ_s (m^3 m^{-3})[d]	0.383	0.393	0.341	0.327	0.336	0.472	0.394	0.428	0.393
α (cm^{-1})[d]	0.087	0.085	0.096	0.094	0.088	0.068	0.086	0.078	0.087
n (−)[d]	1.339	1.326	1.271	1.223	1.192	1.240	1.314	1.290	1.319
K_{sat} (mm h^{-1})[d]	76.41	76.32	48.79	24.52	6.41	75.79	76.20	76.08	76.25
CTEN (cm)[e]	10	10	10	10	10	10	10	10	10
θ_b (m^3 m^{-3})[f]	0.332	0.343	0.325	0.319	0.332	0.422	0.344	0.378	0.343
K_b (mm h^{-1})[f]	1.413	1.316	0.793	0.516	0.409	0.789	1.202	1.083	1.246
ASCALE (mm)[f]	15	15	150	150	15	15	15	15	15
ZN (−)[f]	4	4	2	2	4	4	4	4	4

Note: The parameters without exponent correspond to measured parameters taken from Carpio et al. (2020).
[a] Data for 0–20, 20–40, 40–60, 60–80 and 80-100 cm soil layers, respectively. The data measured for the 80-100 cm layer were used to parameterize the 100–160 cm layer.
[b] $\theta_{initial}$ at 40–60, 60–80 and 80–160 cm depth were 0.166, 0.177 and 0.193 m^3 m^{-3} for S + SMS and 0.171, 0.144 and 0.166 m^3 m^{-3} for S + GC, respectively.
[c] Estimated by Rosetta's pedotransfer functions (Šimůnek et al., 2008).
[d] Estimated by HYPRES pedotransfer functions (Wösten et al., 1999).
[e] Default value (Larsbo and Jarvis, 2003).
[f] Estimated using the pedotransfer functions included in MACRO 5.2.

29, 64, 127, 142, 181, and 225 days after the second application), every 10 cm from 0 to 100 cm. Then they were analysed by ion chromatography and HPLC-DAD-MS for Br^- and herbicide concentrations, respectively. The analytical methods are described in detail in (Marín-Benito et al., 2019).

2.3. Modelling strategy

Simulations were run from 29 November 2016 to 30 November 2018 according to field dataset. One period out of the two experimental periods was used for models calibration (between 29 November 2016 and 12 November 2017), and another one to test the performance of the models (from 13 November 2017 to 30 November 2018). Therefore, the strategy of simulation was first to calibrate the models against the field measurements of water, Br^-, chlorotoluron and flufenacet contents in the control and amended soil profiles over the calibration period. Then soil water contents and chemicals transport were simulated without any further models calibration, and the results were compared to soil moisture, Br^-, chlorotoluron and flufenacet concentrations measured in the soils over the test period.

2.4. Models parameterization

The control, SMS- and GC-amended soil profiles of 1.6 m were split into five horizons of various thicknesses (Table 1). The soil physicochemical characteristics were measured at the experimental site (Carpio et al., 2020). For each soil layer, water contents at field capacity (θ_{FC}, pF = 2.5) and at wilting point (θ_{WP}, pF = 4.2), as needed in PRZM, were estimated using Rosetta pedotransfer functions (Šimůnek et al., 2008). For MACRO parameterization, the pedotransfer functions of HYPRES (Wösten et al., 1999) were used to calculate the van Genuchten soil-water retention parameters (θ_r, θ_s, α and n) and the saturated hydraulic conductivities (K_{sat}) (Table 1). The soil characteristics of the macropore region, such as the water content corresponding to the boundary soil water pressure head between micropores and macropores (θ_b), the boundary hydraulic conductivity (K_b), the parameter controlling the exchange of both water and solute between the micropore and macropore flows (ASCALE), and the pore size distribution index in the macropores (ZN), were estimated using the pedotransfer functions included in MACRO 5.2 (Moeys et al., 2012). The boundary soil water pressure head between micropores and macropores was set to MACRO default value (CTEN = 10 cm) (Table 1).

Table 2
Crop input parameters for winter wheat in unamended control (S)/SMS-amended (S + SMS)/GC-amended (S + GC) soils. COVMAX: Maximum areal coverage of the canopy (for PRZM model), LAI: Leaf area index.

Date	Crop development	COVMAX (%)[a]	LAI (m^2 m^{-2})[b]	Root depth (m)[a]	Root distribution[a,c]	Crop height (m)[a]
14 November 2016	Sowing					
3 December 2016	Emergence		0.00	0.01/0.01/0.01		0.01/0.01/0.01
5 May 2017	Flowering	10/75/20	0.30/2.25/0.60	0.21/0.21/0.21	0.90/0.90/0.90	0.55/0.65/0.65
3 July 2017	Harvest		0.30/2.25/0.60	0.21/0.21/0.21		0.55/0.65/0.65
2 November 2017	Sowing					
23 November 2017	Emergence		0.00	0.00/0.01/0.01		0.00/0.01/0.01
30 April 2018	Flowering	0/75/50	0.00/2.25/1.50	0.00//0.21/0.21	0.00/0.90/0.90	0.00/0.67/0.67
24 July 2018	Harvest		0.00/2.25/1.50	0.00//0.21/0.21		0.00/0.67/0.67

[a] Determined from field measurements or observations.
[b] Data estimated from COVMAX (−) = LAI / 3 for MACRO (Kroes et al., 2008).
[c] Fraction of root density in the uppermost 25% of the root depth for MACRO.

Crop parameters including emergence, flowering and harvest dates, maximum height and rooting depth of the wheat plants, root distribution and the maximum soil cover fraction (COVMAX in PRZM) corresponded to field site observations and relied on expert judgement (Table 2). The wheat maximum leaf area index (LAI) was estimated from the observed maximum soil cover fraction according to COVMAX = LAI / 3 (Kroes et al., 2008).

Sorption coefficients (K_d) of chlorotoluron and flufenacet in the control and amended soil profiles, their topsoil half-lives (DT_{50}) and the effect of temperature on herbicides degradation rate (Q_{10} in PRZM and TRESP in MACRO) were obtained from laboratory experiments on soil samples taken *in situ* at the beginning of the field experiment (Table 3) (Marín-Benito et al., 2019). However, in some cases a calibration step was done for DT_{50} and/or K_d to improve the goodness-of-fit statistics of the models (see Section 3.1). The variation of DT_{50} with depth was calculated according to the recommendations of FOCUS (2000). The dispersivity (DV for MACRO) and the hydrodynamic dispersion (DISP for PRZM) coefficients for each soil treatment were fitted manually from the observed Br^- concentrations in the corresponding soil profiles over the calibration period (29 November 2016–12 November 2017) (Table 3) (see Section 3.1). The crop uptake factor was set to zero for both herbicides, and to 0.5 for the non-sorbed Br^- tracer (FOCUS, 2000).

Topsoil temperature and soil moisture monitored at the beginning of the experiment along the soil profiles were used as initial conditions for the simulations. Soil temperature in deep soil layers was assumed to be 1 °C below those observed on the topsoil (Marín-Benito et al., 2014b). For MACRO, a constant hydraulic gradient equal to 1 was assumed as bottom boundary condition.

Climatic data (rainfall, maximum, minimum and average air temperature) were daily monitored using a meteorological station located at the field site. Measured daily and cumulative rainfall over the calibration and test periods are shown in Fig. S1 (Supplementary Material). Solar radiation, evapotranspiration and wind speed data were obtained from the station of Matacan airport (23 km away from Muñovela farm). Both meteorological stations are operated by the AEMET (Spanish Agency of Meteorology).

Table 3
Main herbicide input parameters used in the simulations. K_d: Sorption coefficient, nf: Freundlich exponent, DT_{50}: Degradation half-life, Q_{10}: Q_{10} factor, TRESP: Exponent in the temperature response function, DISP: Pesticide hydrodynamic solute dispersion coefficient, DV: Dispersivity, S: unamended control soil, S + SMS: Soil amended with spent mushroom substrate, S + GC: soil amended with green compost.

Parameter	Soil layer (cm)	Chlorotoluron			Flufenacet		
		S	S + SMS	S + GC	S	S + SMS	S + GC
Sorption							
K_d (mL g^{-1})[a]	0–10	0.773	4.773 (1.114)	2.563 (0.783)	1.038	6.340 (1.479)	2.909 (0.889)
	11–30	0.873	0.747 (0.336)	1.655 (0.855)	1.118	1.092 (0.492)	1.180 (0.610)
	31–55	0.419	0.419	0.419	0.316	0.316	0.316
	56–90	0.155	0.155	0.155	0.077	0.077	0.077
	91–160	0.105	0.105	0.105	0.073	0.073	0.073
n_f[b]	0–10	0.83	0.92	0.92	0.85	0.99	0.80
	11–30	0.83	0.92	0.92	0.85	0.99	0.80
Degradation							
DT_{50} (days)	0–10[c]	38.6	51.3 (10.3)	67.6 (16.9)	49.3	93.9 (18.8)	91.7 (22.9)
	11–30	38.6	51.3 (10.3)	67.6 (16.9)	49.3	93.9 (18.8)	91.7 (22.9)
	31–55	77.2	102.6 (20.5)	135.2 (33.8)	98.6	187.8 (37.6)	183.4 (45.9)
	56–100	128.7	171.0 (34.2)	225.3 (56.3)	164.3	313.0 (62.6)	305.7 (76.4)
	101–160[d]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Q_{10}[e]		2.3	1.9	2.8	2.3	2.3	2.5
TRESP (K^{-1})[f]		0.083	0.064	0.103	0.083	0.083	0.092
Other characteristics							
DISP (cm^2 day^{-1})[g]		2.5	2	2.5	2.5	2	2.5
DV (cm)[g]		10	12	10	10	12	10

[a] From laboratory experiments with control and amended soil samples taken *in situ* (Carpio et al., 2020). Values in brackets correspond to calibrated values for PRZM and/or MACRO models (see Section 3.1).
[b] Freundlich exponents from laboratory experiments with the unamended control S, and amended with SMS- and GC soils at laboratory scale (García-Delgado et al., 2020). The n_f values as determined in the top 30 cm of S were used for S, S + SMS and S + GC in 31–160 cm depth.
[c] From laboratory experiments with unamended control and amended soil samples taken *in situ* at 6 °C and 40% of the maximum soil water holding capacity (Marín-Benito et al., 2019). Variation of the degradation rate k (k (d^{-1}) = ln (2) / DT_{50}) with depth: k for 0–30 cm, k × 0.5 for 30–60 cm, k × 0.3 for 60–100 cm, k = 0 for >100 cm (FOCUS, 2000). Values in brackets correspond to calibrated values for PRZM model.
[d] n.d. = no degradation.
[e] From Marín-Benito et al. (2019).
[f] Estimated from TRESP = (ln Q_{10}) / 10.
[g] Fitted manually from the observed Br^- concentrations.

2.5. Evaluation of models performance

The performance of the models was evaluated by calculating four statistical indices: the efficiency (*EF*), the coefficient of residual mass (*CRM*), the Pearson correlation coefficient (*r*), and the root mean square error (*RMSE*) (Smith et al., 1996).

$$EF = 1 - \left[\sum_{i=1}^{n}(S_i - O_i)^2 / \sum_{i=1}^{n}(O_i - O_m)^2\right] \tag{1}$$

$$CRM = \left(\sum_{i=1}^{n} O_i - \sum_{i=1}^{n} S_i\right) / \sum_{i=1}^{n} O_i \tag{2}$$

$$r = \sum_{i=1}^{n}(O_i - O_m) \times (S_i - S_m) / \left[\sum_{i=1}^{n}(O_i - O_m)^2\right]^{1/2} \times \left[\sum_{i=1}^{n}(S_i - S_m)^2\right]^{1/2} \tag{3}$$

$$RMSE = (100/O_m)\left[\sum_{i=1}^{n}(S_i - O_i)^2 / n\right]^{1/2} \tag{4}$$

where O_i and S_i are the observed and simulated values, respectively, O_m and S_m are the mean observed and simulated values, respectively, and n is the number of data. The optimum value of *EF* and *r* is +1, and that of RMSE and *CRM* is zero. If *CRM* > 0 (<0), then there is an under(over)estimation of observed values.

3. Results and discussion

3.1. Models calibration

The models calibration was done in two steps. First, the coefficients describing the dispersive characteristics (DV and DISP) of the soils were manually fitted from the observed Br^- concentrations over the calibration period (Table 3). Previous studies have shown the key role of the dispersion coefficients on the simulation of pesticides leaching (Boesten, 2004; Marín-Benito et al., 2015). Second, once the dispersion coefficients were optimized for each soil treatment, the K_d and DT_{50} of chlorotoluron and flufenacet were calibrated to minimize the marked overestimation of their retention in the 0–10 cm soil layer as simulated by PRZM and MACRO (results not shown). This essential calibration step is consistent with the findings of Dubus et al. (2003) who showed that K_d and DT_{50} were two of the most influential parameters in predicting pesticide losses with these models. The calibration of K_d and DT_{50} was different for each soil treatment, herbicide and model. While experimental K_d and DT_{50} values of both herbicides were directly used to simulate their mobility in unamended control soil with PRZM and MACRO, both coefficients had to be calibrated in SMS- and GC-amended soils for

Fig. 1. Observed and simulated soil water contents in 0–20, 20–40, 40–60, 60–80 and 80–100 cm soil layers of the unamended control (S), SMS- and GC-amended (S + SMS and S + GC) soils over the whole experimental period (29 November 2016 to 30 November 2018). Error bars represent the standard deviation of mean observed values of plots treated (n = 3).

PRZM modelling. For MACRO simulations, only the experimental K_d values of chlorotoluron, as determined on the amended soils, were calibrated.

The calibration of K_d and DT_{50} was carried out considering that the dissolved organic carbon (DOC) of the SMS and GC amendments decreased the effective sorption of the herbicides on the soil, enhancing their bioavailability for degradation and their transport along the amended soil profiles (Barriuso et al., 2011; Briceño et al., 2008; Carpio et al., 2020; Marín-Benito et al., 2014a). Quantitatively, the calibration was done from the "DOC of SMS- or GC-amended soil/DOC of unamended soil" ratio at the first application date of the herbicides (Table 3). This calibration assumes that the role of the soil endogenous OC in chlorotoluron and flufenacet sorption was small compared to that of the DOC (Carpio et al., 2020). However, it should be noted that this assumption is right for soils with low endogenous OC contents like ours (Table 1) while it should be tested for soils with higher native OC contents. Jarvis et al. (2000) also severely underpredicted the field dissipation of bentazone herbicide in a soil amended with pig slurry and green manure from yellow mustard, using parameterization based on laboratory measurements of degradation. This discrepancy can be explained by (i) different microbial activity in the laboratory degradation experiments compared to that of the undisturbed population activity in the

Table 4
Goodness-of-fit statistics for PRZM and MACRO modelling of the soil water content (θ), and vertical distribution of Br-, chlorotoluron and flufenacet in unamended control (S), SMS- and GC-amended (S + SMS and S + GC) soil profiles for the whole simulated period (29 November 2016 to 30 November 2018). EF: Efficiency, CRM: Coefficient of residual mass, r: Pearson correlation coefficient, RMSE: Root mean square error.

	PRZM				MACRO			
	EF (−)	CRM (−)	r (−)	RMSE (%)	EF (−)	CRM (−)	r (−)	RMSE (%)
S								
θ	0.18	0.00	0.74	17.9	0.84	0.00	0.92	8.04
Br^-	0.92	0.03	0.96	55.1	0.90	0.26	0.96	61.5
Chlorotoluron	0.78	−0.38	0.91	126	0.91	0.19	0.96	80.4
Flufenacet	0.82	−0.27	0.93	108	0.85	0.28	0.93	99.4
S + SMS								
θ	−0.93	−0.09	0.54	22.0	0.67	−0.02	0.85	9.07
Br^-	0.94	0.00	0.97	54.6	0.91	−0.07	0.96	66.0
Chlorotoluron	0.85	−0.07	0.93	127	0.86	−0.05	0.93	126
Flufenacet	0.88	0.06	0.94	95.2	0.94	0.07	0.97	69.4
S + GC								
θ	−0.74	−0.08	0.62	22.3	0.71	−0.02	0.87	9.14
Br^-	0.92	−0.05	0.96	60.7	0.91	−0.25	0.97	64.9
Chlorotoluron	0.85	−0.20	0.92	129	0.88	−0.05	0.94	116
Flufenacet	0.83	0.03	0.91	114	0.96	0.08	0.98	58.6

field, (ii) significant herbicide dissipation pathways in the field that are not observed under laboratory conditions and are not included in the model code. But it has to be underlined that they did not calibrate the DT_{50} from DOC. On the other hand, Vereecken et al. (2011) concluded that K_d values from laboratory batch experiments are not representative of the field conditions. These results corroborate the need to calibrate K_d and DT_{50}, when they are measured in laboratory, to model field conditions.

3.2. Modelling of soil water content in soil profiles

Over the whole experiment, the addition of organic residues was found to increase the soil water holding capacity in the 0–20 cm soil layer, following the order S < S + GC < S + SMS (Table 1; Fig. 1). The higher soil moisture together with the higher OC content of amended soils led to higher soil fertility and, consequently, to higher crop-growing performance (Table 2). As a result, water and solute dynamics in the amended soil profiles below 20 cm depth were modified compared to those observed in the unamended control plots (Carpio et al., 2020) (Fig. 1). The increased fertility and capacity of amended soils to retain water has been often cited as some of the great benefits of this agricultural practice (García Izquierdo and Lobo Bedmar, 2008).

In any case, *i.e.* amended and unamended soils, MACRO successfully simulated the observed soil water contents at the five different soil depths for the whole simulated period (29 November 2016–30 November 2018), as shown by the high values of r (0.85 to 0.92) and EF (0.67 to 0.84), and the low values of RMSE (<9.14) and CRM (−0.02 to 0.00) (Table 4). According to Ritter and Muñoz-Carpena (2013), the performance of a model is unsatisfactory if EF < 0.65, acceptable if 0.65 < EF < 0.80, good if 0.80 < EF < 0.90, or very good if EF ≥ 0.90. Therefore, the performance of MACRO to simulate the soil water content can be denoted as acceptable for S + SMS and S + GC, and good for unamended soil S. On the contrary, PRZM did not predict satisfactorily the water dynamics along the soil profiles. The best simulation results were obtained in the wheat root influence zone (0–20 cm) for the three soil treatments (Fig. 1). At this depth, the observed fluctuations of soil moisture linked to precipitation events were well described by the model. However, in the absence of rainfall, PRZM overestimated the evapotranspiration, and the simulated soil water content corresponded to the wilting point (Fig. 1; Fig. S1). Below 20 cm depth, PRZM predicted that the water contents of control and amended soils were most of the time at field capacity. Indeed, there is no sink for water under the maximum root depth (21 cm), and consequently PRZM simulated soil moistures at field capacity once it was reached. Nevertheless, the values of some statistical indexes were acceptable (Table 4), probably because of compensation between PRZM underestimation and overestimation of the observations as a function of the depth and/or of the period. The inability of capacity models such as PRZM to represent the soil moisture with an acceptable goodness-of-fit has often been observed (Gottesbüren et al., 2000; Marín-Benito et al., 2014b; Vanclooster and Boesten, 2000). Due to these differences between soil water content observations and simulations, and to the influence of soil moisture content on the herbicide degradation rate, PRZM might not be able to simulate herbicide leaching.

3.3. Modelling of bromide distribution in control and amended soil profiles

Following dispersion coefficients fitting, the ability of the models to simulate the Br^- behavior (peak concentrations and maximum depths reached by the tracer) was very good (Ritter and Muñoz-Carpena, 2013), and similar for the three soils treatments as showed by the narrow ranges of variation of each statistical index (0.96 < r < 0.97, 0.90 < EF < 0.94, 54.6 < RMSE <66.0) (Figs. 2 and 3; Figs. S2 and S3; Table 4). The main difference between the simulation results of the different treatments is that PRZM and MACRO underestimated (CRM > 0) the observed Br^- concentrations in the unamended soil profile while these concentrations were, in general, overestimated (CRM ≤ 0) in S + SMS and S + GC profiles. For the three treatments, the leached amounts of Br^- followed the rainfall regimes (Figs. 2 and 3; Figs. S1 to S3): low Br^- amounts (<1.0 to 2.6% of the amount applied) leached down to 100 cm depth over the first period (273.2 mm of cumulated precipitation) while high amounts (from 16 to 20%) of Br^- did so over the second period (525.4 mm, 2.5 times that of the first period) (Carpio et al., 2020) (Figs. S1 to S3).

The fitted dispersivity (DV for MACRO) and hydrodynamic dispersion (DISP for PRZM) values were similar for unamended soil and S + GC treatments, but different than those obtained for S + SMS (Table 3). This can be due to different soil saturation degrees as simulated by PRZM and MACRO in S + SMS compared to unamended and S + GC soils. The DV value fitted for unamended soil is in agreement with the dispersivity values reviewed for coarse-textured soils under field conditions by Vanderborght and Vereecken (2007). Regarding amended soil, Chalhoub et al. (2013) estimated larger dispersivity values for a control bare soil than for a soil amended with urban wastes composts of different nature under field conditions. However, in undisturbed silt loam soil columns, Pot et al. (2011) found no statistically significant effect of compost application on solute hydrodynamic dispersion, which agrees with our results despite they were obtained in field conditions. Finally, though Vanderborght and Vereecken (2007) observed that dispersion coefficients strongly depend on soil saturation conditions (there are larger dispersivities for saturated than for unsaturated flow conditions), the resulting DV and DISP calibrated values can be considered optimum for simulations under both wet and dry climatic conditions as those recorded in our field experiment.

3.4. Modelling of herbicides distribution in control and amended soil profiles

By increasing the soil OC content, the addition of SMS and GC amendments enhanced the herbicides sorption in the top 20 cm and decreased their downward mobility, which was also favoured by the increase in the soil water retention (see Section 3.2) (Figs. 4 to 7; Figs. S4 to S7). This effect was mainly observed for flufenacet, the most hydrophobic herbicide, whose mobility was slower than that of chlorotoluron. A high mobility of chlorotoluron through the three soil profiles was observed after the first application: the herbicide was detected in the whole control, SMS- and GC-amended soil profiles 33 days after its application because of the rainfall events occurring shortly after the application (Carpio

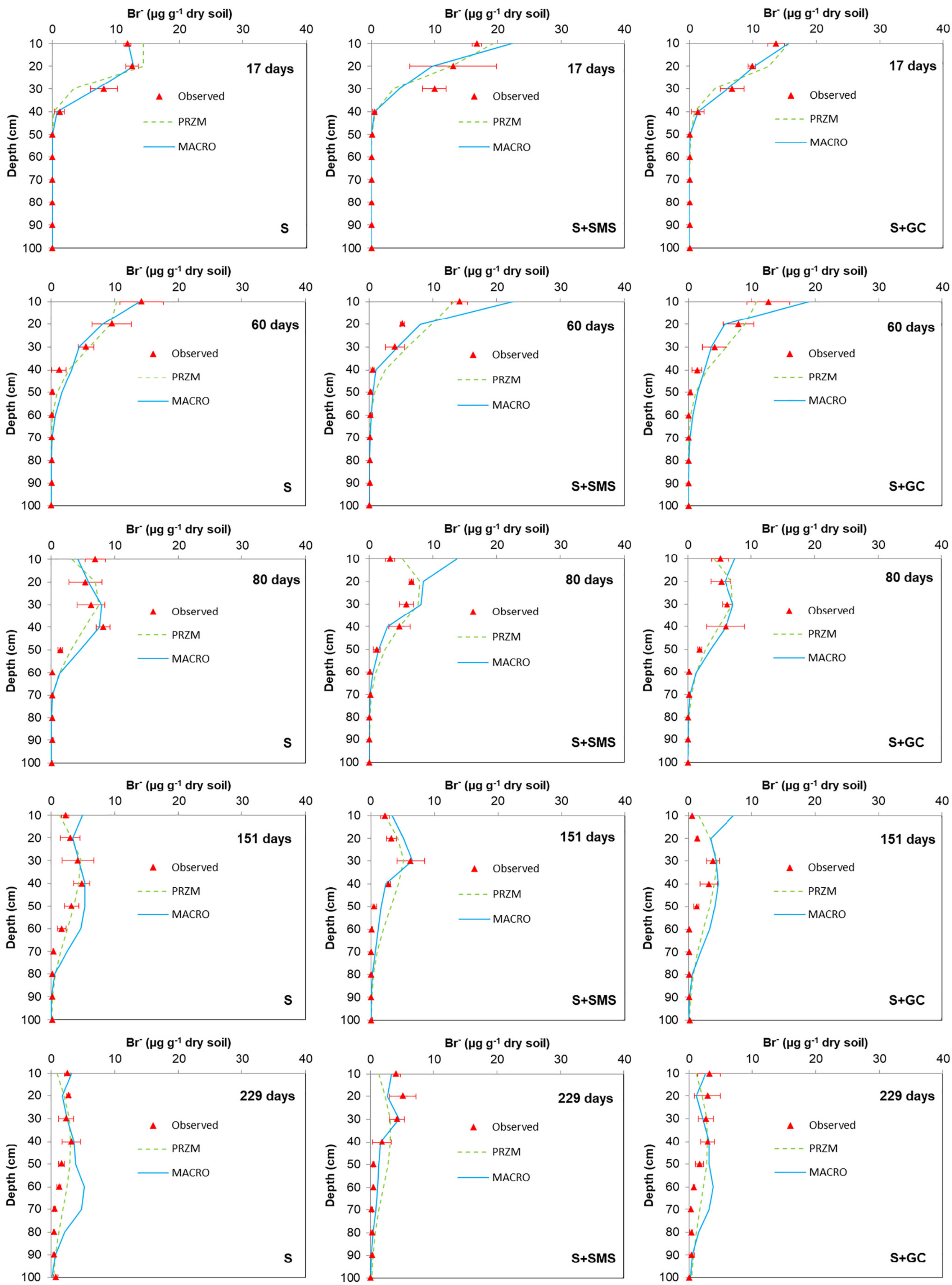


Fig. 2. Observed and simulated distribution in the unamended control (S), SMS- and GC-amended (S + SMS and S + GC) soils profiles of bromide (Br^-) at selected sampling times after the first bromide application (calibration period: 29 November 2016 to 12 November 2017). Error bars represent the standard deviation of mean observed values of plots treated (n = 3).

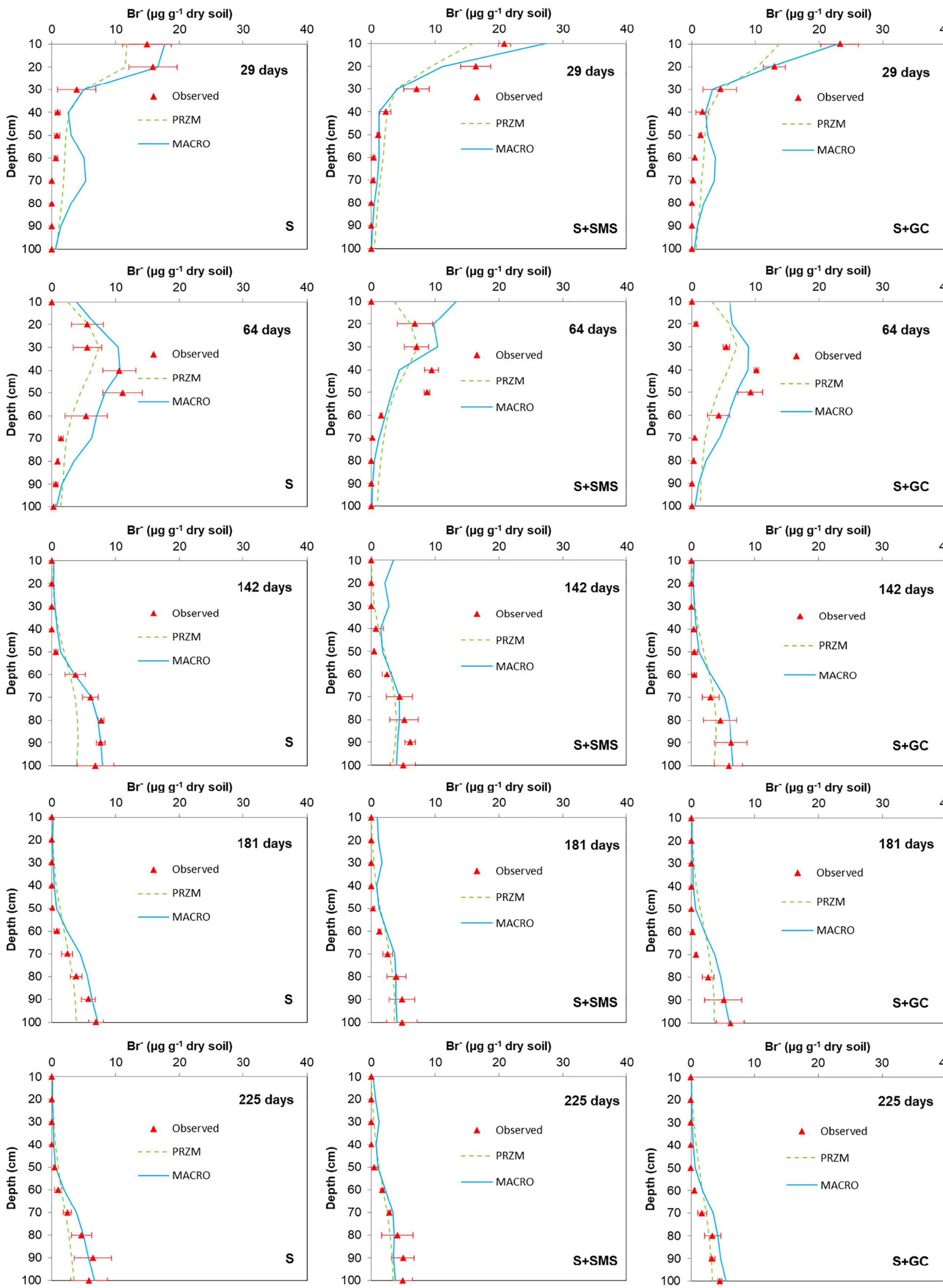


Fig. 3. Observed and simulated distribution in the unamended control (S), SMS- and GC-amended (S + SMS and S + GC) soils profiles of bromide (Br^-) at selected sampling times after the second bromide application (test period: 13 November 2017 to 30 November 2018). Error bars represent the standard deviation of mean observed values of plots treated (n = 3).

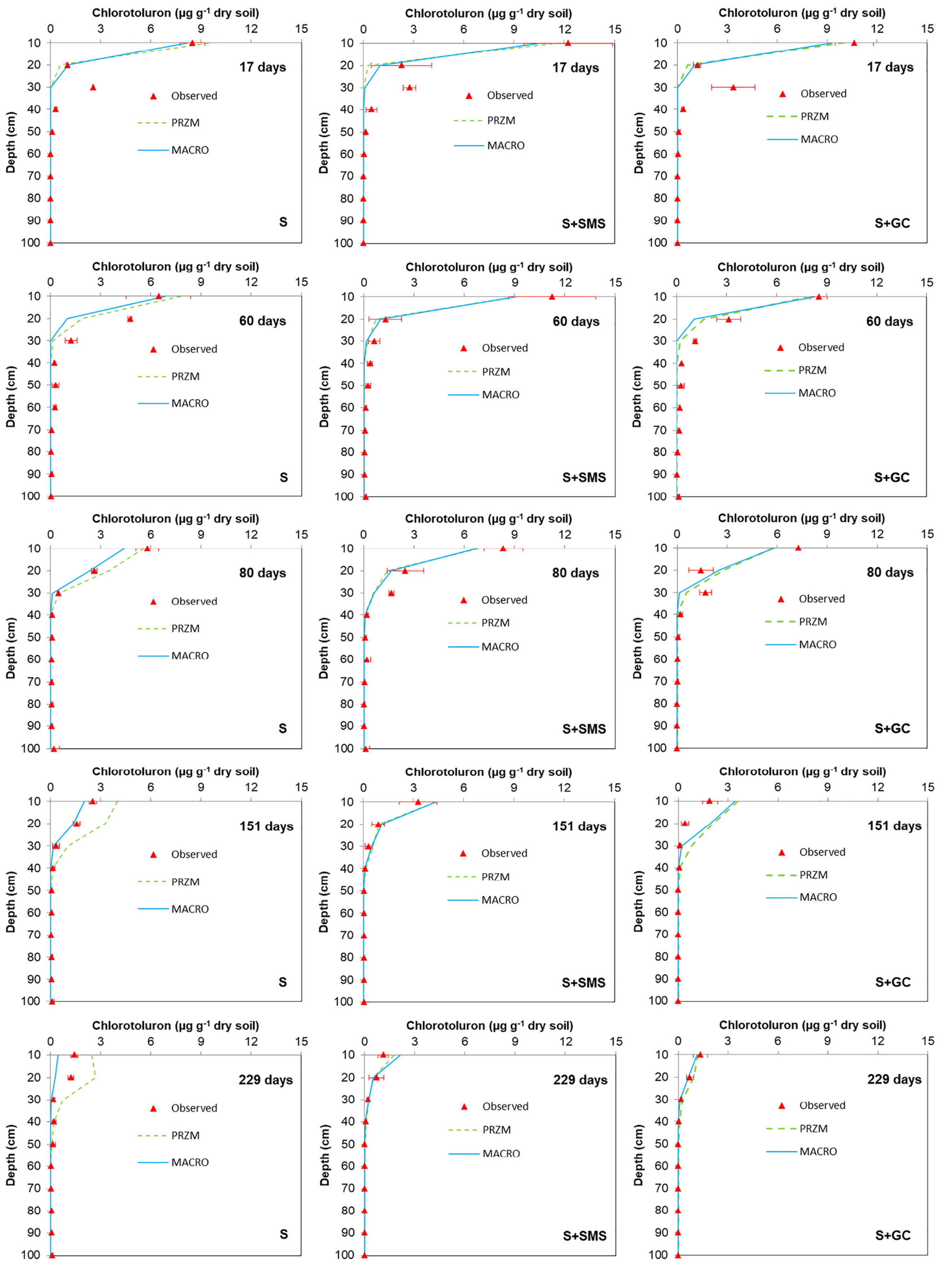


Fig. 4. Observed and simulated distribution in the unamended control (S), SMS- and GC-amended (S + SMS and S + GC) soils profiles of chlorotoluron at selected sampling times after the first herbicide application (calibration period: 29 November 2016 to 12 November 2017). Error bars represent the standard deviation of mean observed values of plots treated (n = 3).

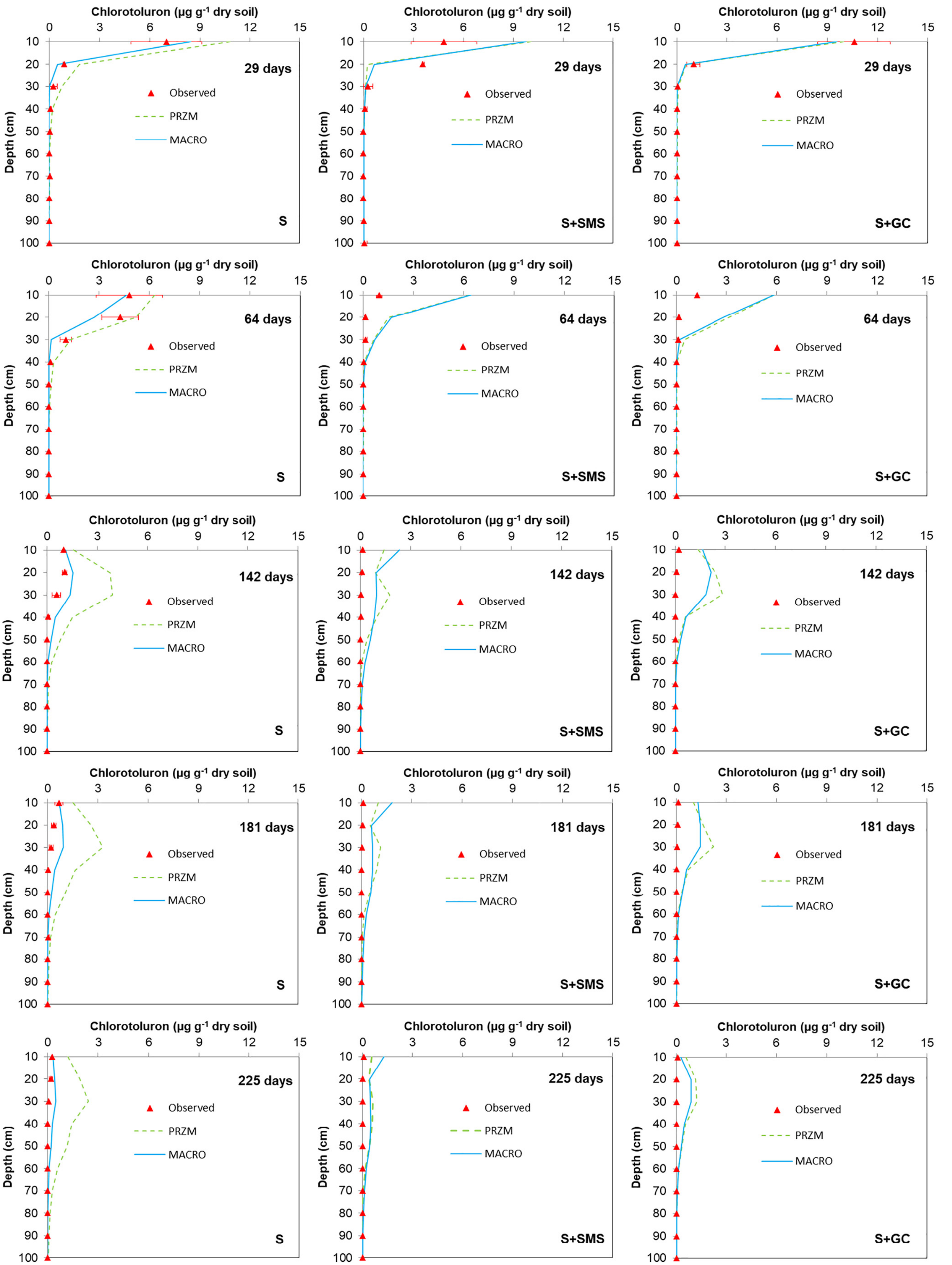


Fig. 5. Observed and simulated distribution in the unamended control (S), SMS- and GC-amended (S + SMS and S + GC) soils profiles of chlorotoluron at selected sampling times after the second herbicide application (test period: 13 November 2017 to 30 November 2018). Error bars represent the standard deviation of mean observed values of plots treated (n = 3).

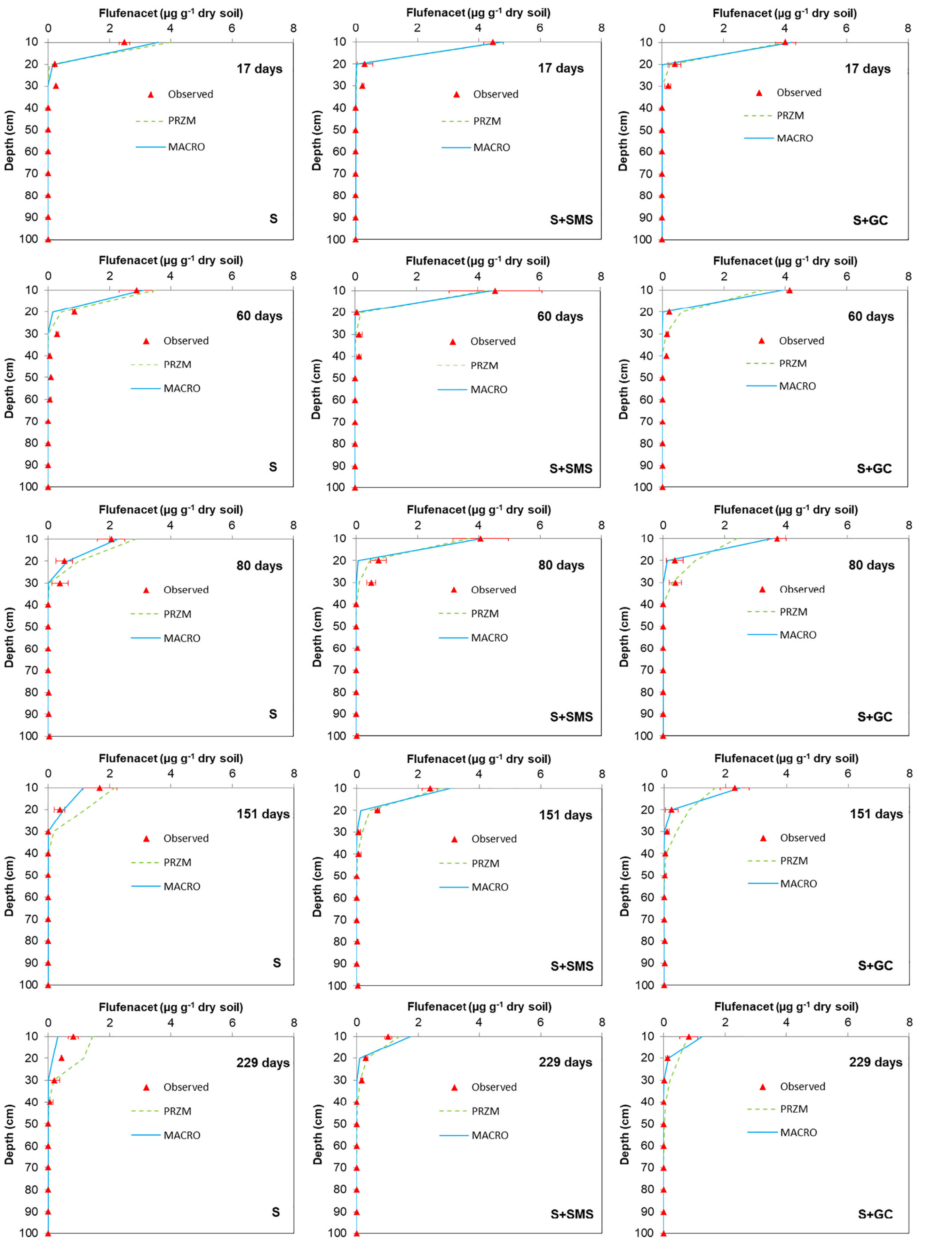


Fig. 6. Observed and simulated distribution in the unamended control (S), SMS- and GC-amended (S + SMS and S + GC) soils profiles of flufenacet at selected sampling times after the first herbicide application (calibration period: 29 November 2016 to 12 November 2017). Error bars represent the standard deviation of mean observed values of plots treated (n = 3).

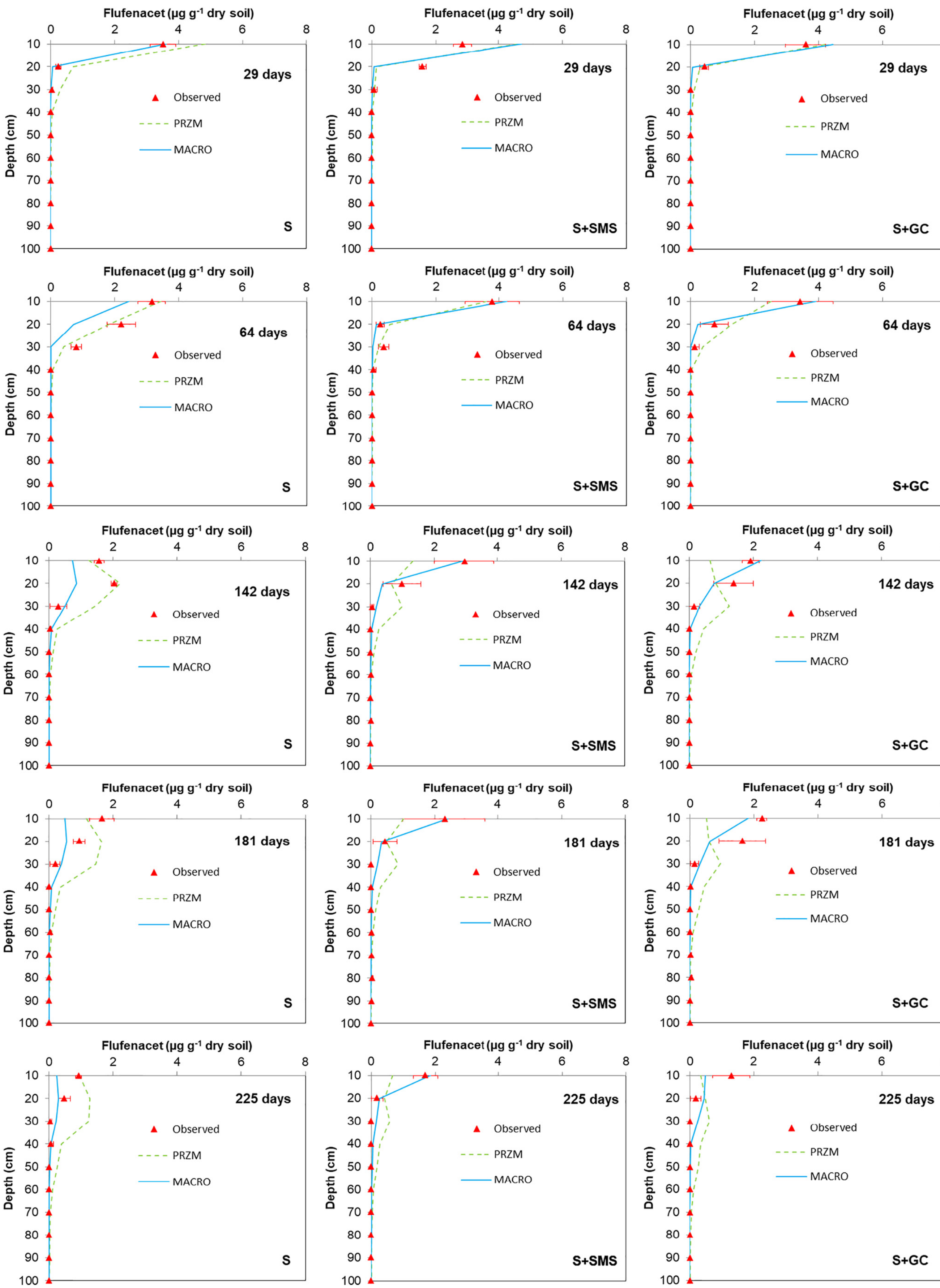


Fig. 7. Observed and simulated distribution in the unamended control (S), SMS- and GC-amended (S + SMS and S + GC) soils profiles of flufenacet at selected sampling times after the second herbicide application (test period: 13 November 2017 to 30 November 2018). Error bars represent the standard deviation of mean observed values of plots treated (n = 3).

et al., 2020) (Fig. S1a and S4). On the contrary, flufenacet needed 33, 80 and 151 days to reach the 90–100 cm soil layer in S + SMS, control and S + GC soils, respectively. The amounts of chlorotoluron (≈1.0 to 2.0%) and flufenacet (<1.0 to 1.3%) that leached down to a depth of 90–100 cm in the three treatments over the first experimental period were higher than those observed in the second period. In this second period, only residual amounts of both herbicides (<1.0%) reached 100 cm depth in the treatment with the highest DOC content, S + SMS, that would have enhanced the transport of chlorotoluron and flufenacet to this depth 29 and 127 days after the second application, respectively (Carpio et al., 2020). In control soil and S + GC, chlorotoluron reached maximum depths of 70 cm and 30 cm, respectively, and no flufenacet was detected below 60 cm and 80 cm, respectively. This behavior might be unexpected as higher rainfall was recorded during the second period of experimentation than in the first one (Fig. S1). However, it indicates that the rainfall events which occurred shortly after the first herbicide applications played a more important role in their high mobility than the high total amounts of rainfall recorded over the second period of experimentation (Willkommen et al., 2019).

Once the degradation and/or sorption coefficients were calibrated, the two models reproduced satisfactorily the observed mobility of both herbicides through the three soil profiles over the whole simulation period (Table 4, Figs. 4–7 and S4–S7). As indicated above, this shows that DOC drives the movement of pesticides (Barriuso et al., 2011; Briceño et al., 2008; Carpio et al., 2020; Marín-Benito et al., 2014a). Nevertheless, MACRO simulated the vertical distribution of chlorotoluron and flufenacet better than PRZM (Table 4). The correspondence between observations and PRZM simulations was acceptable for both herbicides ($0.78 < EF_{Chlorotoluron} < 0.85$, $0.82 < EF_{Flufenacet} < 0.88$) while it was good and very good for MACRO ($0.86 < EF_{Chlorotoluron} < 0.91$, $0.85 < EF_{Flufenacet} < 0.96$) (Ritter and Muñoz-Carpena, 2013). The lowest performance of PRZM to reproduce the herbicides mobility agrees with its poor simulations of the water dynamics, especially in the amended soil profiles (Table 4, Fig. 1). It is important to highlight that the experimental DT_{50} values of the herbicides in the amended soils, which depends on the soil moisture, had to be calibrated only for PRZM (Table 3). Marín-Benito et al. (2014b) also obtained a better fit of the dynamics of other herbicides with models based on the Richards equation (MACRO and PEARL) than with the PRZM capacity model.

The results also showed that the EF of both models for herbicides concentrations decreased over the test period compared to the calibration one. This decrease in EF was higher for PRZM than for MACRO: from 0.90–0.98 to 0.51–0.88, and from 0.90–0.99 to 0.54–0.93, respectively (data not shown). It was more outstanding for chlorotoluron than for flufenacet, and especially in the S + SMS treatment. This is in agreement with the highest DOC content in S + SMS (Table 1), and with the high influence of this parameter on the mobility of the less hydrophobic herbicide chlorotoluron (Carpio et al., 2020) that could not have been perfectly taken into account through the calibration step. In a previous modelling study with PRZM, including two SMS with different DOC contents and two fungicides with very different hydrophobicities, Marín-Benito et al. (2015) also determined the lowest EF values for the less hydrophobic fungicide in the soil which was the richest one in DOC. The decrease in EF could result from the variation of pesticide sorption in amended soils with the natural decay of soil OM load by mineralization (Marín-Benito et al., 2012). However, in our study, the variation of OC contents in the amended topsoils over time was negligible (Carpio et al., 2020), and consequently it was not taken into account in models parameterization.

According to the CRM values (Table 4), MACRO underestimated (CRM > 0) the observed concentrations of the two herbicides in the unamended soil profile while PRZM overestimated them (CRM < 0). In the amended soils, both models overestimated chlorotoluron concentrations whereas those of flufenacet were underestimated. The overestimation of the vertical distribution of chlorotoluron in the S + SMS and S + GC profiles as simulated by both models was mainly marked in the test period when the highest DOC contents in the amended soil profiles were observed (Fig. 5 and S5) (Carpio et al., 2020). Processes linked to the higher DOC content of amended soils and not described in PRZM and MACRO could have facilitated the bioavailability of chlorotoluron in solution to be mineralized (EC, 2005) and/or degraded by soil microorganisms. Among these processes, the formation of herbicide-DOC mobile complexes has been observed for chlorotoluron and other phenylurea herbicides in presence of high DOC amounts (Song et al., 2008; Thevenot et al., 2009). The limits underlined here are some of the well-known limits affecting pesticide leaching models, as shown at field and laboratory scales (Mamy et al., 2008; Marín-Benito et al., 2015; Thevenot and Dousset, 2015).

4. Conclusions

The ability of PRZM and MACRO models to simulate the fate of chlorotoluron and flufenacet herbicides under amended soils was assessed and compared. The models were calibrated and tested based on a two-year field-scale leaching study carried out in experimental plots without amendment, and with spent mushroom substrate (SMS) and green compost (GC) amendments. Both models successfully predicted the vertical distribution of Br^-, chlorotoluron and flufenacet along the three soil profiles. In general, MACRO showed a higher performance than PRZM, which did not simulate satisfactorily the water dynamics. The needed calibration of K_d and DT_{50} parameters was based on the initial DOC contents of control and amended soils, because DOC is known to drive some processes that modify the behavior of pesticides (*e.g.* formation of herbicide-DOC mobile complexes), however they are not considered in the models.

PRZM and MACRO could be successfully used as predictive tools against groundwater contamination by herbicides in amended soils, at least at a bi-annual scale, after calibrating DT_{50} and/or K_d. The results also emphasize the need of modelling the pesticide fate in amended soil scenarios in the regulatory context. However, as the calibration of pesticide parameters is not possible when these models are used for risk assessment for European pesticides registration, a module allowing to correct the DT_{50} and K_d values according to the DOC of the amended soils should be added. Finally, due to the decrease in models efficiency with simulation time (mainly for PRZM) to predict the herbicides mobility in the amended soils, they should be tested for longer periods.

This work showed that models such as PRZM and MACRO are able to simulate the fate of pesticides in amended soils, and it serves as a first step in identifying where future modelling efforts might most profitably be directed. In this sense, further modelling studies should focus on other pedoclimatic and pesticide-organic residues combinations, and for longer time periods. Then, the models will help to optimize the application rates of organic wastes to avoid water pollution.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was financially supported by MINECO/FEDER UE (Project AGL2015-69485-R) and MCIU/AEI/FEDER, UE (Project RTI2018-101587-J-I00). M. J. Carpio thanks for her predoctoral contract co-funded by European Social Fund (ESF) and the Consejería de Educación (Junta de Castilla y León Government). J.M. Marín-Benito thanks MINECO for his Juan de la Cierva-Incorporación (IJCI-2014-19538) contract.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.137019.

References

Barriuso, E., Andrades, M.S., Benoit, P., Houot, S., 2011. Pesticide desorption from soils facilitated by dissolved organic matter coming from composts: experimental data and modelling approach. Biogeochemistry 106, 117–133.

Boesten, J.J.T.I., 2004. Influence of dipersion length on leaching calculated with PEARL, PELMO and PRZM for FOCUS groundwater scenarios. Pest Manag. Sci. 60, 971–980.

Boesten, J.J.T.I., Van der Pas, L.J.T., 2000. Movement of water, bromide and the pesticides ethoprophos and bentazone in a sandy soil: the Vredepeel data set. Agric. Water Manag. 44, 21–42.

Briceño, G., Demanet, R., Mora, M.D., Palma, G., 2008. Effect of liquid cow manure on andisol properties and atrazine adsorption. J. Environ. Qual. 37, 1519–1526.

Carpio, M.J., Rodríguez-Cruz, M.S., García-Delgado, C., Sánchez-Martín, M.J., Marín-Benito, J.M., 2020. Mobility monitoring of two herbicides in amended soils: a field study for modeling applications. J. Environ. Manag. 260, 110161. https://doi.org/10.1016/j.jenvman.2020.110161 (In Press).

Carsel, R., Imhoff, J., Hummel, P., Cheplick, J., Donigian, A., Suarez, L., 2005. PRZM-3, a Model for Predicting Pesticide and Nitrogen Fate in the Crop Root and Unsaturated Soil Zones: User's Manual for Release 3.12.2. US Environ. Prot. Agency (EPA) (420 pp).

Chalhoub, M., Coquet, Y., Vachier, P., 2013. Water and bromide dynamics in a soil amended with different urban composts. Vadose Zone J. 12.

Chen, Y., Camps-Arbestain, M., Shen, Q., Singh, B., Cayuela, M.L., 2018. The long-term role of organic amendments in building soil nutrient fertility: a meta-analysis and review. Nutr. Cycl. Agroecosyst. 111, 103–125.

Dubus, I.G., Brown, C.D., Beulke, S., 2003. Sensitivity analyses for four pesticide leaching models. Pest Manag. Sci. 59, 962–982.

EC (European Commission. Directorate-General Health & Consumer Protection), 2005. Review Report for the Active Substance Chlorotoluron (54 pp.).

Filipović, V., Coquet, Y., Pot, V., Houot, S., Benoit, P., 2014. Modeling the effect of soil structure on water flow and isoproturon dynamics in an agricultural field receiving repeated urban waste compost application. Sci. Total Environ. 499, 546–559.

FOCUS (FOrum for Co-ordination of pesticide fate models and their Use), 2000. FOCUS Groundwater Scenarios in the EU Review of Active Substances. Report of the FOCUS Groundwater Scenarios Workgroup EC Document Reference Sanco/321/ 2000 Rev.2 (202 pp.).

FOCUS (FOrum for Co-ordination of pesticide fate models and their Use), 2009. Assessing Potential for Movement of Active Substances and Their Metabolites to Ground Water in the EU. Report of the FOCUS Groundwater Workgroup EC Document Reference Sanco/13144/2010 Version 1 (604 pp.).

García Izquierdo, C., Lobo Bedmar, M.C., 2008. Rehabilitación de suelos degradados y contaminados mediante la aplicación de compost. In: Moreno Casco, J., Moral Herrero, R. (Eds.), Compostaje. Mundi Prensa, Madrid, pp. 425–448.

García-Delgado, C., Marín-Benito, J.M., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., 2020. Organic carbon nature determines the capacity of organic amendments to adsorb pesticides in soil. J. Hazard. Mater., 122162 https://doi.org/10.1016/j.jhazmat.2020.122162 (In press).

Ghirardello, D., Morselli, M., Semplice, M., Di Guardo, A., 2010. A dynamic model of the fate of organic chemicals in a multilayered air/soil system: development and illustrative application. Environ Sci Technol 44, 9010–9017.

Giannouli, D.D., Antonopoulos, V.Z., 2015. Evaluation of two pesticide leaching models in an irrigated field cropped with corn. J. Environ. Manag. 150, 508–515.

Gottesbüren, B., Aden, K., Bärlund, I., Brown, C., Dust, M., Görlitz, G., Jarvis, N., Rekolainen, S., Schäfer, H., 2000. Comparison of pesticide leaching models: results using the Weiherbach data set. Agric. Water Manag. 44, 153–181.

Herrero-Hernández, E., Andrades, M.S., Marín-Benito, J.M., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., 2011. Field-scale dissipation of tebuconazole in a vineyard soil amended with spent mushroom substrate and its potential environmental impact. Ecotox. Environ. Safe. 74, 1480–1488.

Houot, S., Pons, M.N., Pradel, M., Tibi, A. (coord.)., Aubry, C., Augusto, L., Barbier, R., Benoit, P., Brugère, H., Caillaud, M.A., Casellas, M., Chatelet, A., Dabert, P., De Mareschal, S., Doussan, I., Etrillard, C., Fuchs, J., Génermont, S., Giamberini, L., Hélias, A., Jardé, E, Le Perchec, S., Lupton, S., Marron, N., Ménasseri, S., Mollier, A., Morel, C., Mougin, C., Nguyen, C., Parnaudeau, V., Patureau, D., Pourcher, A.M., Rychen, G., Savini, I., Smolders, E., Topp, E., Vieublé, L., Viguié, C., 2014. Valorisation des matières fertilisantes d'origine résiduaire sur les sols à usage agricole ou forestier, impacts agronomiques, environnementaux, socio-économiques. Expertise scientifique collective, rapport, INRA-CNRS-Irstea (France). [http://institut.inra.fr/Missions/Eclairer-les-decisions/Expertises/Toutes-les-actualites/Expertise-Mafor-effluents-boues-et-dechets-organiques]. (930 pp.).

Hughes, L., Webster, E., Mackay, D., 2008. An evaluative screening level model of the fate of organic chemicals in sludge-amended soils including organic matter degradation. Soil Sediment Contam. 17, 564–585.

IUSS Working Group WRB, 2015. World Reference Base for Soil Resources 2014: International Soil Classification Systems for Naming Soils and Creating Legends for Soil Maps. World Soil Resources Reports No. 106. ISSN 0532-0488. FAO, Rome (181 pp.).

Jarvis, N.J., Brown, C.D., Granitza, E., 2000. Sources of error in model predictions of pesticide leaching: a case study using the MACRO model. Agric. Water Manag. 44, 247–262.

Klein, M., 1995. PELMO: Pesticide Leaching Model, User Manual V 2.01. Fraunhofer-Institut für Umweltchemie und Ökotoxikogie, p. D57392.

Kroes, J.G., Van Dam, J.C., Groenendijk, P., Hendriks, R.F.A., Jacobs, C.M.J., 2008. SWAP Version 3.2. Theory Description and User Manual. Alterra Report 1649, Swap32 Theory Description and User Manual (Wageningen, The Netherlands (262 pp.)).

Larsbo, M., Jarvis, N., 2003. MACRO 5.0. A Model of Water Flow and Solute Transport in Macroporous Soil. Technical Description. Rep Emergo, Swedish University of Agricultural Sciences, Uppsala, Sweden (49 pp.).

Leistra, M., van der Linden, A.M.A., Boesten, J.J.T.I., Tiktak, A., van den Berg, F., 2001. PEARL Model for Pesticide Behaviour and Emissions in Soil-Plant Systems: Description of the Processes. Alterra Rep 13. Wageningen University and Research Centre, Wageningen, The Netherlands (115 pp).

López-Piñeiro, A., Peña, D., Albarrán, A., Becerra, D., Sánchez-Llerena, J., 2013. Sorption, leaching and persistence of metribuzin in Mediterranean soils amended with olive mill waste of different degrees of organic matter maturity. J. Environ. Manag. 122, 76–84.

Mamy, L., Gabrielle, B., Barriuso, E., 2008. Measurement and modelling of glyphosate fate compared with that of herbicides replaced as a result of the introduction of glyphosate-resistant oilseed rape. Pest Manag. Sci. 64, 262–275.

Marín-Benito, J.M., Andrades, M.S., Rodríguez-Cruz, M.S., Sánchez-Martín, M.J., 2012. Changes in the sorption–desorption of fungicides over time in an amended sandy clay loam soil under laboratory conditions. J. Soils Sediments 12, 1111–1123.

Marín-Benito, J.M., Herrero-Hernández, E., Andrades, M.S., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., 2014a. Effect of different organic amendments on the dissipation of linuron, diazinon and myclobutanil in an agricultural soil incubated for different time periods. Sci. Total Environ. 476–477, 611–621.

Marín-Benito, J.M., Pot, V., Alletto, L., Mamy, L., Bedos, C., Barriuso, E., Benoit, P., 2014b. Comparison of three pesticide fate models with respect to the leaching of two herbicides under field conditions in an irrigated maize cropping system. Sci. Total Environ. 499, 533–545.

Marín-Benito, J.M., Rodríguez-Cruz, M.S., Sánchez-Martín, M.J., Mamy, L., 2015. Modeling fungicides mobility in undisturbed vineyard soil cores unamended and amended with spent mushroom substrates. Chemosphere 134, 408–416.

Marín-Benito, J.M., Barba, V., Ordax, J.M., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., 2018. Recycling organic residues in soils as amendments: effect on the mobility of two herbicides under different management practices. J. Environ. Manag. 224, 172–181.

Marín-Benito, J.M., Carpio, M.J., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., 2019. Previous degradation study of two herbicides to simulate their fate in a sandy loam soil: effect of the temperature and the organic amendments. Sci. Total Environ. 653, 1301–1310.

Moeys, J., Larsbo, M., Bergström, L., Brown, C.D., Coquet, Y., Jarvis, N.J., 2012. Functional test of pedotransfer functions to predict water flow and solute transport with the dual-permeability model MACRO. Hydrol. Earth Syst. Sci. 16, 2069–2083.

Pot, V., Benoit, P., Etievant, V., Bernet, N., Labat, C., Coquet, Y., Houot, S., 2011. Effects of tillage practice and repeated urban compost application on bromide and isoproturon transport in a loamy Albeluvisol. Eur. J. Soil Sci. 62, 797–810.

PPDB, 2019. Pesticide properties data base. University of Hertfordshire, UKhttp://sitem.herts.ac.uk/aeru/ppdb/en/index.htm.

Ritter, A., Muñoz-Carpena, R., 2013. Performance evaluation of hydrological models: statistical significance for reducing subjectivity in goodness-of-fit assessments. J. Hydrol. 480, 33–45.

Siimes, K., Kämäri, J., 2003. A review of available pesticide leaching models: selection of models for simulation of herbicide fate in Finnish sugar beet cultivation. Boreal Environ. Res. 8, 31–51.

Šimůnek, J., Van Genuchten, M.T., Šejna, M., 2008. Development and applications of the HYDRUS and STANMOD software packages and related codes. Vadose Zone J. 7, 587–600.

Smith, J., Smith, P., Addiscott, T., 1996. Quantitative methods to evaluate and compare soil organic matter (SOM) models. NATO ASI Series 38, 181–199.

Song, N.H., Chen, L., Yang, H., 2008. Effect of dissolved organic matter on mobility and activation of chlorotoluron in soil and wheat. Geoderma 146, 344–352.

Thevenot, M., Dousset, S., 2015. Compost effect on diuron retention and transport in structured vineyard soils. Pedosphere 25, 25–36.

Thevenot, M., Dousset, S., Hertkorn, N., Schmitt-Kopplin, P., Andreux, F., 2009. Interactions of diuron with dissolved organic matter from organic amendments. Sci. Total Environ. 407, 4297–4302.

Vanclooster, M., Boesten, J.J.T.I., 2000. Application of pesticide simulation models to the Vredepeel dataset. I. Water, solute and heat transport. Agric. Water Manag. 44, 105–117.

Vanderborght, J., Vereecken, H., 2007. Review of dispersivities for transport modeling in soils. Vadose Zone J. 6, 29–52.

Vereecken, H., Vanderborght, J., Kasteel, R., Spiteller, M., Schäffer, A., Close, M., 2011. Do lab-derived distribution coefficient values of pesticides match distribution coefficient values determined from column and field-scale experiments? A critical analysis of relevant literature. J. Environ. Qual. 40, 879–898.

Willkommen, S., Pfannerstill, M., Ulrich, U., Guse, B., Fohrer, N., 2019. How weather conditions and physico-chemical properties control the leaching of flufenacet, diflufenican, and pendimethalin in a tile-drained landscape. Agric. Ecosyst. Environ. 278, 107–116.

Wösten, J.H.M., Lilly, A., Nemes, A., Le Bas, C., 1999. Development and use of a database of hydraulic properties of European soils. Geoderma 90, 169–185.