FIELD MEASUREMENT AND MODELLING OF CHLOROTOLURON AND FLUFENACET PERSISTENCE IN UNAMENDED AND AMENDED SOILS

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1   **ABSTRACT**

2   The dissipation and persistence of two cereals herbicides, chlorotoluron and flufenacet,

3   were studied in a field experiment including three replicated plots of unamended soil

4   (S), soil amended with spent mushroom substrate (S+SMS), and soil amended with

5   green compost (S+GC), during the winter wheat cultivation campaign. The SMS and

6   GC organic residues were applied to the soil at rates of 140 or 85 t residue ha^{-1}, and

7   herbicides were sprayed as Erturon® and Herold® formulations for chlorotoluron and

8   flufenacet, respectively. Concentrations of both herbicides and of their metabolites were

9   regularly measured in the three soil treatments (0-10 cm) from 0 to 339 days. The

10   dissipation kinetics fitted well the single first order (SFO) model, except that of

11   chlorotoluron that fitted the first order multi-compartment (FOMC) model better in the

12   unamended soil. The dissipation rates of herbicides were lower in amended than in

13   unamended soils. The results also showed that the DT$_{50}$ of chlorotoluron (66.2-88.0

14   days) and flufenacet (117-145 days) under field conditions were higher than those

15   previously obtained at laboratory scale highlighting the importance of the changing

16   environmental conditions on the dissipation process. Similarly, the formation of

17   chlorotoluron and flufenacet metabolites under field conditions was different from that

18   previously observed in the laboratory. The performance of the MACRO pesticide fate

19   model, parameterized with laboratory data, was then tested against field data. There was

20   a very good agreement between measured and simulated chlorotoluron residue levels in

21   the three soil treatments, while the ability of the model to reproduce the dissipation of

22   flufenacet was good in the unamended soil and very good in S+SMS and S+GC soils.

23   MACRO might be used to estimate the remaining amounts of herbicides in amended

24   soils from degradation data previously obtained at laboratory scale. This would help to

2

manage herbicide doses in different environmental conditions to preserve the

sustainability of agricultural systems.

Keywords: field dissipation, herbicides, soil, spent mushroom substrate, green compost,

MACRO model

1. Introduction

Winter wheat is an extensively grown crop with great economic relevance in dry

farmland areas of Spain (www.mapa.gob.es), and one of the most important one

worldwide. It is cultivated on more than 200 Mha, contributing approximately to 30%

(~800 Mt) of the total world cereal production (OECD-FAO, 2019). Climatic conditions

(temperature and rainfall) are known to have a great impact on crop yields under the

current Mediterranean scenario, but the influence of other common agricultural

practices such as the application of herbicides and organic residues remains to be

evaluated. Herbicides are needed to control weeds, and many active ingredients are

available on the market, especially for certain crops such as cereals (Bai et al., 2018;

Thiour-Mauprivez et al., 2019). The application of organic residues guarantees soil

fertility and maintains correct organic matter (OM) content and nutrients to obtain crops

of good quality and quantity, and at the same time to avoid soil degradation

(Palansooriya et al., 2019).

The application of both herbicides and organic residues on soil became a

frequent agricultural practice, which could affect the fate of these compounds in the

environment (Marín-Benito et al., 2018; Vieublé Gonod et al., 2016). For example,

composted spent mushroom substrate (SMS) and green compost (GC) have been

efficiently tested for preventing and/or controlling soil and water contamination by

pesticides (Kodesová et al., 2012; Marín-Benito et al., 2018). Among the processes that control the behavior of herbicides under field conditions, their dissipation in the topsoil is the most important one. It is due to abiotic and biotic degradation, loss by volatilization, plant uptake, runoff and/or leaching. Herbicides dissipation in amended soils has been widely studied under laboratory conditions (Barba et al., 2019; Cassigneul et al., 2018; Marín-Benito et al., 2019; Su et al., 2019). On the contrary, herbicides persistence and dissipation in amended soils have been scarcely studied under field conditions (Cañero et al., 2012; García-Delgado et al., 2019).

Chlorotoluron and flufenacet herbicides are recommended for pre- and post-emergence weed control in cereals and various other crops. Chlorotoluron is an urea herbicide with moderate solubility in water and low hydrophobicity, it is moderately persistent and mobile in the soil profile (EC, 2005; PPDB, 2019). Chlorotoluron dissipation/persistence in soils has been rarely studied at field scale (EC, 2005). A few results showed that the dissipation rate increased when the herbicide was repeatedly applied for 12 years (Rouchaud et al., 2000), and that its persistence depends on irrigation and fertilization (Rodríguez-Liébana et al., 2014). Flufenacet is an oxyacetamide herbicide moderately soluble in water and with a high hydrophobic character. It has a low persistence and a medium mobility in soil (EC, 2003; PPDB, 2019). Very few studies report the flufenacet dissipation in field unamended soils (Bloomberg et al., 2002; Rouchaud et al., 1999, 2001). The dissipation rate of the herbicide depends on the season of the year when flufenacet was applied since temperature influences the microbial activity and consequently the biodegradation of this herbicide (Milan et al., 2013; Rouchaud et al., 1999, 2001). The field dissipation of flufenacet is also influenced by soil texture and herbicide characteristics (Rouchaud et al., 2001), but not by the dose (Rouchaud et al., 1999).

74   Working at field scale has some important drawbacks: it is time consuming and

75   cost prohibitive, and it should be carried out over long time periods to understand the

76   effect of the variable climatic conditions on the fate of pesticide (Boesten and van der

77   Pas, 2000; Holvoet et al., 2007; Willkommen et al., 2019). These disadvantages are

78   often responsible for the shortage of this type of studies. Therefore, the combination of

79   laboratory and modelling studies can represent an interesting alternative to field studies,

80   provided that models efficiency had been previously tested by comparison with field

81   data. Numerous pesticide fate models, which were parameterized with sensitive data

82   from laboratory studies such as pesticide adsorption and degradation coefficients

83   (Dubus et al., 2003), and tested against field data, have been successfully used to assess

84   the mobility and/or persistence of herbicides in soils (Garrat et al., 2002; Martínez et al.,

85   1994). However, these numerical models were rarely tested to simulate the fate of

86   herbicides in amended soils (Marín-Benito et al., 2020). Finally, the use of model able

87   to simulate the persistence of herbicides in amended soils would be of great interest to

88   assess soil residual amounts of pesticides which may affect subsequent crops. Indeed,

89   some studies have shown that high herbicide residue levels in non-amended soils, due to

90   the long persistence of these compounds in certain conditions, may result in damage to

91   successive crops (James et al., 1999; Palhano et al., 2018; Scursoni et al., 2017).

92   Therefore, the objectives of this work were: (i) to study the field dissipation

93   kinetics of the chlorotoluron and flufenacet herbicides, and the formation of their

94   metabolites, in an agricultural soil without amendment (S) and amended with spent

95   mushroom substrate (S+SMS) or with green compost (S+GC), (ii) to fit their dissipation

96   to the most simple and acceptable kinetic model by using statistical indexes, and (iii) to

97   assess the ability of the MACRO pesticide fate model to simulate the persistence of

98   these herbicides.

99

2. Materials and methods

2.1. Experimental site, soil sampling and processing

The field experiment was set up at the Muñovela experimental farm belonging to the Institute of Natural Resources and Agrobiology of Salamanca, Spain (40º54´15´´N latitude and 5º46´26´´W longitude), during the 2016-2017 winter wheat cultivation campaign. The experiment involved randomized complete blocks with nine plots of 9 m × 9 m 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) (Carpio et al., 2020). The soil was an Eutric-Chromic Cambisol (IUSS Working Group WRB, 2015) with sandy-loam texture (80.4% sand, 4.7% silt, and 14.9% clay). The soil physicochemical characteristics were determined by standard analytical methods (Carpio et al. 2020; Sparks, 1996) (**Table S1** in Supplementary Material). The SMS and GC organic residues were applied at rates of 140 and 85 t ha^{-1} (dry weight basis), respectively, and incorporated into the top 20 cm at the beginning of the experiment. The SMS is originated from *Agaricus bisporus* and *Pleurotus ostreatus* (2:1) cultivation, and the GC from the pruning of plants and trees in parks and gardens. 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 main characteristics of both organic residues were determined in air-dried and sieved (< 2 mm) samples (**Table S2** in Supplementary Material) using the methods reported by Carpio et al. (2020). Winter wheat was sown on 14 November 2016 and harvested on 3 July 2017. After harvest, a bare soil was maintained during the fallow period. The field experiment ended on 5 November 2017 (339 days after the herbicide application).

Chlorotoluron and flufenacet (**Table S3** in Supplementary Material) were sprayed at 15 and 5 kg a.i. ha^{-1}, respectively, as Erturon® (chlorotoluron 50% w/v, Cheminova Agro S.A., Madrid, Spain) and Herold® (flufenacet 40% w/v, Bayer Crop Science S.L., Valencia, Spain) commercial formulations. The chemicals were jointly applied in pre-emergence using a sprayer attached to a tractor on 1 December 2016. According to the experimental farm's records, none of the chemicals had ever been applied to the experimental field, as an initial onsite background analysis did not detect any residues.

The herbicides dissipation was studied in unamended, SMS- and GC-amended soils from 0 to 339 days after their application. At each sampling time (1, 5, 10, 13, 17, 21, 33, 38, 45, 53, 60, 70, 80, 89, 104, 124, 145, 151, 173, 199, 229, 269, 311 and 339 days), five 10-cm soil subsamples were randomly sampled in each plot, and representative average soil samples of each plot were obtained by mixing the five subsamples. The composite samples were then put into plastic bags and transported in portable refrigerators to the laboratory, where they were homogenised and sieved (< 2 mm), and stored at 4°C until their analysis.

For modelling studies, climatic data (rainfall, maximum, minimum and average air temperature) were daily monitored using a meteorological station located at the field site. Additional evapotranspiration data were obtained from the station of Matacan airport (23 km away from Muñovela farm).

2.2. *Herbicides extraction and 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.

149 (Madrid, Spain) (**Table S3**). The extraction and analysis of both herbicides and of their

150 major metabolites were done according to Marín-Benito et al. (2019). Briefly, triplicate

151 subsamples of moist soil (6 g) from each composite sample of unamended or amended

152 soils, taken at each sampling time, were extracted with acetonitrile (12 mL). Then, they

153 underwent an ultrasonic bath (1 h, 20 ºC), and they were shook (24 h, 20 ºC),

154 centrifuged (5045 g, 15 min), and filtrated (< 0.45 μm). Extracts (8 mL) were

155 evaporated until dryness at 25 ºC under a nitrogen stream using an EVA-EC2-L

156 evaporator (VLM GmbH, Bielefeld, Germany). The residue was dissolved in 0.75 mL

157 of acetonitrile and transferred to a glass vial for analysis. The herbicides and their

158 metabolites were determined by HPLC-DAD-MS using a Waters chromatograph

159 (Waters Assoc., Milford, USA).

160

161 *2.3. Modelling of herbicides dissipation*

162 To model the dissipation of herbicides in the field, the MACRO model (version

163 5.2) was selected because it is used at the European level for pesticide registration

164 (FOCUS, 2000) and because it is one of the most efficient to simulate the fate of

165 pesticides in the environment, and especially in amended soils (Marín-Benito et al.,

166 2020).

167 MACRO is a process-based, one-dimensional, dual-permeability model able to

168 simulate preferential flow processes. The model is presented in detail in Larsbo and

169 Jarvis (2003). In few words, the soil pore system is partitioned into micropore and

170 macropore domains with separate flow rate and solute concentration for each domain.

171 The boundary between the two domains is defined by a given soil water pressure head,

172 and by the corresponding water content and hydraulic conductivity. In the micropores,

173 water flow and solute transport are described by the Richards' equation and the

convection–dispersion equation, respectively. Water flow in the macropores is treated as a gravity driven process, and solute transport is assumed to be solely convective. The adsorption of pesticide is assumed to be linear, instantaneous, and reversible, and its degradation follows first-order kinetic. The model implements physically based expressions using an effective aggregate half-width to calculate the water and solute exchange between the micropore and macropore domains.

The model was mainly parameterized with site-specific data (soil, crop, climate, herbicides), and the parameterization was completed using data from the literature, pedotransfer functions and defaults values for parameters that cannot be measured such as some hydraulic ones. Detailed description of the parameterization and calibration of the model for the 1.6-m unamended, SMS- and GC-amended soil profiles can be found in Marín-Benito et al. (2020) together with the parameter values. **Table S1** summarizes the main physicochemical and hydraulic input parameters for the top 10 cm of S, S+SMS and S+GC soils, and the main crop and herbicide input parameters are shown in **Tables S4** and **S5** (in Supplementary Material), respectively. It has to be highlighted that the DT_{50} (time to 50% degradation, days) values used to parameterize the model were taken from laboratory experiments with unamended control and amended soil samples taken *in situ*, at 6ºC and 40% of the maximum soil water holding capacity (Marín-Benito et al., 2019).

2.4. Data analysis

FOCUS work group guidelines were followed to select the best kinetic model for each herbicide and soil treatment (FOCUS, 2006). According to these guidelines, herbicide dissipation kinetics were initially fitted to single first-order (SFO) and first order multi-compartment (FOMC) kinetic models. The coefficient of determination and

199 the chi-square test were calculated as indicators of the goodness of fit. Based on the

200 acceptability criterion of these guidelines included in Supplementary Material, no more

201 models reported in FOCUS (2006) and also in the literature (Sarmah and Close, 2009;

202 Srinivasan et al., 2014) were tested. The herbicide concentrations, which were measured

203 one day after the application in the three soil treatments, were considered as 100% of

204 the amounts applied. The DT_{50} values were used to characterize the decay curves and to

205 compare the variations in dissipation rates. The kinetic model parameters were

206 estimated using the Excel Solver add-in Package (FOCUS, 2006). An additional

207 description of the dissipation kinetic models is included in Supplementary Material.

208 The performance of MACRO was assessed using three statistical indices, the

209 efficiency (*EF*), the coefficient of residual mass (*CRM*), and the root mean square error

210 (*RMSE*), which were additionally estimated for the kinetic models (Smith et al., 1996):

211 $$EF = 1 - [\sum_{i=1}^{n}(S_i - O_i)^2 / \sum_{i=1}^{n}(O_i - O_m)^2] \qquad (1)$$

212 $$CRM = (\sum_{i=1}^{n} O_i - \sum_{i=1}^{n} S_i) / \sum_{i=1}^{n} O_i \qquad (2)$$

213 $$RMSE = (100/O_m)[\sum_{i=1}^{n}(S_i - O_i)^2/n]^{1/2} \qquad (3)$$

214 where S_i and O_i are the simulated and observed (measured) values, respectively, O_m is

215 the mean observed value, and *n* is the number of data. The optimum value of *EF* is +1

216 and that of *CRM* and *RMSE* is zero. If *CRM*>0 (<), then there is an under (over)

217 estimation of observed values.

218

219 **3. Results and discussion**

220 *3.1. Dissipation kinetics of chlorotoluron in field unamended and amended soils*

221 The dissipation kinetics of chlorotoluron fitted best the FOMC model in the

222 unamended soil S, and the SFO one in S+SMS and S+GC soils (**Fig. 1, Table 1**). This

223 differs from the results of previous works showing that the dissipation kinetic of

chlorotoluron in unamended soil followed SFO, while it fitted bi-phasic double first-order in parallel model (DFOP) in organic-amended soil (Rodríguez-Liébana et al., 2014; Rouchaud et al., 2000). At the end of the experiment (339 days), higher concentrations of chlorotoluron were detected in unamended soil S (15.7%) than in S+SMS (5.97%) or S+GC (8.77%) soils (**Fig. 1**). In the unamended soil, the DT_{50} of chlorotoluron was found to be 66.2 days (**Table 1**), which is consistent with published values ranging from 26 to 64 days (PPDB 2019; Rouchaud et al., 2000). For all soils (unamended and amended), the field DT_{50} were higher than those obtained in laboratory conditions (Marín-Benito et al., 2019) highlighting the importance of the variable environmental conditions on the dissipation process.

In the unamended soil S, more than 26% of chlorotoluron were dissipated 33 days after its application. This high dissipation rate of the herbicide could be explained by its high mobility to deeper soil layers (Carpio et al., 2020; PPDB, 2019). The dissipation rate of chlorotoluron in S+SMS soils was lower than in the unamended soil S, but the dissipation rates were almost similar in S and S+GC (**Table 1**). The lower dissipation rate of chlorotoluron in S+SMS soil can be explained by the decrease in its leaching through the soil profile because of higher adsorption: K_d values as determined by Carpio et al. (2020) were 0.773 L kg^{-1} in S soil and 4.773 L kg^{-1} in S+SMS (**Table S5**). High adsorption of chlorotoluron by amended soils leads to a decrease in the bioavailability of the herbicide to be degraded, as reported previously for this herbicide (Kodešová et al., 2012; Marín-Benito et al., 2019) and for other compounds (Barba et al., 2019; Su et al., 2019). On the contrary, Rodríguez-Liébana et al. (2014) found a rapid dissipation of chlorotoluron (DT_{50} = 2.4 days) in a field amended soil. They related this result to the low water solubility and high hydrophobicity of chlorotoluron, but also indicated a possible increase of aged residues of herbicide over time.

The dissipation of chlorotoluron was consistent with the detection of its desmethyl chlorotoluron metabolite in the soils over the entire experimental period (**Table S3**). The N-dealkylation, giving desmethyl chlorotoluron, has indeed been reported as the main degradation pathway of chlorotoluron in soils (Gross et al., 1979; EC, 2005; PPDB, 2019). This metabolite was also observed in laboratory degradation experiments at 6ºC and 16ºC in similar soils (Marín-Benito et al., 2019). In the unamended soil S, the concentration of desmethyl chlorotoluron increased from the first day of experiment up to 80 days, and then it remained constant up to 339 days. However, its formation was delayed in the S+SMS and S+GC soils as it was only detected after 33 and 13 days, respectively. Then, the concentrations of desmethyl chlorotoluron increased up to 80 days in S+SMS and S+GC, and decreased up to 173 days, when the metabolite was not detected (**Fig. 3**). The amounts of metabolite that were formed in the soils followed the order: S > S+GC > S+SMS. This is consistent with the increase in the adsorption coefficients of chlorotoluron in these soils, so with a concomitant decrease in herbicide bioavailability. Peaks of metabolites were detected at 89 and 151 days in unamended soil S, and at 80 days in S+SMS and S+GC soils (**Fig. 3**). The corresponding concentrations were 0.184 and 0.177 µg g^{-1} dry soil in unamended soil S, 0.053 and 0.194 µg g^{-1} in S+SMS and S+GC, respectively, and the total cumulative amount accounted for 23.5%, 2.83% and 10.6% of the applied herbicide.

These results were similar to those found for the degradation of chlorotoluron under laboratory conditions, where the cumulative amount of desmethyl chlorotoluron was lower in S+SMS than in S and S+GC soils (Marín-Benito et al., 2019), indicating that the herbicide degradation mechanisms were different in S+SMS than in S and S+GC treatments. The high adsorption of chlorotoluron by S+SMS could explain a low

274   bioavailability of the herbicide to be degraded and consequently the low amount of

275   metabolite produced in this soil. However, it should be noted that the dissipation and/or

276   mobility of chlorotoluron could be affected by the dissolved organic carbon (DOC),

277   especially in S+SMS which had the highest DOC content (Carpio et al., 2020).

278   Chlorotoluron could remain adsorbed by the soil OC but also adsorbed by DOC in

279   solution, what enhances its mobility and/or its degradation by microorganisms (Marín-

280   Benito et al., 2012). A high retention of the metabolite by S+SMS or the formation of

281   non-extractable residues could also have occurred. The formation of bound residues for

282   desmethyl chlorotoluron has not been reported previously in the literature, although it

283   would be possible according to its higher Koc (248 mL g^{-1}), compared to the parent

284   compound (196 mL g^{-1}) (**Table S3**) (PPDB, 2019). The greater ability metabolites have

285   to form bound residues than their parent compounds has been reported in the literature

286   for other pesticides (Marín-Benito et al., 2012; Papadopoulou et al., 2016).

287   Finally, mineralization and/or the formation of bound residues of chlorotoluron

288   could also have happened (EC, 2005). Both additional dissipation pathways may have

289   been facilitated in the S+SMS and S+GC soils because of a higher content of both DOC

290   (more herbicide in solution) and OC (higher adsorption of herbicide), respectively,

291   compared to unamended soil S, as observed for other pesticides (Marín-Benito et al.,

292   2012).

293

294   *3.2. Dissipation kinetics of flufenacet in field unamended and amended soils*

295   The dissipation of flufenacet was initially slower in amended soils than in the

296   unamended soil, but the dissipation rates were faster after the DT_{50} were reached. The

297   dissipation kinetics of flufenacet fitted well the SFO model for the three soil treatments

298   (**Table 2**, **Fig. 2**). This is consistent with the results of Bloomberg et al. (2002) and

299 Rouchaud et al. (1999, 2001), who showed that the flufenacet dissipation kinetics

300 followed the SFO model in unamended soil under field conditions. At the end of the

301 experiment (339 days), the residues of flufenacet were 7.02% in S, 7.89% in S+SMS

302 and 2.67% in S+GC (% of initial amounts), showing that flufenacet dissipation

303 increased for all soil treatments at the end of the experimental period. The degradation

304 rates of flufenacet were lower than those of chlorotoluron in the three soils (**Tables 1**

305 **and 2**), although the residual amounts of flufenacet after 339 days were lower than

306 those of chlorotoluron in S and S+GC soils. This is in agreement with what is frequently

307 observed as flufenacet is less water soluble and more hydrophobic than chlorotoluron

308 (PPDB, 2019). The DT_{50} of flufenacet were higher in amended soils than in unamended

309 soil following the order: S < S+SMS < S+GC (**Table 2**). Sixty days after treatment, the

310 residual amounts of flufenacet in S+SMS (90% of initial applied) and S+GC (92%) soils

311 were strongly higher than in the unamended soil S (69%) (**Fig. 2**). The rapid dissipation

312 of flufenacet in S soil compared to that in S+SMS and S+GC is related to its adsorption

313 as K_d values increase as follows: S (1.038 L kg^{-1}) < S+ GC (2.909 L kg^{-1}) < S+SMS

314 (6.340 L kg^{-1}) (Carpio et al., 2020) (**Table S5**). This is in agreement with the findings of

315 Gajbhiye and Gupta (2001), who observed an increase in the persistence of flufenacet in

316 soils with higher adsorption capacity.

317   The DT_{50} of flufenacet in the unamended soil S (117 days) was found to be

318 higher than those reported for unamended agricultural soils under field conditions (from

319 14.2 to 68.1 days) (PPDB, 2019). This result can be explained by the different seasons

320 of the year during which the dissipation studies were carried out. Indeed, the dissipation

321 of flufenacet under field conditions was shown to be accelerated during spring and

322 summer when temperatures were higher than in winter because of the associated

323 increased microbial activities in soil (Rouchaud et al, 1999, 2001). In our study, the

324 herbicides were applied at the end of autumn (1 December 2016) with minimum

325 temperatures ranging from -11.6 to 8.8 ºC up to the DT_{50} of flufenacet was reached in

326 all treatments (145 days after the application, **Table 2**). These low temperatures could

327 have contributed to a decrease in the soil microbial activity, knowing that microbial

328 degradation drives flufenacet dissipation (Milan et al., 2013). It has to be noted that the

329 dissipation pattern of flufenacet in the field was different from that observed in

330 laboratory, as shown for chlorotoluron, since flufenacet was more persistent in the field

331 than in the laboratory (Marín-Benito et al., 2019). These results also corroborate the

332 DT_{50} reported by the Pesticide Properties DataBase (PPDB, 2019).

333   In any case over the experimental period, the flufenacet ESA metabolite was not

334 detected, and the flufenacet OA metabolite was only detected at concentrations below

335 the LOQ, although the formation of flufenacet metabolites in unamended soil under

336 field conditions has been reported (Bloomberg et al., 2002, Lam et al., 2002), as well as

337 their formation under laboratory conditions (Marín-Benito et al., 2019). However, in our

338 field experiment, the high DOC content of S+SMS and S+GC soil may have enhanced

339 the degradation and/or the downward mobility of the herbicide over time (Marín-Benito

340 et al., 2020). In addition, other processes contributing to flufenacet dissipation, such as

341 mineralization and/or the formation of bound residues, could have occurred (EC, 2003).

342

343 *3.3. Modelling herbicide persistence*

344   The performance of MACRO to simulate the dissipation of chlorotoluron in the

345 top 10 cm of the three soil treatments was very good, as shown by the high EF values

346 (Ritter and Muñoz-Carpena, 2013), the CRM values close to zero and the low RMSE

347 values (**Table 3, Fig. 1**). The measured concentrations of chlorotoluron in S and

348 S+SMS soils were weakly underestimated by MACRO while they were weakly

349   overestimated in the S+GC treatment (**Table 3**). For flufenacet, the simulated

350   concentrations values agreed closely with the observed data (**Fig. 2**), and the ability of

351   MACRO to reproduce the dissipation of this herbicide can be denoted as good for the

352   unamended soil S and very good for S+SMS and S+GC soils (Ritter and Muñoz-

353   Carpena, 2013) (**Table 3**). MACRO slightly overestimated the dissipation of flufenacet

354   in the three soil treatments (CRM < 0, **Table 3**). In general, for both herbicides in the

355   three soils, the MACRO simulation results were within the standard deviation of the

356   mean remaining percentages observed (**Figs. 1 and 2**).

357   The comparison of fitted and simulated DT_{50} and DT_{90} (time to 90% dissipation,

358   days) values showed that they closely agreed for chlorotoluron in the three soils (**Table**

359   **4, Figs. 1 and 2**). The coefficients of variation (CV) of the DT_{50} and DT_{90} in the

360   unamended and amended soils ranged from 4% to 16% and from 4% to 32%,

361   respectively (**Table 4**). For flufenacet, MACRO predictions were worse than for

362   chlorotoluron in most of the soil treatments, with CV of the DT_{50} ranging from 10% to

363   28%, and those of DT_{90} ranging from 7% to 39% (**Table 4, Fig. 2**). As indicated above,

364   processes such as the formation of non-extractable residues, which are not simulated by

365   MACRO, could explain the higher ability of the model to estimate the fitted DT_{50} and

366   DT_{90} of chlorotoluron than of flufenacet with higher adsorption capacity (**Table S5**).

367   For both herbicides, the simulated DT_{90} (persistence) were generally lower than

368   the fitted ones in all soil treatments (**Table 4**). The high CV of DT_{90} compared to those

369   of DT_{50} in the unamended soils (**Table 4**) indicate that the model efficiency to

370   reproduce the dissipation of the herbicides in natural soils decreases with simulation

371   time. The model showed a tendency to underestimate the remaining amounts of both

372   herbicides in the unamended soils one year after the application. This tendency could

373   reduce the use of the pesticide fate model as predictive tool in unamended soils. This is

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374 consistent with the results of Garrat et al. (2002) and Martínez et al. (1994).

375 Nevertheless, the use of DT_{50} obtained from laboratory experiments as input in the

376 MACRO model allows satisfactory simulation of the dissipation of chlorotoluron and

377 flufenacet under amended field conditions, and especially that of chlorotoluron which

378 has the lowest persistence.

379

4. Conclusions

381 The field dissipation kinetics of two cereals herbicides, chlorotoluron and flufenacet,

382 fitted well the SFO model in unamended and amended soils, except that of

383 chlorotoluron that fitted the FOMC model better in the unamended soil. The application

384 of the SMS and GC organic amendments to soil slowed down the dissipation rates of

385 chlorotoluron and flufenacet compared to unamended soils as previously observed

386 under controlled laboratory conditions. However, the DT_{50} of chlorotoluron and

387 flufenacet under field conditions were higher than those obtained in laboratory

388 highlighting the importance of changing environmental conditions on the dissipation

389 process. These changes also affected the formation rates of their metabolites at field

390 scale compared with those at laboratory.

391 The field dissipation kinetics of both herbicides were then simulated with the

392 MACRO pesticide fate model parameterized with laboratory data. The results showed

393 that MACRO might be reasonably used as a tool to estimate the remaining amounts of

394 herbicides in the root zone of amended soils knowing their DT_{50} and K_d previously

395 obtained from laboratory experiments. Therefore, MACRO can help to assess if an

396 herbicide can be applied in amended soils without causing damage on succeeding crop.

397 This would help to manage herbicide doses in different environmental conditions to

398 preserve the sustainability of agricultural systems.

399

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553

Figure captions

Fig. 1. Measured, fitted (SFO and FOMC) and simulated (MACRO) dissipation kinetics of chlorotoluron in unamended (S), spent mushroom substrate (S+SMS)- and green compost (S+GC)-amended soils. Bars indicate the standard deviation of the mean value (n=9). SFO: Single first-order model, FOMC: First order multi-compartment model.

Fig. 2. Measured, fitted (SFO) and simulated (MACRO) dissipation kinetics of flufenacet in unamended (S), spent mushroom substrate (S+SMS)- and green compost (S+GC)-amended soils. Bars indicate the standard deviation of the mean value (n=9). SFO: Single first-order model.

Fig. 3. Formation of desmethyl chlorotoluron, in unamended (S), spent mushroom substrate (S+SMS)- and green compost (S+GC)-amended soils over time. Bars indicate the standard deviation of the mean (n=9).

Table 1. Dissipation rate parameters (k, α, β) and dissipation half-lives (DT_{50}) of chlorotoluron in unamended (S), spent mushroom substrate- and green compost-amended soils (S+SMS and S+GC) according to the single first-order (SFO) and first order multi-compartment model (FOMC) models, and goodness of fit statistics.

Sample/SFO	k (days^{-1})		DT_{50} (days)[a]	χ^2	R^2	*EF* (-)[c]	*CRM* (-)[d]	*RMSE* (%)[e]
S	0.009		73.7	7.2	0.991	0.98	0.02	8.53
S+SMS	0.008		88.0	10.1	0.961	0.96	-0.01	12.0
S+GC	0.009		73.6	11.3	0.957	0.96	-0.01	13.4
Sample/FOMC	α	β	DT_{50} (days)[b]	χ^2	R^2	*EF* (-)[c]	*CRM* (-)[d]	*RMSE* (%)[e]
S	2.80	236	66.2	6.0	0.985	0.99	0.00	7.02
S+SMS	5.10×10^4	6.47×10^6	88.0	10.3	0.961	0.96	-0.01	12.0
S+GC	6.09×10^4	6.47×10^6	73.6	11.5	0.957	0.96	-0.01	13.4

[a] $DT_{50} = \ln2 / k$

[b] $DT_{50} = \beta \times [2^{(1/\alpha)} - 1]$

[c] Efficiency.

[d] Coefficient of residual mass.

[e] Root mean square error.

Table 2. Dissipation rate parameters (k, α, β) and dissipation half-lives (DT_{50}) of flufenacet in unamended (S), spent mushroom substrate- and green compost-amended (S+SMS and S+GC) soils according to the single first-order (SFO) and first order multi-compartment model (FOMC) models, and goodness of fit statistics.

Sample/SFO	k (days^{-1})		DT_{50} (days)^{a}	χ^2	R^2	*EF* (-)^{c}	*CRM* (-)^{d}	*RMSE* (%)^{e}
S	0.006		117	12.3	0.905	0.90	0.00	14.7
S+SMS	0.006		123	9.7	0.945	0.94	-0.01	11.5
S+GC	0.005		145	9.9	0.924	0.92	-0.01	11.8
Sample/FOMC	α	β	DT_{50} (days)^{b}	χ^2	R^2	*EF* (-)^{c}	*CRM* (-)^{d}	*RMSE* (%)^{e}
S	3.83×10^4	6.47×10^6	117	12.6	0.905	0.90	0.00	14.7
S+SMS	3.62×10^4	6.47×10^6	123	9.8	0.945	0.94	-0.01	11.5
S+GC	3.11×10^4	6.51×10^6	145	10.1	0.924	0.92	-0.01	11.8

[a] $DT_{50} = \ln2 / k$

[b] $DT_{50} = \beta \times [2^{(1/\alpha)} - 1]$

[c] Efficiency.

[d] Coefficient of residual mass.

[e] Root mean square error.

Table 3. Goodness-of-fit statistics for MACRO modeling of the dissipation of chlorotoluron and flufenacet in the top 10 cm of the unamended (S), spent mushroom substrate- and green compost-amended (S+SMS and S+GC) soils.

	EF (-)[a]	CRM (-)[b]	$RMSE$ (%)[c]
S			
Chlorotoluron	0.94	0.01	14.5
Flufenacet	0.82	-0.02	20.3
S+SMS			
Chlorotoluron	0.95	0.04	13.1
Flufenacet	0.91	-0.10	14.2
S+GC			
Chlorotoluron	0.94	-0.03	15.1
Flufenacet	0.97	-0.02	6.8

[a] Efficiency.

[b] Coefficient of residual mass.

[c] Root mean square error.

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Table 4. Fitted (SFO or FOMC) and simulated (MACRO) DT_{50} and DT_{90} (days) of chlorotoluron and flufenacet in the top 10 cm of the unamended (S), spent mushroom substrate- and green compost-amended (S+SMS and S+GC) soils, and coefficients of variation (CV, %).

Parameter	Chlorotoluron			Flufenacet		
	S	S+SMS	S+GC	S	S+SMS	S+GC
$DT_{50 \text{ fitted}}$	66.2	88.0	73.6	117	123	145
$DT_{50 \text{ MACRO}}$	72.5	93.0	92.0	96.0	184	167
CV DT_{50}	6	4	16	14	28	10
$DT_{90 \text{ fitted}}$	301	292	245	389	411	482
$DT_{90 \text{ MACRO}}$	191	277	230	220	452	375
CV DT_{90}	32	4	4	39	7	18

Note: DT_{50} and DT_{90}, dissipation time values observed in Figs. 1 and 2 when dissipation of 50% or 90% of the herbicide was reached taking into account fitted (SFO or FOMC) and simulated (MACRO) kinetic curves.
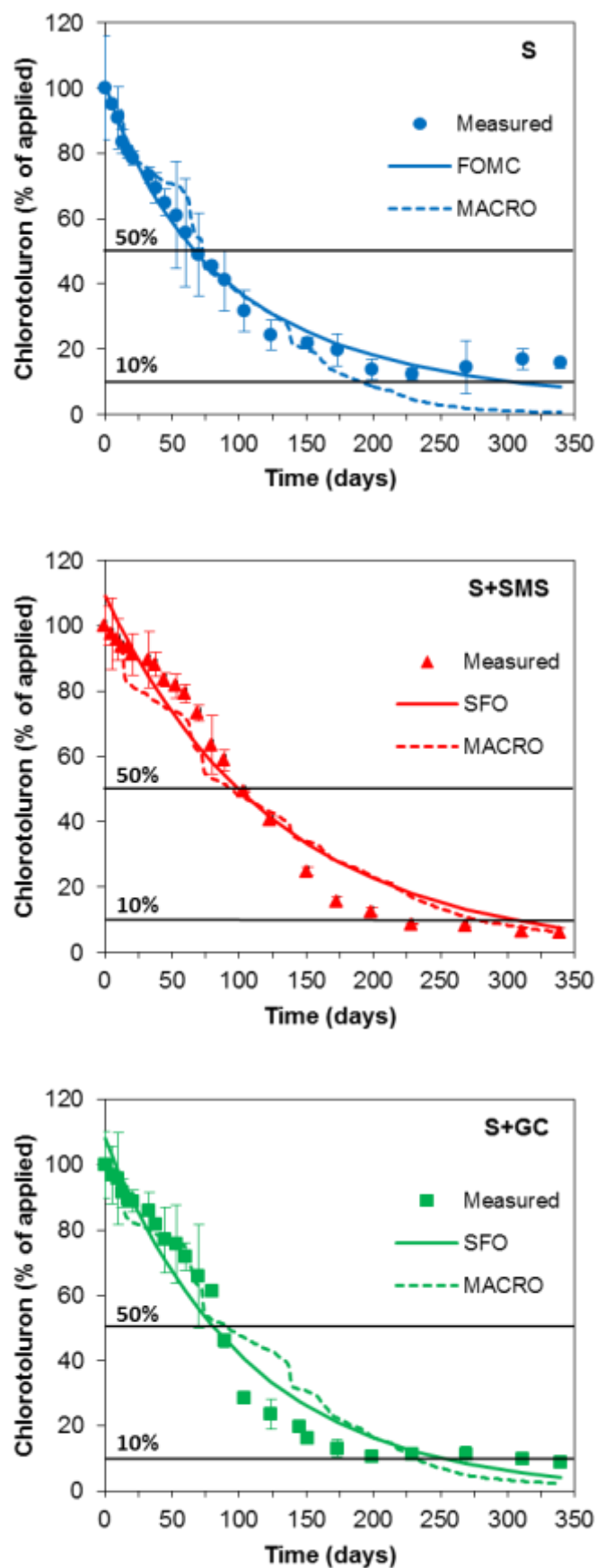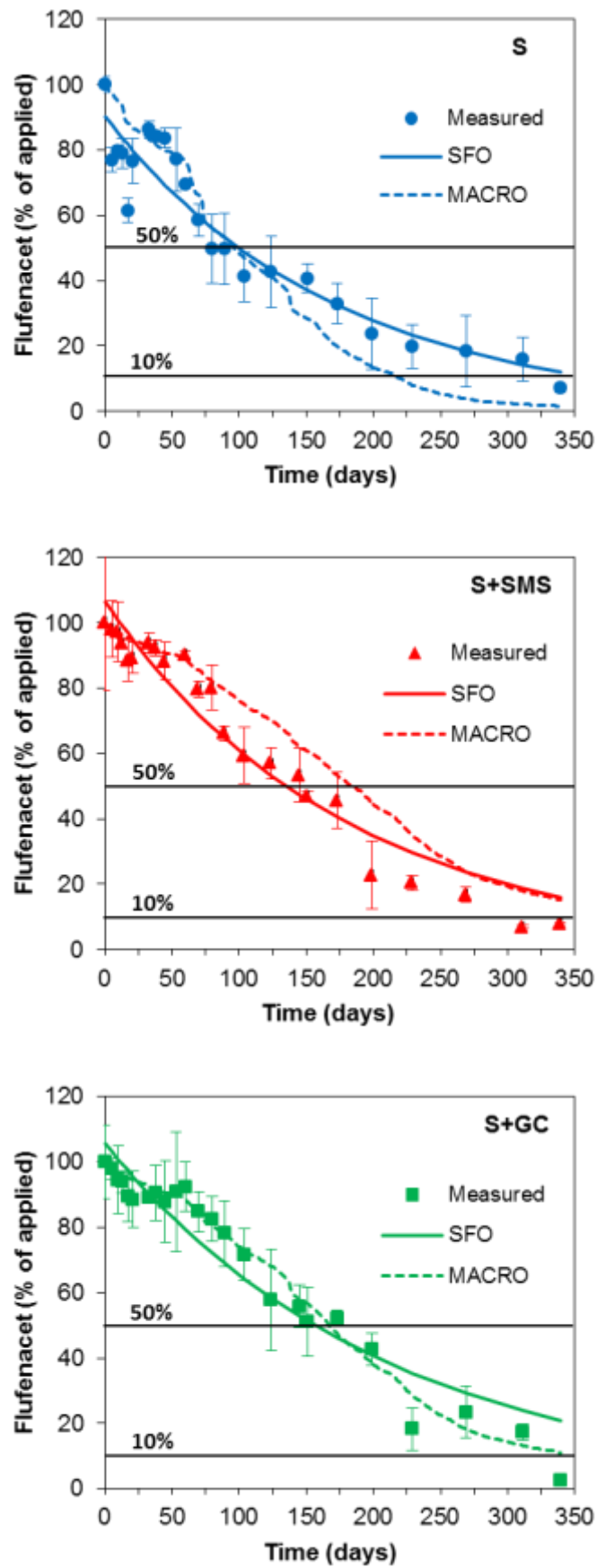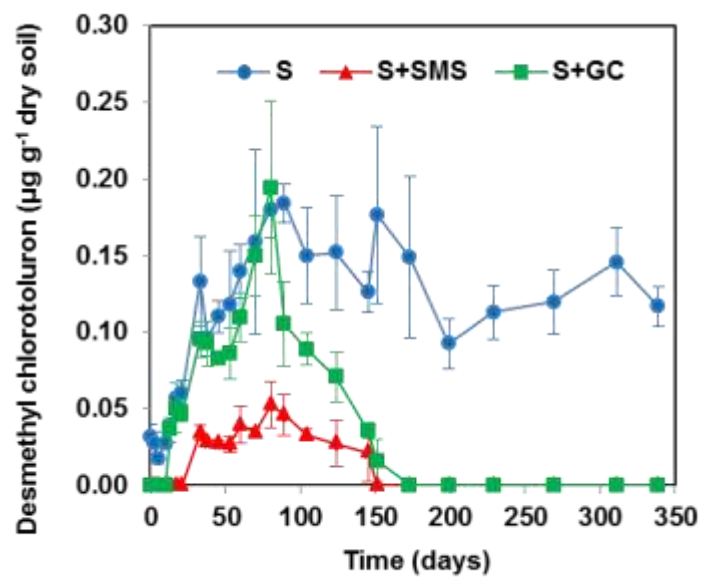
Fig. 1

Fig. 2

Fig. 3

FIELD MEASUREMENT AND MODELLING OF CHLOROTOLURON AND FLUFENACET PERSISTENCE IN UNAMENDED AND AMENDED SOILS

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Number of Pages: 7

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Table S1. Main physicochemical and hydraulic characteristics of the top 10 cm of unamended (S), spent mushroom substrate (S+SMS)- and green compost (S+GC)-amended soils.

	S	S+SMS	S+GC
Sand (%)	80.4	76.7	78.7
Silt (%)	4.7	5.8	4.7
Clay (%)	14.9	16.5	16.6
pH	6.34	7.11	6.99
Bulk density (g cm^{-3})	1.48	1.23	1.34
OC (%)	0.77	2.64	1.69
DOC (mg g^{-1})	0.12	0.50	0.38
$\theta_{initial}$ (m^3 m^{-3})	0.183	0.279	0.244
θ_r (m^3 m^{-3})[a]	0.01	0.01	0.01
θ_s (m^3 m^{-3})[a]	0.383	0.472	0.428
α (cm^{-1})[a]	0.087	0.068	0.078
n (−)[a]	1.339	1.240	1.290
K_{sat} (mm h^{-1})[a]	76.41	75.79	76.08
CTEN (cm)[b]	10	10	10
θ_b (m^3 m^{-3})[c]	0.332	0.422	0.378
K_b (mm h^{-1})[c]	1.413	0.789	1.083
ASCALE (mm)[c]	15	15	15
ZN (−)[c]	4	4	4

Note: The parameters without exponent correspond to measured values taken from Carpio et al. (2020).

[a] Estimated by HYPRES pedotransfer functions (Wösten et al., 1999).
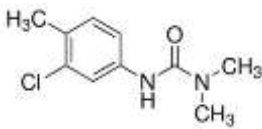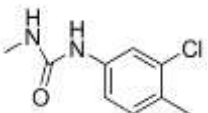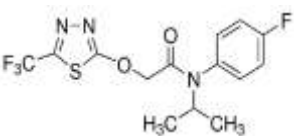
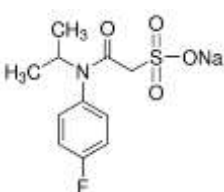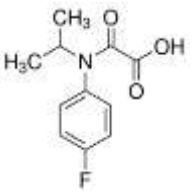[b] Default value (Larsbo and Jarvis, 2003).

[c] Estimated using the pedotransfer functions included in MACRO 5.2.

Table S2. Characteristics of the organic amendments: spent mushroom substrate (SMS) and green compost (GC) (% on a dry weight basis).

	SMS	GC
pH	7.9	7.2
electric conductivity (S/m)	0.78	0.22
ash (%)	40.6	54.0
moisture (%)	37.7	48.6
OM[a] (%)	59.4	46.0
DOC[b] (mg g^{-1})	11.9	7.2
OC[c] (%)	35.0	26.7
N (%)	2.3	1.1
C/N	15.2	24.3
CEC[d] (cmol$_c$ kg^{-1})	35.1	41.4
P_2O_5 (mg/100g)	59.5	40.3
K_2O (mg/100g)	858	458
CaO (mg/100g)	1774	757.3
MgO (mg/100g)	177.7	126.5

[a] Organic matter; [b] Dissolved organic carbon; [c] Organic carbon; [d] Cationic exchange capacity.

Table S3. Main characteristics of herbicides and their metabolites.

Common name Chemical structure	IUPAC name	WS[a] (mg L^{-1})	Log Kow[b]	Field DT$_{50}$[c] (days)	GUS index[d]	K$_{oc}$[e] (mL g^{-1})
Chlorotoluron	3-(3-chloro-p-tolyl)-1,1-dimethylurea	74	2.5	34	3.02	196
Desmethyl chlorotoluron	3-(3-chloro-p-tolyl)-1-methylurea	-	-	60	2.84	248
Flufenacet	4'-fluoro-*N*-isopropyl-2-[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yloxy]acetanilide	51	3.5	39.0	2.02	401
Flufenacet ESA	2-(4-fluoro-*N*-propan-2-ylanilino)-2-oxoethanesulfonic acid	5500	-	302	7.20	12.5
Flufenacet OA	((4-fluorophenyl)(isopropyl)amino)(oxo)acetic acid	-	-	11.1	2.98	14.0

[a] WS, water solubility at 20ºC; [b] Octanol/water partition coefficient at pH 7 and 20ºC; [c] Half-life dissipation time in field conditions; [d] Groundwater Ubiquity Score (Gustafson, 1989); [e] Adsorption coefficient corrected for soil organic carbon content (PPDB, 2019).

Table S4. Crop input parameters for winter wheat in unamended (S) / spent mushroom substrate-amended (S+SMS) / green compost-amended (S+GC) soils.

Date	Crop development	LAI $(m^2 m^{-2})$[b]	Root depth (m)[a]	Root distribution[a,c]
14 Nov. 2016	sowing			
3 Dec. 2016	emergence	0.00	0.01/0.01/0.01	
5 May 2017	flowering	0.30/2.25/0.60	0.21/0.21/0.21	0.90/0.90/0.90
3 July 2017	harvest	0.30/2.25/0.60	0.21/0.21/0.21	

[a] Determined from field measurements or observations.

[b] Estimated from COVMAX (-) = LAI / 3 (Kroes et al., 2008), where COVMAX is the maximum areal coverage of the canopy determined from field measurements (=10%, 75% and 20% for S, S+SMS and S+GC, respectively), and LAI is the leaf area index.

[c] Fraction of root density in the uppermost 25% of the root depth.

Table S5. Main herbicide input parameters used in the simulations in unamended (S), spent mushroom substrate (S+SMS)- and green compost (S+GC)-amended soils.

	Chlorotoluron			Flufenacet		
	S	S+SMS	S+GC	S	S+SMS	S+GC
Adsorption						
K_d (mL g^{-1})[a]	0.773	4.773	2.563	1.038	6.340	2.909
		(1.114)	(0.783)			
n_f[b]	0.83	0.92	0.92	0.85	0.99	0.80
Degradation						
DT_{50} (days)[c]	38.6	51.3	67.6	49.3	93.9	91.7
TRESP (K^{-1})[d]	0.083	0.064	0.103	0.083	0.083	0.092
Other characteristics						
DV (cm)[e]	10	12	10	10	12	10

[a] Adorption coefficients from laboratory experiments with unamended and amended soil samples taken *in situ* (Carpio et al., 2020). Values in brackets correspond to calibrated values according to DOC (Marín-Benito et al., 2020).

[b] Freundlich exponents from laboratory experiments with the unamended control S, and amended with SMS- and GC soils at laboratory scale (García-Delgado et al., 2020).

[c] Degradation half-life from Marín-Benito et al. (2019).

[d] Exponent in the temperature response function estimated from TRESP= (ln Q_{10}) / 10, where Q_{10} factor is taken from Marín-Benito et al. (2019).

[e] Dispersivity fitted manually from the observed Br$^-$ concentrations (Marín-Benito et al., 2020).

Dissipation kinetic models

The dissipation kinetics for the herbicide was fitted to a single first-order (SFO) kinetic model ($C = C_0 \, e^{-kt}$) or first order multi-compartment (FOMC) model ($C = C_0 / ((t / \beta) + 1)^{\alpha}$), known also as the Gustafson and Holden model. C is the herbicide concentration at time t, C_0 is the initial herbicide concentration, k (day^{-1}) is the dissipation rate, α is a shape parameter determined by the coefficient of variation of k values and β is a location parameter. For the selection of the kinetic model that best describes the dissipation results, FOCUS work group guidance recommendations were followed (FOCUS, 2006). The coefficient of determination (r^2) and the chi-square (χ^2) test were calculated as indicators of the goodness of fit. The χ^2 test considers the deviations between observed and calculated values relative to the uncertainty of the measurements for a specific fit, and was used to compare the goodness of fit of the two models tested. The error value at which the χ^2 test is fulfilled at a given degree of freedom should be below 15% (at 5% significance level). The time to 50% and 90% dissipation, or DT_{50} and DT_{90} values, were used to characterise the decay curves and compare variations in dissipation rates. The parameters of the kinetic models were estimated using the Excel Solver add-in Package (Marín-Benito et al., 2012).

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Highlights

- Field dissipation of chlorotoluron and flufenacet was studied in amended soils

- Measured field dissipation of herbicides was simulated with the MACRO model

- Field herbicide dissipation and metabolite formation were different from laboratory ones

- Herbicides´ persistence increased due to the changing field environmental conditions

- MACRO is an efficient tool to estimate remaining herbicide amounts in amended soils

Graphical Abstract

Field plots: unamended, SMS- and GC-amended soils