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Effects of olive mill wastes with different degrees of maturity on behaviour of S-metolachlor in three soils

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Abstract

Laboratory and field experiments were conducted on three Mediterranean agricultural soils in so as to investigate the effects of de-oiled two-phase olive mill waste (D) and two-phase olive mill waste (W) and their level of organic matter maturity on the environmental fate of the herbicide S-metolachlor (SM). Three Mediterranean agricultural soils were amended with fresh (D and W) and composted W (CW) wastes under laboratory conditions. Furthermore, under field conditions, one of the soils was also amended with both wastes (D and W) over 9 years in order to assess the effects of the "aging" transformation (AD and AW treatments, respectively). Significant increases in SM adsorption were observed in all the amended soils, with no reduction in the herbicide's effectiveness. The adsorption process was more reversible with the fresh organic amendments (D or W) than with CW or (even more so) with AD or AW. The fresh amendments also increased the persistence of SM; however the field-aged and composted amendments enhanced its dissipation as a result increased soil microbial activity showed by high levels of soil dehydrogenase activity. The AD- and AW-amended soils, showed the greatest decrease in leaching loss of SM (from 51.9% in original soil to 9.33% in AD and 8.05% in AW), reflecting the strong influence of adsorption-desorption processes on SM leaching. This study has shown that the application of olive mill wastes as organic amendments may be considered a useful strategy to reduce leaching of SM in soils poor in organic matter, especially if those wastes have a high level of organic matter maturity.

Keywords – Adsorption; Dehydrogenase activity; Dissipation; Leaching; Olive mill waste; S-metolachlor

Abbreviations: SM, S-metolachlor; W, two-phase olive mill waste; D, de-oiled two-phase olive mill waste; HPLC, high-performance liquid chromatography; CW, composted two-phase olive mill waste; AD, aged de-oiled two-phase olive mill waste; AW, aged two-phase olive mill waste; TOC, total organic carbon; HA, humic acids; FA, fulvic acids; WSOC, water-soluble organic carbon; HI, humification index; EC, electrical conductivity; DHA, Dehydrogenase activity; H, hysteresis coefficients

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48 **1. Introduction**

49 The herbicide S-metolachlor (SM) is widely used to control weeds in different crops such as maize, soybean, cotton,
50 and tomato as a selective chloroacetanilide herbicide. Indeed, SM is one of the ten most used active ingredients in the
51 European Union (Eurostat and European Commission, 2007). In the environment, SM has been detected in samples of
52 waters at superior concentrations to 0.1 μg L^{-1}, limit established by the European Union for drinking water (Palma et
53 al., 2014; Pérez et al., 2010). This is due to its high water solubility (488 mg L^{-1}), intensive use, low retention potential,
54 and high persistence in soils (Peña et al., 2013; López-Piñeiro et al., 2014). It is therefore quite important to develop
55 effective strategies to avoid or reduce water contamination by SM.
56 Mediterranean agricultural systems are environments at high risk of water pollution by herbicides, mainly because their
57 soils are very often poor in organic matter content (Gámiz et al., 2012). Hence, the application of organic amendments
58 to agricultural soils is a common agronomic practice to increase crops productivity and soils fertility. However, this
59 practice strongly influences the properties of the soil, and can thus affect the adsorption-desorption, dissipation, and
60 leaching of pesticides (e.g., García-Jaramillo et al., 2016; Kerminen et al., 2018; Trigo et al., 2016).
61 In Spain, the current process used in olive oil extraction generates a main by-product which is known as two-phase
62 olive mill waste (W). Generally, W is subjected to extraction to recover the oil still present, process that generates a by-
63 product, which is known as de-oiled two-phase olive mill waste (D). In the Mediterranean region, more than 15 Mt of
64 these wastes are produced during the months of October-December each year (Volpe et al., 2018), which constitutes a
65 critical issue for the industry. These wastes (W and D) are characterised by a high organic matter contents and plant
66 mineral nutrients, as well as lack pathogenic organisms and heavy metals. Therefore, its application to soils as organic
67 amendments, whether fresh or composted, may be a great alternative for their disposal (Gámiz et al., 2012; Peña et al.,
68 2016; Serramiá et al., 2013). Moreover, such waste management practices would be found according to the Circular
69 Economy Strategy of the European Union (COM, 2017), based on resources are conserved and waste is reused. It is
70 especially important to assure the suitable management of organic waste (Hueso-González et al., 2018).
71 Different studies have observed that the application of W and D represents an inexpensive source of nutrients for the
72 crops that could replace the need for chemical fertilizers (Ayoub et al., 2014; Vella et al., 2016), and can enhance crop
73 yields (Chatzistathis & Koutsos, 2017). In addition, the application of W and D as organic amendments can modify the
74 properties of the soils, and therefore also the environmental behaviour of herbicides (Delgado-Moreno et al., 2017;
75 López-Cabeza et al., 2017; López-Piñeiro et al., 2014). Generally, the adsorption of herbicides increases with increasing
76 of organic matter content in the soil, and thus their mobility decreases. However, the fate of herbicides in amended soils
77 is a difficult subject because the effects depends on many factors, such as the soil and amendment types, the organic

matter content and its degree of maturity, amendment dosage, pH, microbial activity (García-Delgado et al., 2019; Wolejko et al., 2017). In addition, the interactions between pesticides and soils may be affected by the evolution and transformation of the amendment´s organic matter under field conditions (Morillo et al., 2002). On the other hand, the properties of the herbicides as their molecular configuration and size, dissociation constant, and water solubility are important factors that affect their behaviour (Mendes et al., 2016). In this sense, the determination of the impacts of W and D on the behaviour of SM in different type of soils would provide valuable information about the safe and effective use of the herbicide in agro-ecosystems.

Although several studies have clearly shown that the application of W and D to soils may provide beneficial effects in soil properties and crop productivity, we only found three studies (Cañero et al., 2015; López-Piñeiro et al., 2014; and Peña et al., 2013) analysing the effects of olive mill wastes on SM behaviour. These studies, however, considered only amendments with the same degree of organic matter maturity and/or only one type of soil.

Previous studies have demonstrated the great importance of the nature and/or degree of decomposition of the organic matter on pesticide adsorption (Aslam et al., 2013; Cassigneul et al., 2015). In the particular case of olive mill wastes, López-Piñeiro et al. (2013a) reported that the highest sorptive capacity for metribuzin was observed with composted olive waste, suggesting that the total organic carbon (TOC) content may not be the principal factor in metribuzin adsorption. Similar results were found by Haberhauer et al. (2001) who observed that in case of MCPA herbicide, an increase of TOC does not necessarily imply an increase on adsorption capacity. However, Cabrera et al. (2010) and López-Piñeiro et al. (2012) found lower K_f coefficients with aged than with fresh amendments to diuron and terbuthylazine herbicides, respectively, due to the lower TOC content observed with aged amendments. These results seems to indicate that the maturity of the organic matter has be to taken into account, since not all organic matter has the same effectiveness for the herbicides sorption (Morillo et al., 2002). Therefore, the objective of the present study was to investigate the effects of olive mill wastes application at different degrees of maturity (fresh, composted, and field-aged) on SM adsorption-desorption, dissipation, and leaching in three Mediterranean agricultural soils. The influence of the olive mill wastes application as organic amendments on the microbial activity of the soil was also analysed due to herbicide persistence largely depends on microbial degradation.

2. Material and Methods

2.1. Herbicide and assays

SM of 96.0 ± 1.0 % purity was purchased from Dr Ehrenstorfer GmbH and its properties were 283.8 g mol^{-1} molecular weight, 3.7 mPa vapour pressure at 25ºC, and 480 mg L^{-1} water solubility at 25°C (BPDB, 2019). For assays, the SM solutions were prepared with this product. High-performance liquid chromatography (HPLC) was used to quantify the herbicide in the different tests. The limits of detection and quantification, calculated as the herbicide concentrations

resulting in signal-to-noise ratios of 3:1 and 10:1, respectively, were 0.061 μM and 0.204 μM, respectively. The conditions of the HPLC analysis are described in text S1 of the Supplementary Material.

2.2. Organic amendments and soils

Two organic amendments (D and W), each with different degree of maturity (fresh, composted, and field-aged), were used in this study. The fresh D and W were obtained from olive oil industries in Beja and Portalegre (Portugal), respectively. The composting process of W (CW) was carried out over 10 months (8 months on a pilot scale and 2 months more for maturation) in a trapezoidal pile with occasional turning and olive leaves added as bulking agent, with water added regularly to maintain appropriate moisture. The physicochemical characteristics of these wastes are given in Table 1.

Three Mediterranean agricultural soils were used in the present study: a loam soil (S1) that contained 239 g kg^{-1} clay, 324 g kg^{-1} silt, and 437 g kg^{-1} sand, a sandy loam soil (S2) that contained 142 g kg^{-1} clay, 323 g kg^{-1} silt, and 535 g kg^{-1} sand. Both soils (S1 and S2) were located in intensive farming systems in the plains of the Guadiana river near to city of Badajoz (Spain), (38°54′N –6°54′W) for S1 and (38°54′N –6°53′W) for S2. The other soil, a sandy clay loam soil (S3) that contained 297 g kg^{-1} clay, 211 g kg^{-1} silt, and 492 g kg^{-1} sand was located on a representative olive grove in Elvas, Portugal (38°53′N–6°59′W). The soil samples (0-30 cm depth) were dried at room temperature and sieved through a 2 mm mesh screen.

In the laboratory, two doses (2.5% and 5% by dry weight) of fresh wastes (D and W) and composted W (CW) were applied separately for each to original soils in order to investigate the impacts of these organic amendments on SM behaviour. Hence the resulting amended samples are labeled as S1D2.5 and S1D5, S2D2.5 and S2D5, and S3D2.5 and S3D5 (2.5% and 5% of D for each of the S1, S2, and S3 soils, respectively), S1W2.5 and S1W5, S2W2.5 and S2W5, and S3W2.5 and S3W5 (2.5% and 5% of W for each of the S1, S2, and S3 soils, respectively), and S1CW2.5 and S1CW5, S2CW2.5 and S2CW5, and S3CW2.5 and S3CW5 (2.5% and 5% of CW for each of the S1, S2, and S3 soils, respectively). Additional information on how the mixtures were made can be found in text S2 of the Supplementary Material.

Field experiment in olive grove of the soil S3 was conducted to investigate the effects of the "aging" transformation of the D and W organic matter on SM behaviour. For this purpose, besides the original S3 soils, four treatments were selected which consisted 27 Mg D ha^{-1} yr^{-1} (equivalent to 0.56% yr^{-1}, S3AD5) and 54 Mg D ha^{-1} yr^{-1} (equivalent to 1.12% yr^{-1}, S3AD10), 30 Mg W ha^{-1} yr^{-1} (equivalent to 0.62% yr^{-1}, S3AW5), and 60 Mg W ha^{-1} yr^{-1} (equivalent to 1.24% yr^{-1}; S3AW10), dry weight equivalents. In this experiment, both amendments have been applied for 9 consecutive years. Additional information on how the mixtures were made can be found in text S2 of the Supplementary Material. Thus, the total amounts of olive mill wastes applied to the field-amended soil and laboratory-

amended soils were similar. For this reason, in the laboratory, the S3 soil was also amended with 10% of fresh D and W, labeled as S3D10 and S3W10, respectively. Selected properties of the original and amended soils are shown in Table 2.

2.3. Analysis of the organic amendments and soils

The properties of the soils and wastes (D, W and CW) analysed were: total organic carbon (TOC), water-soluble organic carbon (WSOC), electrical conductivity (EC) and pH. Humic acids (HA) and fulvic acids (FA) were extracted with 0.1 M of tetrasodium pyrophosphate, and to precipitate HA the supernatant was acidified to pH 2 with sulphuric acid. The TOC associated with each fraction of HA and FA was determined by dichromate oxidation and measurement of the absorbance at 590 nm. The Humification index (HI) was calculated as ((HA/TOC) x 100).
These analyses were developed as described by Peña et al. (2016).

2.4. Adsorption-desorption studies

Adsorption-desorption studies were developed as described by López-Piñeiro et al. (2014). Briefly, the SM concentrations used were 5, 10, 20, 40, and 50 µM. Following the adsorption analysis, desorption of the SM was studied, replacing the 5 mL of the supernatant removed for the adsorption analysis with 5 mL of 0.01 M $CaCl_2$.
Although Freundlich, Langmuir, and linear models were tested, the sorption kinetics of SM were best described by the Freundlich model which produced the best fit with the highest regression coefficients and lowest sum of squared errors. A complete description of the methodology can be found in text S3 of the Supplementary Material.

2.5. Dissipation of SM

The dissipation study was carried out according to the conditions described in Peña et al. (2013). Briefly, the herbicide was applied to get 1.5 mg SM kg^{-1} of concentration. Herbicide-treated soil samples were incubated for 103 days at 20±2°C. Periodically, soils samples were taken and then frozen until assay. Although biphasic and first-order multicompartment models were also tested, dissipation of SM was best described by a first-order kinetics model. This produced the best fit with the highest regression coefficients and lowest sum of squared errors. For this reason, first-order kinetics was used to analyse the dissipation data of this herbicide and to calculate the half-life ($t_{1/2}$) (this last was done after fitting the data to a first-order kinetics equation). A complete description of the methodology can be found in text S4 of the Supplementary Material.

2.6. Dehydrogenase activity

Dehydrogenase activity (DHA) was determined following the method described in García et al. (1993). A complete description of the methodology can be found in text S5 of the Supplementary Material.

169 ***2.7. Column leaching tests***

170 Disturbed soil columns were used to the leaching experiments as described by Peña et al. (2016). A concentration of 1.5
171 mg of SM kg^{-1} was added to the top of the columns and, then 50 mL of calcium chloride was applied to leach the
172 columns every day. At the end of the leaching tests, the columns were sectioned into 5-cm deep portions in order to
173 determine the residual amount of SM at the different depths of the soil column. A complete description of the leaching
174 study is shown in text S6 of the Supplementary Material.

175 ***2.8. Herbicide extraction***

176 For soils samples of the dissipation and leaching studies, SM were extracted with methanol using a ratio of 2:1 (v/w) by
177 shaking mechanically for 24 hours in an end-over-end shaker at 20±2°C. Then, the samples were centrifuged the
178 samples for 7 minutes at 3500 rpm and filtered. Finally, the SM concentration in the extracts was determined by HPLC.
179 Preliminary studies showed that this extraction procedure recovered ≥95% of the SM applied to the soils.

180 ***2.9. Bioassays***

181 In order to assess how application of the organic amendments affected SM's efficacy, its antigermination potential was
182 measured on *Lolium perenne* L., due to is a plant sensitive to SM. The treatments selected for this experiment were: S1,
183 S1D5, S1W5, S1CW5, S2, S2D5, S2W5, S2CW5, S3, S3D5, S3D10, S3W5, S3W10, S3CW5, S3AD10, and S3AW10.
184 In each case, two sets of pots were carried out, one set with SM applied at a dose rate of 1.5 kg ha^{-1}, and the other set
185 without herbicide to be used as controls. 50 seeds were carefully spread by hand on the surface of the soil in the pot as
186 homogeneously as possible before the SM application. The pots were under optimal conditions for germination. After
187 14 days of the sowing, the seedlings in each pot were counted and their lengths measured.

188 ***2.10. Statistical analysis***

189 IBM SPSS Statistics 22.0 program was used to the statistical test. The results were subjected to a one-way ANOVA
190 model and multiple pairwise comparisons were performed using the Duncan test to determine significant differences
191 between results at a $p<0.05$ level of probability. Pearson's correlation coefficient was employed to find possible
192 correlations between the various parameters.

193 **3. Results and Discussion**

194 ***3.1. Adsorption-desorption studies***

195 The experimental data of the adsorption-desorption studies fit Freundlich equation well, with $R^2 \geq 0.944$ (Table 3). A
196 high level of linearity was observed for the SM adsorption isotherms ($n_f \approx 1$, Table 3), especially with the fresh and
197 aged amendments (D, W, AD, and AW). This behaviour is coherent with that observed by Peña et al. (2013) for SM

198 adsorption in a Cutanic Luvisol using D- and W-amendments. However, Baran & Gourcy (2013) found n_f values of less
199 than unity for SM in different agricultural soils, showing that the soil's affinity for the herbicide molecules decreases as
200 the herbicide concentration increases. The k_f values for SM adsorption in the original soils ranged from 1.41 for S3 to
201 3.02 for S1. These relatively low values agree with Cañero et al. (2015) who found values of 1.0 and 1.57 in a sandy
202 soil and a clayey soil, respectively, and suggest that these soils have a very weak capacity to bind SM. The low TOC
203 content observed in the soils of the present study could be the reason to the relatively low k_f values found. Indeed, for
204 some soils in the USA with TOC values from 8.70 to 32.5 g kg^{-1}, much higher than those of our study (Table 2), Shaner
205 et al. (2006) reported k_f values ranging from 1.58 to 6.93. Likewise, Bedmar et al. (2011) report a k_f of 29.2 in a no-
206 tillage soil for four years, witch a TOC value of 25 g kg^{-1}. The fresh amendments (D and W) had a significant influence
207 on the adsorption of SM (Table 3). Their k_f values were greater than those of the original soils; however the magnitudes
208 are different between soil and according to the amendment applied. Thus, for the 5% D applications, the k_f was greater
209 by factors of 1.33 in S1, 2.11 in S2, and 3.60 in S3, whereas for the 5% W applications, the corresponding factors were
210 2.00 in S1, 3.01 in S2, and 4.82 in S3. These results suggest that W had a higher affinity for SM than D. Similar
211 findings had been found by Albarrán et al. (2003) for simazine sorption, with the increase produced by a D amendment
212 being significantly less pronounced than that found with a W amendment. These differences may be due to not only to
213 the higher TOC content of W (535 g kg^{-1}) than of D (516 g kg^{-1}), but especially to the higher HA content of W (51.8 g
214 kg^{-1}) than of D (30.7 g kg^{-1}). In fact, in our study, k_f was positively and significantly (p<0.01) correlated with HA
215 (r=0.744), and this correlation was higher than that with TOC (r=0.657).
216 The adsorption of SM was greater in the soils amended with W than CW (Table 3). This could be attributable to the
217 higher content of TOC into the fresh W-amended soils than the CW-amended soils (Table 2). In particular, for 5% of
218 fresh W treatments, the TOC content increased by factors of 3.54, 4.85, and 4.11 in S1, S2, and S3, respectively,
219 whereas, for 5% of composted W (CW treatments), the factors were 2.73, 3.83, and 2.67 in S1, S2, and S3, respectively.
220 Previous work with SM has found that SM sorption coefficients were correlated with the soil's organic matter content
221 (Patakioutas & Albanis, 2002; Westra et al., 2015).
222 In the field-amended soils, the application of both amendments (D and W) significantly (p<0.05) increased SM
223 adsorption (Table 3). The increase was greater in the D-amended soils, suggesting that D had a higher affinity for SM
224 than W when both wastes had been transformed in the soils under long-term field conditions, unlike the situation
225 observed with fresh amendments (D and W). These results could be to explain by the greater TOC content observed in
226 the AD treatments than in the AW treatments (Table 2). In the present study, the highest SM sorption values were found
227 in the field-amended soils despite their having lower TOC contents (Table 2) than the laboratory-amended soils (Table
228 2 and 3). Hence, increased TOC content by itself does not necessarily led to a greater SM sorption. This finding is
229 further supported by the k_{foc} values which were lower for laboratory-amended soils than for field-amended soils (Table

3). This could be understood in terms of the soils' organic matter quality (Delgado-Moreno et al., 2007) due to the interactions between SM and organic matter also depends on the quality of the material (Haberhauer et al., 2001). In fact, k_{foc} was significantly and positively correlated with HI (r=0.564, p<0.01) and negatively with WSOC (r=-0.398, p<0.05), confirming that the evolution and transformation of organic matter in the studied soils was also important for SM adsorption. The calculated SM k_{foc} values (around 214 for all treatments) are coherent with the values given in the EU review report (mean 226, range 110–369) (SANCO, 2004).

The values of hysteresis coefficients (H) in fresh-amended soils (D and W treatments) were significantly lower than in those amended with composted W (CW treatments) or in the field (AD and AW treatments) (Table 3). Consequently, the adsorbed SM could be easily desorbed in D- and W-amended soils if the amendments are not mature. In fact, H was significantly and positively with HI (r=0.384, p<0.05) and negatively with WSOC (r= -0.437). Although the correlations are statistically significant, they explain less than 20% of the variability, and therefore should be regarded as minor factors. SM desorption was correlated negatively (p<0.05) with HA and HI (r= -0.398 and r= -0.462, respectively), indicating the importance of the level of humification in the adsorption-desorption of SM. Similar results have been reported previously in soils where these wastes were incorporated: for MCPA (López-Piñeiro et al., 2013b; Peña et al., 2015) and for metribuzin (López-Piñeiro et al., 2013a; Peña et al., 2016). Also, Cañero et al. (2015) indicated that SM sorption was more reversible in amended than original soils, although they considered only fresh W as organic amendment.

3.2. Dissipation studies

The SM dissipation curves for both original and amended soils are shown in Fig. 1. The data for all the treatments fit well to first-order kinetics with R^2≥0.827 (Table 3). The SM half-lives ($t_{½}$) in the original soils (18.1-27.0 days) were similar to those found in other studies which range from 11.1 to 28.0 days in different soil types (e.g., Shaner et al., 2006; Wolejko et al., 2017). According to these $t_{½}$ values (Table 3), the SM dissipation rates in original soils followed the trend of sandy loam soil (S2) < loam soil (S1) < sandy clay loam soil (S3). These dissipation rate differences could be caused by the differences in pH, since this was highest in S3 and lowest in S2 (Table 2). The results agree with those of Alletto et al. (2013) who observed that SM mineralization was heavily influenced by pH, indicating that a higher soil pH can foster the growth of soil microbial activity and so the dissipation of SM (Wolejko et al., 2017). In fact, in our study, $t_{½}$ was significantly (p<0.01) and negatively correlated with pH (r= -0.826) and DHA (r= -0.618).

Independently of the soils type, the application of fresh D or W in the laboratory (D and W treatments) substantially reduced the SM dissipation (Fig. 1), and consequently caused significant increases in $t_{½}$, (Table 3). Usually, adsorption is found to limit dissipation because it reduces the available herbicide concentration. For example, SM mineralization rates are inversely correlated with the herbicide's adsorption (Bedmar et al., 2017; Cañero et al., 2015). The observed

increase in SM adsorption in the D- and W-amended soils could thus be the cause for its high persistence (Table 3). However, the greatest k_f values were found in the field soils amended with both wastes (AD and AW treatments of the S3 soil) (Table 3). Their half-lives ($t_{½}$ values of 20.1, 18.8, 15.3, and 18.8 days for S3AD5, S3AD10, S3AW5, and S3AW10, respectively) were significantly shorter than those of the laboratory soils amended with D and W, and very close to the value of the original soil (18.1 days in S3). In our soils therefore, SM adsorption can not explain the results observed in the dissipation studies. Thus, although a correlation could have been expected between k_f and $t_{½}$, no such significant relationship was found (the results of the correlation study were r= -0.068, p>0.05).

Rodríguez-Cruz et al. (2012) found that high rate of herbicide degradation may be caused by increase in soil microbial activity. In our study, the field amended soils showed the greatest initial DHA values (1.89, 2.17, 1.97, and 2.71 µg INTF g^{-1} h^{-1} in S3AD5, S3AD10, S3AW5, and S3AW10, respectively) (Table 2). Throughout the dissipation study, DHA was on average about 1.27 and 1.73 times greater in the S3AD5 treatment than in S3 and S3D5, respectively and 1.42 and 1.48 times greater in S3AW5 than in S3 and S3W5, respectively. Therefore, the greater DHA observed in the field-amended treatments with both wastes (AD and AW) could mainly explain the short persistence of SM.

However, although the activity of soil microbial can increase with increasing in organic carbon content of the soil (Pose-Juan et al., 2015) the DHA values of D and W treatments (regardless of dosage) fell to even below those of original soils (Table 2). Again throughout the dissipation study, DHA was on average about 2.77, 1.61, and 1.37 times lower in S1D5, S2D5, and S3D5 than in the corresponding original soils S1, S2, and S3, respectively, and 3.09, 1.40, and 1.04 times lower in S1W5, S2W5, and S3W5 than in the corresponding original soils S1, S2, and S3, respectively. Thus, independently of the soil type, the greater SM $t_{½}$ values found in the D2.5, D5, W2.5, and W5 treatments, could be caused to the inhibitory effect of these amendments on microbial activity (Sampedro et al., 2009). The observed differences in DHA between laboratory and field-amended soils could be a reflection of a possible adaptation of the soil microorganisms to the two wastes (D and W) after 9 years of field application and so it favours the SM biodegradation (Cabrera et al., 2010).

In contrast with the trend observed for the laboratory fresh W-amended soils, the CW amendment significantly shortened the SM half-life, regardless of the soil type. In particular, the application of CW at the higher rate (5%) reduced $t_{½}$ from 23.9 days in the original S1 soil to 22.9 days, from 27.0 days in the original S2 soil to 18.5 days, and from 18.1 days in the original S3 soil to 12.3 days (Table 3). This effect could be attributed to increased microbial activity in the CW-amended soils. As can be seen by Fig. 1, the lines of DHA in soils amended with CW are far above the corresponding line of the original soils. Considering all the incubation times together, the DHA was on average 1.21, 4.95, and 1.13 times greater in S1CW5, S2CW5, and S3CW5 than S1, S2, and S3, respectively and 3.73, 6.90, and 1.18 times greater in S1CW5, S2CW5, and S3CW5 than S1W5, S2W5, and S3W5, respectively. The different rates of dissipation observed with CW and W agree with the water-soluble phenols (WSP) values of the two amendments (2.40

293 g kg^{-1} and 7.30 g kg^{-1} for CW and W, respectively), implying greater toxicity of W than of CW for soil microorganisms
294 (Piotrowska et al., 2011; Sampedro et al., 2009).
295 The low values of $t_{½}$ observed in the CW-amended soils and field D- and W-amended soils may be due to the fact that
296 the soil microorganisms are consuming the herbicide as a carbon and energy resource rather than the available organic
297 substrates (WSOC), which was significantly reduced in these treatments with greater HI (Table 2). Indeed, $t_{½}$ was
298 positively correlated (p<0.01) with WSOC (r=0.558) and negatively with HI (r= -0.510), indicative of the importance of
299 the level of organic matter humification for the dissipation of SM.
300 One of the findings of our dissipation study was the significant increase in DHA values after SM application (2 hours),
301 demonstrating that this product does not any toxicity risk to microorganisms at dose used (1.5 kg ha^{-1}). Similarly,
302 Wolejko et al. (2017) reported that, in two agricultural soils, the application of SM at doses of 1.2 and 1.5 kg ha^{-1} may
303 have contributed to an increase in DHA values from the 2nd to the 28th days after the herbicide's application.

304 ***3.3. Leaching studies***

305 Breakthrough cumulative curves from the original and amended soils are shown in Fig. 2. The amendments led to
306 retardation of SM breakthrough, independently of the amendment applied or the soil type. This situation is coherent
307 with the greater k_f values found in the amended soils (Table 3).
308 The total percentage of SM eluted for the original soils ranged from 51.9% to 54.1% of the initially applied dose (Table
309 3). While similar SM leaching losses were observed by Cañero et al. (2015) in a Mediterranean olive grove soil, López-
310 Piñeiro et al. (2014) recovered 12.4% of the applied SM in leachates, although in this case through undisturbed soil
311 columns.
312 For all soils studied, the amendments application had a significant influence (p<0.05) on SM leaching losses, though the
313 magnitudes of those losses depended on the soil and waste type (Table 3, Fig. 2). In the particular case of the laboratory
314 fresh D-amended soils, the effect differed according to the dose rate. Whereas for 5% of D application, the SM leaching
315 losses were lower by factors of 1.20 in S1 and 1.36 in S3, for the 2.5% rate of D application the leaching losses were
316 even slightly greater than those of the original soils (Table 3). In contrast, the laboratory fresh W-amended soils showed
317 significantly reduced SM leaching losses relative to the original soils (by factors of 2.70, 2.37, and 1.53 for S1W5,
318 S2W5, and S3W5, respectively). The higher WSOC found with the use of D than with W could explain this difference,
319 because this material can act as co-transporter in leaching the herbicide (Peña et al., 2015). Thus, considering the 5%
320 dose rates, the WSOC content of the W5 treatments was 1.40, 1.49, and 1.63 times lower than that of the corresponding
321 D5 treatment in the S1, S2, and S3 soils, respectively.
322 The CW amendment significantly reduced the percentage of herbicide leached by greater factors than the fresh W
323 amendment (Table 3, Fig. 2). Thus, the percentages of herbicide in the leachates relative to the original soils were lower

by factors of 2.71, 3.36, and 2.62 for S1CW5, S2CW5, and S3CW5, respectively. The above findings seem to demonstrate that the amendment's degree of maturity is even more important than its organic matter content with regard to the leaching of SM. In fact, the amount of SM leached was correlated negatively with both TOC ($p<0.05$, $r= -0.393$) and HA ($p<0.01$, $r= -0.541$).

The percentage of SM leached from the field amended soils was significantly less than from the original and laboratory-amended soils, independently of the amendment applied (Table 3; Fig. 2). In coherence with the adsorption, the greatest k_f and H values corresponded to the field-amended soils (Table 3). In fact, various authors have suggested that adsorption-desorption processes are key factors in the transport and environmental fate of herbicides in soils (e.g., Cox et al., 2001; Gianelli et al., 2014; Hiller et al., 2010). The percentage of SM leached was significantly ($p<0.01$) and negatively correlated with k_f ($r= -0.757$) and H ($r= -0.544$), showing that adsorption and desorption processes were also responsible for the leaching behaviour of SM.

In most cases, the application of either waste, independently of its degree of organic matter maturity, increased the amount of SM extracted from the soil columns, suggesting that relatively fresh organic matter allows intra-organic matter diffusion and absorption, thus preventing the compound from biodegradation (Table 3). Fig. 3 shows the distribution of SM at the different depths of the soil columns once the study was finalized. The pattern of this distribution differs markedly between the original and the amended soil columns. In the former, large amounts of herbicide were recovered from the bottom layer (15-20 cm), but in the latter, the opposite was the case with the amounts of SM declining with column depth. These results are consistent with those described above for the adsorption process. Certainly, the amount of SM extracted was significantly ($p<0.01$) and positively correlated with k_f ($r=0.543$).

3.4. Herbicidal activity

Table 4 lists the germination percentages obtained in the bioassay study. Although the organic waste amendments (independently of the type of waste and the degree of organic matter maturity) increased SM adsorption (Table 3), they did not reduce the herbicide's efficacy. Indeed, the germination percentages were zero when SM was applied (Table 4). Furthermore, the application of organic amendments did have a significant influence ($p<0.05$) on the germination of the *Lolium perenne* L. seeds in the control pots without herbicide application. The magnitude of this influence depended on the type of waste applied and its degree of organic matter maturity (Table 4). Relative to the original soils, the germination percentages were lower in the laboratory D- and W-amended soils, especially with D (Table 4). Thus, for 5% D addition, the germination decreased by factors of 3.28 in S1, 18.5 in S2, and 3.09 in S3, and for 5% W addition, these factors were 1.64 in S1, 2.31 in S2, and 1.08 in S3. For the CW-amended soils however, the germination percentages were significantly greater than for the W-amended soils, and quite similar to the original soils, independently of soil type. Various experiments performed with olive-mill by-products and wastes have linked their

355 phytotoxicity to phenols (Alburquerque et al., 2006; Pinho et al., 2017). The present results might therefore be
356 attributable to the different WSP contents of the wastes – 2.40 g kg^{-1} in CW, 7.30 g kg^{-1} in W, and 14.6 g kg^{-1} in D.
357 In the field-amended soils, the repeated applications of D and W significantly increased the germination percentages. In
358 particular, compared to the original S3 soil, these increases were by factors of 1.21 and 1.08 for S3AD10 and S3AW10,
359 respectively, and, compared to S3D10 and S3W10 (laboratory-amended soils), they were by factors of 7.51 and 1.73 for
360 S3AD10 and S3AW10, respectively.
361 The seedling length results were similar (Fig. 4). The values for the field-amended soils (10.2 cm and 9.16 cm for
362 S3AD10 and S3AW10, respectively) were significantly greater than for the laboratory fresh-amendment soils (3.20 cm
363 and 7.24 cm for S3D10 and S3W10, respectively). The seedling lengths in the laboratory W- and D-amended soils
364 (especially the latter) were smaller than in the original soils, independently of soil type (Fig. 4). Thus, at the 5% dose
365 rate, these differences were by factors of 1.51 and 1.35 on average for the D and W treatments, respectively. Again
366 however, the case was different with CW as organic amendment (the CW5 treatments), for which the lengths were
367 similar to those of the original soils.
368 These findings therefore indicate that the phytotoxicity of the fresh olive mill wastes (D and W) reflected in the lower
369 germination percentages and shorter seedling lengths disappears with both the natural transformation under field
370 conditions (AD and AW treatments) and the composting process (CW treatments) (Asses et al., 2018).

371 **4. Conclusions**

372 The results found in this study have shown that application of olive mill wastes (D and W) as organic amendments to
373 Mediterranean agricultural soils greatly influences the behaviour of SM. However these effects depend on soil and
374 amendment type, dose rate of amendment, and above all, on the degree of maturity. Amendments with fresh (D and W),
375 composted (CW), and field-aged (AD and AW) olive mill wastes led to increased SM adsorption capacity, although
376 without reducing the herbicide's effectiveness. The application of SM at a dose rate of 1.5 kg ha^{-1} was not toxic for the
377 soil microorganisms, as was shown by the greater values of DHA found after two hours herbicide application. However,
378 the addition of the organic amendments influenced the soils' microbial activity, and therefore the persistence of SM, but
379 the magnitude of the effect depended on the maturity of the amendment. Thus, the application of fresh wastes (D and
380 W) increased the persistence of SM in all soils, whereas the CW and the AD and AW amendments had the opposite
381 effect, reducing the persistence of herbicide due to increase in the soils' microbial activity. The application of olive mill
382 wastes (D and W) as organic amendments may be considered as a useful strategy in order to reduce the leaching of SM
383 in soils poor in organic matter, especially if those wastes have previously been aged in the soil or composted.
384 Furthermore, these types of wastes should be applied in preference to fresh type so as to ensure that there are no
385 phytotoxicity concerns.

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Figure Captions

Fig. 1. Effects of D and W application (fresh, composted, and aged) on SM dissipation (left) and dehydrogenase activity (right). Error bars represent one standard error of the mean (in some cases, they are smaller than the symbols).

Fig. 2. Effects of D and W application (fresh, composted, and aged) on the cumulative breakthrough curves of SM. Error bars represent one standard error of the mean (in some cases, they are smaller than the symbols).

Fig. 3. Effects of D and W application (fresh, composted, and aged) on SM extracted from different depths of the soil columns of the leaching experiment. Error bars represent one standard error of the mean.

Fig. 4. Effects of D and W application (fresh, composted, and aged) on seedling length (*Lolium perenne* L). Error bars represent one standard error of the mean.

Fig. S1. Effects of D and W (fresh, composted, and aged) application on the SM adsorption isotherms. Treatments are (○) original; (▼)W2.5; (■)W5; (▲)W10; (▽) CW2.5; (□) CW5; (▼) D2.5; (■) D5; (▲) D10; (●) AW5; (◆) AW10; (●) AD5, and (◆) AD10. Vertical bars represent one standard error of the mean which were lower than the symbols in all cases.

Fig. S2. The symbols indicate the experimental data points of SM dissipation studies whereas the lines correspond to the fits to first-order dissipation kinetics for those experimental data. Error bars denote standard errors of triplicate measurements.

Supplementary Material

Text S1.

The SM concentration was determined by high-performance liquid chromatography (HPLC) model Waters 600E using a device equipped with a UV diode-array detector (model Waters 996) and a Nova-Pack column C18 (150 × 3.9 mm, 4 µm particle size). The injection volume was 25 µL, the flow rate 1 mL min^{-1}, and the column temperature 30°C. The mobile phase was 50% distilled water and 50% acetonitrile. The wavelength used for detection was 204 nm. The SM concentrations were quantified against a linear calibration curve of chromatographic peak area versus SM standards (0.2–50 µM). The standards were prepared in the same medium as the samples – in $CaCl_2$ 0.01M for the adsorption-desorption and leaching experiments, and in methanol for the dissipation experiment.

Text S2.

In the laboratory, the amendments were added to the unamended soils at 2.5 and 5% (w/w) by adding the corresponding amount of amendment to a pre-weighed amount of soils and then mixing with a stainless steel spatula to homogenize the mixtures. The mixtures were made manually for each sample and each study in order to be able to ensure their correct proportion. In the case of the field conditions, the amendments were applied annually, spreading the waste on the soil surface manually, followed by arable-level homogenization using a mould-board plough.

Text S3.

Soil samples (5 g) were treated with 10 mL of SM solution. The initial concentration of SM ranged between 5 and 50 µM in 0.01 M $CaCl_2$ and each concentration was replicated three times. Samples were equilibrated by shaking mechanically at 20 ± 2 ºC for 24 hours. Preliminary kinetic studies were carried out to determine the optimal soil:solution ratio and the equilibrium time according to OECD guideline 106 (OECD, 2000). Equilibrium concentrations in the supernatants were determined by HPLC. The amount of SM adsorbed (C_s) was calculated from the difference between the initial (C_i) and equilibrium (C_e) solution concentrations. The measurements with control samples containing only SM showed that there were no losses of SM due to dissipation, volatilization or adsorption onto the surface of the tubes.

Following the adsorption experiment, the desorption of SM from the soils was measured by successive remove-refill from the 50 µM initial concentration points. The 5 mL of supernatant removed for adsorption analysis was replaced with 5 mL of 0.01 M $CaCl_2$. The samples were re-suspended, shaken for 24 hours, centrifuged and filtered, and the equilibrium concentration in the supernatant was determined. This desorption procedure was repeated three times. All treatments had three replicates. Preliminarily studies indicated that no measurable degradation occurred during the sorption-desorption period. The herbicide adsorption and desorption results were fitted by the Freundlich model, $C_s=k_f C_e^{nf}$, where C_s (µM kg^{-1}) is the amount of herbicide adsorbed at the equilibrium concentration C_e (µM L^{-1}), and k_f and n_f

are the Freundlich coefficients that characterize the relative adsorption capacity and the adsorption intensity, respectively, of the herbicide. The organic carbon soil adsorption coefficient (k_{foc}) was calculated from the k_f values as $k_{foc}= (k_f \times 100)/TOC\%$. Hysteresis coefficients (H), for the adsorption-desorption isotherms were calculated as $H = n_a/n_d$, where n_a and n_d are the Freundlich constants obtained from the adsorption and desorption isotherms, respectively. The desorption percentage was calculated as $\%D = ((C_{sa}-C_{sd})/C_{sa}) \times 100$, where C_{sa} is the amount of SM adsorbed in adsorption process and C_{sd} is the amount of SM adsorbed in desorption process.

Text S4.

The dissipation of SM in original and amended soils was determined by incubation experiments in which 500 g of original and amended soils samples were spiked with SM at a rate of 1.5 mg of active ingredient kg^{-1} soil. The moisture content was adjusted to 40% field capacity, and then the samples were thoroughly mixed by passing them several times through a 2 mm-sieve. Herbicide-treated soil samples were transferred to 1-L glass jars where they were incubated at 20± 2 °C for 103 days in the dark. The moisture content was maintained at a constant level throughout the experiment by adding distilled water as necessary, followed by vigorous shaking using a sterilized spatula. The soils were sampled periodically, and finally frozen until assay, 5 g of soil samples in triplicates were extracted with 10 mL of methanol for 24 hours, and the SM concentration in the extracts was determined by HPLC. Incubation data were fitted to first-order herbicide dissipation kinetics: $Ln\ C = Ln\ Co - k \cdot t$, where *C* is the herbicide concentration at time *t* (days), *Co* is the initial herbicide concentration, and *k* (days $^{-1}$) is the first-order dissipation constant. The half-live ($t_{1/2}$) was calculated as $t_{1/2}=0.693/k$.

Text S5.

Dehydrogenase activity (DHA) was determined in original and amended soil samples from the dissipation study by the method of García et al. (1993). One gram of soil was incubated for 20 hours at 20 °C in the dark with 0.2 mL of 0.4% 2-(p-Iodophenyl)-3(p-nitrophenyl)-5-phenyl tetrazoliumchloride (INT) as substrate. At the end of the incubation, the iodonitrotetrazoliumformazan (INTF) produced was extracted with 10 mL of methanol and the absorbance measured at 490 nm.

Text S6.

Leaching experiments were carried out using disturbed-soil columns (30-cm length × 5-cm i.d.) constructed of PVC. To minimize losses of soil during the experiment, the top 5 cm of the columns was filled with sea sand and the bottom 5 cm with sea sand plus glass wool. The remaining 20 cm was hand-packed with original or amended air-dried soil. The experiment was performed with triplicates of the original and amended soil samples. The soil columns were saturated with 0.01 M $CaCl_2$, allowed one to drain for 24 hours, and then the amount of SM corresponding to an application rate of 1.5 kg ha^{-1} dissolved in water was applied to the top of the columns. Each day the columns were leached with 0.01 M

694 $CaCl_2$ at a rate of 50 mL day^{-1} until no herbicide was detected in the leachates. Leachates containing the herbicide were
695 collected daily, filtered, and assayed by HPLC. At the end of the monitoring period, the columns were sectioned into
696 four depths (0–5 cm, 5–10 cm, 10–15 cm, and 15–20 cm), and SM extracted by shaking (24 hours at 20 ºC) 5 g of soil
697 with 10 mL of methanol. The suspensions were centrifuged, filtered, and assayed by HPLC in order to determine the
698 residual amount of herbicide at the different depths of the soil column.
699

700 References of Supplementary Material

701 OECD, 2000. OECD guideline for testing of chemicals. Method 106. Adsorption-desorption using batch equilibrium
702 method. OECD, Paris, p. 45.

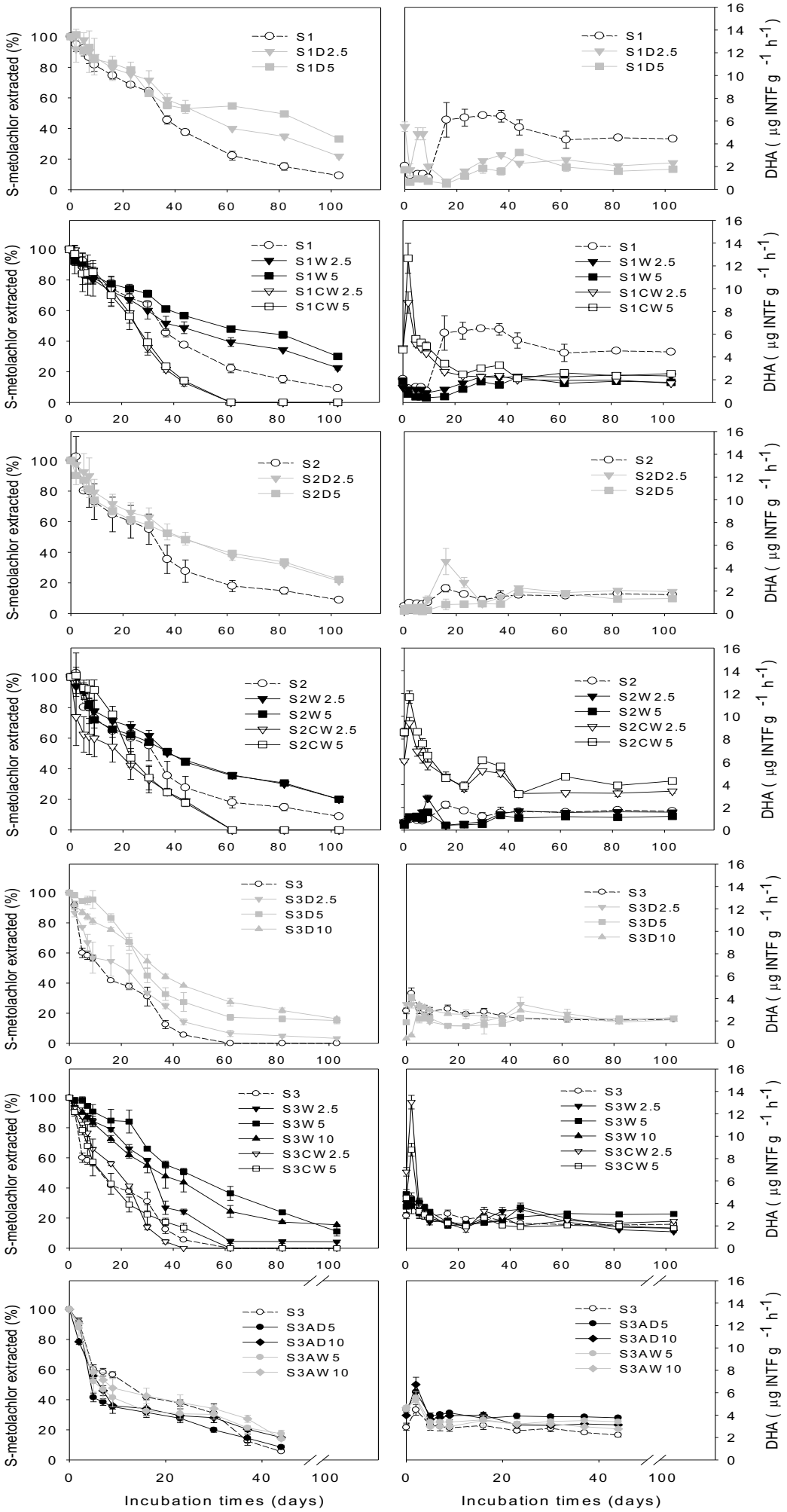
S-metolachlor extracted (%)
DHA (µg INTF g -1 h-1)
Incubation times (days)
S1
S1D2.5
S1D5
S1W2.5
S1W5
S1CW2.5
S1CW5
S2
S2D2.5
S2D5
S2W2.5
S2W5
S2CW2.5
S2CW5
S3
S3D2.5
S3D5
S3D10
S3W2.5
S3W5
S3W10
S3CW2.5
S3CW5
S3AD5
S3AD10
S3AW5
S3AW10

Figure 1

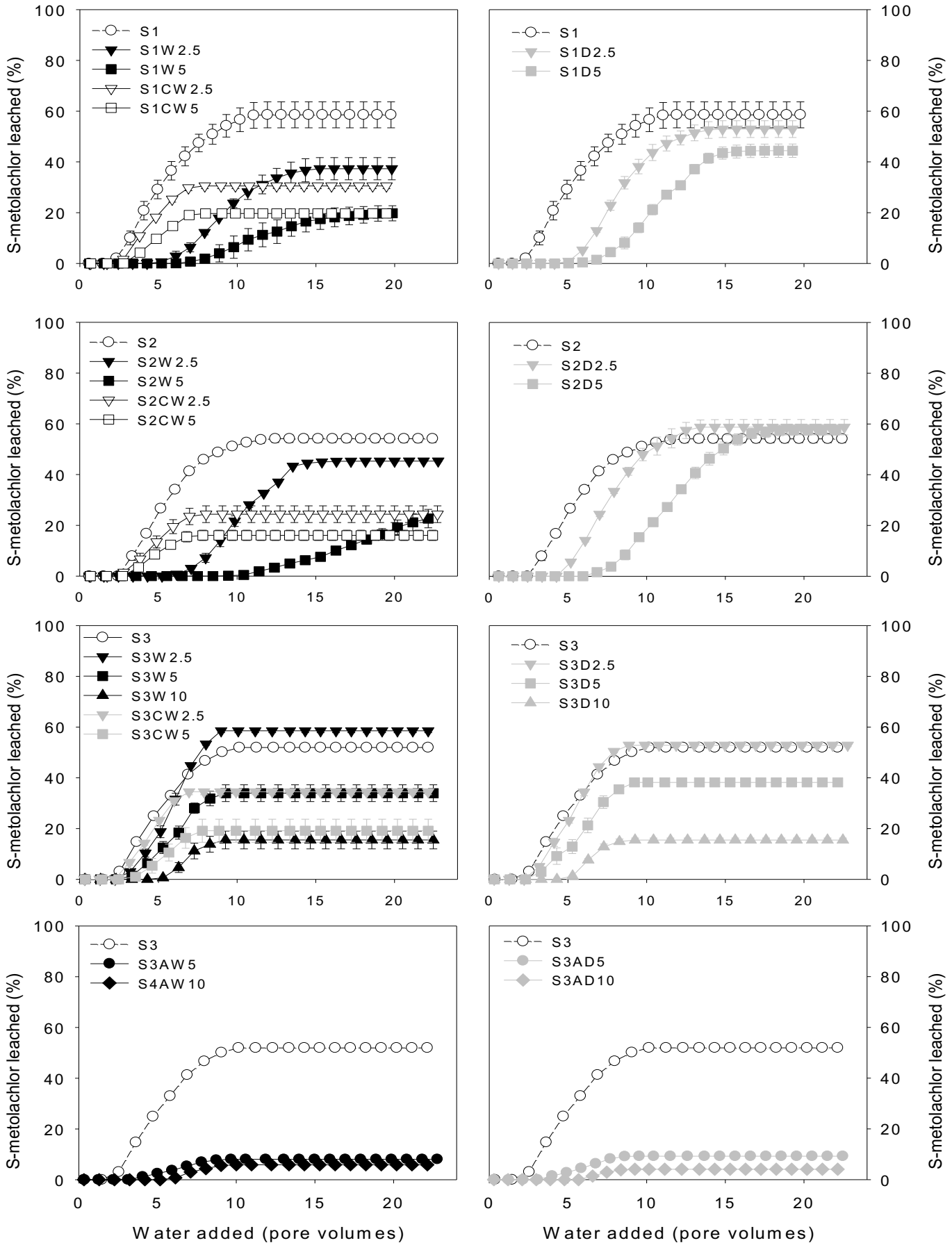
S-metolachlor leached (%)
Water added (pore volumes)
S1
S1W2.5
S1W5
S1CW2.5
S1CW5
S1
S1D2.5
S1D5
S2
S2W2.5
S2W5
S2CW2.5
S2CW5
S2
S2D2.5
S2D5
S3
S3W2.5
S3W5
S3W10
S3CW2.5
S3CW5
S3
S3D2.5
S3D5
S3D10
S3
S3AW5
S4AW10
S3
S3AD5
S3AD10

Figure 2

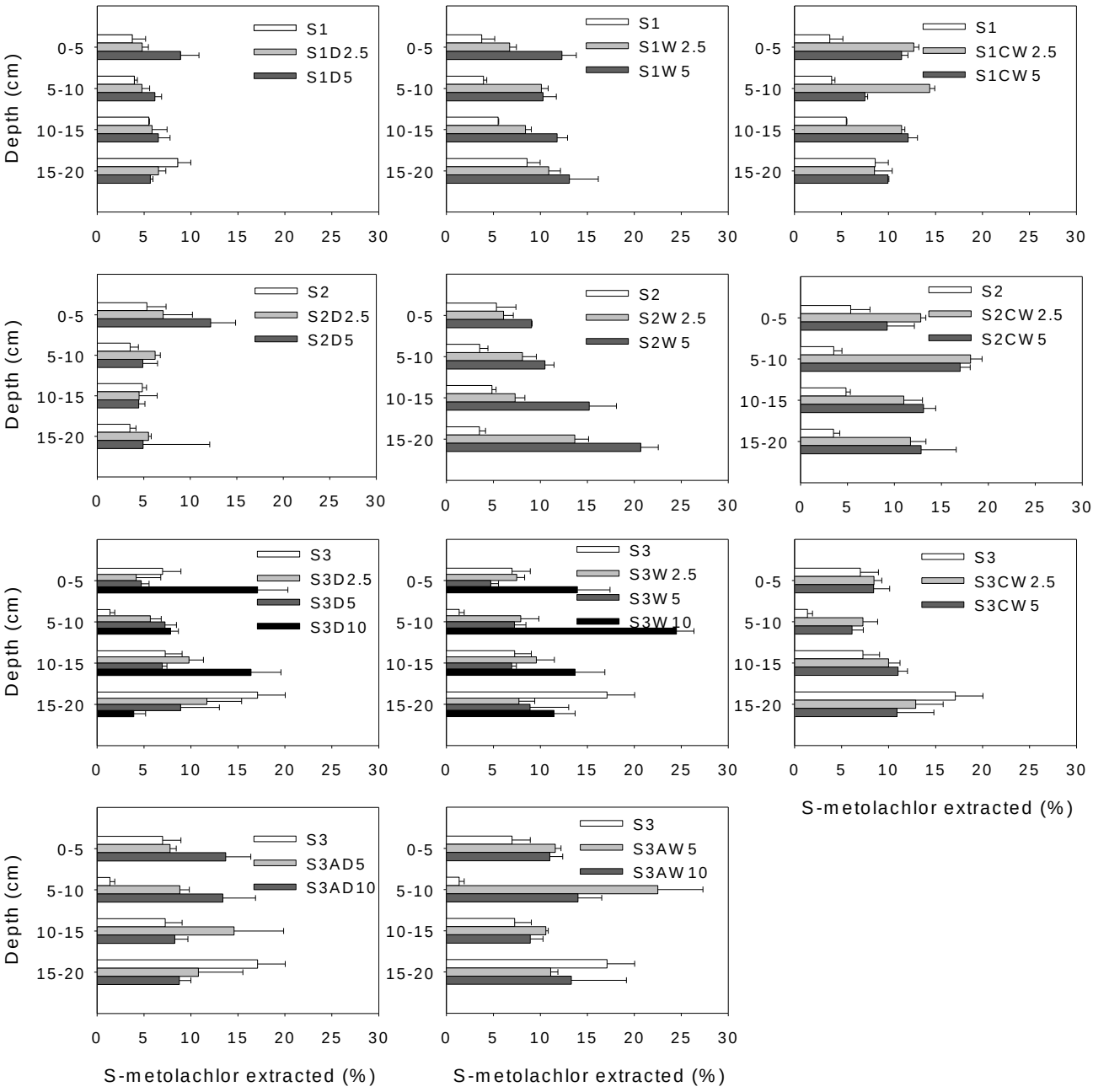
Depth (cm)
0-5
5-10
10-15
15-20
S1
S1D2.5
S1D5
S1W2.5
S1W5
S1CW2.5
S1CW5
S2
S2D2.5
S2D5
S2W2.5
S2W5
S2CW2.5
S2CW5
S3
S3D2.5
S3D5
S3D10
S3W2.5
S3W5
S3W10
S3CW2.5
S3CW5
S3AD5
S3AD10
S3AW5
S3AW10
0 5 10 15 20 25 30
S-metolachlor extracted (%)

Figure 3

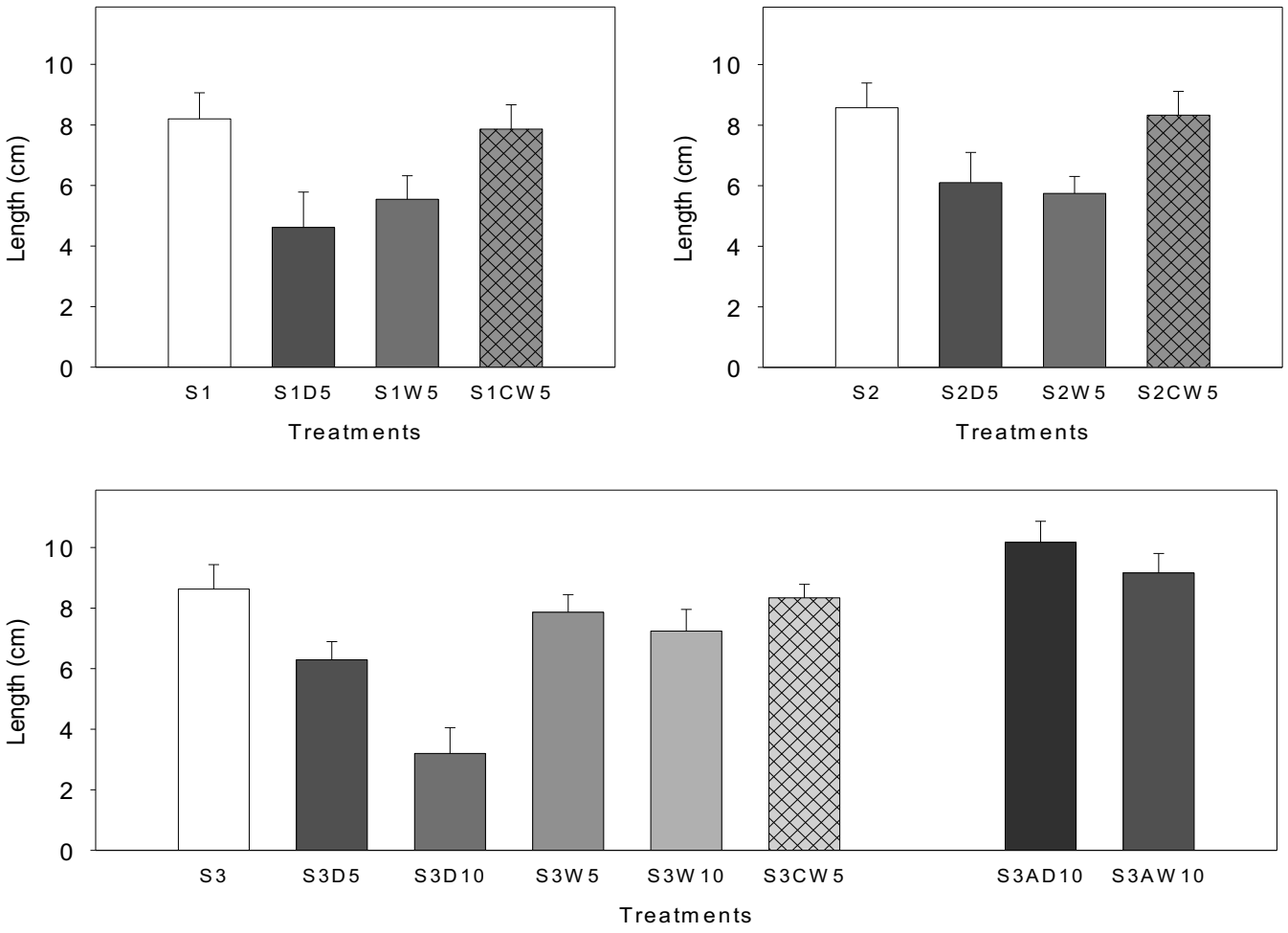
Length (cm)
0
2
4
6
8
10
S1
S1D5
S1W5
S1CW5
Treatments
S2
S2D5
S2W5
S2CW5
Treatments
S3
S3D5
S3D10
S3W5
S3W10
S3CW5
S3AD10
S3AW10
Treatments

Figure 4

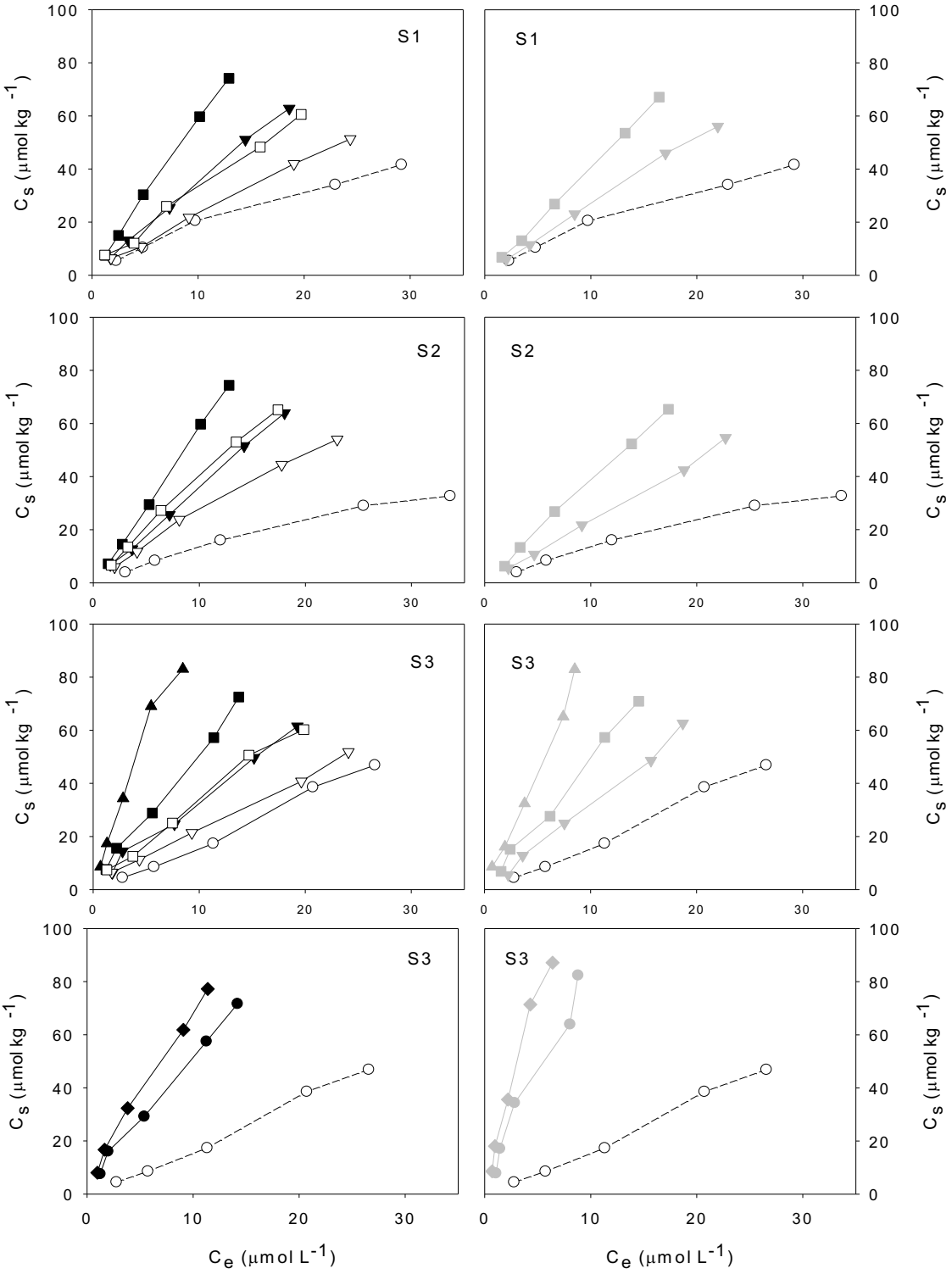
S1
S1
S2
S2
S3
S3
S3
S3
C_s (µmol kg $^{-1}$)
C_e (µmol L^{-1})
0
10
20
30
0
20
40
60
80
100

Figure S1

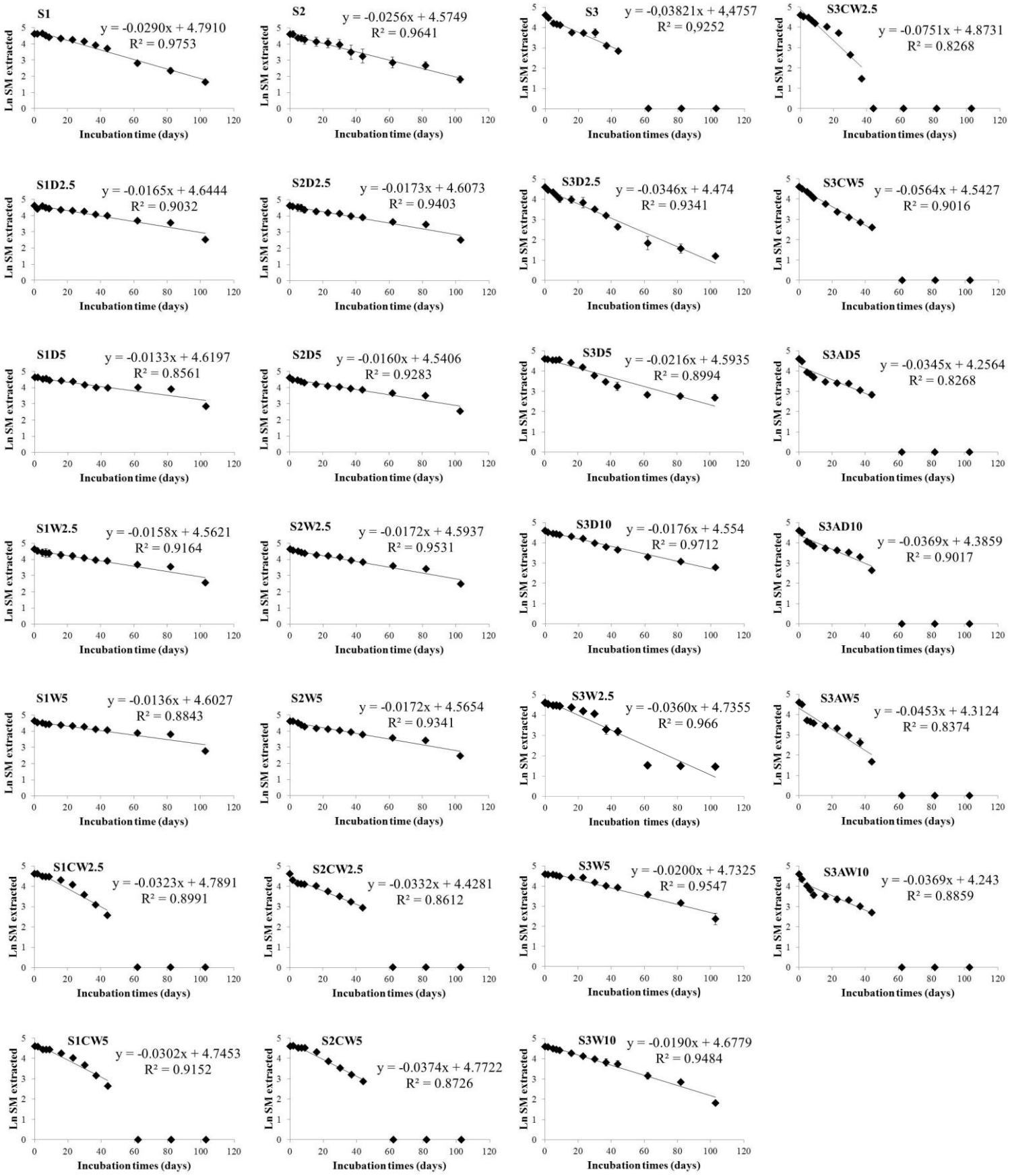
S1
y = -0.0290x + 4.7910
R² = 0.9753
S2
y = -0.0256x + 4.5749
R² = 0.9641
S3
y = -0,03821x + 4,4757
R² = 0,9252
S3CW2.5
y = -0.0751x + 4.8731
R² = 0.8268
S1D2.5
y = -0.0165x + 4.6444
R² = 0.9032
S2D2.5
y = -0.0173x + 4.6073
R² = 0.9403
S3D2.5
y = -0.0346x + 4.474
R² = 0.9341
S3CW5
y = -0.0564x + 4.5427
R² = 0.9016
S1D5
y = -0.0133x + 4.6197
R² = 0.8561
S2D5
y = -0.0160x + 4.5406
R² = 0.9283
S3D5
y = -0.0216x + 4.5935
R² = 0.8994
S3AD5
y = -0.0345x + 4.2564
R² = 0.8268
S1W2.5
y = -0.0158x + 4.5621
R² = 0.9164
S2W2.5
y = -0.0172x + 4.5937
R² = 0.9531
S3D10
y = -0.0176x + 4.554
R² = 0.9712
S3AD10
y = -0.0369x + 4.3859
R² = 0.9017
S1W5
y = -0.0136x + 4.6027
R² = 0.8843
S2W5
y = -0.0172x + 4.5654
R² = 0.9341
S3W2.5
y = -0.0360x + 4.7355
R² = 0.966
S3AW5
y = -0.0453x + 4.3124
R² = 0.8374
S1CW2.5
y = -0.0323x + 4.7891
R² = 0.8991
S2CW2.5
y = -0.0332x + 4.4281
R² = 0.8612
S3W5
y = -0.0200x + 4.7325
R² = 0.9547
S3AW10
y = -0.0369x + 4.243
R² = 0.8859
S1CW5
y = -0.0302x + 4.7453
R² = 0.9152
S2CW5
y = -0.0374x + 4.7722
R² = 0.8726
S3W10
y = -0.0190x + 4.6779
R² = 0.9484
Ln SM extracted
Incubation time (days)
Incubation times (days)

Figure S2

Text in this colour has been included in the amended manuscript GEODER_2018_1936_R1

Table 1. Physicochemical characteristics of the fresh D and W, and composted W (CW)

Properties	D[a]	W[b]	CW[b]
TOC (g kg^{-1})	516	535	383
WSOC (g kg^{-1})	74.3	42.6	16.5
HA (g kg^{-1})	30.7	51.8	69.0
FA (g kg^{-1})	62.2	34.6	79.2
HI	5.94	9.68	18.0
EC (dS m^{-1})	5.30	5.02	3.10
pH	5.30	5.70	8.72
Total Kjeldahl N (g kg^{-1})	24.0	16.0	28.6
WSP (g kg^{-1})	14.6	7.30	2.40

TOC: Total Organic Carbon; WSOC: Water-Soluble Organic Carbon; HA: Humic Acids; FA: Fulvic Acids; HI: Humification Index; EC: Electrical Conductivity, WSP: Water-Soluble Phenols

[a] From Peña et al. (2016)

[b] From López-Piñeiro et al. (2013a)

Table 2. Selected properties of the original, D- and W-amended soils (fresh, composted, and aged)

Properties	TOC ($g\ kg^{-1}$)	WSOC ($mg\ kg^{-1}$)	HA ($g\ kg^{-1}$)	FA ($g\ kg^{-1}$)	HI	EC ($dS\ m^{-1}$)	pH	DHA ($\mu g\ INTF\ g^{-1}\ h^{-1}$)
S1	9.69a	131a	1.35a	0.769a	13.9e	2.47a	6.81b	0.968c
S1D2.5	21.1c	2135e	2.03b	2.81e	9.64c	4.48d	6.45a	0.214a
S1D5	32.9f	3975g	2.80c	4.20f	8.50ab	6.67e	6.05a	0.131a
S1W2.5	22.3d	1692d	2.05b	1.52c	9.19bc	3.05b	6.40a	1.02c
S1W5	34.3g	2849f	2.69c	2.07d	7.84a	3.90c	6.20a	0.490b
S1CW2.5	19.4b	613b	2.04b	1.13b	10.5d	2.79b	6.96b	1.14d
S1CW5	26.5e	986c	2.98d	1.50c	11.2d	3.59c	7.09b	1.37e
S2	6.67a	103a	0.962a	0.584a	14.4d	3.08a	5.70cd	0.747c
S2D2.5	19.4b	2647e	1.65b	2.60f	8.52c	5.31d	5.44b	0.203a
S2D5	31.3d	4434g	2.07c	4.38g	6.60a	7.84e	5.18a	0.093a
S2W2.5	19.8b	1841d	1.58b	1.30c	7.98bc	3.70b	5.74d	0.395b
S2W5	32.4d	2975f	2.37d	1.98e	7.31ab	4.36c	5.67c	0.168a
S2CW2.5	18.9b	590b	1.58b	1.04b	8.36c	3.12a	6.62e	1.22d
S2CW5	25.6c	967c	2.28d	1.51d	8.91c	3.92bc	6.85f	1.46d
S3	9.86a	69.0a	1.02a	0.960a	10.3cde	0.426a	7.80ef	1.37c
S3D2.5	24.9cd	3149e	1.64b	2.75c	6.57a	3.78e	7.08d	1.31c
S3D5	39.0ef	5372f	2.40c	4.75d	6.15a	6.57g	6.54b	1.11b
S3D10	58.6g	10297h	4.13e	7.58e	7.05a	10.6h	5.96a	0.541a
S3W2.5	25.9cd	1638d	2.49c	1.55b	9.61c	1.80c	7.05d	1.54d
S3W5	40.6f	3305e	4.09e	1.94bc	10.1cd	2.91d	6.79c	1.56d
S3W10	62.5g	7208g	6.83f	2.93cd	10.9def	4.58f	6.45b	1.42cd
S3CW2.5	18.0b	597b	2.13c	1.40b	11.8f	1.12b	8.03g	1.55d
S3CW5	26.3d	1093c	3.02d	1.68b	11.5f	2.96d	7.89fg	1.71e
S3AD5	20.4bc	444b	2.27c	1.23a	11.1ef	0.940b	7.97g	1.89f
S3AD10	34.2e	686b	2.92d	1.67b	8.54b	1.56c	7.69e	2.17fg
S3AW5	17.6b	399b	2.46c	1.74b	14.0fg	0.52a	7.92fg	1.97f
S3AW10	27.6d	524b	4.01e	2.44c	14.5g	1.52c	7.74e	2.71g

Values with the same letter within a column, for a given soil, are not significantly different at the $p<0.05$ level of probability.

TOC: Total Organic Carbon; WSOC: Water-Soluble Organic Carbon; HA: Humic Acids; FA: Fulvic Acids; HI: Humification Index; EC: Electrical Conductivity; DHA: Dehydrogenase activity

Table 3. Effects of D and W application (fresh, composted, and aged) on the adsorption-desorption coefficients, half-life ($t_{1/2}$), and percentages leached and extracted from the soil columns

	n_f	k_f $\mu mol^{1-nf} kg^{-1} L^{nf}$	k_{fOC}	R^2	H	D (%)	$t_{1/2}$ (days)	R^2	$t_{1/2}$ (days)*	Leached (%)	Extracted (%)
S1	0.788a	3.02a	312d	0.992	3.26d	28.5b	23.9a	0.975	32	53.5d	21.8a
S1D2.5	0.957b	2.96a	140a	0.999	2.98c	33.1b	42.0b	0.903	50	52.9d	22.0a
S1D5	0.998b	4.04c	123a	0.998	2.06b	30.9b	52.1c	0.856	74	44.4c	27.2a
S1W2.5	0.954b	3.91c	175b	0.999	1.42a	39.1c	43.8b	0.916	44	37.3c	36.2b
S1W5	0.989b	6.06e	177b	0.999	1.56a	31b	50.8c	0.884	60	19.8a	47.5c
S1CW2.5	0.825a	3.55b	183b	0.986	7.40f	15.8a	21.4a	0.899	26	30.5b	47.0c
S1CW5	0.767a	5.65d	213c	0.961	5.57e	22.3a	22.9a	0.915	26	19.7a	40.9b
S2	0.873a	1.67a	250d	0.989	4.38d	25.7a	27.0b	0.964	34	54.1d	17.3a
S2D2.5	0.984cd	2.43b	125a	0.999	2.59c	34.7b	40.1c	0.940	48	58.7d	23.3b
S2D5	1.04de	3.53c	113a	0.994	2.06b	34.2b	43.4c	0.928	48	57.6d	26.5b
S2W2.5	0.947bc	4.05d	205c	0.996	1.47a	40.3c	40.1c	0.953	42	45.3c	35.2c
S2W5	1.06e	5.02e	155b	0.999	1.35a	32.9ab	40.2c	0.934	42	22.8b	55.5d
S2CW2.5	0.910ab	3.25c	172b	0.997	5.51e	24.5a	20.8a	0.861	20	24.4b	53.6d
S2CW5	0.980cd	4.14d	162b	0.998	5.55e	29.4a	18.5a	0.873	22	16.1a	52.2d
S3	1.06c	1.41a	143a	0.995	5.49g	15.4b	18.1c	0.925	14	51.9d	32.7abc
S3D2.5	1.07c	2.71b	109a	0.984	3.10d	36.4e	20.0c	0.934	22	52.9d	31.4ab
S3D5	0.985c	5.09e	131a	0.979	2.80c	26.5c	32.1d	0.899	28	38.2c	27.8a
S3D10	0.919b	10.3j	176a	0.984	3.51e	20.3c	39.4e	0.971	34	15.8b	45.2bcd
S3W2.5	0.881b	4.51d	174a	0.967	2.19b	35.3e	19.3c	0.966	32	58.5e	32.7abc
S3W5	0.886b	6.80f	167a	0.991	1.64a	25.4c	34.7d	0.955	44	33.9c	27.8a
S3W10	0.927b	12.8k	205a	0.991	3.14d	13.5ab	36.6de	0.948	40	15.9b	63.6e
S3CW2.5	0.799a	3.79c	211a	0.993	5.09f	30.2d	9.23a	0.827	20	34.9c	38.6abc
S3CW5	0.804a	5.28e	201a	0.977	4.73f	20c	12.3ab	0.902	12	19.8b	36.4abc
S3AD5	0.971c	9.86i	525c	0.988	10.5j	8.27a	20.1c	0.827	5	9.33a	42.0bcd
S3AD10	1.01c	15.1l	442c	0.944	12.9k	7.86a	18.8c	0.902	7	4.11a	44.1bcd
S3AW5	0.862b	7.23g	441c	0.995	6.67h	12.8ab	15.3bc	0.837	6	8.05a	55.8d
S3AW10	0.877b	9.35h	349b	0.980	8.73i	11.6ab	18.8c	0.886	9	5.88a	47.2cd

Values with the same letter within a column, for a given soil, are not significantly different at the $p<0.05$ level of probability.

k_{fOC}: k_f normalized for organic carbon content; H: hysteresis coefficients; D: percentage of SM desorbed.

* Values of $t_{1/2}$ determined visually from the SM dissipation curves.

Table 4. Effects of SM, D and W application (fresh, composted, and aged) on *L. perenne* germination

	Germination with herbicide (%)	Germination without herbicide (%)
S1	0a	80.0c
S1D5	0a	24.4a
S1W5	0a	48.9b
S1CW5	0a	86.6c
S2	0a	82.2c
S2D5	0a	4.44a
S2W5	0a	35.6b
S2CW5	0a	77.8c
S3	0a	82.2d
S3D5	0a	26.6b
S3D10	0a	13.3a
S3O5	0a	75.6d
S3O10	0a	51.1c
S3CW5	0a	84.4d
S3AD10	0a	100d
S3AW10	0a	88.8de

Values with the same letter within a column, for a given soil, are not significantly different at the $p<0.05$ level of probability.

Table 1. Physicochemical characteristics of the fresh D and W, and composted W (CW)

Properties	D[a]	W[b]	CW[b]
TOC (g kg^{-1})	516	535	383
WSOC (g kg^{-1})	74.3	42.6	16.5
HA (g kg^{-1})	30.7	51.8	69.0
FA (g kg^{-1})	62.2	34.6	79.2
HI	5.94	9.68	18.0
EC (dS m^{-1})	5.30	5.02	3.10
pH	5.30	5.70	8.72
Total Kjeldahl N (g kg^{-1})	24.0	16.0	28.6
WSP (g kg^{-1})	14.6	7.30	2.40

TOC: Total Organic Carbon; WSOC: Water-Soluble Organic Carbon; HA: Humic Acids; FA: Fulvic Acids; HI: Humification Index; EC: Electrical Conductivity, WSP: Water-Soluble Phenols

[a] From Peña et al. (2016)

[b] From López-Piñeiro et al. (2013a)

Table 2. Selected properties of the original, D- and W-amended soils (fresh, composted, and aged)

Properties	TOC ($g\ kg^{-1}$)	WSOC ($mg\ kg^{-1}$)	HA ($g\ kg^{-1}$)	FA ($g\ kg^{-1}$)	HI	EC ($dS\ m^{-1}$)	pH	DHA ($\mu g\ INTF\ g^{-1}\ h^{-1}$)
S1	9.69a	131a	1.35a	0.769a	13.9e	2.47a	6.81b	0.968c
S1D2.5	21.1c	2135e	2.03b	2.81e	9.64c	4.48d	6.45a	0.214a
S1D5	32.9f	3975g	2.80c	4.20f	8.50ab	6.67e	6.05a	0.131a
S1W2.5	22.3d	1692d	2.05b	1.52c	9.19bc	3.05b	6.40a	1.02c
S1W5	34.3g	2849f	2.69c	2.07d	7.84a	3.90c	6.20a	0.490b
S1CW2.5	19.4b	613b	2.04b	1.13b	10.5d	2.79b	6.96b	1.14d
S1CW5	26.5e	986c	2.98d	1.50c	11.2d	3.59c	7.09b	1.37e
S2	6.67a	103a	0.962a	0.584a	14.4d	3.08a	5.70cd	0.747c
S2D2.5	19.4b	2647e	1.65b	2.60f	8.52c	5.31d	5.44b	0.203a
S2D5	31.3d	4434g	2.07c	4.38g	6.60a	7.84e	5.18a	0.093a
S2W2.5	19.8b	1841d	1.58b	1.30c	7.98bc	3.70b	5.74d	0.395b
S2W5	32.4d	2975f	2.37d	1.98e	7.31ab	4.36c	5.67c	0.168a
S2CW2.5	18.9b	590b	1.58b	1.04b	8.36c	3.12a	6.62e	1.22d
S2CW5	25.6c	967c	2.28d	1.51d	8.91c	3.92bc	6.85f	1.46d
S3	9.86a	69.0a	1.02a	0.960a	10.3cde	0.426a	7.80ef	1.37c
S3D2.5	24.9cd	3149e	1.64b	2.75c	6.57a	3.78e	7.08d	1.31c
S3D5	39.0ef	5372f	2.40c	4.75d	6.15a	6.57g	6.54b	1.11b
S3D10	58.6g	10297h	4.13e	7.58e	7.05a	10.6h	5.96a	0.541a
S3W2.5	25.9cd	1638d	2.49c	1.55b	9.61c	1.80c	7.05d	1.54d
S3W5	40.6f	3305e	4.09e	1.94bc	10.1cd	2.91d	6.79c	1.56d
S3W10	62.5g	7208g	6.83f	2.93cd	10.9def	4.58f	6.45b	1.42cd
S3CW2.5	18.0b	597b	2.13c	1.40b	11.8f	1.12b	8.03g	1.55d
S3CW5	26.3d	1093c	3.02d	1.68b	11.5f	2.96d	7.89fg	1.71e
S3AD5	20.4bc	444b	2.27c	1.23a	11.1ef	0.940b	7.97g	1.89f
S3AD10	34.2e	686b	2.92d	1.67b	8.54b	1.56c	7.69e	2.17fg
S3AW5	17.6b	399b	2.46c	1.74b	14.0fg	0.52a	7.92fg	1.97f
S3AW10	27.6d	524b	4.01e	2.44c	14.5g	1.52c	7.74e	2.71g

Values with the same letter within a column, for a given soil, are not significantly different at the $p<0.05$ level of probability.

TOC: Total Organic Carbon; WSOC: Water-Soluble Organic Carbon; HA: Humic Acids; FA: Fulvic Acids; HI: Humification Index; EC: Electrical Conductivity; DHA: Dehydrogenase activity

Table 3. Effects of D and W application (fresh, composted, and aged) on the adsorption-desorption coefficients, half-life ($t_{1/2}$), and percentages leached and extracted from the soil columns

	n_f	k_f $\mu mol^{1-nf} kg^{-1} L^{nf}$	k_{fOC}	R^2	H	D (%)	$t_{1/2}$ (days)	R^2	$t_{1/2}$ (days)*	Leached (%)	Extracted (%)
S1	0.788a	3.02a	312d	0.992	3.26d	28.5b	23.9a	0.975	32	53.5d	21.8a
S1D2.5	0.957b	2.96a	140a	0.999	2.98c	33.1b	42.0b	0.903	50	52.9d	22.0a
S1D5	0.998b	4.04c	123a	0.998	2.06b	30.9b	52.1c	0.856	74	44.4c	27.2a
S1W2.5	0.954b	3.91c	175b	0.999	1.42a	39.1c	43.8b	0.916	44	37.3c	36.2b
S1W5	0.989b	6.06e	177b	0.999	1.56a	31b	50.8c	0.884	60	19.8a	47.5c
S1CW2.5	0.825a	3.55b	183b	0.986	7.40f	15.8a	21.4a	0.899	26	30.5b	47.0c
S1CW5	0.767a	5.65d	213c	0.961	5.57e	22.3a	22.9a	0.915	26	19.7a	40.9b
S2	0.873a	1.67a	250d	0.989	4.38d	25.7a	27.0b	0.964	34	54.1d	17.3a
S2D2.5	0.984cd	2.43b	125a	0.999	2.59c	34.7b	40.1c	0.940	48	58.7d	23.3b
S2D5	1.04de	3.53c	113a	0.994	2.06b	34.2b	43.4c	0.928	48	57.6d	26.5b
S2W2.5	0.947bc	4.05d	205c	0.996	1.47a	40.3c	40.1c	0.953	42	45.3c	35.2c
S2W5	1.06e	5.02e	155b	0.999	1.35a	32.9ab	40.2c	0.934	42	22.8b	55.5d
S2CW2.5	0.910ab	3.25c	172b	0.997	5.51e	24.5a	20.8a	0.861	20	24.4b	53.6d
S2CW5	0.980cd	4.14d	162b	0.998	5.55e	29.4a	18.5a	0.873	22	16.1a	52.2d
S3	1.06c	1.41a	143a	0.995	5.49g	15.4b	18.1c	0.925	14	51.9d	32.7abc
S3D2.5	1.07c	2.71b	109a	0.984	3.10d	36.4e	20.0c	0.934	22	52.9d	31.4ab
S3D5	0.985c	5.09e	131a	0.979	2.80c	26.5c	32.1d	0.899	28	38.2c	27.8a
S3D10	0.919b	10.3j	176a	0.984	3.51e	20.3c	39.4e	0.971	34	15.8b	45.2bcd
S3W2.5	0.881b	4.51d	174a	0.967	2.19b	35.3e	19.3c	0.966	32	58.5e	32.7abc
S3W5	0.886b	6.80f	167a	0.991	1.64a	25.4c	34.7d	0.955	44	33.9c	27.8a
S3W10	0.927b	12.8k	205a	0.991	3.14d	13.5ab	36.6de	0.948	40	15.9b	63.6e
S3CW2.5	0.799a	3.79c	211a	0.993	5.09f	30.2d	9.23a	0.827	20	34.9c	38.6abc
S3CW5	0.804a	5.28e	201a	0.977	4.73f	20c	12.3ab	0.902	12	19.8b	36.4abc
S3AD5	0.971c	9.86i	525c	0.988	10.5j	8.27a	20.1c	0.827	5	9.33a	42.0bcd
S3AD10	1.01c	15.1l	442c	0.944	12.9k	7.86a	18.8c	0.902	7	4.11a	44.1bcd
S3AW5	0.862b	7.23g	441c	0.995	6.67h	12.8ab	15.3bc	0.837	6	8.05a	55.8d
S3AW10	0.877b	9.35h	349b	0.980	8.73i	11.6ab	18.8c	0.886	9	5.88a	47.2cd

Values with the same letter within a column, for a given soil, are not significantly different at the $p<0.05$ level of probability.

k_{fOC}: k_f normalized for organic carbon content; H: hysteresis coefficients; D: percentage of SM desorbed.

* Values of $t_{1/2}$ determined visually from the SM dissipation curves.

Table 4. Effects of SM, D and W application (fresh, composted, and aged) on *L. perenne* germination

	Germination with herbicide (%)	Germination without herbicide (%)
S1	0a	80.0c
S1D5	0a	24.4a
S1W5	0a	48.9b
S1CW5	0a	86.6c
S2	0a	82.2c
S2D5	0a	4.44a
S2W5	0a	35.6b
S2CW5	0a	77.8c
S3	0a	82.2d
S3D5	0a	26.6b
S3D10	0a	13.3a
S3O5	0a	75.6d
S3O10	0a	51.1c
S3CW5	0a	84.4d
S3AD10	0a	100d
S3AW10	0a	88.8de

Values with the same letter within a column, for a given soil, are not significantly different at the $p<0.05$ level of probability.