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Previous degradation study of two herbicides to simulate their fate in a sandy loam soil: Effect of the temperature and the organic amendments

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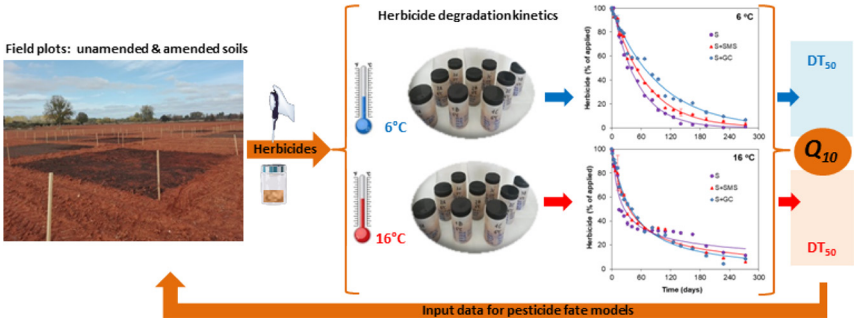
HIGHLIGHTS

- Impact of organic amendments and temperature on two herbicides degradation in soil was evaluated.
- Degradation rate decreased by application of organic amendments and increased by temperature.
- Major metabolites of both herbicides were found and evaluated in all conditions assayed.
- Kinetic parameters at different temperatures allowed calculation of Q_{10} factor in amended soils.
- Q_{10} values will allow simulating pesticide leaching in amended soils with FOCUS models.

GRAPHICAL ABSTRACT



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ABSTRACT

A laboratory study was designed to assess the following: i) the degradation kinetics of chlorotoluron and flufenacet at two different temperatures, 6 °C and 16 °C, in an unamended agricultural soil and one amended with spent mushroom substrate (SMS) and green compost (GC), and ii) the formation of the main metabolites of both herbicides with potential risk for water pollution over degradation time. The aim was to determine the dependence of these herbicide degradations on temperature (Q_{10} factor) using kinetic parameters, which is essential information for the later simulation of herbicide environmental fate with FOCUS models. SMS and GC were applied in situ to the natural soil as organic amendments at rates of 140 or 85 t residue ha^{-1}, respectively. Unamended and amended soils were taken from the 0–10 cm topsoil of experimental plots (three replicates/treatment) located on an agricultural farm. Samples of soil + herbicides were incubated at 6 °C or 16 °C under laboratory conditions. The degradation curves of chlorotoluron and flufenacet were fitted to single first-order and first-order multicompartment kinetic models, respectively. The flufenacet degradation, the more hydrophobic herbicide, was slower than that of chlorotoluron in all the treatments. The application of the organic amendments to soil increased the half-lives (DT_{50}) for both herbicides incubated at 6 °C (1.3–1.9 times) and 16 °C (1.4–1.9 times) due to their higher sorption and lower bioavailability for degradation in amended soils. The herbicides recorded a faster degradation at 16 °C than at 6 °C (Q_{10} = 1.9–2.8) due to the increased microbial biomass and/or activity with temperature. The metabolites desmethyl chlorotoluron, flufenacet ESA and flufenacet OA were detected in all the soil treatments at both incubation temperatures. The determination of Q_{10} factors in amended soils is very valuable for generating accurate input data for pesticide fate models such as FOCUS in order to improve the evaluation of the leaching of herbicides and their transformation products, which is a relevant goal to maintain the sustainability of agricultural systems.

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1. Introduction

The main challenge facing agriculture now and in the future is to ensure a food supply for the world's growing population while preserving the environment. The increase in crop yields is often based on the use of pesticides (AEPLA, 2018). The omnipresent competition between crops and weeds for soil nutrients turns herbicides into the most commonly used type of pesticides to ensure crop development and boost yields (FAOSTAT, 2018). Productive agriculture, however, depends not only on the use of pesticides but also on soil quality and fertility. Accordingly, the application to the soil of organic residues rich in nutrients and organic matter (OM) as organic amendments is a common practice in sustainable agriculture for stopping it from degrading (Bastida et al., 2015; Yazdanpanah et al., 2016). The herbicide-organic amendment combination is therefore an attractive farming practice from a productive viewpoint. However, the addition of organic amendments to the soil can control the environmental fate of herbicides through the modification of the processes that govern their dynamics in natural soil, including degradation (Briceño et al., 2007; Marín-Benito et al., 2016, 2018; Rodríguez-Cruz et al., 2012a; Rodríguez-Liébana et al., 2014). The combination of both farming practices needs to be carefully studied in order to assess and minimize their potential environmental risk on soil and water quality, especially considering the increasing presence of herbicides in aquatic media and the consequent social concern (Carabias-Martínez et al., 2003; Guzzella et al., 2006; Herrero-Hernández et al., 2013, 2017; Kotrikla et al., 2006; Ulrich et al., 2018).

Multiple factors besides the pesticides' own properties are responsible for controlling their degradation rates in the soil, ranging from their physicochemical properties (e.g., pH, texture, OM and clay content/composition), biological properties (variety, density and activity of microbial population), pesticide combinations, and/or weather conditions, through to the regulation of other main variables such as soil water content and soil temperature (varying throughout the day and on a seasonal scale from site to site) (García-Delgado et al., 2018; Gupta and Gajbhiye, 2002; Hussain et al., 2015; Kah et al., 2007; Walker et al., 1992, 1997). Numerous studies have been conducted to assess how the herbicides' degradation rate is modified, and consequently their environmental fate, by altering one or several of these factors through the application of organic amendments to the soil. In some cases, a decreased bioavailability of herbicides to be degraded by soil microbial communities has been reported as a result of their enhanced sorption by the OM of the amendments (Coppola et al., 2011; Marín-Benito et al., 2014a; Rodríguez-Cruz et al., 2012b).In other cases, the opposite effect has been observed, with higher herbicide degradation promoted by the soluble carbon from the organic amendments or by the activity of added microbial communities (García-Delgado et al., 2018; Grenni et al., 2012; Hussain et al., 2015; Marín-Benito et al., 2014a).The numerous residues potentially used as organic amendments include those from agricultural and industrial activities, such as composted spent mushroom substrate (SMS) and green compost (GC) (García-Delgado et al., 2018; Marín-Benito et al., 2014a).

The impacts temperature and soil water content have on the degradation rate of herbicides has been widely investigated (Alletto et al., 2006; Jurado-Exposito and Walker, 1998; Walker et al., 1992, 1997). In general, a higher temperature and more soil moisture increase the biodegradation rate. Natural soils were used in all these studies, although no similar studies including amended soils have yet been published. In reference to the particular dependence of degradation on temperature, the use of the Arrhenius equation is generally accepted for properly describing that dependence through the activation energy E_a (Walker and Brown, 1983). This dependence can also be described with the Q_{10} factor, which is defined as the ratio of pesticide degradation rate coefficients (k_2/k_1) at temperatures T2 and T1, with T_1 being 10 °C lower than T_2 (EFSA, 2007). The Q_{10} factor or the equated E_a in the Arrhenius equation is used as an input in the four pesticide fate models PELMO, PRZM, PEARL and MACRO used for risk assessment in European pesticide registration to account for the impact of different temperatures (FOCUS, 2000; Marín-Benito et al., 2014b). As a default, the value of $Q_{10} = 2.2$ was proposed by FOCUS (1997) and updated to $Q_{10} = 2.58$ by the European Food Safety Authority (EFSA, 2007). EFSA recommends using pesticide-specific Q_{10} values instead of the default value in modeling or risk assessment whenever they are available because it means models provide more accurate predictions of residues in the soil and/or water (Mamy et al., 2008)). In addition, the default Q_{10} value reported by EFSA is the result of multiple pesticide degradation studies including only natural soils. Thus, its extrapolation to modeling studies with amended soils could under- or overestimate the effect of temperature on pesticide degradation rates and not properly reproduce their environmental fate (Marín-Benito et al., 2015) in a model of sustainable agriculture.

On the other hand, and besides the pesticide half-life (DT_{50}) and sorption characteristics, the Q_{10} factor is considered to have the biggest influence on the prediction of pesticide loss, so it is critical information used in pesticide fate modeling and risk assessment (Dubus et al., 2003). Despite the sensitivity of FOCUS models toward these parameters, to the best of our knowledge no studies have been published assessing the influence of temperature on rates of herbicide degradation in amended soils.

The herbicides chlorotoluron (3-(3-chloro-*p*-tolyl)-1,1-dimethylurea) and flufenacet (4′-fluoro-*N*-isopropyl-2-[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yloxy] acetanilide) are widely used in the pre- and post-emergence control of grasses and some broad-leaved weeds in cereal and potato crops. Chlorotoluron is a phenylurea with a high potential for leaching due to its moderate solubility in water and low hydrophobicity (EC, 2005; PPDB, 2018). Indeed, chlorotoluron has frequently been detected in surface and ground waters, and in some cases at higher concentrations than those permitted by the EU for individual pesticides in drinking water (0.1 μg L^{-1}) (Carabias-Martínez et al., 2003; Kotrikla et al., 2006). Under laboratory conditions, chlorotoluron DT_{50} values ranged between 13 and 92 days (EC, 2005). The dissipation of this herbicide is mainly due to microbial transformation (ElGouzi et al., 2015). Its major metabolite in soil is desmethyl chlorotoluron (3-(3-chloro-*p*-tolyl)-1-methylurea), which is characterized by a high mobility and DT_{50} values ranging from 52 to 66 days (EC, 2005; PPDB, 2018).

Flufenacet belongs to the chemical group oxyacetamide and is moderately soluble in water, with high sorption and hydrophobicity (EC, 2003). Flufenacet DT_{50} values ranged between 15 and 64 days under laboratory conditions, with flufenacet ESA (2-[(4-fluorophenyl)-isopropyl-amino]-2-oxo-ethanesulfonic acid) and flufenacet OA (2-[(4-fluorophenyl)-isopropyl-amino]-2-oxo-acetic acid) being its two major degradation products in soil (EC, 2003). The persistence of flufenacet ESA in soil ($DT_{50} = 230$ days) is higher than that of flufenacet OA ($DT_{50} = 11$ days), posing a serious threat to water quality due to its huge potential for leaching (GUS index = 7.20) (EC, 2003; PPDB, 2018; (Ulrich et al., 2018). By contrast, low mobility has been reported for flufenacet (Milan et al., 2015; Rouchaud et al., 1999), although the risk of groundwater contamination in highly permeable soils is also high (USEPA, 1998).

Very few studies have been published on flufenacet degradation and its transformation products in soil (Gupta et al., 2001; Gupta and Gajbhiye, 2002; Rouchaud et al., 1999), and none including amended soils. By contrast, more and more varied studies have reported on chlorotoluron degradation and its major metabolite in soil (Badawi et al., 2009; Hussain et al., 2015; Kördel et al., 1995) although again, the effect of organic amendment on their degradation/formation has been little studied (Rodríguez-Liébana et al., 2014).

Accordingly, the objectives here were to study the following: i) the degradation kinetics of chlorotoluron and flufenacet at two different temperatures, 6 °C and 16 °C, in an unamended agricultural soil and one amended with spent mushroom substrate (SMS) and green compost (GC) under laboratory conditions in order to determine the

respective Q_{10} factors essential for the later simulation of their environmental fate with FOCUS models, and ii) the formation of the main metabolites of both herbicides over degradation time in soils with different treatments to assess the effect of organic amendments and temperature in the formation of these metabolites with a potential risk for water pollution. This work contributes to get relevant sustainable development goals inside an ongoing project on the evaluation of the leaching of these herbicides and their transformation products applied to experimental field plots cropped with wheat in soils previously amended with SMS or GC.

2. Materials and methods

2.1. Herbicides

The soils were spiked with 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). Analytical standards of chlorotoluron, flufenacet (>99.5% purity) and their metabolites desmethyl chlorotoluron, flufenacet ESA sodium salt and flufenacet OA (>99.3% purity) were supplied by Sigma Aldrich Química S.A. (Madrid, Spain). Their main characteristics are included in Table 1 (PPDB, 2018).

2.2. Organic residues

Spent mushroom substrate (SMS) from *Agaricus bisporus* and *Pleurotus ostreatus* (2:1) cultivation was composted under aerobic conditions (Sustratos de la Rioja S.L., Pradejon, Spain). Green compost (GC) is a vegetal residue from the pruning of plants and trees in parks and gardens (El Arca, S.L., Salamanca, Spain), also composted under aerobic conditions. Their main characteristics were determined by the methods reported previously (Marín-Benito et al., 2012) for air-dried samples (Table 2).

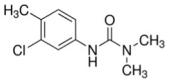
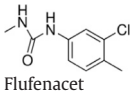
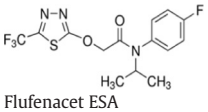
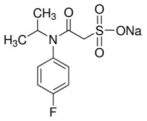
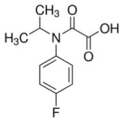
2.3. Soils and treatments

Topsoil samples (0–10 cm) were collected from experimental field plots (9 m × 9 m) corresponding to an experimental layout designed to simulate the environmental fate of herbicides. The field experiment was in a Eutric-Chromic Cambisol soil with sandy loam texture (14.9% clay, 4.7% silt, and 80.4% sand) located in the Muñovela experimental farm belonging to the Institute of Natural Resources and Agrobiology of Salamanca, Spain. Experimental plots corresponded to unamended soil (S), SMS-amended soil (S + SMS) at a rate of 140 t SMS ha^{-1}, and GC-amended soil (S + GC) at a rate of 85 t GC ha^{-1} on a dry weight basis. SMS and GC were homogenously spreading with a tractor at field and then they were incorporated into the 20 cm topsoil with a rotavator. The soil's characteristics were determined by standard analytical methods (Marín-Benito et al., 2012; Sparks, 1996) (Table 2). Samples were collected and characterized after 30 days of organic residue application just before the application of herbicides in the field experiment to reproduce as faithfully as possible the initial state of the soil samples at field conditions. This time was considered appropriate for previous conditioning of the organic residue in the soil.

2.4. Degradation experiment

Freshly collected samples of unamended and amended soils were individually homogenized and sieved (<2 mm). Triplicate soil samples (600 g) for each treatment (S, S + SMS and S + GC) were then spiked with a combined dose of chlorotoluron (14 mg) and flufenacet (5.5 mg) per kg of dry soil using the commercial formulations Erturon and Herold, respectively. The soil moisture content was adjusted to 40% of the maximum soil water holding capacity in agreement with the moisture content of each sample previously determined. Then herbicide doses corresponding to five times the recommended agronomic doses for natural soils were applied. The samples were subsequently incubated for different time periods in the dark at two temperatures, 6 °C

Table 1
Main characteristics of herbicides and their metabolites.

Common name / chemical structure	IUPAC name	WS[a] (mg L^{-1})	Log Kow[b]	Koc/Kfoc[c] (mL g^{-1})	DT_{50}[d] (days)	GUS index[e]
Chlorotoluron 	3-(3-chloro-*p*-tolyl)-1,1-dimethylurea	74	2.5	196	59	3.02
Desmethyl chlorotoluron 	3-(3-chloro-*p*-tolyl)-1-methylurea	–	–	248	60	2.84
Flufenacet 	4′-fluoro-*N*-isopropyl-2-[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yloxy]acetanilide	51	3.5	273.3	19.7	2.02
Flufenacet ESA 	2-(4-fluoro-*N*-propan-2-ylanilino)-2-oxoethanesulfonic acid	5500	–	12.5	302	7.20
Flufenacet OA 	((4-fluorophenyl) (isopropyl)amino) (oxo)acetic acid	–	–	14.0	11.1	2.98

[a] WS, water solubility at 20 °C.
[b] Octanol/water partition coefficient at pH 7 and 20 °C.
[c] Sorption coefficient normalized to organic carbon content.
[d] Time to degradation 50% of compound.
[e] Gustafson mobility index (PPDB, 2018).

Table 2
Characteristics of the organic residues and unamended and amended soil (0–10 cm depth).

	SMS	GC	S[c]	S + SMS	S + GC
pH	7.9	7.2	6.34	7.11	6.99
OM (%)[a]	59.4	46.0	1.33	4.36	2.81
DOC (%)[b]	0.8	0.7	0.008	0.023	0.018
N (%)	2.3	1.1	0.05	0.24	0.14
C/N	15.2	24.3	14.5	10.7	12.0

[a] Organic matter, [b] Dissolved organic carbon, [c] Unamended soil.

(average winter temperature where the experimental plots were located) or 16 °C. A sterilized soil sample was also prepared for each soil treatment by autoclaving soil at 120 °C for 1 h on three consecutive days. The sterilized soils were treated with the herbicides and incubated as indicated above, and these samples were used as controls to check the chemical degradation of the herbicides. Soil sampling was performed at different times up to 67 or 273 days according to each herbicide's degradation rate.

2.5. Herbicide extraction and analysis

At each sampling time, duplicate soil samples (6 g) of each triplicate treatment of S, S + SMS and S + GC were extracted with acetonitrile (12 mL) with an ultrasonic bath for 1 h at 20 °C and shaking for 24 h at 20 °C in glass test-tubes. The samples were then centrifuged at 5045*g* for 15 min, and the herbicide extracts were filtered (<0.45 μm). Extracts (8 mL) were evaporated until dry 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 acetonitrile and transferred to a glass vial for analysis. The recoveries of the extraction method were determined by spiking three soil samples in each treatment with analytical grade herbicide to a final concentration of 3 mg kg^{-1}, performing the extraction procedure as described above. The mean recovery values varied between 101% and 115% for chlorotoluron, and 95% and 101% for flufenacet.

The herbicides were determined by HPLC-DAD-MS using a Waters chromatograph (Waters Assoc., Milford, USA) with a Phenomenex Luna (3 μm C18, 150 × 4.6 mm) column. The mobile phase was acetonitrile:water +1% formic acid (80:10). The flow rate was 0.4 mL min^{-1} and the sample injection volume was 20 μL. The detection by DAD was at 243 nm for chlorotoluron and 232 nm for flufenacet. The positive molecular ions (*m/z*) [M + H^+] monitored with a MS detector were 213.04 for chlorotoluron and 364.03 for flufenacet. The retention times were 6.1 min for chlorotoluron and 7.9 min for flufenacet. Monitoring also involved positive molecular ions (*m/z*) [M + H^+] 198.65 for desmethyl chlorotoluron, and negative molecular ions (*m/z*) [M-Na^+] 274.26 for flufenacet ESA and [M-H^+] 224.15 for flufenacet OA, respectively. The formation of metabolites during the dissipation experiment was quantified. The limits of detection (LOD) and quantification (LOQ) for flufenacet ranged from 0.003 (S + SMS) to 0.005 μg mL^{-1} (S + GC), and from 0.009 (S + SMS) to 0.016 μg mL^{-1} (S + GC), respectively. In the case of chlorotoluron, the LOD was 0.002 μg mL^{-1} for all the soil treatments, and the LOQ varied between 0.006 (S + GC) and 0.008 μg mL^{-1} (S + SMS).

2.6. Sorption study

The possible effect of sorption on herbicide degradation was assessed by determining the amount of herbicide sorbed in the unamended and amended soils. Duplicate samples of soils (5 g) were equilibrated with 10 mL of a 0.01 M $CaCl_2$ Milli-Q ultrapure water solution of both herbicides (commercial formulations) at concentrations of 10 μg mL^{-1}. The suspensions were shaken at 6 °C or 16 °C for 24 h in a thermostatted chamber, with intermittent shaking for 2 h at three-hour intervals. The suspensions were subsequently centrifuged at 5045*g* for 15–30 min, and the herbicide's equilibrium concentrations (Ce, μg mL^{-1}) were determined. The amount of herbicide sorbed (Cs, μg g^{-1}) was considered to be the difference between that initially present in the solution and that remaining after equilibration with the soil.

2.7. Data analysis

The degradation kinetics for each herbicide and soil treatment was fitted to a single first-order (SFO) kinetic model or first order multi-compartment (FOMC) model. FOCUS work group guidelines were followed (FOCUS, 2006) for selecting the kinetic model that best describes the degradation results. The coefficient of determination and the chi-square test were calculated as indicators of the goodness of fit. The time to 50% degradation, or DT_{50} value (days), was used to characterize the decay curves and compare variations in degradation rates. The kinetic models' parameters were estimated using the Excel Solver add-in Package (FOCUS, 2006).

The incubation temperature's effect on herbicide degradation was determined by the factor $Q_{10} = DT_{50}$ (6 °C)/DT_{50} (16 °C).

The distribution coefficients, Kd (mL g^{-1}), for each herbicide and soil treatment were determined from the relationship between Cs and Ce.

Analysis of variance (ANOVA) was used to evaluate the effects the different factors (soil treatment and temperature) had on herbicide dissipation. Standard deviation (SD) was used to indicate variability among replicates, and the least significant difference (LSD), at a confidence level of 95%, was determined to evaluate the effects of different soil treatments and temperatures on DT_{50} values. Statgraphics Plus version 5.1 statistical software (Statgraphics Plus Corp., Princeton, NJ) was used.

3. Results and discussion

3.1. Degradation kinetics of herbicides in unamended and amended soils at different temperatures

Figs. 1 and 2 include the degradation curves of herbicides in the unamended and amended soils during the incubation times of 273 and 67 days for chlorotoluron at 6 °C and 16 °C, and 273 days for flufenacet at both temperatures assayed, respectively. The degradation curves of chlorotoluron indicate a continuous degradation with time and, in general, they fitted the SFO model well for all the soil treatments and temperatures (Fig. 1). Only one replicate of soil amended with GC fitted the FOMC model better. Degradation was almost complete at the end of the incubation periods, with the percentages of herbicide residues being 1–10% after 273 days at 6 °C and 5–8% after 67 days at 16 °C. The degradation of flufenacet was initially fast for both temperatures and soil treatments, but the degradation rate subsequently slowed down (Fig. 2). The degradation curves of flufenacet always fitted the FOMC model better, independently of the incubation temperature and the treatment studied. In contrast to this research, other authors have reported that the degradation curves of flufenacet in unamended soil fit the SFO model well (Bloomberg et al., 2002; Gupta and Gajbhiye, 2002; Rouchaud et al., 1999). The percentages of flufenacet residues at the end of the incubation (273 days) were higher than those of chlorotoluron: 36–38% at 6 °C and 5–9% at 16 °C.

Tables 3 and 4 include the DT_{50} values for chlorotoluron and flufenacet in S, S + SMS and S + GC at 6 °C and 16 °C, respectively. The degradation rates of flufenacet were lower than those of chlorotoluron for all the soil treatments and incubation temperatures, according to the longer persistence of flufenacet at 273 days, as previously indicated. Both herbicides have a moderate solubility in water, but a different hydrophobic nature. Flufenacet records a higher hydrophobicity, sorption and persistence in soil than chlorotoluron (PPDB, 2018). The DT_{50} values reported for flufenacet in agricultural soils at 25 °C (10.1–31.0 days) were close to the value found in this work at 16 °C (21.2 days) (Gupta and Gajbhiye, 2002), although as expected

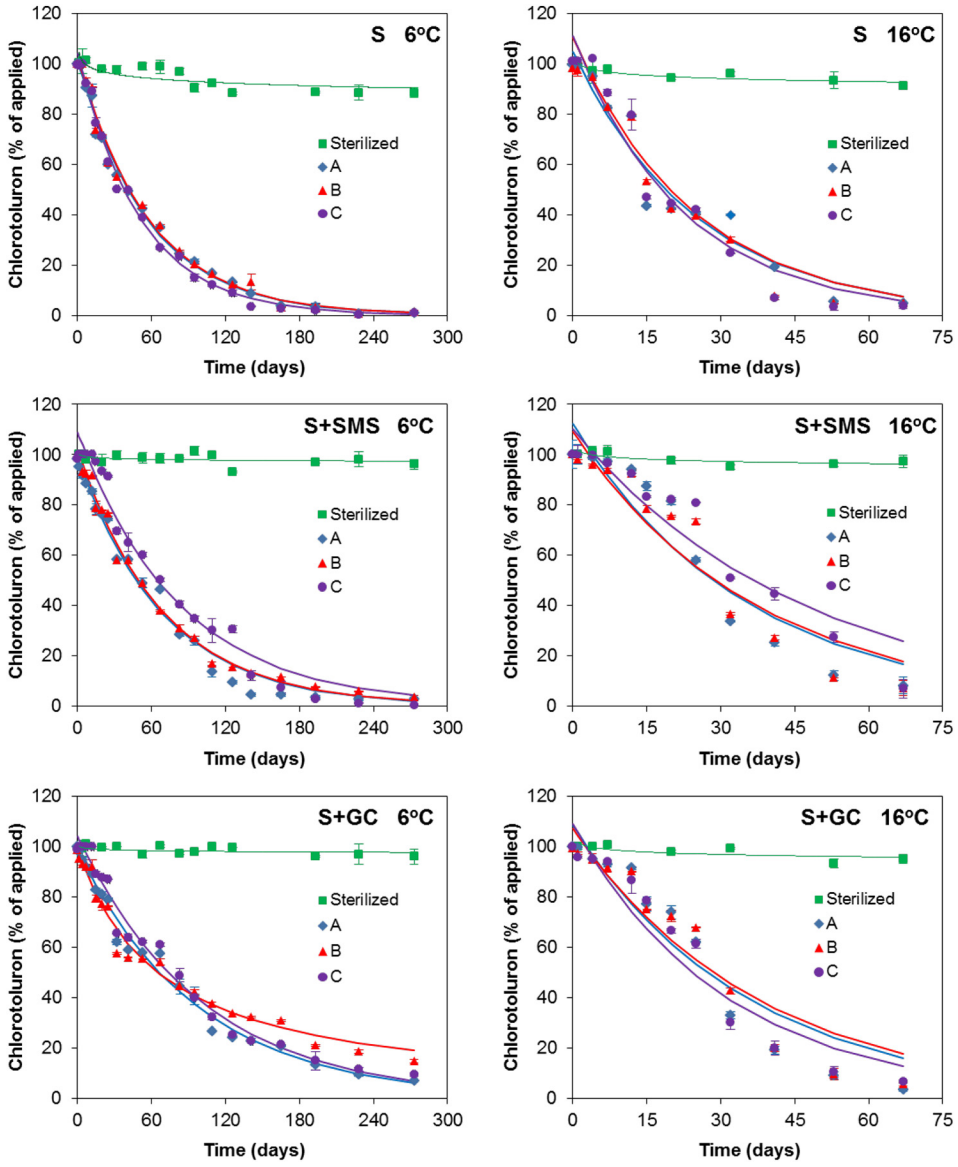


Fig. 1. Degradation kinetics of chlorotoluron in sterilized and non-sterilized unamended (S) and SMS- and GC-amended (S + SMS and S + GC) soils incubated at 6 °C (273 days) and 16 °C (67 days). Bars indicate the standard deviation of the mean ($n = 2$). A, B and C correspond to the three replicates per soil treatment.

they were different under other laboratory incubation conditions (49.3 days, at 6 °C). Gupta and Gajbhiye (2002) have observed that the degradation of flufenacet is slower in soils with a high adsorption capacity and slower desorption. Under laboratory conditions, the mean DT_{50} value for chlorotoluron in unamended soils was 59 days at 20 °C (PPDB, 2018), which was higher than the value calculated here at 16 °C (16.8 days).

The application of SMS and GC to the soil increased the DT_{50} values of both herbicides incubated at 6 °C and 16 °C (Tables 3 and 4). In amended soils, the DT_{50} values increased between 1.3 and 1.7 times for chlorotoluron, and between 1.7 and 1.9 times for flufenacet when compared with the values for the unamended soil. The DT_{50} values followed the order: S < S + GC < S + SMS for flufenacet at both incubation temperatures and for chlorotoluron at 16 °C, with this order being consistent with the higher soil OM content. However, for chlorotoluron incubated at 6 °C, the DT_{50} values followed the order: S < S + SMS < S + GC (Table 2).

The slower degradation in amended soils than in unamended soils is related to the higher sorption of chlorotoluron and flufenacet by amended soils, and therefore a lower bioavailability of the herbicides to be degraded. Sorption was evaluated by the distribution coefficients determined at temperatures of 6 °C and 16 °C (Table 5). The Kd values indicate that the sorption of chlorotoluron by amended soils increased, being up to 4.6 times higher for S + SMS and up to 2.8 times for S + GC than for the unamended soil, comparing all Kd values at both temperatures. Similar increases were recorded for the sorption of flufenacet by amended soils. Small increases in the sorption coefficients of both herbicides for the amended soils were recorded at higher temperatures, as reported for some compounds (Kaur and Kaur, 2018), although it has also been reported that an increase, decrease or no change in sorption could be caused by an increase in temperature (Ten Hulscher and Cornelissen, 1996). However, the small increases in the sorption of herbicides by amended soils or by the higher temperature did not help to explain the different degradation rate of both herbicides.

The higher DT_{50} values found for flufenacet than for chlorotoluron could only be explained by the higher sorption in the SMS amended soil. The influence of sorption for decreasing the degradation rate has also been observed for other pesticides (Álvarez-Martín et al., 2016; Marín-Benito et al., 2014a; Marín-Benito et al., 2012). The more rapid dissipation of chlorotoluron could be due to an apparent dissipation, as reported for other phenylurea herbicides such as linuron, which was explained by the formation of non-extractable bound residues in

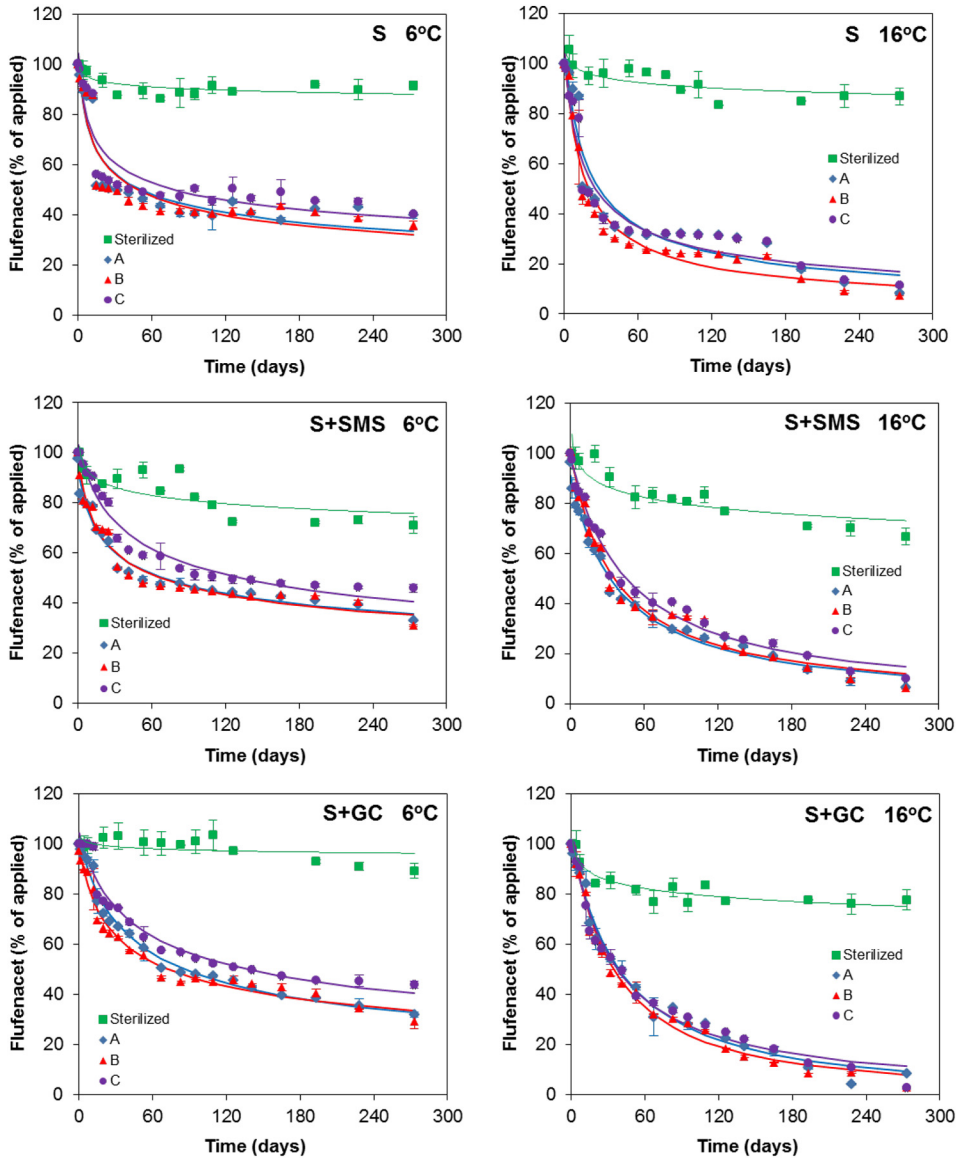


Fig. 2. Degradation kinetics of flufenacet in sterilized and non-sterilized unamended (S) and SMS- and GC-amended (S + SMS and S + GC) soils incubated at 6 °C and 16 °C (273 days). Bars indicate the standard deviation of the mean (n = 2). A, B and C correspond to the three replicates per soil treatment.

amended soils (Marín-Benito et al., 2014a). The influence of the herbicide's chemical structure for the formation of non-extractable bound residues and for subsequent biodegradation has also been reported (Barriuso et al., 2008). These results would indicate that degradation rates depend on the soil amendment and herbicide characteristics.

The degradation of herbicides was also studied in sterilized soils. No degradation of chlorotoluron was observed in either of the treatments at both temperatures (89–96% remaining at 273 days) (Fig. 1). For flufenacet a slower degradation in sterilized soils than in non-sterilized ones was observed (Fig. 2), with the percentages of residues remaining at 6 °C being slightly higher (71–92%) than at 16 °C (67–87%). The dissipation of flufenacet in sterilized soils may be influenced by other abiotic factors over the incubation time. Herbicide photodegradation was not considered, as soils were kept in the dark during incubation. It is also possible that soil sterilization was incomplete, especially in the amended soils with higher soil microbial biomass and activity, as indicated previously (ElGouzi et al., 2015). These results show that the degradation of chlorotoluron and flufenacet was mainly caused by microorganisms, as reported previously (ElGouzi et al., 2015; EC, 2003).

3.2. Metabolism of the herbicides in unamended and amended soil at different temperatures

Simultaneously to the degradation of herbicides, some metabolites of chlorotoluron and flufenacet were produced in all the soil treatments. The concentrations of desmethyl chlorotoluron, flufenacet OA and flufenacet ESA (μg metabolite g^{-1} dry soil) were evaluated over the incubation period of herbicides in the soils (Fig. 3).

Different amounts of desmethyl chlorotoluron were detected in unamended and amended soils. Peaks of metabolite concentrations were detected at short times at the beginning of the experiment conducted at 6 °C (up to 25 days), and they could explain the degradation of chlorotoluron in S and in S + GC. The concentrations detected were 0.49 and 0.59 μg g^{-1} dry soil in S and S + GC, respectively, and the total cumulative amount accounted for 21.9 and 18.1% of the dose of herbicide applied. Lower concentration peaks were

Table 3
Dissipation parameters and goodness of fit for chlorotoluron in unamended and SMS- or GC-amended soils incubated at 6 °C and 16 °C calculated by fitting the data to a SFO model.

Sample/temperature	k (days^{-1})	DT_{50} (days)	χ^2	R^2	Q_{10}[a]
S/6 °C	0.017	40.0	5.2	0.993	
	0.017	40.4	5.8	0.992	
	0.020	35.5	9.5	0.994	
		38.6 ± 2.72c			
S/16 °C	0.039	17.6	11.2	0.952	
	0.040	17.2	15.0	0.966	
	0.045	15.5	12.2	0.954	
		16.8 ± 1.12a			2.3
S + SMS/6 °C	0.014	48.2	6.7	0.987	
	0.014	48.0	4.4	0.993	
	0.012	57.6	8.8	0.976	
		51.3 ± 5.49d			
S + SMS/16 °C	0.028	24.4	14.9	0.906	
	0.027	25.5	15.0	0.906	
	0.022	32.0	10.6	0.908	
		27.3 ± 4.11b			1.9
S + GC/6 °C	0.010	67.7	5.1	0.986	
	1.034–69.0[b]	65.9	5.2	0.981	
	0.010	69.3	5.7	0.982	
		67.6 ± 1.70e			
S + GC/16 °C	0.029	24.3	14.8	0.926	
	0.027	25.8	12.8	0.924	
	0.032	21.5	14.9	0.926	
		23.9 ± 2.18ab			2.8

[a] Estimated from Q_{10} = DT_{50} (6 °C)/DT_{50} (16 °C).
[b] α and β values from the fitting of the degradation curve to the FOMC model.
Different letters in DT_{50} values indicate significant differences among samples and treatments (LSD = 8.91, $p < 0.05$).

determined throughout the degradation process. The maximum concentration of desmethyl chlorotoluron (0.12 μg g^{-1}) and the cumulative amount (5.14% of herbicide applied) were lower in S + SMS, indicating that the herbicide's degradation mechanism was different to that observed in S and S + GC treatments. The highest sorption of chlorotoluron by S + SMS could explain a lower bioavailability of the herbicide to be degraded and the lower amount of metabolite produced in this soil. However, the degradation rate was higher than in S + GC, which means another chlorotoluron degradation pathway could be involved in this soil, such as mineralization or the formation of other metabolites.

Table 4
Dissipation parameters and goodness of fit for flufenacet in unamended and SMS- or GC-amended soils incubated at 6 °C and 16 °C calculated by fitting the data to a FOMC model.

Sample/temperature	α	β	DT_{50} (days)	χ^2	R^2	Q_{10}[a]
S/6 °C	0.245	2.7	43.6	11.3	0.870	
	0.262	3.2	41.9	11.8	0.872	
	0.211	2.4	62.3	10.4	0.857	
			49.3 ± 11.3a			
S/16 °C	0.590	10.7	23.9	14.4	0.924	
	0.656	9.1	17.1	11.4	0.957	
	0.501	7.5	22.5	11.8	0.942	
			21.2 ± 3.59a			2.3
S + SMS/6 °C	0.257	6.6	91.3	4.8	0.963	
	0.262	5.6	73.1	5.2	0.964	
	0.307	13.7	117.4	4.5	0.964	
			93.9 ± 22.3b			
S + SMS/16 °C	1.000	38.8	38.8	6.1	0.983	
	0.950	32.8	35.2	7.4	0.979	
	0.967	44.4	46.5	5.6	0.984	
			40.2 ± 5.77a			2.3
S + GC/6 °C	0.419	19.1	81.0	3.6	0.982	
	0.328	10.5	76.7	4.3	0.972	
	0.337	17.2	117.4	4.7	0.964	
			91.7 ± 22.4b			
S + GC/16 °C	1.381	59.1	38.6	6.1	0.984	
	1.380	50.8	33.2	5.8	0.989	
	1.069	39.9	36.4	6.1	0.984	
			36.1 ± 2.72a			2.5

[a] Estimated from Q_{10} = DT_{50} (6 °C)/DT_{50} (16 °C). Different letters in DT_{50} values indicate significant differences among samples and treatments (LSD = 38.4, $p < 0.05$).

Table 5
Sorption coefficients (Kd) for chlorotoluron and flufenacet in unamended and SMS- and GC-amended soils incubated at 6 °C and 16 °C calculated for an initial concentration of 10 μg mL^{-1}.

	Chlorotoluron		Flufenacet	
	6 °C	16 °C	6 °C	16 °C
	Kd ± SD (mL g^{-1})	Kd ± SD (mL g^{-1})	Kd ± SD (mL g^{-1})	Kd ± SD (mL g^{-1})
S	1.56 ± 0.37a	1.57 ± 0.24a	1.62 ± 0.22a	1.54 ± 0.03a
S + SMS	6.93 ± 0.47c	7.28 ± 0.92c	7.44 ± 0.26c	8.24 ± 0.08c
S + GC	4.05 ± 0.73b	4.37 ± 0.43b	3.98 ± 0.27b	4.36 ± 0.55b

SD, standard deviation of replicates (n = 2). Different letters in Kd values indicate significant differences among samples and treatments (LSD = 1.81, $p < 0.05$).

The degradation rate of chlorotoluron in the soils was faster when the temperature increased to 16 °C, but the pattern of metabolite formation was similar to that observed at 6 °C. However, the maximum peaks were obtained at lower times (up to 15 days), and the total cumulative amounts were lower than those determined at 6 °C (9.8, 15.7 and 3.4% of herbicide applied in S, S + GC and S + SMS, respectively) (Fig. 3). Desmethyl chlorotoluron is reported to be the main metabolite of chlorotoluron detected in soils (EC, 2005; PPDB, 2018) in amounts > 10% of the chlorotoluron applied (Badawi et al., 2009; EC, 2005). Furthermore, the degradation mechanism of chlorotoluron by demethylation in soil prevails over the oxidation of the ring-methyl group (Gross et al., 1979).

The metabolites flufenacet OA and flufenacet ESA were also detected in unamended and amended soils. At 6 °C, maximum concentration peaks of 0.34 and 0.08 μg g^{-1} were detected in S for flufenacet OA and flufenacet ESA after 12 and 109 days of herbicide application, respectively. At the end of the experiment (273 days), the cumulative amount of flufenacet OA (2.2 μg g^{-1}) and flufenacet ESA (0.32 μg g^{-1}) reached 40.0% and 5.8% of the amount of herbicide applied, respectively. In S + GC, peaks of flufenacet OA and flufenacet ESA were also recorded, although their concentrations were lower (0.15 and 0.03 μg g^{-1}) and were delayed or advanced compared to S, respectively (Fig. 3). The total formation of flufenacet OA (0.66 μg g^{-1}) and flufenacet ESA (0.23 μg g^{-1}) represented 12.0% and 4.2% of the amount of herbicide applied to S + GC after 273 days, respectively. In S + SMS, the maximum concentrations of flufenacet OA (0.06 μg g^{-1}) and flufenacet ESA (0.05 μg g^{-1}) were observed after 32 and 41 days of herbicide application. Similar to results in S + GC, these concentrations were lower in S + SMS than in S, and smaller amounts of flufenacet OA and flufenacet ESA were accumulated at the end of the experiment (0.48 and 0.33 μg g^{-1} representing 8.7% and 6.0% of the herbicide applied, respectively). These results indicate a different herbicide degradation mechanism in this soil. The higher sorption of flufenacet by S + SMS could explain a lower bioavailable amount of compound and the lower amount of metabolite produced.

The flufenacet degradation rate in soils was faster when the temperature increased to 16 °C than for chlorotoluron (Fig. 3). Only a slight change in the metabolites concentrations was recorded in S + GC and S + SMS with increasing temperature. The formation of these metabolites was reported in studies on flufenacet degradation in unamended soils under laboratory or field conditions (Bloomberg et al., 2002).

The results reflect the influence of organic residues for modifying the herbicide degradation mechanism, possibly being determined by the sorption characteristics and the influence of this process on the bioavailability of herbicide, or by the nature of microorganisms provided by the organic residues for enhancing degradation.

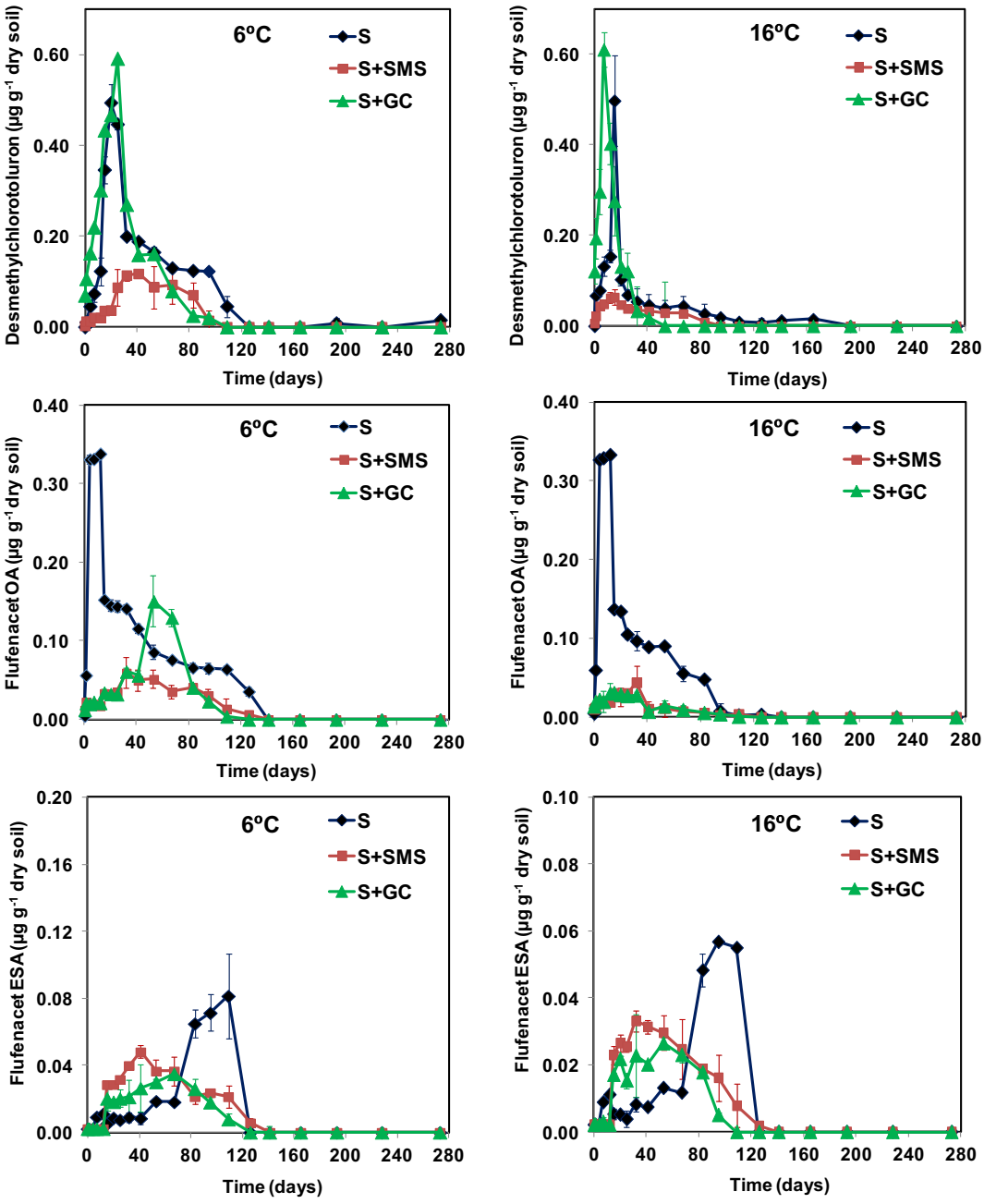


Fig. 3. Formation of desmethyl chlorotoluron, flufenacet OA and flufenacet ESA in non-sterilized unamended (S) and SMS- and GC-amended (S + SMS and S + GC) soils incubated at 6 °C and 16 °C over time. Bars indicate the standard deviation of the mean ($n = 6$).

3.3. Influence of soil treatment in the Q_{10} factor

The degradation of both herbicides was more rapid at 16 °C than at 6 °C, as observed for other pesticides (El Azhari et al., 2018; Walker et al., 1992; Walker and Jurado-Exposito, 1998) probably due to the increase in microbial structure and/or activity with temperature. Temperature can regulate the structure and functions of the soil microbiome. In fact, it has been reported that microbial communities in soil collected during the summer and winter differ not only in composition, but also in their overall function (Reedich et al., 2017).

The DT_{50} values determined at two temperatures permitted the calculation of the Q_{10} factor. The Q_{10} factor values varied between 1.9 and 2.8 for chlorotoluron (Table 3) and between 2.3 and 2.5 for flufenacet (Table 4). This factor was the same for both herbicides in the unamended soil, while the effect of temperature on the degradation rate of herbicides in the amended soils was greater for flufenacet ($Q_{10} = 2.3$) in the S + SMS than for chlorotoluron ($Q_{10} = 1.9$). However, incubation temperature had a greater impact on S + GC for chlorotoluron ($Q_{10} = 2.8$) than for flufenacet ($Q_{10} = 2.5$).

The Q_{10} values determined for the unamended soil agree with those reported for herbicides, as well as for other pesticides under laboratory conditions. Mamy et al. (2008) have simulated the fate of the herbicides glyphosate, trifluralin and metazachlor in a clay loam calcareous soil using Q_{10} values ranging from 1.7 to 2.3, which were determined experimentally at 18 °C and 28 °C. El Azhari et al. (2018) have also reported a Q_{10} value of 2.3 for tebuconazole in a laboratory study under two temperature regimes (20 °C and 2–9 °C simulating winter conditions), differing by approximately 10 °C. Previously, Rouchaud et al. (1999) have

observed decreasing DT_{50} values (up to 1.75 times) of flufenacet at higher temperatures (spring and summer) than at lower temperatures (winter) under field conditions, being due to higher soil microbial activities. For chlorotoluron, an increase in DT_{50} values of 2.66 times was reported when the temperature decreased from 20 °C to 10 °C under aerobic laboratory conditions (EC, 2005).

The Q_{10} values calculated in this work for chlorotoluron and flufenacet considering both unamended and amended soils include the value of 2.58 recommended by default for modeling studies (EFSA, 2007). From a comparative viewpoint, the Q_{10} values determined for both herbicides in the unamended soil were slightly lower than the default value. However, this comparison cannot, or at least should not, be made for amended soils, as the default value recommended by EFSA was averaged from a database that includes degradation studies of pesticides from different chemical groups, being carried out solely with unamended soils due to the lack of similar studies with amended soils. It is important to obtain these data for amended soils through laboratory experiments because they are required for highly accurately parameterizing pesticide fate models (e.g. FOCUS models) in order to avoid overestimating or underestimating the temperature effect on the pesticide degradation rate in simulation studies that include this agricultural practice.

4. Conclusions

Incubation temperature and organic amendments had no significant impact on the kinetic model that best fits the experimental degradation curves of chlorotoluron and flufenacet in an agricultural soil. This impact depended solely on the herbicide. However, the application of the organic amendments to soil decreased the degradation rates of both herbicides due to their higher sorption and lower bioavailability for degrading. This effect of the amendments differed depending on the herbicide and incubation temperature. An expected faster degradation was observed for both herbicides at 16 °C than that at 6 °C, possibly because the increased microbiological activity with the higher temperature meant a significant presence of metabolites in all the soil treatments and incubation temperatures. The estimated Q_{10} values showed the need to carry out these laboratory studies for amended soils, as the parameterization of pesticide fate models with the default values recommended for Q_{10} factor by EFSA (2007) could overestimate or underestimate the effect of temperature on the degradation rate of pesticides in amended soils. These effects have consequences on the environmental impact of pesticides and their consideration is relevant in order to maintain a sustainable development agricultural systems.

Acknowledgements

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References

AEPLA, 2018. Asociación Empresarial para la Protección de las Plantas. Available online. www.aepla.es, Accessed date: 21 May 2018.

Alletto, L., Coquet, Y., Benoit, P., Bergheaud, V., 2006. Effects of temperature and water content on degradation of isoproturon in three soil profiles. Chemosphere 64, 1053–1061. https://doi.org/10.1016/j.chemosphere.2005.12.004.

Álvarez-Martín, A., Sánchez-Martín, M.J., Pose-Juan, E., Rodríguez-Cruz, M.S., 2016. Effect of different rates of spent mushroom substrate on the dissipation and bioavailability of cymoxanil and tebuconazole in an agricultural soil. Sci. Total Environ. 550, 495–503. https://doi.org/10.1016/j.scitotenv.2016.01.151.

El Azhari, N., Dermou, E., Barnard, R.L., Storck, V., Tourna, M., Beguet, J., Karas, P.A., Lucini, L., Rouard, N., Botteri, L., Ferrari, F., Trevisan, M., Karpouzas, D.G., Martin-Laurent, F., 2018. Science of the total environment the dissipation and microbial ecotoxicity of tebuconazole and its transformation products in soil under standard laboratory and simulated winter conditions. Sci. Total Environ. 637–638, 892–906. https://doi.org/10.1016/j.scitotenv.2018.05.088.

Badawi, N., Rønhede, S., Olsson, S., Kragelund, B.B., Johnsen, A.H., Jacobsen, O.S., Aamand, J., 2009. Metabolites of the phenylurea herbicides chlorotoluron, diuron, isoproturon and linuron produced by the soil fungus *Mortierella* sp. Environ. Pollut. 157, 2806–2812. https://doi.org/10.1016/j.envpol.2009.04.019.

Barriuso, E., Benoit, P., Dubus, I.G., 2008. Formation of pesticide nonextractable (bound) residues in soil: magnitude, controlling factors and reversibility. Environ. Sci. Technol. 42, 1845–1854. https://doi.org/10.1021/es7021736.

Bastida, F., Selevsek, N., Torres, I.F., Hernández, T., García, C., 2015. Soil restoration with organic amendments: linking cellular functionality and ecosystem processes. Sci. Rep. 5, 1–12. https://doi.org/10.1038/srep15550.

Bloomberg, A.M., Shadrick, B.A., Arthur, E.L., Clay, V.E., 2002. Outdoor soil metabolism of [phenyl-U-^{14}C] flufenacet on California. Soil, 167–182 https://doi.org/10.1021/bk-2002-0813.ch012.

Briceño, G., Palma, G., Durán, N., 2007. Influence of organic amendment on the biodegradation and movement of pesticides. Crit. Rev. Environ. Sci. Technol. 37, 233–271. https://doi.org/10.1080/10643380600987406.

Carabias-Martínez, R., Rodríguez-Gonzalo, E., Fernández-Laespada, M.E., Calvo-Seronero, L., Sánchez-San Román, F.J., 2003. Evolution over time of the agricultural pollution of waters in an area of Salamanca and Zamora (Spain). Water Res. 37, 928–938. https://doi.org/10.1016/S0043-1354(02)00366-4.

Coppola, L., Castillo, Pilar, Del, M., Vischetti, C., 2011. Degradation of isoproturon and bentazone in peat- and compost-based biomixtures. Pest Manag. Sci. 67, 107–113. https://doi.org/10.1002/ps.2040.

Dubus, I.G., Brown, C.D., Beulke, S., 2003. Sensitivity analyses for four pesticide leaching models. Pest Manag. Sci. 59, 962–982. https://doi.org/10.1002/ps.723.

EC (European Commission. Directorate-General Health & Consumer Protection), 2003. Review Report for the Active Substance Flufenacet (30 pp).

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

EFSA, 2007. Scientific opinion of the panel on plant protection products and their residues on a request from EFSA related to the default Q10 value used to describe the temperature effect on transformation rates of pesticides in soil. EFSA J. 622, 1–32.

Elgouzi, S., Draoui, K., Chtoun, E.H., Dolores Mingorance, M., Peña, A., 2015. Changes in the persistence of two phenylurea herbicides in two Mediterranean soils under irrigation with low- and high-quality water: a laboratory approach. Sci. Total Environ. 538, 16–22. https://doi.org/10.1016/j.scitotenv.2015.07.146.

FAOSTAT. Food and Agriculture Organization of the United Nations, 2018. Available online. http://faostat3.fao.org, Accessed date: 24 May 2018.

FOCUS, 1997. Soil Persistence Models and EU Registration 29.2.97 (77 pp).

FOCUS, 2000. Focus groundwater scenarios in the EU review of active substances. Report of the FOCUS Groundwater ScenariosWorkgroup EC Document Reference Sanco/321/2000 Rev.2 (202 pp).

FOCUS, 2006. Guidance Document on estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration. Report of the FOCUS Work Group on Degradation Kinetics. EC Documents Reference Sanco/10058/2005 Version 2.0.

García-Delgado, C., Barba, V., Marín-Benito, J.M., Igual, J.M., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., 2018. Simultaneous application of two herbicides and green compost in a field experiment: implications on soil microbial community. Appl. Soil Ecol. 127, 30–40. https://doi.org/10.1016/j.apsoil.2018.03.004.

Grenni, P., Rodríguez-Cruz, M.S., Herrero-Hernández, E., Marín-Benito, J.M., Sánchez-Martín, M.J., Caracciolo, A.B., 2012. Effects of wood amendments on the degradation of terbuthylazine and on soil microbial community activity in a clay loam soil. Water Air Soil Pollut. 223, 5401–5412. https://doi.org/10.1007/s11270-012-1289-z.

Gross, D., Laanio, T., Dupuis, G., Esser, H.O., 1979. The metabolic behavior of chlorotoluron in wheat and soil. Pestic. Biochem. Physiol. 10, 49–59. https://doi.org/10.1016/0048-3575(79)90007-5.

Gupta, S., Gajbhiye, V.T., 2002. Effect of concentration, moisture and soil type on the dissipation of flufenacet from soil. Chemosphere 47, 901–906. https://doi.org/10.1016/S0045-6535(02)00017-6.

Gupta, S., Gajbhiye, V.T., Agnihotri, N.P., 2001. Adsorption – desorption, persistence, and leaching behavior of flufenacet in alluvial soil of India. Bull. Environ. Contam. Toxicol., 9–16 https://doi.org/10.1007/s001280000198.

Guzzella, L., Pozzoni, F., Giuliano, G., 2006. Herbicide contamination of surficial groundwater in northern Italy. Environ. Pollut. 142, 344–353. https://doi.org/10.1016/j.envpol.2005.10.037.

Herrero-Hernández, E., Andrades, M.S., Álvarez-Martín, A., Pose-Juan, E., Rodríguez-Cruz, M.S., Sánchez-Martín, M.J., 2013. Occurrence of pesticides and some of their degradation products in waters in a Spanish wine region. J. Hydrol. 486, 234–245. https://doi.org/10.1016/j.jhydrol.2013.01.025.

Herrero-Hernández, E., Rodríguez-Cruz, M.S., Pose-Juan, E., Sánchez-González, S., Andrades, M.S., Sánchez-Martín, M.J., 2017. Seasonal distribution of herbicide and insecticide residues in the water resources of the vineyard region of La Rioja (Spain). Sci. Total Environ. 609, 161–171. https://doi.org/10.1016/j.scitotenv.2017.07.113.

Hussain, S., Arshad, M., Springael, D., Sørensen, S.R., Bending, G.D., Devers-Lamrani, M., Maqbool, Z., Martin-Laurent, F., 2015. Abiotic and biotic processes governing the fate of phenylurea herbicides in soils: a review. Crit. Rev. Environ. Sci. Technol. 45, 1947–1998. https://doi.org/10.1080/10643389.2014.1001141.

Jurado-Exposito, M., Walker, A., 1998. Degradation of isoproturon, propyzamide and alachlor in soil with constant and variable incubation conditions. Weed Res. 38, 309–318. https://doi.org/10.1046/j.1365-3180.1998.00099.x.

Kah, M., Beulke, S., Brown, C.D., 2007. Factors influencing degradation of pesticides in soil. J. Agric. Food Chem. 55, 4487–4492. https://doi.org/10.1021/jf0635356.

Kaur, P., Kaur, P., 2018. Time and temperature dependent adsorption-desorption behaviour of pretilachlor in soil. Ecotoxicol. Environ. Saf. 161, 145–155. https://doi.org/10.1016/j.ecoenv.2018.05.081.

Kördel, W., Wahle, U., Knoche, H., Hund, K., 1995. Degradation capacities of chlorotoluron and simazine in subsoil horizons. Sci. Total Environ. 171, 43–50. https://doi.org/10.1016/0048-9697(95)04688-2.

Kotrikla, A., Gatidou, G., Lekkas, T.D., 2006. Monitoring of triazine and phenylurea herbicides in the surface waters of Greece. J. Environ. Sci. Health B 41, 135–144. https://doi.org/10.1080/03601230500364336.

Mamy, L., Gabrielle, B., Barriuso, E., 2008. Measurement and modelling of glyphosate fate compared with that of herbicides replaced as a result of the introduction of glyphosate-resistant oilseed rape. Pest Manag. Sci. 64, 262–275. https://doi.org/10.1002/ps.

Marín-Benito, J.M., Andrades, M.S., Rodríguez-Cruz, M.S., Sánchez-Martín, M.J., 2012. Changes in the sorption-desorption of fungicides over time in an amended sandy clay loam soil under laboratory conditions. J. Soils Sediments 12, 1111–1123. https://doi.org/10.1007/s11368-012-0525-x.

Marín-Benito, J.M., Herrero-Hernández, E., Andrades, M.S., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., 2014a. Effect of different organic amendments on the dissipation of linuron, diazinon and myclobutanil in an agricultural soil incubated for different time periods. Sci. Total Environ. 476–477, 611–621. https://doi.org/10.1016/j.scitotenv.2014.01.052.

Marín-Benito, J.M., Pot, V., Alletto, L., Mamy, L., Bedos, C., Barriuso, E., Benoit, P., 2014b. Comparison of three pesticide fate models with respect to the leaching of two herbicides under field conditions in an irrigated maize cropping system. Sci. Total Environ. 499, 533–545. https://doi.org/10.1016/j.scitotenv.2014.06.143.

Marín-Benito, J.M., Rodríguez-Cruz, M.S., Sánchez-Martín, M.J., Mamy, L., 2015. Modeling fungicides mobility in undisturbed vineyard soil cores unamended and amended with spent mushroom substrates. Chemosphere 134, 408–416. https://doi.org/10.1016/j.chemosphere.2015.04.103.

Marín-Benito, J., Sánchez-Martín, M., Rodríguez-Cruz, M., 2016. Impact of spent mushroom substrates on the fate of pesticides in soil, and their use for preventing and/or controlling soil and water contamination: a review. Toxics 4, 17. https://doi.org/10.3390/toxics4030017.

Marín-Benito, J.M., Barba, V., Ordax, J.M., Andrades, M.S., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., 2018. Application of green compost as amendment in an agricultural soil: Effect on the behaviour of triasulfuron and prosulfocarb under field conditions. J. Environ. Manag. 207, 180–191. https://doi.org/10.1016/j.jenvman.2017.11.024.

Milan, M., Ferrero, A., Fogliatto, S., Piano, S., Vidotto, F., 2015. Leaching of *S*-metolachlor, terbuthylazine, desethyl-terbuthylazine, mesotrione, flufenacet, isoxaflutole, and diketonitrile in field lysimeters as affected by the time elapsed between spraying and first leaching event. J. Environ. Sci. Health B 50, 851–861. https://doi.org/10.1080/03601234.2015.1062650.

PPDB, 2018. Pesticide Properties Data Base. University of Hertfordshire, UK http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm.

Reedich, L.M., Millican, M.D., Koch, P.L., 2017. Temperature impacts on soil microbial communities and potential implications for the biodegradation of turfgrass pesticides. J. Environ. Qual. 46, 490–497. https://doi.org/10.2134/jeq2017.02.0067.

Rodríguez-Cruz, M.S., Herrero-Hernández, E., Ordax, J.M., Marín-Benito, J.M., Draoui, K., Sánchez-Martín, M.J., 2012a. Adsorption of pesticides by sewage sludge, grape marc, spent mushroom substrate and by amended soils. Int. J. Environ. Anal. Chem. 92, 933–948. https://doi.org/10.1080/03067319.2011.609933.

Rodríguez-Cruz, M.S., Marín-Benito, J.M., Ordax, J.M., Azejjel, H., Sánchez-Martín, M.J., 2012b. Influence of pine or oak wood on the degradation of alachlor and metalaxyl in soil. J. Environ. Manag. 95, S228–S232. https://doi.org/10.1016/j.jenvman.2010.10.043.

Rodríguez-Liébana, J.A., ElGouzi, S., Mingorance, M.D., Castillo, A., Peña, A., 2014. Irrigation of a Mediterranean soil under field conditions with urban wastewater: effect on pesticide behaviour. Agric. Ecosyst. Environ. 185, 176–185. https://doi.org/10.1016/j.agee.2013.12.026.

Rouchaud, J., Neus, O., Cools, K., Bulcke, R., 1999. Flufenacet soil persistence and mobility in corn and wheat crops. Bull. Environ. Contam. Toxicol. 63, 460–466. https://doi.org/10.1007/s001289901002.

Sparks, D.L., 1996. Methods of Soil Analysis. Part 3-Chemical Methods. Soil Science Society of America, Inc., Madison, WI.

Ten Hulscher, T.E.M., Cornelissen, G., 1996. Effect of temperature on sorption equilibrium and sorption kinetics of organic micropollutants - a review. Chemosphere 32, 609–626. https://doi.org/10.1016/0045-6535(95)00345-2.

Ulrich, U., Hörmann, G., Unger, M., Pfannerstill, M., Steinmann, F., Fohrer, N., 2018. Lentic small water bodies: variability of pesticide transport and transformation patterns. Sci. Total Environ. 618, 26–38. https://doi.org/10.1016/j.scitotenv.2017.11.032.

USEPA, 1998. United States Environmental Protection Agency Pesticide Fact Sheet – Flufenacet. USEPA, Washington, DC (31 pp).

Walker, A., Brown, P.A., 1983. Measurement and prediction of chlorsulfuron persistence in soil. Bull. Environ. Contam. Toxicol. 30, 365–372. https://doi.org/10.1007/BF01610146.

Walker, A., Jurado-Exposito, M., 1998. Adsorption of isoproturon, diuron and metsulfuron-methyl in two soils at high soil:solution ratios. Weed Res. 38, 229–238. https://doi.org/10.1046/j.1365-3180.1998.00087.x.

Walker, A., Moon, Y.-H., Welch, S.J., 1992. Influence of temperature, soil moisture and soil characteristics on the persistence of alachlor. Pestic. Sci. 35, 109–116. https://doi.org/10.1002/ps.2780350203.

Walker, A., Helweg, A., Jacobson, O.S., 1997. Temperature and pesticide degradation. Soil Persistence Models and European Union Pesticide Registration: Final Report of the FOCUS Working Group. European Union Document DOC 7617/VI/96, pp. 10–21.

Yazdanpanah, N., Mahmoodabadi, M., Cerdà, A., 2016. The impact of organic amendments on soil hydrology, structure and microbial respiration in semiarid lands. Geoderma 266, 58–65. https://doi.org/10.1016/j.geoderma.2015.11.032.