Transport of ^{14}C-prosulfocarb through soil columns under different amendment, herbicide incubation and irrigation regimes

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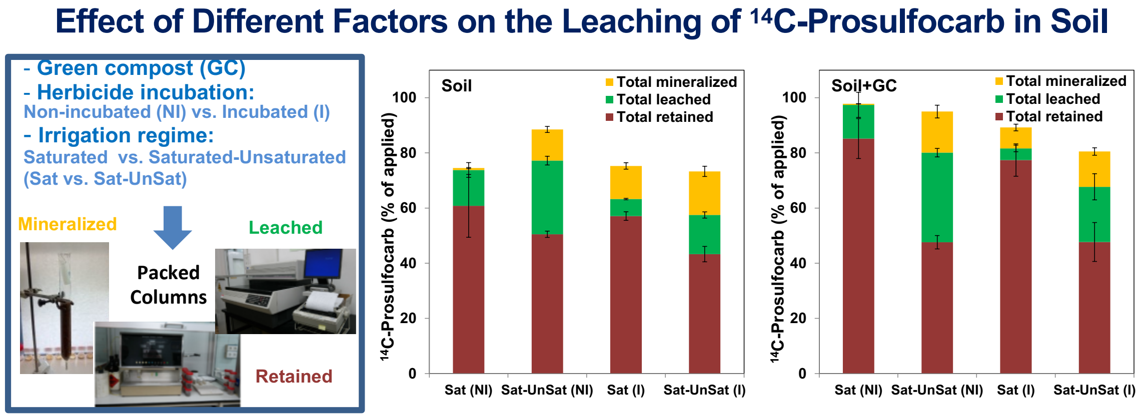
Highlights

- Leaching of prosulfocarb in green compost-amended soil (S+GC) columns was studied
- The leached amounts decreased when the herbicide was incubated for 28 days in S and S+GC
- The total retained amounts were lower in S than in S+GC columns under saturated flow
- Prosulfocarb was retained in the first segment of S and S+GC columns under all conditions
- Herbicide incubation notably increased the mineralized amount under saturated flow

Graphical Abstract



Abstract

This study sets out to evaluate the effect on the leaching of prosulfocarb through packed soil columns of applying green compost (GC) as an organic amendment (20% w/w), herbicide ageing over 28 days in the soil (incubation vs. no incubation), and two different irrigation regimes (saturated or saturated-unsaturated flows). Peak concentrations decreased after herbicide incubation in the columns for both unamended (S) and amended (S+GC) soils under both flow regimes. The leached amounts decreased when the herbicide was incubated for 28 days in S (2.1 and 1.9 times) and S+GC (2.9 and 1.6 times), under saturated or saturated-unsaturated flow, respectively. In the S columns, the total amounts retained (43.3%-60.8%) were lower than the ones obtained for the S+GC columns under saturated flow (77.4%-85.2%), suggesting a stronger interaction between the herbicide and the GC-amended soil. This behaviour was not observed under saturated-unsaturated flow, as the total amounts retained were similar in both the S and S+GC columns. Prosulfocarb was primarily retained in the first segment of the S (> 28%) and S+GC (> 43%) columns under all conditions. Incubation time did not greatly affect the herbicide retention, but it significantly increased the mineralized amount under saturated flow. The total balances of ^{14}C-prosulfocarb were > 73% and > 80% in the S and S+GC columns, respectively, indicating that amendment decreased prosulfocarb loss by volatilization. Several factors, such as amendment, herbicide ageing and water flow, proved to be important for controlling the leaching of this herbicide through the soil profile.

Keywords

Prosulfocarb, soil, green compost, leaching, water saturation, ageing

1. Introduction

The application of pesticides on different crops to increase yields may lead to the release of pollutants and residues into waters and soils (Climent et al., 2019; Herrero-Hernández et al., 2016; Pose-Juan et al., 2015). Prosulfocarb (S-(phenylmethyl)-dipropylcarbamothioate) is a thiocarbamate herbicide used at pre- and post-emergence for weed control in different crops, such as potatoes or winter cereals. It is a hydrophobic herbicide with low water solubility, a Kf_{oc} of 1367-2339 mL g^{-1}, and a GUS index of 0.84, indicating high sorption and low leachability in soil (EFSA, 2007; PPDB; 2019). Prosulfocarb could reach surface water after its application to different agricultural soils through point sources (Neumann et al., 2003), spray drift (Arts et al., 2006), recycled water (Busetti et al., 2015), and rainwater contamination (Bernhardt et al., 2004). However, to our knowledge, there are no studies on prosulfocarb's potential to reach groundwater.

Our previous studies have reported the dissipation and mobility of prosulfocarb in a soil with two different green compost (GC) amendments and different irrigation regimes under field conditions (Marín-Benito et al., 2018a,b). The simultaneous application of GC increases the herbicide's persistence in the soil. Prosulfocarb's leaching through the soil profile was influenced mainly by soil water content and dissolved organic carbon (DOC) content. A low amount of water in the soil means the herbicide is less mobile toward deeper soil layers. By contrast, the effect of the DOC of GC-amended soil could favour herbicide mobility (Marín-Benito et al., 2018b). We therefore need to further our knowledge of the influence these factors have on the leaching of prosulfocarb in organically-amended soils. In a previous laboratory study, the herbicide prosulfocarb recorded faster dissipation and higher bioavailability in the unamended soil than in the GC amended soil due to its lower sorption regardless of the dose of herbicide applied (Barba et al., 2019).

The application of organic amendments to soils is a common agricultural practice used to increase nutrient content and organic carbon (OC). This practice could prevent the possible contamination of groundwater by pesticides due to the modification of their bioavailability and retention by the soil (Marín-Benito et al., 2018c; Pose-Juan et al., 2018). Organic residues are characterized by high OC content, which is one of the main factors influencing the adsorption process in soils. Organic amendments could act as a sorbent to prevent the spread or leaching of pesticides through the soil profile (Álvarez-Martín et al., 2016; Marín-Benito et al., 2013, 2018c). Leaching may be reduced by structural changes in the porosity induced by the change in OC content (Worrall et al., 2001). In addition, high levels of dissolved organic matter (DOM) could cause the formation of complexes with pesticides, due to their adsorption by the DOC in solution, increasing their mobility to deeper soil layers (García-Jaramillo et al., 2014; Marín-Benito et al., 2009; Thevenot et al., 2009).

Leaching studies have been carried out in columns of soils amended with olive mill waste (Aharonov-Nadborny et al., 2016), spent mushroom substrate (SMS) (Álvarez-Martín et al., 2017), sheep manure, spent coffee grounds, composted pine bark, and coir (Fenoll et al., 2014), biochar (Gámiz et al., 2017), manure and fly ash (Majumdar and Singh, 2007), and grape marc, pine wastes, urban solid wastes, sewage sludge, and SMS (Marín-Benito et al., 2018c). These studies have reported a reduction in pesticide leaching due to enhanced pesticide sorption in organically-amended soils. Leaching can be decreased due to the pesticide's retention by the solid organic matter (OM) of the amendments (Majumdar and Singh, 2007), although simultaneously leaching can also increase by the DOC from the OM of organic amendments.

Mobility studies in soil amended with organic residues have been carried out under saturated or saturated-unsaturated flow regimes, but studies under both flow conditions are rare (Álvarez-Martín et al., 2017). Experiments conducted under a saturated flow condition simulate the worst-case scenario (Cederlund et al., 2017; Ghosh and Singh, 2012, Larsbo et al., 2013), while experiments carried out under a saturated-unsaturated flow condition are closer to real field conditions, as they simulate rainfall and irrigation events (Aharonov-Nadborny et al., 2016; Fenoll et al., 2014).

Leaching studies have usually been conducted without pesticide ageing in the amended soil (Gámiz et al., 2017; Majumdar and Singh, 2007). Leaching pesticides under different ageing states in unamended and amended soils is relevant because this factor and the flow regime largely determine the transport of these compounds and the potential risk of groundwater contamination (Álvarez-Martín et al., 2017; Milan et al., 2015). There is evidence to show that the timing of rainfall or irrigation relative to the time of pesticide application may be the major factor controlling leaching losses (Walker et al., 2005). The incubation of a soil-amendment-pesticide system could transform soil OM, altering the way pesticides interact with amended soils (Marín-Benito et al., 2012).

Because the lack of knowledge about prosulfocarb mobility through soil profile taking into account the factors pointed above, it is necessary to study the influence of the application of organic amendments to soil on this process under different conditions of herbicide incubation in the soil and irrigation. Results from this study will be relevant to complete our knowledge about the fate of prosulfocarb in the soil environment.

This paper's objective was to study the leaching of the herbicide prosulfocarb through packed soil columns. The effect of the following factors was evaluated: 1) the application of GC as an organic amendment to soil; 2) the incubation time following herbicide application to the soil; soil column washing started at Day 1 (non-incubated) or 28 days (incubated) after herbicide application; and 3) the irrigation regime applied; saturated with continuous irrigation or saturated-unsaturated with intermittent irrigation.

2. Materials and methods

2.1. Chemicals

A non-labelled prosulfocarb analytical standard (PESTANAL®, > 98.9% purity) was supplied by Sigma-Aldrich Química S.A. (Madrid, Spain). The labelled [Ring-U-^{14}C] prosulfocarb (specific activity 3.16 MBq mg^{-1}, 94.8% purity) was supplied by IZOTOP (Budapest, Hungary). Prosulfocarb has a water solubility of 13.2 mg L^{-1} (20°C), and a log K_{ow} of 4.48 (pH 7, 20°C) (PPDB, 2019).

2.2. Organic amendment

The green compost (GC) came from the pruning of plants and trees in gardens and parks, and it was supplied by the nursery El Arca (Salamanca, Spain). Its characteristics were determined in samples that were first homogenized and sieved (< 2 mm) (Barba et al., 2019). The GC's characteristics (on a dry weight basis) were as follows: pH 7.20, total OC content 24.1%, DOC content 0.703%; total N content 1.11%, C/N ratio 21.8, ash percentage 54.0%, and moisture content 48.6% (**Table S1**).

2.3. Unamended and amended soil characterization

The soil used in this study was classified as a Typic Haploxerept with sandy clay loam texture (57.63% sand, 16.97% silt, 24.98% clay, and 0.21% carbonate content). It was taken from the surface horizon (0-30 cm) at the Muñovela experimental farm (40º55'56"N latitude and 5º52'53"W longitude) belonging to the Institute of Natural Resources and Agrobiology of Salamanca (IRNASA-CSIC).

The amended soil was prepared by uniformly mixing soil with GC (S+GC) at a rate of 20% w/w (180 t ha^{-1}) on a dry weight basis. The soil and GC were mixed after sieving (< 2 mm), and its characteristics were determined (Barba et al., 2019). The pH, total OC, N content, and DOC were 7.35, 1.30%, 0.12% and 0.006%, respectively, in the unamended soil (S), and 7.30, 4.66%, 0.42% and 0.027% in the GC-amended soil (S+GC), also respectively (**Table S1**).

2.4. Soil column setup and leaching studies

Four herbicide leaching experiments were performed, following OECD guidelines (OECD, 2007), in triplicate for each soil treatment in glass columns of 3 cm (i.d.) x 25 cm (length) packed with 100 g of unamended or GC-amended soils (**Table S2**). These columns were oversaturated with distilled water to their maximum water-holding capacity, and then allowed to drain off the excess water for 24 hours, so the humidity conditions were the same as field capacity. The pore volume (PV) of the packed columns was estimated by the difference in weight between the water-saturated columns and dry columns (**Table 1**). Prosulfocarb was evenly applied by adding 1 mL of a 1000 μg mL^{-1} prosulfocarb solution in methanol to the top of the columns for a concentration of 10 mg kg^{-1} (2.5 times the agronomic dose), and an activity of approximately 10 kBq mL^{-1}. This concentration was similar to the concentration applied in the field (Marín-Benito et al., 2018b) to simulate the worst case scenario of these compounds leaching in soils (Khorram et al., 2015).

Leaching was carried out one day after herbicide application (non-incubated columns, NI) or after incubating the herbicide at 20ºC in the dark for 28 days (incubated columns, I) (**Table S2**). This incubation period was selected taking into account the relatively short half-life of prosulfocarb (Barba et al., 2019). A $CaCl_2$ aqueous solution (0.01M) was used instead of water to wash the columns to minimize the disruption of the soil mineral balance. Two different washing flow regimes were studied: saturated and saturated-unsaturated (**Table S2**). Under saturated flow regime, 500 mL of a 0.01M $CaCl_2$ solution were pumped continuously at a rate of 1 mL min^{-1}, always keeping the top of the column in contact with the water. Under the saturated-unsaturated flow regime, the same volume of $CaCl_2$ solution was added for 25 days (20 mL per day). Herbicide mineralization was measured over incubation time in the column, or when a saturated-unsaturated flow was applied. A ^{14}C trap consisting of a scintillation vial containing 1M NaOH (1 mL) was attached to the top of the column via a stainless-steel clip (Reid et al., 2002), and $^{14}CO_2$ from mineralized ^{14}C-prosulfocarb was periodically determined.

A Gilson MINIPULS 3 peristaltic pump (Gilson Inc. Middleton, WI, USA) was used to maintain the leaching flow constant. Fractions of leaching solution (20 mL) were collected by a Gilson F203 automated fraction collector. Once the leaching had been completed, the columns were cut into three segments (0-5, 5-10 and 10-15 cm), and the soil contained in each segment was dried and weighed.

2.5. Analysis of ^{14}C-prosulfocarb residues

The radioactivity of the leached fractions was measured in disintegrations per minute (dpm) on a Beckman LS 6500 liquid scintillation counter (Beckman Instruments Inc., Fullerton, CA). These measurements were determined in duplicate by mixing 1 mL of extract with 4 mL of scintillation cocktail (Ecoscint^{TM} A, National Diagnostics, Atlanta, GA). The dpm values recorded were compared to the dpm value obtained for the prosulfocarb standard solution. The quantification limit for the ^{14}C-prosulfocarb was determined as the background radioactivity (18.2-23.1 dpm) in the leached $CaCl_2$ solution. Determinations were carried out in duplicate for all the solutions, and the range of the coefficient of variation was always between 0.1% and 2%. $^{14}CO_2$ from mineralized ^{14}C-prosulfocarb trapped in the scintillation vial containing 1M NaOH (1 mL) was determined by adding 4 mL of scintillation cocktail, as previously indicated.

The remaining ^{14}C-prosulfocarb retained in the soil after leaching was determined by the combustion of triplicate 1 g samples of dried soil using a Biological Oxidizer (RJ. Harvey OX-500 Instrument Corporation, NJ) under O_2 excess at 900ºC. The $^{14}CO_2$ generated was trapped in a mixture of ethanolamine (1 mL) and scintillation cocktail (Oxysolve C-400, Zinsser Analytic, Berkshire, UK, 15 mL), and determined as indicated before. The oxidizer´s efficiency was calculated prior to sample combustion as the ratio between ^{14}C-standard activity applied in an inert material (mannitol) after combustion in an oven and ^{14}C-standard activity without combustion. ^{14}C-prosulfocarb recovery was always > 98%.

2.6. Chloride ion leaching in soil columns

Chloride ion (KCl) was used as an ion tracer to describe the dispersive characteristics of the columns used for herbicide leaching. An amount of 47 mg of chloride ion was applied per column (1 mL of a 100 g L^{-1} KCl aqueous solution). Chloride ion leaching was carried out with similar water flow regimes to those used in herbicide leaching (saturated flow and saturated-unsaturated flow). Chloride ion concentrations were determined using a Metrohm Ion Chromatograph (Metrohm Ltd., Switzerland) with a conductivity detector, following the method described by Rodríguez-Cruz et al. (2011).

2.7. Data analysis

The retardation factors, R, were determined as indicators of the peak shifts of the BTC for herbicide leaching relative to the chloride tracer in the unamended and amended soil columns. These factors were estimated according to the expression $R = 1 + K \rho / \theta$ (Marín-Benito et al., 2013), assuming that sorption–desorption isotherms are linear and reversible. In this expression, ρ is the bulk density of the soil (g cm^{-3}), θ is the volumetric water content or PV in the packed column divided by the total volume (cm^3 cm^{-3}), and K is the distribution coefficient for the linear adsorption of herbicide by soil (mL g^{-1}). K values were determined from the linearized adsorption isotherms obtained by the batch equilibrium technique for prosulfocarb with the soils used here (unpublished results). The parameters of the soil columns and the calculated values of adsorption constants (K) and retardation factors (R) are included in **Table 1**.

Standard deviation (SD) was used to indicate the variability in the leached, retained, or mineralized amounts of herbicide among replicates. Retained, leached, mineralized and total amounts of ^{14}C-prosulfocarb were subjected to an analysis of variance (ANOVA) to measure the effects of herbicide incubation and irrigation. IBM SPSS statistics v24 software package was used (SPSS Inc. Chicago, USA).

3. Results and discussion

3.1. Chloride ion leaching in soil columns

The chloride ion is widely used as a water flow tracer in soil columns because it is a conservative ion that is not retained or degraded in soils. The chloride breakthrough curves (BTC) were obtained for both unamended and amended soils (**Fig. 1**). They were symmetric, and maximum leaching occurred at about 1 PV, as expected in the percolation of conservative ions. An amount of chloride ion close to 100% of the ion applied was recovered at the end of the leaching process. This indicates that water flow is uniform in the columns used; tracer ion leaching is not affected by the water flow regime applied, and there are no preferential flows throughout the soil columns. The peak concentration recorded for the amended soil decreased with respect to the unamended soil (38% and 47%, respectively). A similar reduction was also observed in soils amended with other organic residues (Álvarez-Martín et al., 2017).

3.2. Breakthrough curves of prosulfocarb in unamended and amended soil columns

Experimental BTCs were obtained corresponding to prosulfocarb leaching in the unamended soil columns (**Fig. 1A,B**) and in the GC-amended soil columns (**Fig. 1C,D**) under two different herbicide incubation times (one day and 28 days of prosulfocarb ageing in soil before leaching) and flow regimes (saturated and saturated-unsaturated).

In general, the BTCs of prosulfocarb in S columns were asymmetrical and different to those of the chloride ion. They recorded a rapid initial leaching of ^{14}C applied to the column for a PV ≤ 1.50, although the BTCs recorded a long tail with shoulders (saturated flow) (**Fig. 1A**) or peaks (saturated-unsaturated flow) (**Fig. 1B**), indicating the steady leaching of the herbicide when up to 500 mL (11PV) of water were pumped under both flow conditions. These asymmetrical BTCs were also reported for other herbicides and fungicides in an unamended soil (Khorram et al., 2017; Marín-Benito et al., 2018c). The peak concentration was recorded at a water volume between 1.10 and 1.28 PV, similar to that recorded for the tracer ion, albeit lower (**Table 2**; **Fig. 1A,B**). This peak represents 2.01%-6.33% of the total ^{14}C applied to the S columns for the non-incubated herbicide under saturated or saturated-unsaturated flow, respectively.

When the herbicide was incubated in the soil column for 28 days, the BTC pattern was similar, albeit with lower peak concentrations. Concentrations decreased up to ~2-3 times compared to those of the non-incubated herbicide (**Table 2; Fig. 1A,B**). Changes in peak concentrations with incubation time were also observed for the leaching of other pesticides in an unamended soil (Álvarez-Martín et al., 2017), although the decrease was not always as significant as observed here.

In the S+GC columns, BTCs recorded early peaks when a saturated flow was applied; the mobility of prosulfocarb was then very slow, and the leaching of ^{14}C was continuously determined up to a water volume of 9-11 PV (**Table 2**). However, the BTCs for prosulfocarb leaching in S+GC columns under saturated-unsaturated flow were different because they recorded a long tail with several peaks. The early peaks of BTCs were recorded for a water volume between 0.79 and 1.50 PV under both flow conditions, similar to those found for the herbicide in the unamended soil and for the chloride ion. The leaching kinetic of prosulfocarb was faster, however, and peak concentration was higher in S+GC (2.99%) than in S under saturated flow, although the adsorption of prosulfocarb by S+GC was higher than by S (**Table 1**). A similar effect was observed for the leaching of the hydrophobic compound tebuconazole in an amended soil using similar experimental conditions (Álvarez-Martín et al., 2017). The DOC content in S+GC (0.027%) was higher than in S (0.006%), and it favoured the compound's initial rapid movement in the column. This effect of DOM or DOC on the adsorption of hydrophobic compounds increasing their mobility has been reported in previous works (García-Jaramillo et al., 2014; Marín-Benito et al., 2018b; Thevenot et al., 2009). There is a decreasing or increasing effect of DOC on the adsorption of hydrophobic compounds by the batch equilibrium technique and on the mobility of compounds under saturated water conditions (Marín-Benito et al., 2016). The effect of rapid leaching was also observed in the early peak concentration for the non-incubated prosulfocarb under saturated-unsaturated flow conditions (4.34%) (**Fig. 1C,D**), although a second peak with a concentration of 2.72% (4.98 PV) was recorded under this saturated-unsaturated flow, and the leaching pattern was closer to that recorded in the unamended soil. This behaviour could be attributed to non-equilibrium sorption due to the time-dependent interactions that occur between the herbicide and soil components and/or organic amendment, which may be more difficult to attain under the conditions of unsaturated water flow (Brusseau et al., 1992; Dousset et al., 2007; Marín-Benito et al., 2009). This asymmetrical behaviour is also commonly observed for other pesticides in amended soils (Fenoll et al., 2014; Khorram et al., 2015; Rodríguez-Cruz et al., 2011).

Peak concentrations decreased after herbicide incubation in the S+GC columns under saturated and saturated-unsaturated flow regimes. They fell within the range 0.65%-1.31% of the total ^{14}C applied to the column for the incubated compound. The first peak of prosulfocarb after incubation is broad and not well defined under saturated-unsaturated flow (**Fig. 1 D**) (**Table 2**). A second peak with concentrations of 1.59% (3.34 PV) was also recorded when incubated herbicide was leached under saturated-unsaturated flow. The BTCs patterns were similar for prosulfocarb leaching when no incubation was carried out and after the incubation of the herbicide in the S+GC column (**Fig. 1C,D**). However, the peak concentrations of herbicide were ~4.6 times and ~3.3 times lower after incubation under saturated or saturated-unsaturated flow, respectively. This decrease in herbicide concentration under all conditions could be due to the increase in the mineralized amount or to the possible formation of bound residues of ^{14}C-herbicide after incubation in soil columns compared to non-incubated ones (**Table 2**), consistent with the dissipation mechanisms of prosulfocarb in S and S+GC described by Barba et al. (2019).

3.3. Leaching of prosulfocarb in unamended and amended soil columns

The total amounts leached for non-incubated prosulfocarb after the application of 10-11 PV to the S columns were 13.0% and 26.7% for saturated and saturated-unsaturated flow, respectively. For the S+GC columns, these values were similar in the case of saturated flow (12.2%) and slightly higher than the one obtained in saturated-unsaturated flow (32.5%). A higher movement of prosulfocarb through the soil profile in the GC-amended soil than in the unamended soil was also recorded in a field experiment (Marín-Benito et al., 2018b).

The leached amounts decreased when the herbicide was incubated for 28 days in the S and S+GC columns. They decreased 2.1 and 1.9 times for the S columns, and 2.9 and 1.6 times for the S+GC columns under saturated or saturated-unsaturated flow, respectively (**Table 2**). Walker et al. (2005) indicated that time-dependent sorption processes are important for controlling pesticide movement in soil. The time elapsed between the application and leaching of the herbicide could explain these results, as the losses of herbicides following their application were higher than when leaching events occur days after an incubation period (Milan et al., 2015). Results obtained are consistent with the prosulfocarb dissipation in the same S and S+GC soils reported by Barba et al. (2019). They found that after a 27-day incubation period the fraction extracted with a 0.01M $CaCl_2$ water solution (potentially leachable) decreased by up to 7% in the unamended soil, being higher in S+GC than in S. Previous studies have also reported a decrease in tebuconazole and cymoxanil leaching after pesticide incubation in an experiment with packed soil columns (Álvarez-Martín et al., 2017).

3.4. Retention of prosulfocarb in unamended and amended soil columns

The total amounts retained after herbicide leaching were lower in S than in S+GC under saturated flow. However, these amounts were similar in both S and S+GC when saturated-unsaturated flow was applied. These values were the same after incubating the herbicide in the column (**Table 2**). They are consistent with the higher adsorption constant of prosulfocarb by S+GC than by S, as previously indicated (**Table 1**), suggesting a stronger interaction between the herbicide and the S+GC soil. Previous leaching studies have reported a higher retention of pesticides by amended soils than by unamended ones (Ghosh and Singh, 2012; Jiang et al., 2016; Khorram et al., 2015; Larsbo et al., 2013). Prosulfocarb retention was higher under saturated than saturated-unsaturated flow for the non-incubated and incubated compounds in agreement with the corresponding amounts leached (**Table 2**), with this effect contradicting our results reported for other pesticides (Álvarez-Martín et al., 2017). The slow leaching kinetic of prosulfocarb in S and S+GC under saturated-unsaturated flow could increase herbicide degradation. The initial amounts retained could not remain in both soils if prosulfocarb metabolites were produced over time with a high leachability capacity. Prosulfocarb has a relatively short half-life, and the formation of degradation products has been reported (Barba et al., 2019;

Braun et al., 2017). Degradation could be enhanced by the organic matter in S+GC, according to the higher amount leached in this soil than in the unamended one (**Table 2**).

The distribution of the ^{14}C amounts retained in the different segments of the columns, expressed as a percentage of the total ^{14}C applied to the columns under all the conditions (**Fig. 2**), indicated that prosulfocarb was primarily retained in the first segment of the columns. The retention in the S columns was > 28% in all cases, and in the S+GC columns it also occurred mainly in the first segment, > 74% under saturated flow, and ~43% under saturated-unsaturated flow, according to the total amount retained as previously indicated. A higher percentage of pesticides remaining in the first segment of the column for unamended soils and soils amended with biochar or fly ash has usually been reported (Gámiz et al., 2017; Ghosh and Singh, 2012; Khorram et al., 2015). The amounts of herbicide present in the lower segments of the S columns were higher than in the S+GC columns. This suggests a stronger binding of the herbicide with the organic amendment in the upper layer, or the formation of bound residues with the soil (Barriuso et al., 2008), which would cause the retention in the upper layer of the column (García-Jaramillo et al., 2014; Marín-Benito et al., 2009). Prosulfocarb may be able to form bound residues, as reported in our previous work (Barba et al., 2019), but these residues may be bioavailable for degradation under saturated-unsaturated flow, as previously indicated, decreasing the remaining prosulfocarb in the first segment and increasing the total amount leached.

3.5. Mineralization of Prosulfocarb in unamended and amended soil columns

The total mineralized amounts of non-incubated ^{14}C-prosulfocard were low (≤ 0.70%) in the S and S+GC columns under saturated flow (**Table 2**). However, under the saturated-unsaturated flow condition, the mineralized amounts were higher (11.3%-

14.9%), probably due to the longer leaching experiment (20 days). In a previous dissipation work, the mineralization of prosulfocarb was > 18% after 27 days incubation in S and > 14% in S+GC (Barba et al., 2019). As regards the incubated herbicide in the soil columns, the total mineralized amounts increased up to 19 times under saturated flow compared to the non-incubated herbicide in the soil column. These results suggest that incubation time did not greatly affect the herbicide's retention, but it significantly increased the mineralized amount under saturated flow. As regards the incubated herbicide in the S and S+GC columns, the mineralized amounts were similar under saturated-unsaturated flow compared to the non-incubated herbicide (**Table 2**).

3.6. Total balance and retardation factors of prosulfocarb in unamended and amended soil columns

The total amounts of prosulfocarb leached, retained and mineralized were determined to evaluate the total balance of ^{14}C-prosulfocarb in the columns. They were expressed as the percentages of the total ^{14}C initially added to the columns, and the values found were between 73% and 88% in the S columns, and between 80% and 97% in the S+GC columns (**Table 2**). Prosulfocarb is considered a slightly volatile compound, so some losses due to volatilization are expected (EFSA, 2007). Prosulfocarb volatilization from soil has been reported (Carlsen et al., 2006), and it has been detected in rainwater or the air (Khalil et al., 2019; Kreuger et al., 2017). The possible volatilization of prosulfocarb after incubation occurred in the S column, and to a lesser extension in the S+GC column. These results are consistent with our previous work, where we studied the dissipation mechanism of prosulfocarb, finding that the total ^{14}C mass balance was 92.4% and 94.9% at time 0 days for S and S+GC soils, respectively, with these percentages decreasing over time (Barba et al., 2019).

Finally, the retardation factors (R) were determined for comparing the BTCs under different conditions (**Table 1**). Their values ranged from 26.3 to 28.2 in S, and from 30.6 to 32.7 in S+GC. The R factors for S+GC are slightly higher than for S soils, but this is not reflected in the PV values corresponding to the initial peaks due to the BTC patterns with various peaks. The R results indicate a lower mobility of prosulfocarb in the S+GC column, although this was not the case for the saturated-unsaturated flow. The high R values found for unamended and amended soils indicate the low leaching potential of prosulfocarb and the highest percentage of herbicide retained under all the conditions assayed.

4. Conclusions

The results obtained in this work show the effects that the application of GC to soil had in the leaching of the herbicide prosulfocarb when different water flow and herbicide ageing conditions were applied. Although the total amount of prosulfocarb leached differed little between unamended and amended soils, the amount of herbicide retained was higher in the amended soil under saturated flow (1.4 times). The amendment had less impact when the saturated-unsaturated water flow was applied after the non-incubation or incubation of the herbicide. However, the presence of the organic amendment decreased the loss of prosulfocarb due to other processes such as volatilization. When the leaching experiment was carried out after 28 days of incubation, the amount of prosulfocarb leached decreased for both the unamended and amended soils, although the amount mineralized increased. The results on the leaching of prosulfocarb from this study complement the field studies carried out in previous works. Several factors, such as amendment, water flow and herbicide ageing, which are related to climate and agronomic factors, have proven to be important for controlling the leaching of this herbicide through the soil profile.

Declarations of interest: none.

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