



Research article

Recycling organic residues in soils as amendments: Effect on the mobility of two herbicides under different management practices



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ABSTRACT

The addition of organic residues to soil to increase its organic matter content is considered as a viable option for sustainable food production in soils sensitive to degradation and erosion. However, the recycling of these organic residues in agricultural soils needs to be previously appraised because they can modify the behaviour of pesticides when they are simultaneously applied in agricultural practices. This study evaluated the changes in the mobility and persistence of two herbicides, triasulfuron and prosulfocarb, after two repeated applications in field experimental plots in an unamended soil and one amended with green compost (GC) for seven months. Different factors were studied: i) soil without amendment (S), ii) soil amended with two doses of GC ($\sim 12 \text{ t C ha}^{-1}$, S + GC1 and 40 t C ha^{-1} , S + GC2), and iii) soils unamended and amended with different irrigation conditions: non-irrigated and with additional irrigation (2.8 mm per week). After the first application of herbicides, the results initially indicated no significant effects of soil treatments or irrigation conditions for triasulfuron mobility in agreement with the residual concentrations in the soil profile. The effect of irrigation was noted after one month of herbicide application and the effect of the soil treatment was significant after two months because the persistence of triasulfuron in S + GC2 was maintained until 50% of the applied amount. For prosulfocarb, the influence of soil amendment was significant for the initial persistence of the herbicide in S + GC2, higher than in S or S + GC1, in agreement with its adsorption constants for this soil. However, dissipation or leaching of the herbicide over time was not inhibited in this soil. After the repeated application of herbicides, the influence of the treatment of soils and/or irrigation was significant for the leaching and dissipation of both herbicides. The initial dissipation/degradation or leaching of herbicides was higher than after the first application, although persistence was maintained after five months of application in amended soils for triasulfuron and in unamended and amended soils for prosulfocarb. The results confirm that high doses of GC increased the persistence of both herbicides. This practice may offer the possibility of applying a tailored dose of GC to soil for striking a balance between residual concentrations and the soil agronomic effect.

1. Introduction

Management strategies are now being implemented for sustainable food production in soils susceptible to degradation and erosion. These strategies involve an increase in soil organic matter (OM) (Martins Gomes et al., 2018) because OM has a direct influence on the physical, chemical and microbiological properties of soils, and hence on soil fertility and plant development (Bastida et al., 2007; Tejada et al., 2009; Yazdanpanah et al., 2016). A possible option is the addition to the soil of amendments or organic wastes from different origins (urban, agricultural or industrial), which are currently generated in large quantities. The improvement in soil properties due to the OM content in these residues has been well documented, so its application as an

organic amendment in agriculture is a common practice (Aranda et al., 2015; Bastida et al., 2015; Ferreras et al., 2006; Tejada and Gonzalez, 2008). In addition, the application of organic wastes represents an opportunity to increase the soil capacity for carbon sequestration, especially lignocellulosic organic wastes (Castellano et al., 2015; Hernandez et al., 2017). These residues have a more recalcitrant or less biodegradable nature than other residues, albeit with greater affinity to bind to the soil's mineral particles, increasing the stable soil carbon pool when protected against decomposition (Nicolás et al., 2017).

After being composted, the plant residues generated in the pruning carried out in parks and gardens have an OM content > 15% on dry weight and could be considered a more stable source of soil OM than that provided by other more biodegradable residues such as biosolids or

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sewage sludge. However, the recycling of these organic residues in agricultural soils has to be previously evaluated because they can modify the behaviour of pesticides when they are simultaneously applied in agricultural practices (Herrero-Hernández et al., 2011). Organic residues can be effective tools for controlling soil and water pollution by pesticides, but the agronomic efficiency of these compounds could be decreased by changing their adsorption, mobility, persistence or bioavailability. In this sense, investigations are necessary before the implementation of these products in agricultural soils to optimize their use in pursuit of pollution control and/or the agronomic effect of pesticides. Some studies related to this subject are reported in the literature for different types of pesticides (Jiang et al., 2016; Marín-Benito et al., 2009a, 2009b; Tejada and Benítez, 2017). In general, these studies are carried out under laboratory conditions, being rarely conducted under field conditions for a more realistic approach to this issue (Herrero-Hernández et al., 2015; Stipičević et al., 2015).

The evaluation of the effect of organic amendments in soils with cereal crops and its possible incidence on the behaviour of simultaneously applied herbicides is of special interest. Cereals are among the most important crops in world agriculture, with Spain devoting over five million ha to this crop. It is one of the crops with the largest amount of active ingredients available to be used as herbicide, and the competition between weeds and the crop will depend on, among other factors, the conditions of the environment and the soil. Compounds of the chemical groups sulfonamide and thiocarbamate, such as triasulfuron and prosulfocarb, are usually recommended for individual or joint use for the control of weeds in rainfed and irrigated cereal crops since provide a good control of weeds (Bajya et al., 2015; Cirujeda and Taberner, 2010; Knežević et al., 2010; Mehmeti et al., 2018).

Triasulfuron (2-(2-chloroethoxy)-N-[[[4-methoxy-6-methyl-1,3,5-triazin-2-yl] amino] carbonyl] benzene sulfonamide) is a sulfonylurea with selective herbicide activity in the pre- and post-emergence control of broadleaf species in barley, oats and wheat. Triasulfuron has a high mobility in the soil due to its high solubility in water and low hydrophobicity (EC, 2000). Prosulfocarb (S-(phenylmethyl) dipropylcarbamothioate) is a systemic thiocarbamate with selective herbicide activity, being applied in early pre- and post-emergence against grasses and broadleaf weeds in crops such as long-cycle barley and wheat. It is a hydrophobic herbicide and has high adsorption, low mobility, and moderate persistence in soil (EFSA, 2007a).

In a previous work, we evaluated the behaviour of these herbicides, triasulfuron and prosulfocarb, in a short field experiment in an unamended soil and one amended with a low dose of green compost (GC) (Marín-Benito et al., 2018). The dissipation and mobility of herbicides were determined from concentrations obtained at various times in the soil surface and at different depths up to 50 cm. Variable effects of organic carbon (OC), dissolved organic carbon (DOC) from GC, soil water infiltration or formulation type (Logran[®], Auros[®] and Auros Plus[®]) on the adsorption/persistence and leaching of herbicides in the soil profile were observed. The interest of these results is sustained considering that the leaching of herbicides from the soil surface shortens the duration of residual weed control and may contaminate groundwater. Furthermore, the amounts retained in the soil profile could exceed the recorded threshold for the sensitivities of susceptible species. The results of previous experiments were obtained after a single application of these herbicides and a single dose of GC. However, in practice, herbicides could be applied repeatedly to the soil-crop system for weed control with different soil amendment doses, and these practices can alter their degradation rate and persistence in soil, making it difficult to forecast their environmental impact.

Considering there are no studies on prosulfocarb mobility in soils in the literature, while the mobility of triasulfuron has been evaluated at field and laboratory scale (Stork, 1995; Weber et al., 1999), although in no case have they been carried out on soils amended with organic wastes, it is deemed of interest to expand the study of the behaviour of both herbicides under broader conditions. Both herbicides are usually

applied as individual formulations or as a joint one when it comes to tackling a weed mixture. A good weed control of winter wheat (> 96.7%) has been reported with the herbicide combinations of prosulfocarb plus triasulfuron (Knežević et al., 2010).

Accordingly, the objective of this paper was to expand the study of the mobility of triasulfuron and prosulfocarb using a joint formulation (Auros Plus[®]) in an agricultural field devoted to cereal cultivation under different conditions: i) soil without amendment, ii) soil amended with two doses of green compost, and iii) soils unamended and amended with different irrigation conditions (non-irrigated and with additional irrigation). These factors were studied in field experimental plots in two time periods (2 + 5 months) during which repeated doses of herbicides were applied, and the results involved the physical, chemical and physicochemical properties of soils.

2. Materials and methods

2.1. Herbicides

The commercial formulation of triasulfuron + prosulfocarb (Auros Plus[®]) (Syngenta Agro S.A., Madrid, Spain) was used in the study. Analytical standards of both compounds were purchased from PESTANAL[®] (purity > 98.9%) (Sigma Aldrich Química S.A., Madrid, Spain). Water solubility is 815 and 13.0 mg L⁻¹ and log Kow is -0.59 and 4.48 for triasulfuron and prosulfocarb, respectively (PPDB, 2018). The chemical structure and general characteristics are included in Table S1 in Supplementary material.

2.2. Green compost residues

Two composted organic residues of vegetal origin (< 5 mm) generated from the pruning of plants and trees in parks in the city of Salamanca (NW-Spain) were used. They were supplied by the City Council (GC1) and by the nursery “El Arca” in Salamanca (Spain) (GC2). Their main physicochemical characteristics on a dry weight basis were determined as indicated in Marín-Benito et al. (2018), and they are pH 7.33 and 7.58, OC% 9.8 and 24.1 and N% 1.04 and 1.10, respectively, for GC1 and GC2.

2.3. Experimental set-up

The field assay was conducted in plots located in the Muñovela experimental farm belonging to the Institute of Natural Resources and Agrobiology of Salamanca, Spain (latitude 40°54'15" N, longitude 5°46'31.51" W). These plots were located in the same experimental field (sandy clay loam soil, Typic Haploxerept) (Soil Survey Staff, 2010) where we carried out a previous experiment in 2015 (Marín-Benito et al., 2018). In February 2016, the experimental layout of randomized complete blocks (18 plots of 3 m × 3 m) was designed as follows: unamended soil (S, 6 plots), soil amended with GC1 at the rate of 120 t ha⁻¹ on a dry weight basis (~12 t C ha⁻¹) (S + GC1, 6 plots) and soil amended with GC2 at the rate of 180 t ha⁻¹ on a dry weight basis (~40 t C ha⁻¹) (S + GC2, 6 plots) (Fig. 1). GC1 and GC2 amendments were used by availability effect to get different OC content in plots. They were incorporated into the 20-cm topsoil layer by using a rototiller. Three plot replicates per treatment received only natural rainfall (NI), and a further three replicates per treatment received additional sprayer irrigation (I, 2.8 mm per week).

Eighteen unamended and amended plots were treated with the combined commercial formulation of both herbicides (Auros Plus[®]). Water herbicide solutions were applied manually using a backpack sprayer (volume of 5 L) shortly after the soil was amended. The doses jointly applied to the plots were 11.25 kg a.i. ha⁻¹ of prosulfocarb as Auros[®] 80% and 250 g a.i. ha⁻¹ of triasulfuron as Logran[®] 20%, corresponding to 2.5 times the maximum agronomic dose for both herbicides recommended for heavy soils with a greater adsorption capacity.



Fig. 1. Location of plots in the experimental farm.

The increase in the soil's capacity for adsorbing the herbicides after an organic amendment supports the use of doses higher than those recommended to maintain the efficacy of the compounds (Worrall et al., 2001). Two repeated applications of herbicides were carried out in this experiment; the first dose was applied in March 2016, and the second one was applied once the dissipation of herbicides had surpassed 50% in May 2016 (68 days after the first application).

The estimated concentrations applied were 0.1923 mg kg⁻¹ and 8.653 mg kg⁻¹ for triasulfuron and prosulfocarb, respectively, calculated considering a soil density of 1.3 g cm⁻³ and a depth of 10 cm. However, the averaged concentrations measured in soil samples to check the dosage applied to soil ranged from 0.169 to 0.270 mg kg⁻¹ and 5.088–8.794 mg kg⁻¹ for triasulfuron and prosulfocarb, respectively, in different plots of unamended and amended soil after the first application. After the second application, the measured concentrations ranged from 0.257 to 0.291 mg kg⁻¹ and 6.857–8.350 mg kg⁻¹ for triasulfuron and prosulfocarb, respectively.

Rainfall and air temperature were monitored over the 215 days of experimentation by a weather station located on site. Air temperature ranged from 1.7 °C to 14.6 °C and from 10.5 °C to 26.3 °C during the first and the second period of the application, 68 and 147 days, respectively. Cumulative rainfall and rainfall + irrigation were 139–150 mm and 46.6–105 mm during the first and the second period

of the application, respectively (Fig. 2).

2.4. Soil sampling and sample processing

Soil sampling was carried out at 13, 28 and 68 days after the first application of herbicides, and after 15, 28, 55, and 147 days after the second application of herbicides (corresponding to 84, 97, 124 and 215 days from the initial application) to study the influence of repeated doses on the downward mobility and persistence of herbicides in the soil samples. Five soil cores from 0 to 50 cm were collected in each plot and then sectioned into five segments of 10 cm each, and composite samples of five cores were transferred to polypropylene bottles. All the samples were transported to the laboratory in portable refrigerators. The moisture content of the bulk sample for each 10-cm soil layer was gravimetrically determined by weight difference, measuring the soil sample mass before and after drying at 110 °C for 24 h. The characteristics of soil samples, previously air-dried overnight if necessary and sieved (< 2 mm), were determined by standard methods, as indicated in Marín-Benito et al. (2018). Dissolved organic carbon (DOC) was determined in soil/Milli-Q ultrapure water extracts (1/2 w/v ratio) after shaking (24 h at 20 °C), centrifugation (20 min at 10000 rpm), and filtering (Minisart NY 25 filter 0.45 µm, Sartorius Stedim Biotech, Germany) using a Shimadzu 5050 (Shimadzu, Columbia, MD, USA) organic carbon analyzer (Table 1). The pH, OC and DOC values were determined at different times after the application of herbicides to evaluate their influence on the behaviour of herbicides (Table 1 and Fig. S1 in Supplementary material). The adsorption capacity of triasulfuron and prosulfocarb by each 10-cm soil layer was determined as a single-point concentration (10 µg mL⁻¹) at the beginning of the experiment, and the distribution coefficients, K_d (mL g⁻¹), were calculated as indicated in Marín-Benito et al. (2018) (Table S2 in Supplementary material).

2.5. Herbicide extraction and analysis

The experimental method of herbicide extraction and analysis was as indicated in Marín-Benito et al. (2018). Briefly, duplicate subsamples of moist soil (6 g) from each section (0–10 cm) of soil cores were extracted with methanol (12 mL) and underwent sonication (1 h), shaking at 20 °C (24 h), and centrifugation (15 min). A volume of 8 mL was then evaporated until dryness at 25 °C under a nitrogen stream using an EVA-EC2-L evaporator (VLM GmbH, Bielefeld, Germany). The residue was dissolved in 0.5 mL of methanol + formic acid (1%) and transferred to a HPLC glass vial for analysis. The analysis of triasulfuron and prosulfocarb was performed in a Waters chromatograph (Waters Assoc.,

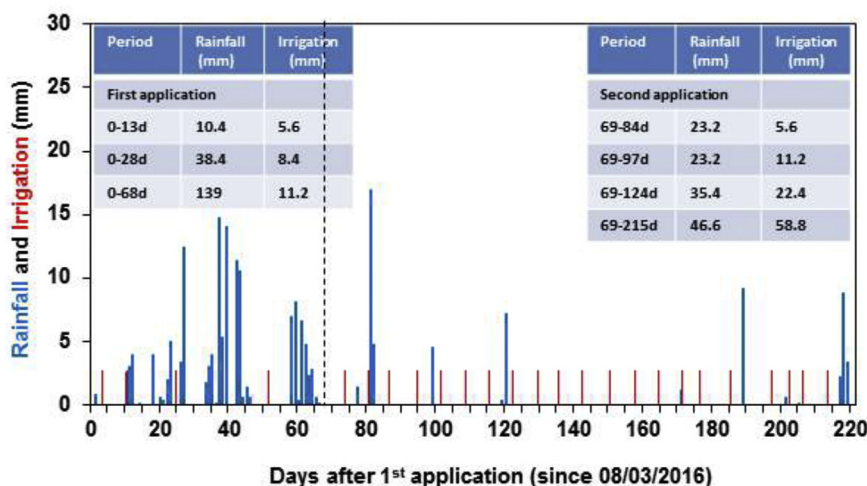


Fig. 2. Rainfall and irrigation evolution over time of experiment.

Table 1
Properties of the soils unamended and amended with green compost (GC1 and GC2) from experimental plots.

Properties	Soil depth (cm)				
	0–10	10–20	20–30	30–40	40–50
Soil texture	Sandy clay loam	Sandy clay loam	Sandy clay loam	Sandy clay loam	Sandy clay loam
pH	7.10–6.57 ^a 7.69–7.35 ^b 7.24–7.34 ^c	7.18–6.78 7.50–7.69 7.26–7.11	7.29–6.76 7.29–7.59 7.21–6.76	7.36–7.22 7.38–7.67 7.45–7.03	7.43–7.67 7.38–7.65 7.56–7.32
OC (%)	1.41–0.95 ^a 2.29–1.89 ^b 5.87–3.34 ^c	1.17–0.88 1.74–1.24 2.16–1.28	0.92–0.86 1.02–0.84 0.04–0.04	0.75–0.68 0.76–0.71 0.04–0.03	0.65–0.57 0.67–0.49 0.66–0.57
DOC (mg g ⁻¹)	0.06–0.02 ^a 0.08–0.07 ^b 0.32–0.19 ^c	0.11–0.03 0.09–0.04 0.07–0.04	0.09–0.03 0.04–0.04 0.05–0.02	0.08–0.03 0.04–0.03 0.02–0.02	0.04–0.05 0.03–0.03 0.03–0.02
N (%)	0.12–0.10 ^a 0.19–0.22 ^b 0.43–0.41 ^c	0.11–0.07 0.12–0.16 0.16–0.15	0.08–0.07 0.09–0.10 0.09–0.09	0.06–0.07 0.08–0.07 0.07–0.07	0.06–0.06 0.13–0.06 0.07–0.06
C/N	11.4–9.04 ^a 11.9–8.93 ^b 11.1–8.11 ^c	11.0–12.0 14.6–7.61 13.3–8.93	11.2–11.8 11.3–8.63 11.5–10.8	10.8–10.0 9.30–10.2 12.2–10.5	10.3–9.42 5.30–7.97 10.1–9.26
CaCO ₃ (%)	0.21 ^a	0.18	0.20	0.22	0.22
Sand (%)	57.63 ^a	58.22	59.15	55.63	51.04
Silt (%)	16.97 ^a	16.95	16.95	16.77	17.60
Clay (%)	24.98 ^a	25.25	25.25	29.10	34.72
Clay mineralogy	K, I, M ^d	K, I, M	K, I, M	K, I, M	K, I, M

Note: The ranges of values included for some parameters correspond to the variation of mean values of these parameters in three replicate plots between 13 and 215 days.

^a Unamended soil.

^b Soil amended with GC1 at 120 t ha⁻¹.

^c Soil amended with GC2 at 180 t ha⁻¹.

^d K, kaolinite; I, illite; M, montmorillonite.

Milford, MA, USA), equipped with a model e2695 multisolvent delivery and autosampler system attached to a ZQ mass spectrometer (MS) detector. Detection involved monitoring the positive molecular ion [m/z] 402.8 [M+H]⁺ (triasulfuron) and 252.4 [M+H]⁺ (prosulphocarb), and the retention times were 6.1 min and 14.1 min, respectively. The method's recoveries were determined by spiking three unamended and amended soil samples with triasulfuron and prosulphocarb at similar concentrations to those applied in the field, and performing the extraction procedure as described above. The mean recovery values were > 80% for both compounds in the unamended and GC-amended soils. The amounts of triasulfuron and prosulphocarb extracted from soils were not corrected for recovery values because matrix-matched calibration method was used.

2.6. Data analysis

Analysis of variance (ANOVA) was used to evaluate the effects of the different soil treatments on herbicide mobility. Standard deviation (SD) was used to indicate variability among replicates. Fisher's least significant difference (LSD) method, at a confidence level of 95%, was determined with SPSS Statistics 22.0 software for Windows (SPSS Inc. Chicago, USA).

3. Results

3.1. Soil characteristics

The values of pH, OC and DOC were determined for soils with different treatments (Table 1 and Fig. S1 in Supplementary material). The pH mean values of soils with different treatments were similar at the beginning (13 days) and at the end (215 days) of the experiment (7.32–7.28), although a significant decrease was recorded after 84–97

days of the application of herbicides (6.96–7.14) (LSD = 0.096, $p < 0.05$). However, significant differences were observed between the pH values of soils with different treatments (6.94–6.99 (S), 7.04–7.20 (S + GC2) and 7.31–7.47 (S + GC1)) or between different depths of soils (6.97–7.20 up to 10–30 cm and 7.39 up to 50 cm) (LSD = 0.088). Changes in the pH of amended soils were noted when additional irrigation was applied.

The soil OC content increased through the addition of organic residues (Table 1 and Fig. S1 in Supplementary material). The OC contents ranged between 1.41 and 0.95% for the unamended topsoil for all experimental times, and these contents increased with the application of GC up to two times in the S + GC1 (2.29–1.89%) and up to five times in the S + GC2 (5.87–3.34%). The soil OC content significantly increased up to 20–30 cm in the soil profile after the application of organic residues (LSD = 0.285, $p < 0.05$), while there were no differences between OC contents below 30 cm in the soil profile in any soil, and the OC contents ranged between 0.67 and 0.49% over the 215 days of experimentation. The increase in soil OC content due to the effect of GC1 was maintained in the different depths throughout the experimentation (seven months). However, the soil OC content after the application of the GC2 showed a higher decrease than after the application of the GC1, with the initial OC content in the topsoil decreasing ≈ 1.5 times by the end of the experiment, possibly due to the oxidation and/or mobility of the most labile forms of carbon. Despite this decrease, a significant increase ($p < 0.05$) in the OC content in the 0–10 cm and 10–20 cm layers was recorded in the amended soils with respect to the unamended soils, indicating that the application of the GC to the soil could improve soil properties over the long term. No significant changes in soil OC contents due to irrigation were observed.

The application of GC gave rise to an increase of DOC in the 0–10 cm layer of the S + GC2. The DOC content of the topsoil was 0.06 mg g⁻¹ and remained almost constant until the end of the experiment. The DOC content increased up to 5–10 times after the addition of the GC2 to the soil, but the increase was only up to two times after the addition of GC1 as regards the unamended soil (Table 1 and Fig. S1 in Supplementary material). The highest mean values of DOC in all the soils were recorded after 13–84 days from the initial time, and the DOC content decreased ≈ 2 times at the end of the experiment in the 10–20 cm layer of the S + GC2. At this depth, only the mean values of DOC of S + GC2 without irrigation or with irrigation were significantly different to those from S and S + GC1 (LSD = 0.076, $p < 0.05$). The DOC may have been leached out of the S + GC2 soil profile, especially under conditions of pH > 7 for the soil studied, as reported by some authors (Temminghoff et al., 1997), and this process might affect the mobility of the herbicides applied.

3.2. Mobility of triasulfuron from Auros Plus[®] formulation

The amounts of triasulfuron in the soil profile (0–50 cm) were determined at different times after the first application (13, 28 and 68 days) and the second one (15, 28, 55 and 147 days) in S, S + GC1 and S + GC2, with and without additional irrigation (Fig. 3).

After 13 days of the first triasulfuron application, the remaining amounts in the 0–10 cm layer were > 70% in the S and S + GC2, and > 50% in the S + GC1 taking the amounts initially determined as the reference of application. In the 10–20 cm layer, the remaining amounts decreased below 5%, 8% and 2% in the S, S + GC1 and S + GC2, respectively. The amounts of triasulfuron in the topsoil (0–10 cm) were the highest in the soil profile, and there were no significant differences between the mean amounts detected in the other layers. The lowest mean amount of triasulfuron was detected in the S + GC1 profile, and the highest in the S profile (LSD = 0.017, $p < 0.05$). The presence of triasulfuron was detected in all the layers of the soil profile with different treatment or irrigation conditions in decreasing amounts up to 40–50 cm (< 0.0075 $\mu\text{g g}^{-1}$).

The distribution pattern of triasulfuron in the soil profile was similar

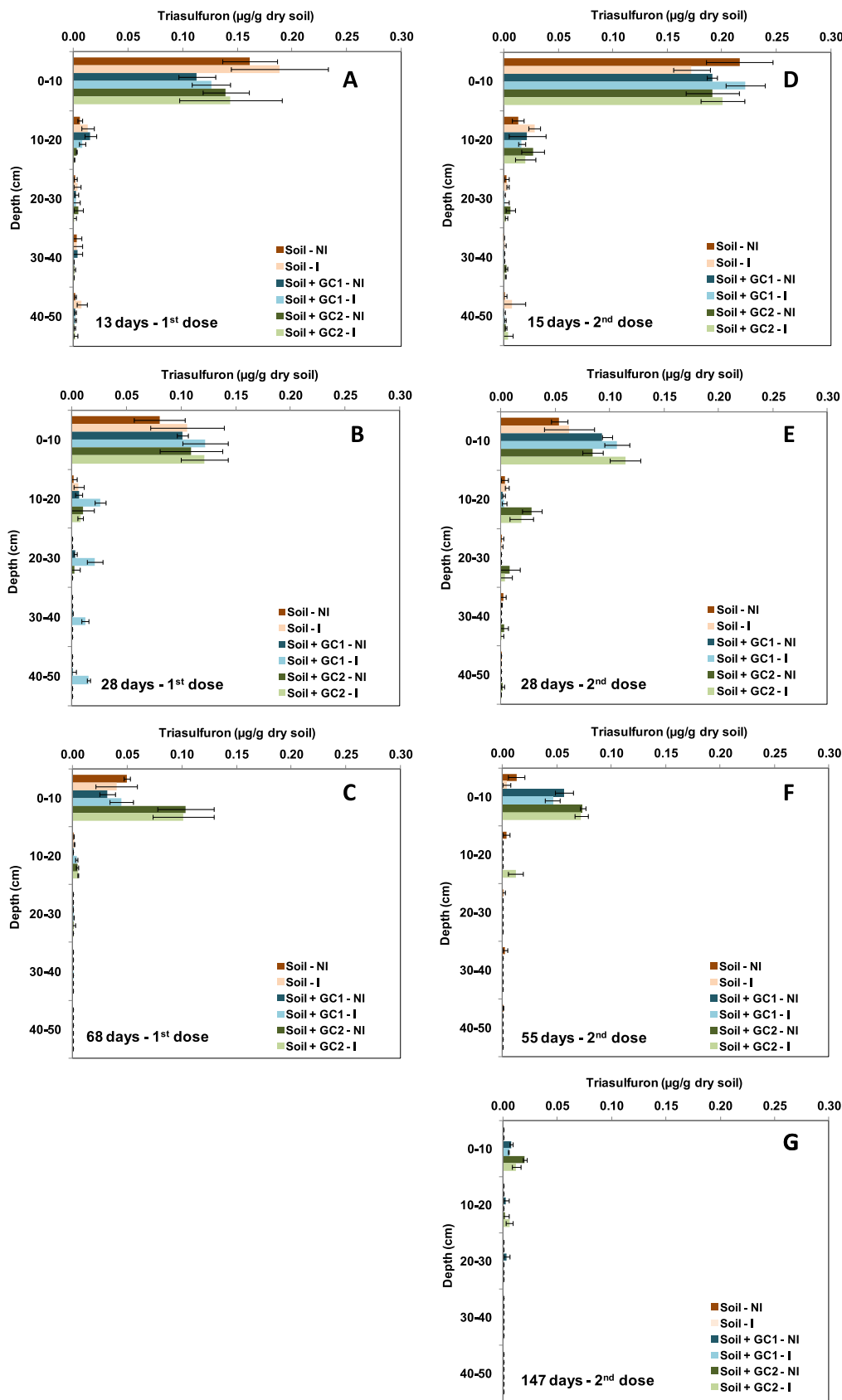


Fig. 3. Distribution profiles of triasulfuron in soil unamended and soil amended with green compost (GC1 and GC2) with non-irrigation (NI) and with additional irrigation (I) at different sampling times after the herbicide application (left graphs (A–C) correspond to the first application and right graphs (D–G) correspond to the second application). Error bars represent the standard deviation of mean values of plots treated ($n = 3$).

after 28 and 68 days of treatment, although the mean residual concentrations decreased in all the soils and layers (LSD = 0.009, $p < 0.05$). The herbicide concentration in the 0–10 cm layer decreased especially in S (28 and 68 days) and in S + GC1 (68 days), but the decrease in S + GC2 was not significant. The effect of GC2 on the persistence of triasulfuron in this soil appeared over time. It is worth noting a significant increase in the triasulfuron concentration recorded in S + GC1-I after 28 days in the 10–20 cm, 20–30 cm, and 40–50 cm layers. The recorded amounts of triasulfuron in the deeper layers of S + GC1 were significantly different to those found in the other soils, and herbicide amounts in the 40–50 cm depth were detected only in S + GC1-I. At this time, the highest mean amounts were recorded in the profile of the amended soils with the application of additional irrigation (S + GC1-I > S + GC2-I > S + GC2 > S + GC1 > S-I > S) (LSD = 0.007, $p < 0.05$). These differences were not observed after 68 days among soils with different treatments in soil layers under 0–10 cm, although a percentage close to 50% was detected in the topsoil of S + GC2, and traces of triasulfuron were found in amended soils up to 20–30 cm depth ($< 0.0007 \mu\text{g g}^{-1}$) in S + GC2 and 30–40 cm depth in S + GC1 ($0.0005 \mu\text{g g}^{-1}$).

The second application of triasulfuron was carried out when the residual concentration of herbicide was in the 15–55% range. The amounts remaining after 15 days were > 67%, > 70% and > 65%, in the soils S, S + GC1 and S + GC2, respectively, as regards those found immediately after the second application. The highest residual concentrations were also found in the 0–10 cm soil layers and were close to those found in the first application of the herbicide. However, an increase in the residual concentrations in the 10–20 layer was found compared to the first application, being significantly higher than those in the other soil profile layers (LSD = 0.011, $p < 0.05$) for soil samples with different treatments. The soil treatment had no influence on the levels of triasulfuron found at this time, and the presence of herbicide was also detected in all the soil profile layers of unamended or amended soils in decreasing amounts up to the 40–50 cm layer ($< 0.0078 \mu\text{g g}^{-1}$).

The distribution pattern of triasulfuron in the soil profile after 28 and 55 days was similar to that determined at 15 days, although the residual concentrations were lower. After 28 days, there were also differences between the residual concentrations in the soils, and the effect of the amendment and the application of additional irrigation were also significant, as in the first application. The detected amounts decreased according to the order S + GC2-I > S + GC2 > S + GC1-I > S + GC1 > S-I > S (LSD = 0.015, $p < 0.05$), and triasulfuron was detected only in the S + GC2 up to 40–50 cm depth ($< 0.002 \mu\text{g g}^{-1}$). Similar to the first application, differences between soil samples and layers below 0–10 cm were not observed after 55 days of treatment. The mean amounts found throughout the soil profile were not significantly different, and only traces of triasulfuron were found up to 10–20 cm depth ($< 0.0012 \mu\text{g g}^{-1}$) in S + GC2-I and to 30–40 cm depth in S ($0.0003 \mu\text{g g}^{-1}$). After 147 days, the residual concentrations of triasulfuron decreased drastically in the 0–10 cm layer, and no residual amounts of triasulfuron were detected in the unamended soil, and only traces of the herbicide were detected in S + GC1 up to 20–30 cm depth ($0.003 \mu\text{g g}^{-1}$) and up to 10–20 cm depth in S + GC2-I ($0.006 \mu\text{g g}^{-1}$) and S + GC2 ($0.002 \mu\text{g g}^{-1}$). The residues of triasulfuron indicated a lower persistence of herbicide in unamended and amended soils after repeated herbicide application.

3.3. Mobility of prosulfocarb from Auros Plus® formulation

The amounts of prosulfocarb in the soil profile (0–50 cm) at different times were recorded after the first application (13, 28 and 68 days) and the second one (15, 28, 55 and 147 days) in S, S + GC1 and S + GC2 with and without additional irrigation (Fig. 4).

After 13 days of the first herbicide application, the remaining amounts in the 0–10 cm layer were > 47%, > 48% and > 90%,

and < 5%, < 9% and < 0.5% in the 10–20 cm layer in S, S + GC1 and S + GC2, respectively, taking as reference the amounts initially determined. Only the amounts found in the 0–10 cm layers were statistically different, and no significant differences were found between the amounts detected in the other layers of the soil profile. The influence of the soil treatment and/or the application of additional irrigation was not significant in the mean amounts found in the soil profile, although the highest amount of prosulfocarb in the topsoil was recorded in S + GC2. The presence of prosulfocarb was detected in all the soil profiles up to 40–50 cm depth in amounts $< 0.2020 \mu\text{g g}^{-1}$.

After 28 and 68 days, the distribution pattern of prosulfocarb in the soil profile was similar to that determined after 13 days of treatment, but the residual concentrations found at 68 days were lower than at 13 and 28 days (LSD = 0.565, $p < 0.05$). The highest herbicide concentration recorded in the 0–10 cm layer decreased significantly after 28 days, especially in S and S + GC1 and regardless of the application of additional irrigation. This decrease was more pronounced after 68 days in the amended soils, with no influence of additional irrigation, and in unamended soil where the dissipation of prosulfocarb was total and no herbicide was detected. After 28 days, traces of the compound were detected up to 20–30 cm in the unamended soil and up to 40–50 cm in the amended soils ($\leq 0.032 \mu\text{g g}^{-1}$ in S + GC1 and $\leq 0.0126 \mu\text{g g}^{-1}$ in S + GC2). After 68 days, traces of the compound were detected up to the 40–50 cm depth ($\leq 0.002 \mu\text{g g}^{-1}$) in the amended soils (S + GC1 and S + GC2).

The second application of prosulfocarb was carried out when the dissipation of the herbicide was total (S) or almost total ($< 1.5\%$ in S + GC1 and $< 3.1\%$ in S + GC2). The amounts of prosulfocarb remaining in S, S + GC1 and S + GC2 after 15 days of the second application varied in the ranges > 6%, > 21% and > 31%, respectively, of that found immediately after its application. Similar to the first application, the highest residual concentrations were found in the 0–10 cm layer of the soil profile, and the residual concentrations of the herbicide in the deeper layers of the soil profile were not statistically different (LSD = 0.487, $p < 0.05$) for soil samples with different treatments. The presence of prosulfocarb was detected in all the layers of the soil profile in decreasing amounts for all soil treatments. Residues of prosulfocarb were detected up to 40–50 cm depth in amounts $\leq 0.1615 \mu\text{g g}^{-1}$. Similar to the first application, no significant differences were found between the mean prosulfocarb amounts in the soil profiles with the different treatments, or with the application of additional irrigation.

The distribution of prosulfocarb in the soil profile 28 and 55 days after the second application was similar to that determined at 15 days, although the residual concentrations were lower, and only the amounts detected in the 0–10 cm layer were significantly different. However, after 28 days, the residual concentrations detected in all S + GC2 layers with or without additional irrigation were significant. The presence of GC2 favoured the leaching of prosulfocarb throughout the soil profile. This effect disappeared after 55 days, and only herbicide traces under the 0–10 cm layer were detected in all the soils. The herbicide amounts were greater in the amended soils (S < S + GC1 < S + GC2), and similar in S + GC2 to that recorded at 55 days, but they always diminished after the application of additional irrigation. After 147 days, the residual concentrations of repeatedly applied prosulfocarb decreased significantly in the 0–10 cm layer, following the same pattern as after 55 days, but residual concentrations were recorded in all the soils and in all soil profiles. It should be noted that residual concentrations of prosulfocarb were higher after 147 days than those obtained 68 days after the first application of the herbicide. The results indicate an increase in the persistence of prosulfocarb in the unamended and amended soils by repeated application of herbicide over time.

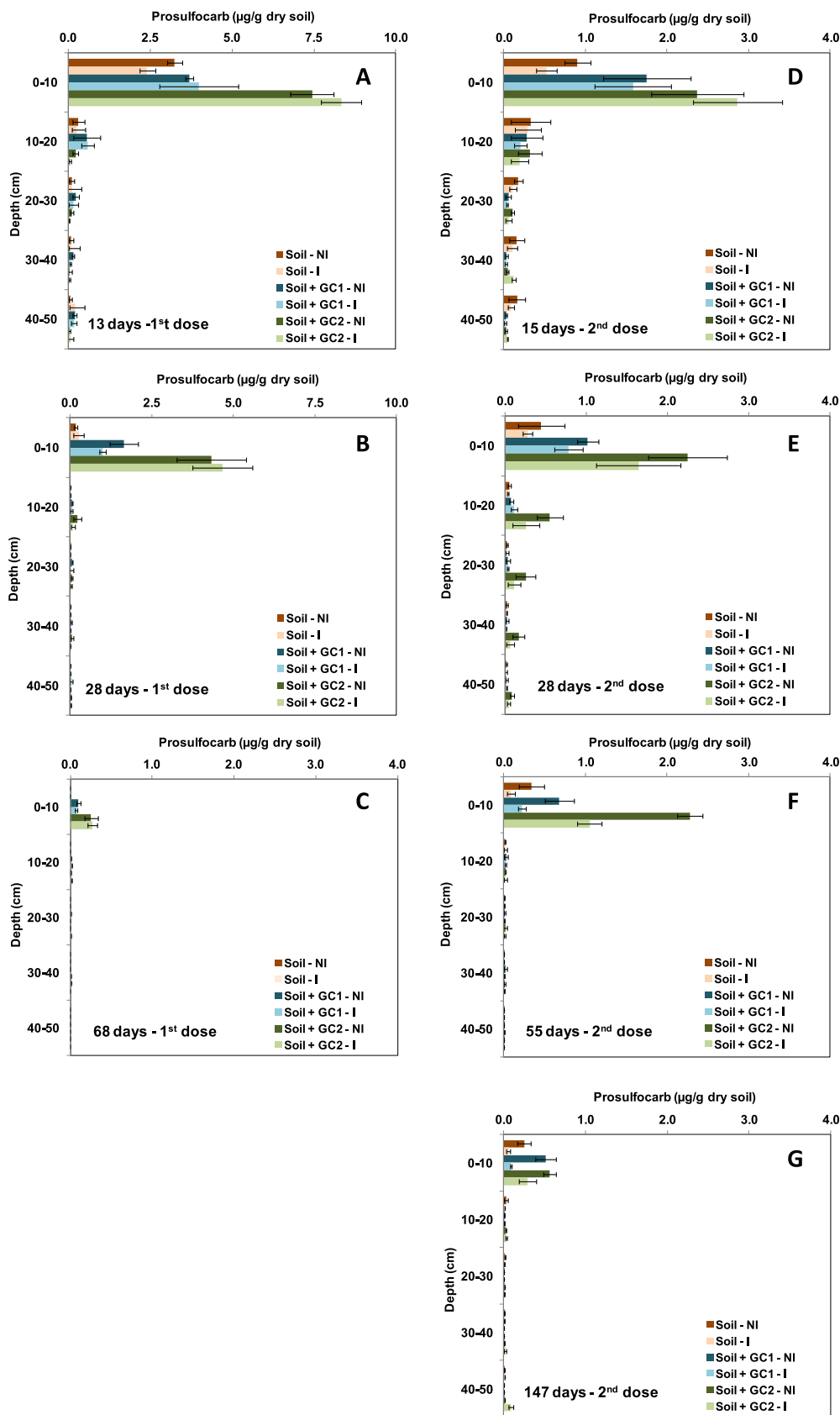


Fig. 4. Distribution profiles of prosulfocarb in soil unamended and soil amended with green compost (GC1 and GC2) with non-irrigation (NI) and with additional irrigation (I) at different sampling times after the herbicide application (left graphs (A–C) correspond to the first application and right graphs (D–G) correspond to the second application). Error bars represent the standard deviation of mean values of plots treated (n = 3).

4. Discussion

4.1. Triasulfuron mobility: effect of organic amendment and irrigation

Triasulfuron mobility was initially observed in the soil profile for all soil treatments. This behaviour is to be expected because sulfonylureas are weak acids and adsorption decreases when soil pH is higher than its pKa (4.64) (Pusino et al., 2003) increasing its mobility. In our experiment, the pH of the 0–10 cm layer was higher than 7, i.e., pH was higher than pKa, and this factor could increase the mobility of the herbicide. In fact, a significant correlation coefficient ($r = -0.863$, $p < 0.05$) was found between triasulfuron amounts in the 0–10 cm layers and soil pH after 13 days of treatment. However, this significant correlation was not observed between the residual concentrations in the soil profile and pH values for each soil, indicating the influence of other factors on herbicide mobility. After one month of the application, the dissipation of the compound was higher in the unamended soil than in the amended soils, with mobility in the soil profile being more significant in these soils. The effect of a rainfall event of 12.4 mm at 27 days, along with the additional irrigation applied, could have affected the mobility observed in S + GC1. Similar changes were also observed after two months of treatment, and the highest amounts of herbicide at this time were found in the surface horizon of S + GC2 with herbicide traces detected up to 20–30 cm (S + GC2 and S + GC1) and 30–40 cm (S + GC1). Herbicide leaching depended on soil treatment and rainfall and/or additional irrigation received after the first application of the herbicide over time (Fig. 2). A rapid transport into deep soil layers by the irrigation flow has been reported for triasulfuron and other different pesticides (Anyusheva et al., 2016; Salazar-Ledesma et al., 2018; Sarmah et al., 2000). Rainfall events at this time were more important for the transport of herbicide than the additional irrigation, although these events did not affect the dissipation of herbicide in S + GC2 to any greater extent.

The increase in the OC content of S + GC2 in the 0–10 cm layer could explain the persistence of more than 50% of the amount of herbicide initially applied in the soil after two months, indicating a slower dissipation of triasulfuron. A significant correlation between the residual concentrations of herbicide and the OC content of soils throughout the soil profile was found for S + GC2 ($r \geq 0.968$, $p < 0.01$) and S + GC1 ($r \geq 0.927$, $p < 0.05$) even though the OC content decreased significantly in the soil profile. This correlation was not significant for the unamended soil. The herbicide's behaviour is also consistent with the higher adsorption coefficients (K_d) for S + GC2, with the highest OC content (S, $0.31 \pm 0.01 \text{ mL g}^{-1}$, S + GC1, $0.38 \pm 0.09 \text{ mL g}^{-1}$ and S + GC2, $0.67 \pm 0.03 \text{ mL g}^{-1}$) (Table S2 in Supplementary material). Similar effects were observed for triasulfuron and other sulfonylureas in soils amended with other organic residues (Delgado-Moreno and Peña, 2008; Said-Pullicino et al., 2004). In addition, herbicide leaching may also be modified by structural changes in soil aggregate stability, porosity, hydraulic conductivity, water holding-capacity, etc. induced by the increase in OC content (Ingelmo Sánchez and Rubio Delgado, 2008; Yazdanpanah et al., 2016). In our study, a higher water holding-capacity of the topsoil in S + GC2 may be responsible for a lower water percolation in the soil profile.

The mobility of triasulfuron in the amended soils detected over the time of application of the herbicide could be explained by the mobilizing effect of the herbicide caused by the DOC in the soil profile considering a $\text{pH} > 7$ for the amended soils. At the basic pH shown by the amended soils (Fig. S1 in Supplementary material), the DOC is more easily mobilized and could favour the leaching of triasulfuron, even though the hydrophobicity of triasulfuron was not high enough to explain its adsorption by the DOC in solution, as indicated in the literature for other compounds of similar character (Marín-Benito et al., 2012; Rodríguez-Liébana et al., 2018; Rodríguez-Liébana and Peña, 2018). However, the DOC content of S + GC1 is relatively low for explaining the mobility of triasulfuron after 28 days. This herbicide mobility in

S + GC1, but not recorded in S and S + GC2, could be due to the existence of random preferential flows in the soil within the individual plots because of its clay content ranging from 25% to 34% in the soil profile, which would facilitate the rapid leaching of the herbicide. In fact, cracks were noted in the S + GC1 plots after additional irrigation was applied. A similar behaviour was explained in previous studies (Sarmah et al., 2000; Anyusheva et al., 2016; Jarvis, 2007; Koestel and Jorda, 2014). The effect, observed only in the S + GC1-I, could not be explained by the greater amount of water applied to irrigated soils. The presence of DOC in the S + GC1 profile as a mobilizing effect of triasulfuron could not be considered because there was no difference between DOC of S and S + GC1 despite the fact that the higher pH of S + GC1 could mobilize the DOC to a greater extent.

4.2. Triasulfuron mobility: effect of repeated doses

After 15 days of treatment, no significant relationship was found between residual concentrations of triasulfuron in the 0–10 cm layers and the pHs of different soils, even though the pH values in the soil profile were higher for amended soils than for the unamended one. The residual concentrations detected in the 10–20 cm layer for all the soils at this time could possibly be influenced by the heavy rainfall recorded (17 mm) in the days prior to soil sampling and herbicide determination.

An increase in herbicide dissipation was observed one month after the repeated application with respect to the first application, consistent with the amounts of triasulfuron found in the topsoils. An accelerated degradation due to microbial adaptation leading to faster metabolism could explain this behaviour, as reported for other compounds (Fang et al., 2018; Singh et al., 2002). The degradation of the herbicide could also be due to the higher air temperatures recorded in the second part of the experiment ($\sim 10^\circ\text{C}$ higher). It is well known that the degradation rate of pesticides in soil depends heavily on the soil moisture and temperature. EFSA (2007b) indicates an average increase of 2.58 times in the degradation rate of pesticides when temperature is increased by 10°C .

Triasulfuron dissipation increased in all the soils, but herbicide mobility in the soil profile also increased in S + GC2 from one month to more than five months of treatment. Residual concentrations of herbicide determined along S + GC2 profile could remain due to adsorption of herbicide by soil. In fact, significant correlations between the residual concentrations in the soil profile and the OC content were observed in this soil. Correlation coefficients (r) varied between 0.973 and 0.984 ($p < 0.01$) for the corresponding sampling times between 15 days and five months.

The DOC from the amended soil S + GC2 could help to promote the mobility of the herbicide in this soil after the second application showing it the persistence of this DOC in the soil profile and its impact on the leaching of triasulfuron over time. As already indicated, the DOC could be mobilized in the soil profile, and adsorb the mobilized triasulfuron, which would be consistent with the significant correlation found between the residual concentrations in S + GC2 and the DOC content in this soil from the second application (r ranged between 0.878 and 0.998, $p < 0.05$). The amount of additional irrigation applied after five months of herbicide application and the light rainfall did not have any relevant effects on the amount of herbicide leached. The herbicide was found to persist five months after its repeated application in the amended soil profile, although it decreased compared to that obtained after the first application.

4.3. Prosulfocarb mobility: effect of organic amendment and irrigation

Prosulfocarb is a non-ionic compound with low solubility in water, but its presence was detected in the soil profile after 13 days of treatment, especially in S and S + GC1. Simultaneously, prosulfocarb recorded a dissipation close to 50% in S and in S + GC1, while only a dissipation close to 10% was observed in S + GC2 in the same period.

After one month of treatment, the dissipation percentage of the compound increased in the unamended and amended soils, and after two months of treatment, the percentage of herbicide detected was < 3% in the amended soils, and it was not detected in the unamended soil. The highest prosulfocarb retention recorded in the 0–10 cm layer could be related to the soils' adsorption coefficients. The K_d adsorption coefficients were similar for S ($21.6 \pm 5.55 \text{ mL g}^{-1}$) and S + GC1 ($24.7 \pm 7.62 \text{ mL g}^{-1}$), but this coefficient increased significantly for S + GC2 ($57.1 \pm 2.09 \text{ mL g}^{-1}$) (Table S2 in Supplementary material) in agreement with the higher residual concentrations found in S + GC2. Prosulfocarb is adsorbed by S + GC2 to a greater extent than by S + GC1 due to the latter's higher OC content (Table 1). A significant correlation coefficient was found between residual concentrations and OC content in the soil profile for S + GC2 ($r \geq 0.976$, $p < 0.01$), S + GC1 ($r \geq 0.923$, $p < 0.05$) and S ($r \geq 0.813$, $p < 0.1$), despite the significant decrease in OC content in the soil profile. According to this, a significant correlation has been reported between the adsorption constants of prosulfocarb and soil OC contents (Marín-Benito et al., 2018; Nègre et al., 2006). Similar effects were observed for other carbamate compounds in unamended or amended soils (Berglöf et al., 2002; Marín-Benito et al., 2012).

The dissipation percentage of prosulfocarb was very high over the experimental period, especially in S and S + GC1. The dissipation in the topsoil layer was more significant than its mobility, as only herbicide traces were detected throughout the soil profile. Prosulfocarb is not very soluble in water, but when adsorbed by soil particles it may be transported out of the soil profile in S and S + GC1 by rainwater or by the additional irrigation applied, especially if random soil cracks occur, as indicated for triasulfuron. However, it should be noted that other dissipation processes could also be responsible for the high dissipation percentage of prosulfocarb, such as the microbiological degradation of the compound or volatilization. Prosulfocarb is considered as slightly volatile (PPDB, 2018) but it has been reported that considerable amounts of herbicide were lost from the soil in volatility experiments (EFSA, 2007a). Recently volatility of prosulfocarb from soils was also reported (Braun et al., 2017) as indicated for other thiocarbamates.

In S + GC2, the addition of the organic amendment might also have reduced the mobility of prosulfocarb by increasing the water holding capacity of the 20-cm topsoil layers, which will be responsible for decreasing the water percolation, as indicated for triasulfuron. This circumstance and the greater adsorption of prosulfocarb by this soil could decrease its dissipation rate, although the prosulfocarb adsorbed by S + GC2 might also be affected by the processes indicated above.

4.4. Prosulfocarb mobility: effect of repeated doses

Similar to triasulfuron, the dissipation of prosulfocarb after repeated application was more rapid than after the first application. The volatilization of the herbicide could explain its high dissipation after 15 days of its application, as it could be favoured by the higher air temperature recorded at this time. On the other hand, the repeated prosulfocarb application could induce a greater soil microbial activity as it was indicated by Rouchaud et al. (1997) and this enhanced soil biodegradation could be favoured by the higher temperature recorded than in the first application. The residual concentrations increased in the order $S < S + GC1 < S + GC2$, following the same pattern as in the first application of the herbicide (Fig. 4). Simultaneously, the amounts recorded in the soil profile indicated the presence of prosulfocarb in all the soils, reaching up to 40–50 cm depth, especially in the case of S, despite the low amount of water received during this second application.

The residual concentrations remaining in the topsoil indicated that dissipation decreased slowly over time, without the complete disappearance of the compound in all the soils after the repeated application. The adsorption of herbicide by the soils could delay its dissipation. It should be noted that mobility in the soil profile was detected

in all the soils, mainly after one month of the application of prosulfocarb, although the amounts retained decreased throughout the soil profile.

The decrease in the dissipation of the compound could be due to the low amount of water present in the soil during the five months following the second application. This circumstance could lower the mobility of the herbicide to deeper soil layers, avoid the presence of the herbicide in solution to be degraded, and/or generate a non-optimum scenario for its degradation by microorganisms. In fact, the influence of more irrigation ($\approx 60 \text{ mm}$) than that supplied by rainfall (45 mm) after the second application could favour herbicide dissipation, as observed for all the soil treatments at different times.

By contrast, the effect of the DOC of S + GC2 could favour herbicide mobility in these amended soils after the second application. This would be consistent with the significant correlation found between the residual concentrations and the soil DOC content for each time (r ranging between 0.986 and 0.993, $p < 0.01$).

5. Conclusions

The results obtained confirm the mobility of triasulfuron and prosulfocarb up to 50 cm in the soil profile in unamended and amended soils with different doses of GC immediately after their application. The influence of the soil treatment (amendment) or environmental conditions (additional irrigation) was noted for both herbicides over time and it was recorded for the first and the second application of herbicides. The persistence in S + GC2 was higher than in S or S + GC1 and was explained by this soil's high capacity for adsorbing herbicides due to its OC content but prosulfocarb dissipated more quickly than triasulfuron. The leaching of both herbicides was affected by irrigation in all the soils although other factors, such as the DOC or water storage capacity may be significant in S + GC2. Both herbicides dissipated more rapidly after the second application than after the first application in all experimental conditions of soil, but residues of both herbicides were found in amended soils after five months of application. An accelerated degradation due to microbial adaptation leading to faster metabolism (triasulfuron and prosulfocarb) or an enhanced volatilization (prosulfocarb) could explain the increased dissipation after second application also enhanced by the increased temperature at this time. The interest of these results is that herbicides leaching from the soil surface may contaminate groundwater, and the amounts retained in the soil profile could exceed the recorded threshold for the sensitivities of susceptible species. Accordingly, establishing new agricultural practices involving organic residues requires the prior evaluation of their characteristics (OC and DOC) and the structural changes in soil aggregate that their application may imply in order to improve soil fertility without an environmental impact.

Conflicts of interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jenvman.2018.07.045>.

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