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Accelerated Dissipation of Two Herbicides after Repeated Application in Field Experiments with Organically-Amended Soil

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Abstract: Organic wastes applied as composted amendments may improve the quality of degraded soils and modify the fate of pesticides. This work has set out to study the dissipation kinetics of the herbicides chlorotoluron and flufenacet during their second-year application in field experimental plots with a sandy-loam agricultural soil without amendment (S) and amended with spent mushroom substrate (S + SMS) or green compost (S + GC). The SMS and GC were applied to the soil during the previous winter's wheat crop campaign (1 year before the second herbicide application) at rates of 140 and 85 t ha^{-1} (dry weight basis), respectively. The experiment involved randomized complete blocks with plots of 81 m^2, including three replicates per soil treatment. Surface soils were sampled after herbicide application for 225 days, and herbicide residues in the soil samples were determined by HPLC-MS. The dissipation curves of both herbicides for the three soil treatments were better fitted to the first order multi-compartment (FOMC) kinetic model. The dissipation rates of the most hydrophobic herbicide, flufenacet, were slower than those for chlorotoluron in both unamended and amended soils. The half-life (DT$_{50}$) values ranged between 20.7 to 41.1 days for chlorotoluron, and 42.9 to 75.6 days for flufenacet, and they followed the order S > S + SMS > S + GC. The DT$_{50}$ values of chlorotoluron were close for S + SMS and S + GC, and the DT$_{50}$ of flufenacet for S was similar to that for S + SMS. These DT$_{50}$ values decreased up to four times with respect to those calculated after the first application indicating an accelerated dissipation of the herbicides after the second application especially in amended soil in comparison with unamended soil. The persistence of chlorotoluron and flufenacet in an agricultural soil was modified by the effect of the organic amendments, weather conditions, and possibly the repeated application of the compounds under real field conditions.

Keywords: chlorotoluron; flufenacet; commercial formulation; repeated application; soil; spent mushroom substrate; green compost; accelerated dissipation; field plot

1. Introduction

The composted organic residues applied to soils as amendments to increase the organic matter (OM) in soils with content <1% is a common agricultural management practice which improves soil fertility and quality, as well as crop yields [1]. The organic residues applied to soil as amendments have a high content of organic carbon (OC) and dissolved organic carbon (DOC), which may modify the dynamics (adsorption, mobility, and degradation) of pesticides applied simultaneously to combat pests and diseases [2–4]. The OC content has been positively correlated with the adsorption of hydrophobic compounds with high affinity by organic soil components and amendments [5,6], although functional groups of OC from amendments are also important factors controlling the adsorption-desorption of pesticides by amended soils [6]. On the one hand, DOC is a diverse mixture of complex compounds with different chemical structures and molecular weights that might enhance the formation of multiple interactions with organic pesticides, controlling their distribution in the soil. This is why DOC may increase the adsorption of organic pesticides through

the formation of complexes that are adsorbed by soils, although on the other hand, it may increase the amount of compound in solution through the formation of complexes leached throughout the soil [7–9]. Moreover, organic residues improve soil microbial activity, which has influence on the degradation of pesticides applied in amended soils [10].

The soil dissipation of pesticides depends on several processes, with the most significant ones being degradation, adsorption, and mobility, which control pesticide behavior [11]. The dissipation rate of pesticides after the repeated application of the same pesticide, or another with a similar chemical structure, during several crop cycles may be accelerated by faster pesticide biodegradation due to microorganism adaptation, which affects their persistence and reduces their efficacy against weeds [12–15]. Furthermore, pesticide dissipation under field conditions in the same soil may be influenced by different weather conditions (temperature, precipitation, and solar irradiation) recorded over time [16]. Accelerated pesticide degradation depends on soil properties, such as soil OC content, clay content, pH, moisture content, pesticide structure, microbial activity, degrader growth, plant exudates, environmental factors, and soil management practices [13,14,17]. This phenomenon is well known and has been reported for pesticides under laboratory conditions [4,18,19]. At field scale, accelerated herbicide dissipation has been reported in unamended and amended soils for atrazine [20], butachlor [16,17], metribuzin [21], and sulfosulfuron [15].

Studies on the dissipation and persistence of pesticides in soils amended with organic residues under field conditions are less frequent, and, in general, they only evaluate dissipation after a single application. However, the repeated application of pesticides during successive cycles of the same crop is a common agricultural practice, especially in conventional agriculture, with the consequent risk of soil and/or water contamination [16,22].

The herbicides chlorotoluron and flufenacet are applied at the pre-emergence stage of cereal crops such as winter wheat. Chlorotoluron belongs to the phenylurea family, and records moderate water solubility (74 mg L^{-1}, 20 °C), low hydrophobicity (log K_{ow} 2.5), and high leaching potential (GUS index 3.02). Flufenacet is an oxyacetamide with moderate water solubility (56 mg L^{-1}, 20 °C), high hydrophobicity (log K_{ow} 3.2), and intermediate capacity for leaching (GUS index 2.23) [23,24].

There are only a few results on the dissipation and persistence of chlorotoluron and flufenacet in unamended and amended soils at field scale [11,25–28], being influenced by soil properties, herbicide characteristics, and environmental conditions. However, the dissipation of chlorotoluron after repeated application in field studies has been assessed solely in unamended soils [29]. To the best of our knowledge, there are no studies on the dissipation of these herbicides after repeated application in field soils amended with organic residues.

This study therefore pursued the following objectives: (i) study the field dissipation kinetics of the herbicides chlorotoluron and flufenacet after their repeated application at the pre-emergence stage of winter wheat in an agricultural soil unamended and amended with two organic residues, (ii) compare their persistence with that observed the previous year after a first application in the same field experiment, and (iii) assess the influence of soil property evolution and weather conditions on the long-term dissipation and persistence of these herbicides. This study is part of a research project carried out under field conditions involving the dissipation and mobility of chlorotoluron and flufenacet over a 2 year experimental period following an initial, single application of the organic residues to the soil [11,30].

2. Materials and Methods

2.1. Field Dissipation Study

The organic wastes used as soil amendments originated from *Agaricus bisporus* and *Pleurotus ostreatus* (2:1) cultivation (SMS), and from the pruning of plants and trees in parks and gardens (GC). They were composted following an aerobic process, and were supplied by Sustratos de la Rioja S.L. (Pradejon, Spain) and Viveros El Arca S.L. (Salamanca,

Spain), respectively. The soil was an Eutric-Chromic Cambisol (IUSS Working Group WRB, 2015) with a sandy-loam texture (80.4% sand, 4.7% silt, and 14.9% clay). The main physicochemical characteristics of both organic residues and unamended and amended soils were determined in air-dried and sieved (<2 mm) samples (Table 1) by standard analytical methods, as reported by Carpio et al. [30]. Briefly, the DOC content was determined in organic residues extracts 1/100 *w/v* or soil extracts 1/2 *w/v* ratio in deionized water after soil shaking 24 h at 20 °C, centrifugation 20 min at 10,000 rpm, and filtering (Minisart NY 25 filter 0.45 µm, Sartorius Stedim Biotech, Germany). DOC, OC and N content was determined on a LECO CN628 (Saint Joseph, MI, USA) elemental analyzer.

Table 1. Characteristics of organic residues spent mushroom substrate (SMS) and green compost (GC), unamended soil (S) and soil amended with SMS (S + SMS) or GC (S + GC). Soil OC and DOC include the range of values determined between 29 and 225 days after the second herbicides' application.

Soil	pH	OC (%) [a]	DOC (mg g^{-1}) [b]	N (%)	C/N	CEC (cmolc kg^{-1}) [c]
SMS	7.9	35.0	11.9	2.3	15.2	35.1
GC	7.2	26.7	7.18	1.1	24.3	41.4
S	6.3	0.76–0.80	0.37–0.18	0.05	15.2–16.0	8.5
S + SMS	7.1	2.22–2.43	0.75–0.45	0.24	9.25–10.1	10.9
S + GC	7.0	1.65–1.72	0.66–0.33	0.14	11.8–12.3	11.0

[a] Organic carbon; [b] dissolved organic carbon; [c] cation exchange capacity.

Herbicides were initially applied during the 2016–2017 winter wheat crop campaign in a field experiment set up at the Muñovela experimental farm belonging to the Institute of Natural Resources and Agrobiology of Salamanca, Spain (40°54′15″ N latitude and 5°46′26″ W longitude) [30]. The experiment involved randomized complete blocks with plots of 81 m^2 corresponding to the following three treatments, each in three replicates: unamended control soil (S), soil amended with spent mushroom substrate (S + SMS), and soil amended with green compost (S + GC). The SMS and GC were applied to the soil once in the previous winter wheat crop campaign (November 2016) at rates of 140 and 85 t ha^{-1} (dry weight basis), respectively, and incorporated into the top 20 cm. The commercial formulations, Erturon® (chlorotoluron 50% *w/v*, Cheminova Agro S.A., Madrid, Spain) and Herold® (flufenacet 40% *w/v*, Bayer Crop Science S.L., Valencia, Spain), were sprayed at the pre-emergence stage at 15 and 5 kg a.i. ha^{-1}, respectively, the first time in November 2016 and 346 days after their first application (in November 2017) at similar concentrations by second time. Herbicide dissipation was evaluated after repeated application.

Weather data (precipitation, maximum, minimum, and average air temperature) were recorded at the Spanish State Agency of Meteorology (AEMET) weather station on the Muñovela farm itself. During the 2017–2018 campaign corresponding to field dissipation experiment after second application of herbicides, the average air temperature was 8.0 °C, with average maximum and minimum temperatures of 13.6 °C and 2.5 °C, respectively. The total precipitation recorded was 411.0 mm during the 225-day-long experiment, starting 10 days after herbicide application. Precipitation >10 mm was recorded 52, 105, 106, 108, 110, 116, 120, 147, 152, 208, and 219 days after herbicide application, so less precipitation was recorded up to 104 days (79.6 mm). The maximum precipitation was 20.0 mm at 208 days after herbicide application (Figure 1).
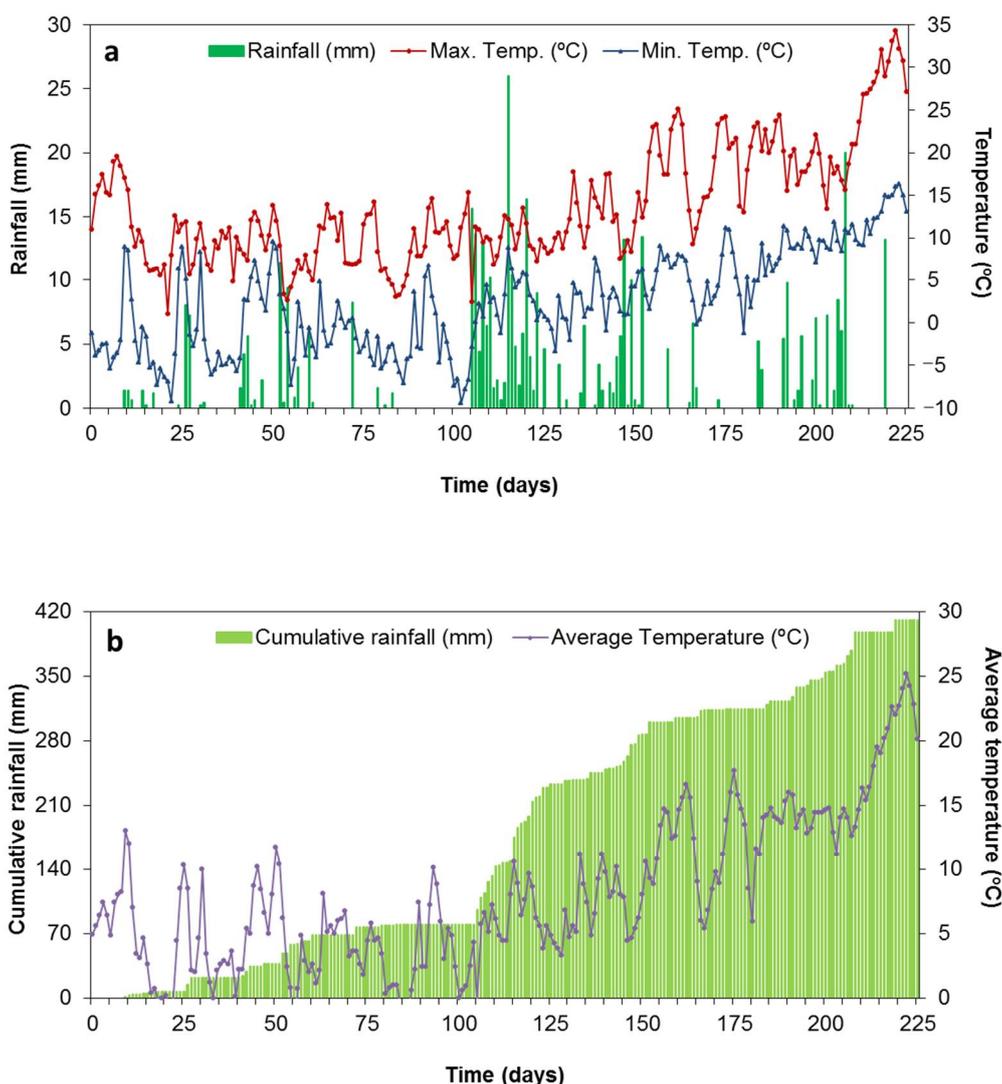
Figure 1. (**a**) Rainfall, maximum and minimum air temperatures; (**b**) cumulative rainfall and average temperature recorded in the Muñovela farm during the field dissipation experiment (225 days).

2.2. Herbicide Extraction and Analysis

Surface soils (0–10 cm) were sampled eighteen different times for 225 days after herbicide application. On each occasion, five soil subsamples were randomly collected in each plot, and representative average samples were obtained for each plot by mixing the five subsamples. The composite samples were homogenized, sieved (<2 mm), and stored at 4 °C until their analysis.

The analytical standards of chlorotoluron and flufenacet (>99.5% purity), and of their major metabolites, desmethyl chlorotoluron, flufenacet ESA sodium salt, and flufenacet OA (>99.3% purity), were supplied by Sigma Aldrich Química S.A. (Madrid, Spain). Both the herbicides and their major metabolites were extracted and analyzed according to [31]. Briefly, triplicate subsamples of moist soil (6 g) from each composite sample of unamended or amended soils taken at each sampling time were extracted with acetonitrile (12 mL). They then underwent an ultrasonic bath (1 h, 20 °C), shaken (24 h, 20 °C), centrifuged (5045 g, 15 min), and filtrated (<0.45 μm). Extracts (8 mL) were 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 0.75 mL of acetonitrile and transferred to a glass vial for analysis. The herbicides and their metabolites were determined by HPLC-DAD-MS using a Waters chromatograph (Waters Assoc., Milford, MA, USA).

2.3. Data Analysis

FOCUS work group guidelines were followed to select the best kinetic model for each herbicide and soil treatment [32]. According to these guidelines, herbicide dissipation kinetics were fitted to single first-order (SFO) and first-order multi-compartment (FOMC) kinetic models. The coefficient of determination and the chi-squared test were calculated as indicators of the goodness of fit. The herbicide concentrations, which were measured 1 day after the application in the three soil treatments, were considered as 100% of the amounts applied. The DT_{50} and DT_{90} values were used to characterize the decay curves and compare the variations in dissipation rates. The kinetic model parameters were estimated using the Excel Solver Add-in Package [32].

3. Results

3.1. Dissipation of Chlorotoluron and Flufenacet during the Second-Year Application

The dissipation curves of the herbicides for the three soil treatments were fitted to the SFO and FOMC kinetic models. Although the fitting of the observed data to both kinetic models was acceptable, the goodness of fit of both herbicides in all soil treatments was better for the FOMC model than for the SFO one (Figure 2, Table 2). The chi-squared (χ^2) test was ≤ 14.7 and the coefficient of determination (R^2 value) was ≥ 0.95 when herbicide dissipation curves were fitted to the FOMC model (Table 2). In a previous work, the dissipation of chlorotoluron in unamended and amended soils under field conditions was better described by the double first-order in parallel (DFOP) model [33]. The dissipation of flufenacet in unamended soils in field trials was more accurately described by the SFO model [25].
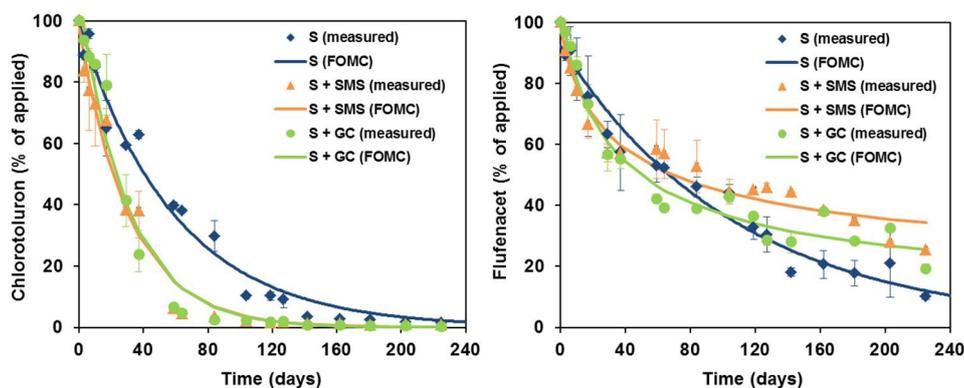
Figure 2. Dissipation curves of chlorotoluron and flufenacet in the unamended soil (S) and soil amended with SMS (S + SMS) or GC (S + GC). Dissipation data were fitted to the FOMC kinetic model (FOCUS, 2006).

Table 2. Dissipation parameters (DT_{50} and DT_{90}) for chlorotoluron and flufenacet in unamended (S) and SMS- and GC-amended (S + SMS and S + GC) soils. Goodness of fit parameters (χ^2 and R^2) obtained from the fitting of dissipation curves to a first-order multi-compartment (FOMC) kinetic model [32].

Soil	M0 (%)	α	β	DT_{50} (Days)	DT_{90} (Days)	χ^2	R^2
				Chlorotoluron			
S	99.21	1.14×exp4	6.75×exp5	41.1	136.5	9.3	0.982
S + SMS	97.54	6.23×exp4	1.96×exp6	21.8	72.3	8.1	0.983
S + GC	107.79	5.39×exp5	1.61×exp7	20.7	68.8	14.7	0.975
				Flufenacet			
S	92.41	64.496	6995.6	75.6	254.3	5.8	0.972
S + SMS	97.98	0.35	11.7	73.6	8515.6	6.4	0.951
S + GC	105.16	0.511	14.9	42.9	1333.5	5.3	0.969

A total of 64 days after its application, the dissipation of chlorotoluron was >60% in S, and >93% in S + SMS and S + GC, indicating rapid dissipation during the first phase of the kinetic curve. This behavior would be related with this compound's characteristics (high solubility in water and low hydrophobicity). For flufenacet, the percentages of dissipation were >47% in S, >43% in S + SMS, and >60% in S + GC at 64 days after its application in the field plots. These results indicate that the flufenacet dissipation rate was slower than for chlorotoluron in both unamended and amended soils. This may be due to flufenacet's lower solubility in water and higher hydrophobicity [23]. However, both herbicides dissipated faster after the second application in field conditions than after their first application previously evaluated in the same unamended and amended soils [11].

The DT_{50} values for chlorotoluron were two times lower in amended soils than in the unamended soil (Table 2). The DT_{50} value for flufenacet was 1.76 times lower in S + GC than in the unamended one. The DT_{50} values of both herbicides followed the order S > S + SMS > S + GC, although the DT_{50} values of chlorotoluron were close for S + SMS and S + GC, while the DT_{50} value of flufenacet for S was similar to that for S + SMS (Figure 2, Table 2). The DT_{50} and DT_{90} values calculated for chlorotoluron were in the same range or lower than those reported in unamended soils under field conditions [23,25]. However, the DT_{50} and DT_{90} values for flufenacet were always higher than those reported for unamended soils [23,26].

The higher DOC content in amended soils (Figure 3) than in unamended one may explain the lower persistence of chlorotoluron, as DOC could increase the amount of chlorotoluron in solution, facilitating its dissipation through different pathways, such as biodegradation by microorganisms or its mobility to lower soil layers, as reported in previous research [30]. Flufenacet recorded a high dissipation rate in amended soils (lower DT_{50} values for S + SMS and S + GC than for S) during the first kinetic phase, probably due to its higher availability in solution enhanced by the DOC content, as shown for chlorotoluron. However, the dissipation rate decreased in S + SMS and S + GC (higher DT_{90} values than for S) during the second kinetic phase (Figure 2, Table 2). The higher OC content of amended soils together with their decreased DOC content over time (Figure 3) could facilitate the formation of bound residues from residual flufenacet, making this herbicide less prone to dissipation over time than chlorotoluron. It has been reported that the formation of non-extractable bound residues for flufenacet at ~100 days after its application varied between 16.3% and 56.2% [26]. Carpio et al. [30] have reported the adsorption and persistence of flufenacet in the soil surface by the OC content as the main parameter influencing its behavior in the soil.
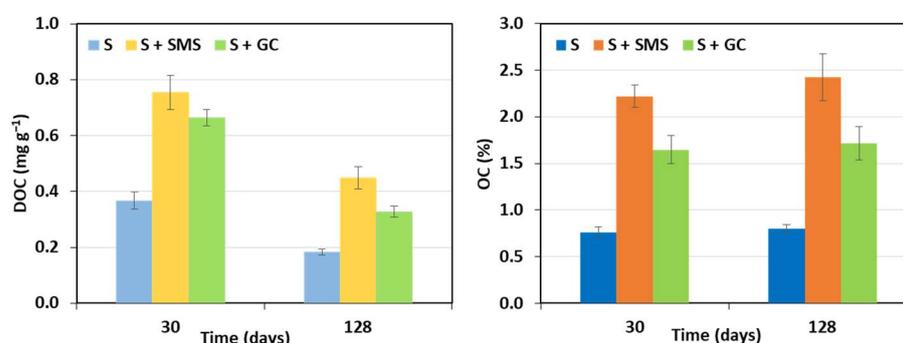
Figure 3. Dissolved organic carbon (DOC) and organic carbon (OC) for unamended soil (S) and soil amended with SMS (S + SMS) or GC (S + GC) at 30 and 128 days after the second application of herbicides.

Over the field experimental period, the metabolite desmethyl chlorotoluron was detected in all three soil treatments assayed (Figure 4). Desmethyl chlorotoluron is the major degradation product of chlorotoluron formed in soil [23], as reported in previous laboratory and field studies [11,25,31]. Its concentrations increased up to 84, 29, and 17 days

in S, S + GC and S + SMS, respectively, and then the metabolite concentrations decreased through to 225 days (Figure 4). The total amounts of metabolite formed in soils over the experimental period (225 days) followed the order: S + SMS (4.9%) < S + GC (7.1%) < S (9.0%) (Figure 4). These results are consistent with the adsorption of chlorotoluron by these soils [11]. The herbicide is therefore less bioavailable for degradation in S + SMS due to it higher adsorption. The metabolite desmethyl chlorotoluron has a higher adsorption constant than chlorotoluron [23], so it could have been adsorbed by S + SMS, forming bound residues as previously reported [11]. The flufenacet–OA metabolite was detected in the soil for all three treatments at different sampling times, but always at lower concentrations than its limit of quantification, indicating that other processes were involved in its dissipation.
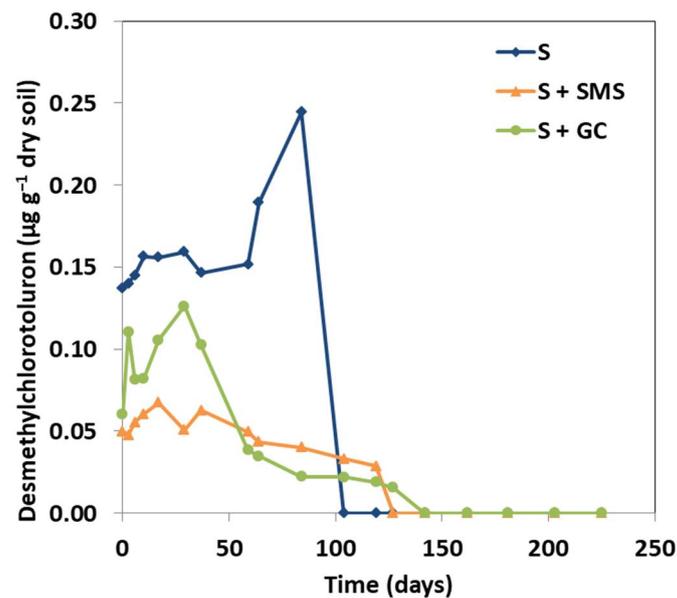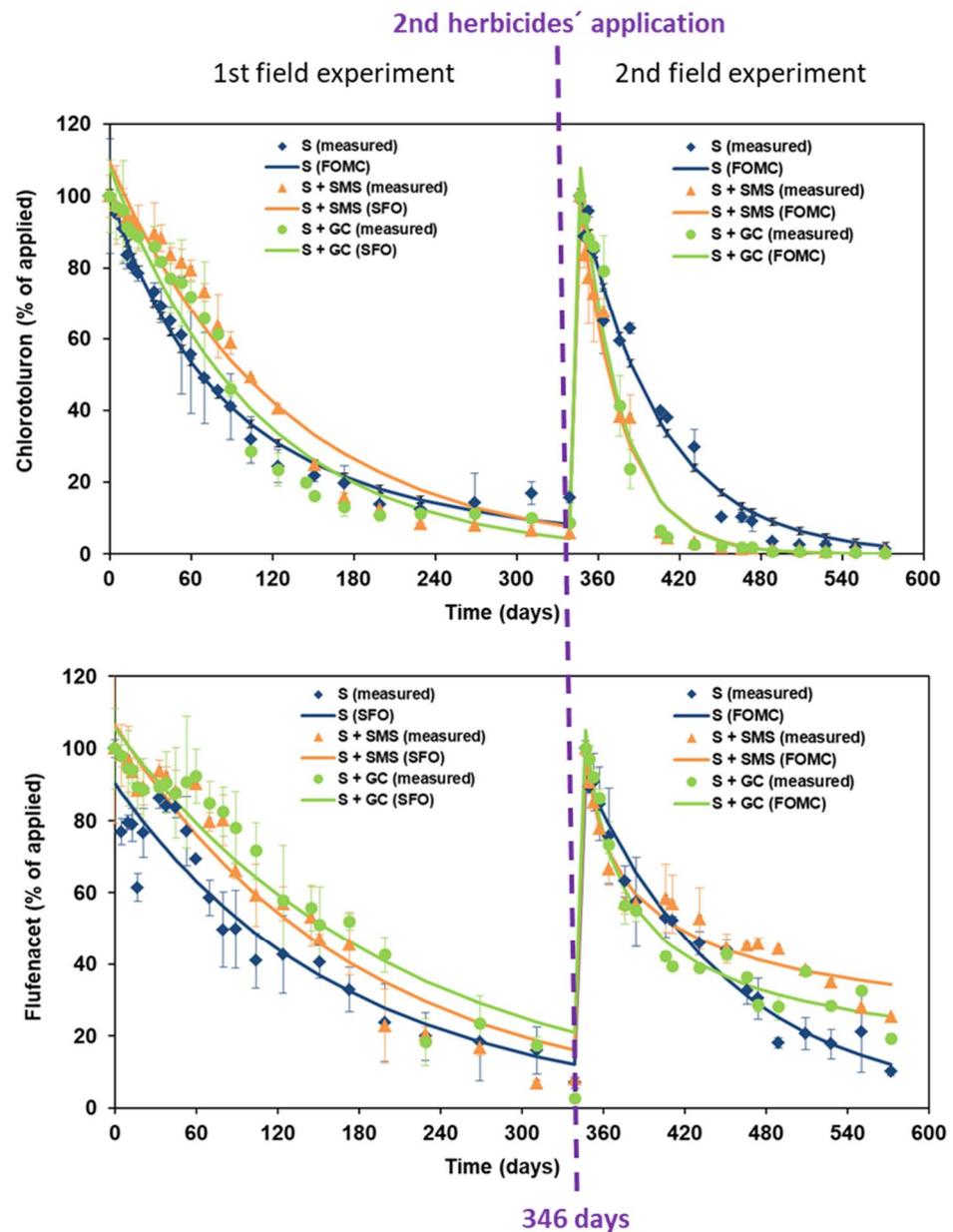

Figure 4. Formation of desmethyl chlorotoluron in unamended soil (S) and soil amended with SMS (S + SMS) or GC (S + GC).

3.2. Comparison of the Dissipation Kinetics of Chlorotoluron and Flufenacet after Repeated Application

The dissipation pattern of chlorotoluron and flufenacet after the second herbicide application was different to the first one, where the herbicide dissipation curves were best described by the SFO and FOMC models after the first and second application, respectively. For comparison purposes, Figure 5 shows these dissipation curves of chlorotoluron and flufenacet during both field experiments in unamended soil and SMS- and GC-amended soils.

The kinetic parameters indicate that chlorotoluron and flufenacet dissipated more quickly after the second application than after the first one. The DT_{50} values of both herbicides were lower by between 1.6 and 4.0 times (chlorotoluron) and by between 1.6 and 3.4 times (flufenacet) than those calculated after the first application [11]. A higher dissipation was observed after the repeated application of both herbicides in the same field plots. Previous studies have detected a similar effect (higher dissipation rate) for chlorotoluron [29] and other herbicides [15,16,20,22] applied repeatedly in field dissipation studies. Other studies have also reported an increase in dissipation rates of 1.35 times for sulfosulfuron [15], 2.0 for atrazine [34], 5.81 for chlorotoluron [29], and up to 8.0 for simazine [35] following repeated herbicide application in unamended soils.

Figure 5. Dissipation kinetics of chlorotoluron and flufenacet in unamended soil and soil amended with SMS (S + SMS) or GC (S + GC) after the first application (0–339 days) and after the second application (346–572 days) of herbicides to field plots.

In this paper changes in some variables such as soil properties (pH, OC, and DOC contents), and the presence of a crop (winter wheat) and amendments (SMS and GC) during both application years may also be responsible for changes in soil microorganisms which could help to explain chlorotoluron and flufenacet dissipation in the soil, as observed in previous studies [15,22,36,37]. It is expected that different dissipation processes, including biodegradation/mineralization and/or mobility in the soil profile, could explain the behavior of chlorotoluron and flufenacet, especially in amended soils after the repeated application, although this was not compared with control plots with a single herbicide application during the second year.

3.3. Relationship between Dissipation Parameters and Weather Conditions

Variations in precipitation and temperature over the different seasons will have an effect on the leaching, degradation, and persistence of herbicides and on their efficacy for

weed control [35,36]. High accumulated precipitation (68.4 mm) at 64 days (Figure 1b) after the second application of the herbicides could have decreased the persistence of these compounds in the topsoil and accelerated their dissipation. Cumulative precipitation at 64 days after the second herbicide application was 2.5 times higher than at 60 days (27.2 mm) after the first herbicides application [11]. The DOC content and the higher cumulative precipitation during the second application of herbicides may facilitate the availability of chlorotoluron for biodegradation, and possibly the greater mobility of flufenacet through the soil profile [30]. Janaki et al. [17] have reported the increased dissipation of butachlor due to higher initial precipitation which might have diluted or entrained the herbicide residues during the rice growing period. Similarly, Liu et al. [36] have reported lower residues of fungicide tricyclazole in rice fields from April to June due to the more frequent precipitation, which could accelerate the dissipation of pesticides by increasing their mobility through the soil profile.

The average temperature at 64 days after the second herbicide application (4.49 °C) was slightly higher than after the first application (3.86 °C) [11]. In a previous laboratory study, Marín-Benito et al. [31] have reported that chlorotoluron and flufenacet degradation rates increase with higher temperature due to higher microbial biomass and/or activity. Rouchaud et al. [27,28] have reported that the field dissipation of flufenacet accelerated with the higher temperatures in spring and summer due to increased soil microbial activities. Similarly, Johnstone et al. [38] have found a relationship between the persistence of the herbicide trifluralin and weather conditions (total precipitation and maximum average temperatures) at 60 days after its repeated application in experimental plots.

4. Conclusions

The dissipation kinetics of chlorotoluron and flufenacet after their repeated application in unamended and amended soils under field conditions followed different patterns from those observed after their initial application. Both herbicides dissipated likely faster in all the soils after the second application and in the presence of SMS and GC residues. Both soil factors (OC and DOC contents) and environmental ones (high cumulative precipitation after herbicide application) are key to explaining the higher dissipation. The possible increased availability of chlorotoluron enhanced by the DOC could increase its dissipation supported by the degradation products specified. However, the DOC content for the more hydrophobic herbicide flufenacet could initially increase its mobility in the soil profile, while the OC content would enhance the retention of residual fractions over time, explaining the high DT_{90} values obtained. This study demonstrates that dissipation rate of herbicides repeatedly applied in amended soils was also affected by weather conditions and soil characteristics. The accelerated dissipation of chlorotoluron and flufenacet facilitates their lower persistence in soils and at the same time a sustainable agricultural management of soils. Further research should focus on: (1) the determination of possible loss of weed control by these herbicides in organically-amended soils; (2) studies on microbial degradation and isolation of herbicides degraders after repeated application; and (3) studies on the effects of different amounts of organic residues on herbicide dissipation after their repeated application.

Author Contributions: Conceptualization, M.J.S.-M. and M.S.R.-C.; methodology, M.J.C. and J.M.M.-B.; software, M.J.C., J.M.M.-B., and M.S.R.-C.; validation, M.J.C., J.M.M.-B., and M.S.R.-C.; formal analysis, M.J.C. and J.M.M.-B.; investigation, M.J.C. and J.M.M.-B.; resources, M.J.S.-M.; data curation, J.M.M.-B. and M.S.R.-C.; writing—original draft preparation, M.S.R.-C.; writing—review and editing, M.J.S.-M., J.M.M.-B., M.J.C., and M.S.R.-C.; visualization, J.M.M.-B.; supervision, M.J.S.-M., J.M.M.-B., and M.S.R.-C.; project administration, M.J.S.-M.; funding acquisition, M.J.S.-M. All authors have read and agreed to the published version of the manuscript.

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