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1 **Leaching and degradation of S-Metolachlor in undisturbed soil cores amended with** 2 **organic wastes**

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14
15 **Abstract:** Organic waste (OW) reuse in agriculture is a common practice fostered by benefits in terms
16 of waste recycling and crop production. However, OW amendments potentially affect the fate of
17 pesticides spread on fields to protect the crops from pests and weeds. The influence of OW on the
18 sorption, degradation and leaching of pesticides is generally studied for each mechanism separately
19 under artificial laboratory conditions. Our study aims at evaluating the balance of these mechanisms
20 under more realistic conditions to clarify the influence of three common OW amendments on the
21 fate, in soil, of the widely used herbicide S-Metolachlor. We performed leaching experiments in large
22 undisturbed soil cores amended with raw sewage sludge, composted sludge and digested pig slurry
23 (digestate), respectively. We monitored S-Metolachlor and its two main metabolites MET-OA and
24 MET-ESA in the leachates during a succession of 10 rainfall events over 126 days. We also quantified
25 the remaining S-Metolachlor and metabolites in the soil at the end of the experiments. S-Metolachlor
26 leaching didn't exceed 0.1% of the applied dose with or without OW amendment. Despite a soil
27 organic carbon increase of 3 to 32 %, OW amendments did not significantly affect the amount of S-
28 Metolachlor that leached through the soil (0.01 to 0.1 %) nor its transformation rate (6.0 to 8.6 %).
29 However, it affected the degradation pathways with an increase of MET-OA relative to MET-ESA
30 formed after OW amendment (28 to 54 %) compared to the controls (8 %). Concentration of S-
31 Metolachlor and metabolites in the leachates of all treatments greatly exceeded the regulatory limit

32 for groundwater intended for human consumption in Europe. These high concentrations were
 33 probably the consequence of preferential macropore flow. Colloids had comparable levels in the
 34 leachates after S-Metolachlor application. Dissolved organic carbon was also comparable in the
 35 controls, digestate and sludge treatments but was 65% higher in the compost amended cores. These
 36 results, along with a great variability among replicates inherent to experiments performed under
 37 realistic conditions, partly explain the limited impact of OW on the transport of S-Metolachlor.

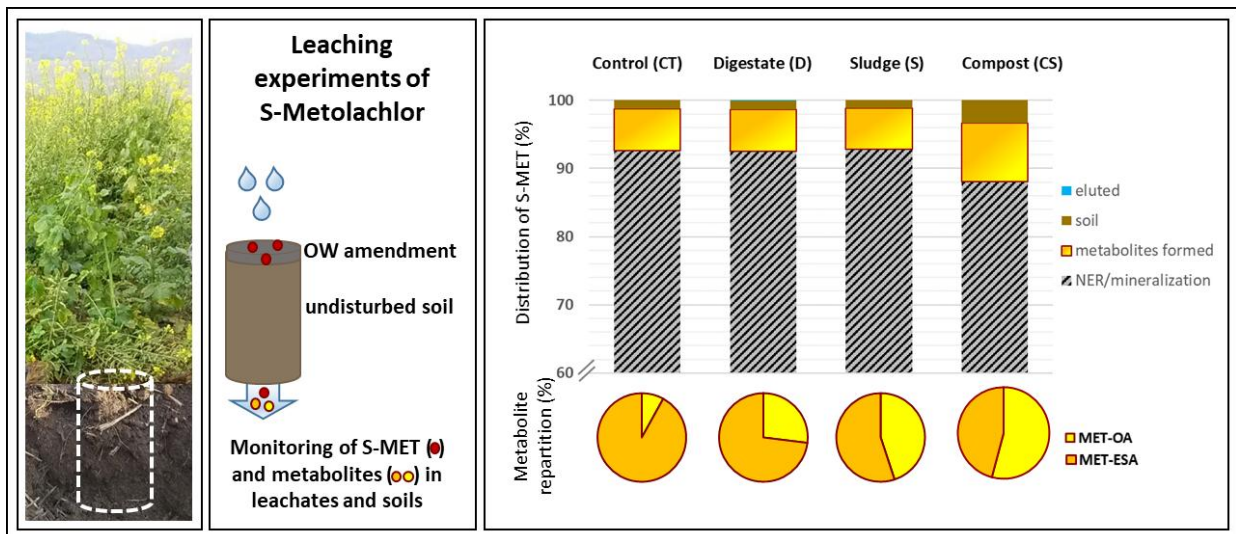
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39 **Keywords:** herbicide; leaching; degradation; sewage sludge; compost; digestate.

40

41 **Graphical abstract:**

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45 **Highlights:**

- 46 • Organic waste (OW) amendments modify the metabolic pathways of S-Metolachlor
- 47 • The MET-OA pathway is stimulated by OW amendments
- 48 • OW don't have a significant impact on S-Metolachlor leaching and transformation rate

- 49 • S-Metolachlor leaching did not exceed 0.1% of the applied dose with or without OW
- 50 • Preferential macropore flow can lead to high herbicide concentrations in leachates

51

52 **1. Introduction**

53 Organic waste (OW) reuse in agriculture is a common practice fostered by multiple benefits both in
54 terms of waste disposal and crop production (Carpio et al., 2021; Houot et al., 2014; Kupper et al.,
55 2014). Indeed, in addition to their high fertilization value, OW amendments have been reported to
56 improve soil physical properties and to increase the organic carbon content of soils (Briceño et al.,
57 2007; Hargreaves et al., 2008; Kupper et al., 2014). OW amendments on agricultural lands also
58 contribute to reduce landfill.

59 The major sources of OW are the agricultural and silvicultural sectors, with the production of
60 manure, slurry and green wastes, that are usually recycled on site with or without post-treatments
61 (Houot et al., 2014). About 1 Mt of raw manure and slurry are spread every year on agricultural lands
62 in France (Houot et al., 2014). Sewage sludge and municipal bio-wastes are the other main sources of
63 OW (Collivignarelli et al., 2019; Meyer-Kohlstock et al., 2015). About 10 Mt of sewage sludge are
64 produced annually in Europe among which, 0.6 Mt is produced in France (Eurostats, 2020). In France,
65 about 70% of the sewage sludge is recycled in agriculture either raw (42%) or composted (31%)
66 (Collivignarelli et al., 2019; Houot et al., 2014).

67 Composting and methanization (anaerobic digestion) are the most common biological post-
68 treatments that either improve the quality and homogeneity of the amendments or produce energy.
69 Composting stabilizes the organic matter and reduces the pathogens and organic pollutants loads
70 (Hargreaves et al., 2008; Houot et al., 2014; Sertillanges et al., 2020). Mixes of several raw materials
71 including green wastes and sewage sludge are usually used for composts. Methanization produces
72 biogas. The raw materials used for methanization are usually more diversified than for composting
73 and include manure, slurry, agricultural green waste or wastes from food industries. The resulting

74 waste, digestate, is also recycled in agriculture either raw or composted (Bartólg et al., 2020;
75 Tambone et al., 2019).

76 OW amendments increase the soil organic matter (SOM), the dissolved organic carbon (DOC) and
77 stimulate the microbial activity, which potentially affect the fate of pesticides spread on fields to
78 protect the crops from pests and weeds (Briceño et al., 2007; Carpio et al., 2021). On the one hand,
79 increased SOM generally promotes the sorption of pesticides, which can reduce their mobility, their
80 bioavailability and resulting degradation and mineralization. On the other hand, increased DOC
81 generally lowers pesticide sorption to immobile soil constituents and enhances their downward
82 transfer and bioavailability due to co-sorption and co-transport mechanisms (Barriuso et al., 2011;
83 Chabauty et al., 2016). A recent review by Carpio et al. (2021) summarizes the data related to OWs'
84 influence on the pesticide sorption, degradation and leaching mechanisms acquired with controlled
85 laboratory studies. A brief overview of the current knowledge is provided hereafter. Several studies
86 with a range of pesticides and OW types have evidenced the enhanced sorption and decreased
87 leaching resulting from OW amendment (Cabrera et al., 2007; Gámiz et al., 2016; Marín-Benito et al.,
88 2013, 2021; Singh, 2003). However, opposite effects have also been reported (Fernandes et al., 2006;
89 Marín-Benito et al., 2013). For exemple, Fernandes et al. (2006) tested different wastes from the
90 olive mill industry and reported lower sorption and higher leaching rate of metalaxyl than in the un-
91 amended soil in contrast with the solid wastes. The influence of OW amendments on degradation is
92 more variable with both increased and decreased half-lives reported for a range of OW and
93 pesticides (Cabrera et al., 2007; Dolaptsoglou et al., 2007; Fernandes et al., 2006; Gámiz et al., 2016;
94 Ghosh and Singh, 2009; Marín-Benito et al., 2014, 2021).

95 The influence of OW amendment on the mechanisms controlling the environmental fate of
96 pesticides has been reported to depend on the OW characteristics and the soil and pesticide
97 properties (Briceño et al., 2007; Morillo et al., 2002; Peña et al., 2019). The influence of OW
98 amendments such as sewage sludge and to a lesser extent, composted sludge, has been investigated

99 for some pesticides including terbutylazin, atrazine, diazinon, methidation, linuron and myclobutanil
100 (Dolaptsoglou et al., 2007; González et al., 2008; Marín-Benito et al., 2014). These studies generally
101 show a weak effect of OW on sorption with slightly increase or un-modified K_d compared to un-
102 amended soils and a significant influence on the degradation with both increased and decreased DT_{50}
103 depending on the pesticides and the soil. However, the effect of digestate on pesticides' leaching
104 has, to our knowledge, not been characterized, with the exception of a study, in a different context
105 and purpose, focusing the effect of digestate on pesticide dissipation (Mukherjee et al., 2016).

106 The OW influence on the sorption, degradation, mineralization and leaching mechanisms of
107 pesticides has generally been investigated separately and in controlled artificial laboratory conditions
108 (Carpio et al., 2021, 2020). Batch experiments were used to investigate sorption and degradation.
109 Repacked soil columns were used to investigate leaching, generally under saturated conditions and
110 with large elution volumes (Fernandes et al., 2006; Graber et al., 1997; Marín-Benito et al., 2021,
111 2014; Peña et al., 2019). However, these mechanisms occur at different time scale and are regulated
112 by the hydrologic conditions and hydrodynamic properties of the soil. Few studies have been carried
113 out under controlled but realistic conditions (e.g. undisturbed soil cores, unsaturated conditions,
114 transient flow during successions of rainfall events over a cropping season) to evaluate the balance
115 between the processes and approach the global behavior of pesticides in soils amended with a range
116 of OW (e.g. Carpio et al., 2020; Pot et al., 2011). Such studies would be of great value (i) for a better
117 assessment of the environmental risks related to pesticide use in relation to the widespread practice
118 of OW recycling in agriculture and (ii) to provide key information for a global assessment of the
119 benefits and risks of the different types of OW post-treatments.

120 Accordingly, the objective of this study was to investigate the influence of three widely used OW: a
121 raw and a composted sewage sludge and a digested pig slurry on the fate of a widely used herbicide
122 under controlled but realistic conditions. Therefore, we used large undisturbed soil cores amended
123 with the three OW and monitored the fate of S-Metolachlor and its major metabolites during a

124 succession of rainy (10 mm h^{-1} rainfall events) and dry periods over a cropping season (126 days). We
125 also monitored colloids and DOC, two potential herbicide carrier phases. This experimental design
126 allows to simultaneously assess the balance of the leaching, sorption and degradation mechanisms.
127 S-Metolachlor was selected for this study because it is a widely used pre-emergent herbicide applied
128 worldwide on a variety of crops including maize and sugar beet (PPDB, 2018). It is classified as
129 moderately mobile due to a low sorption affinity for soils. As a consequence, it has been frequently
130 detected in surface and groundwater in the USA and EU (Baran and Gourcy, 2013; Bexfield et al.,
131 2021; Kupfersberger et al., 2018; Toccalino et al., 2014; Zambito Marsala et al., 2020). The major
132 metabolites of S-Metolachlor are Metolachlor oxanilic acid (MET-OA) and Metolachlor ethane
133 sulfonic acid (MET-ESA). Whether S-Metolachlor's fate is influenced or not by sewage sludge,
134 composted sludge or digestate amendments remains to be characterized.

135

136

137 **2. Material and methods**

138

139 **2.1. Soil cores sampling and preparation**

140 The soil cores were taken from an experimental field located in Colmar, France (48.059777,
141 7.327474) which is part of the SOERE PRO network (SOERE PRO, 2015). This network gathers long
142 term field experimental stations mainly over France where the impacts of organic waste
143 amendments on crop yields, soil and water quality are evaluated. The crop rotation in the Colmar
144 experimental field consists in a succession of wheat, corn, sugar beets and barley. Cover crops are
145 established during the winter seasons. The plots have an history of S-Metolachlor application. The
146 climate at the site is temperate with an average yearly rainfall of 552 mm (INRAE, 2020). The soil of
147 the tilled horizon (0-28 cm depth) has a bulk density of 1.3 g/cm^3 , a pH of 8.3 an OC content of 1.21

148 %, a cation exchange capacity of 16.9 cmol/kg and a texture of 10.9 - 64.5 - 24.6 % (sand-silt-clay).
149 The soil belongs to the Calcisols group according to the WRB (FAO, 2014).

150 PVC cylinders, 18.6 cm internal diameter and 30 cm long, were used to sample undisturbed soil cores
151 in the tilled horizon. Twenty cores were sampled in the control plot having no history of organic
152 waste amendment. The beveled cylinders were gently pushed into the soil down to a depth of 25 cm.
153 Then the surrounding soil was excavated to extract the undisturbed cores. Each core was positioned
154 onto a stainless steel screen (2-mm circular openings on 42% of its surface area). The screen was
155 maintained immobile by an annular sample holder.

156 The top 2 cm soil was manually excavated from each core and stored in separate containers at 4°C.
157 To allow the relaxation of the mechanical stresses undergone by the soil during extraction and
158 handling, a succession of three low intensity rainfall events (5 mm/h, 3 h each) separated with a 2-
159 week interval were performed onto each core (Michel et al., 2010).

160

161 **2.2. Organic waste amendments**

162 The OW origin, processing and physico-chemical properties are thoroughly described in Sertillanges
163 et al. (2020). The main physico-chemical properties are also reported in Table 1. The first OW we
164 used is an activated and dewatered sewage sludge (S) from a domestic treatment plant (Site Urb II,
165 Sertillanges et al., 2020). The second is a compost (CS) of the previous sewage sludge mixed with
166 green wastes (66% co-substrate, Site Urb II, Sertillanges et al., 2020). The last is a raw digestate (D)
167 after anaerobic digestion of pig slurry in a methanizing plant (Site Agri I, Sertillanges et al., 2020).

168 For each OW treatment, three cores were randomly selected among the 20 sampled cores. Three
169 control cores were left un-amended. Each treatment was established in triplicate hereafter named A,
170 B and C.

171 The OW were thoroughly mixed with the previously excavated top 2 cm soil (section 2.2) and the
172 OW-soil mixture was repacked on top of the cores. The digestate being liquid, was not mixed with
173 the soil but spread over the repacked soil. Ponding occurred during digestate spreading and part of it
174 percolated directly through the cores and was collected at the output (40.3%, 18.3% and 12.2% of
175 the applied mass for the replicates A, B and C, respectively). The OW amendments rates were 76
176 t/ha, 63 t/ha and 128 t/ha for the sewage sludge, the compost and the digestate, respectively. The
177 OW amendment rates were calculated based on their nitrogen content and are in the high range of
178 the recommended amendment doses in France (Houot et al., 2014).

179

180 **2.3. Selected herbicide and metabolites**

181 S-Metolachlor is moderately hydrophobic ($\log K_{ow} = 3.05$) and has a relatively low water solubility
182 (480 mg/L). Its degradation half-life in soils varies between 15 and 92 days (PPDB, 2018). It is
183 classified as moderately mobile due to a low sorption affinity for soils ($K_{oc} 112-368$ L/kg). Both
184 metabolites MET-ESA and MET-OA are more persistent than S-Metolachlor with a DT50 of 325 and
185 400 days for MET-OA and MET-ESA, respectively (PPDB, 2018). They also have a sorption affinity for
186 soil about 10 to 20 times lower than that of S-Metolachlor ($K_{oc} 2-63$ L/kg for MET-OA and $K_{oc} 9$ L/kg
187 for MET-ESA) (PPDB, 2018).

188

189 **2.4. Leaching experiments**

190 Each core was submitted to a succession of 10 rainfall events with a two-week interval between each
191 rainfall. The rainfall intensity for all events was 10 mm/h which is in the high range of rainfall
192 intensities recorded in Colmar (INRAE, 2020). Each rainfall event lasted for two hours. The cumulated
193 rainfall volume for the whole experimental campaign was representative of the cumulated rainfall
194 during the cropping season in Colmar. The artificial rain solution consisted in a 1.8×10^{-4} mol/L $CaCl_2$

195 solution in ultrapure water to approach the ionic strength of natural rain (e.g., Sequeira and Lung,
196 1995). It was applied to the cores using a rainfall simulator described in Michel et al. (2014). Free
197 drainage was allowed at the bottom of the cores. Between the rainfall events the cores were covered
198 and stored at room temperature ($25 \pm 3^\circ\text{C}$). The whole leaching experiment lasted for 126 days. This
199 relatively long elution period was chosen to permit the transformation of the amended organic
200 matter during the experiment, as it occurs during the cropping season.

201 S-Metolachlor was applied between the second and third rainfall events, 28 days after the organic
202 waste amendments, to stay as close as possible to the field conditions. Indeed, OW amendment is
203 usually performed several weeks before crop seeding and weeding to enable the degradation of the
204 organic matter and the release of nutrients. S-Metolachlor, dissolved in water at a concentration of
205 390 mg/L, was evenly sprayed on top of the cores to reach the agricultural relevant dose of 1.58
206 kg/ha.

207 During the rainfall events and the following two hours' elution periods, 30 mL fraction of the
208 effluents were collected in polypropylene vials. Sorption of S-Metolachlor and metabolites was
209 negligible on the polypropylene vials. The vials were weighed before and after sampling and the
210 exact time of sampling was recorded to enable the calculation of the outflow. The cores were also
211 weighed every 10 seconds during rainfall and elution to estimate the evolution of their water
212 content. About 16 samples were collected for each rainfall event. For the analysis of S-Metolachlor
213 and its main metabolites in the leachates four combined samples per rainfall event were generated
214 due to analytical cost constraints. For the combined samples 3 mL of the fractions 1 to 4; 5 to 8; 9 to
215 12 and 13 to 16 were combined, respectively. The samples were deep frozen (-18°C) in PET amber
216 vials until analysis. Sorption of S-Metolachlor and metabolites was negligible on the PET vials.

217 At the end of the experimental campaign the cores were sliced to establish the soil concentration
218 profiles of S-Metolachlor and its main metabolites at depth 0-4, 4-8, 8-16 and 16-25 cm. The
219 collected soil samples were stored at -18°C until analysis.

220

221

222 **2.5. Analyses**

223

224 **2.5.1. Analysis of the herbicide carrier-phases**

225 **2.5.1.1. Colloids**

226 Colloids contents were measured in all 30 mL elution fractions using a UV-Visible spectrophotometer.
227 The absorbance at 400 nm was converted into colloids concentration using a calibration curve
228 established beforehand as detailed in Michel et al. (2010).

229

230 **2.5.1.2. Dissolved organic carbon**

231 For the control and digestate treatments, 8 combined samples per rainfall event were generated due
232 to analytical costs constraints, whereas, for the compost and sludge treatments the dissolved organic
233 carbon was quantified in all of the fractions. The samples were centrifuged at 3000 rpm (1660 g) for 2
234 minutes to remove the large suspended particles and acidified with high purity trace metal analytical
235 grade nitric acid (2%). The acidified samples were stored in the fridge at 4°C until analysis. The
236 dissolved organic carbon analyses were performed by the CIRAD UR 78 Laboratory with the Non-
237 Purgeable Organic Carbon (NPOC) method (NF ISO 10694 & NF ISO 13878) on a Total Organic Carbon
238 Analyzer (TOC-L Series Shimadzu). Samples were bubbled for 90 s with 1.5% HCl (1N) to eliminate
239 carbonates before injection into the combustion tube with a platinum catalyst (720 °C). Each sample
240 was analysed 3 to 5 times until standard deviation was lower than 0.1 and the variation coefficient
241 between the replicates of the multiple injections became lower than 2%. The average of replicates
242 was used for the treatment of the experimental results.

243

244 **2.5.2. S-Metolachlor and metabolites**

245 The elution fractions were acidified and analysed by online solid phase extraction and ultra-high-
246 performance-liquid chromatography coupled with triple quadrupole mass spectrometry (online SPE -
247 UHPLC-MS-MS) with the method described for soil and water samples by Bourdat-Deschamps et al.,
248 (2014). Soil samples were extracted by ultrasonic extraction, purified using a modified QuEChERS
249 method and analysed by online SPE – UHPLC-MS-MS as described by Ferhi et al. (2016). Mass
250 spectrometrer transitions for the quantification of S-Metolachlor, MET-OA and MET-ESA were 284.3
251 > 252.3 (positive electrospray ionization), 278.07 > 206.2 (negative electrospray ionization) and
252 328.16 > 79.95 (negative electrospray ionization), respectively. Other transitions were also used for
253 confirmation of the compounds. The compound concentrations were determined by internal
254 quantification-isotope dilution (polynomial calibration curves; weighting 1/X; coefficients of
255 determination higher than 0.97 and residues below 20%) in order to correct both
256 extraction/purification losses and potential matrix effects in mass spectrometry. Soils and elution
257 fractions were therefore spiked with a solution of (\pm)-Metolachlor-d₆ (propyl-d₆) from Cluzeau Infor
258 Labo (Sainte-Foy-La-Grande, France).

259

260 **2.6. Statistical analyses**

261

262 One-way independent sample ANOVA analyses were performed using the R software (R Core Team,
263 2020) to compare the difference between the four OW treatments (Control, Digestate, Sludge,
264 Compost). When the difference was significant according to the ANOVA ($p < 0.05$), pairwise Student
265 t-test were conducted. Graphical representation of the analysed data, means and 95% confidence
266 intervals, are presented in Fig. S1 of the supplementary information.

267

268

269 **3. Results and discussion**

270

271 **3.1. S-Metolachlor leaching**

272 S-Metolachlor breakthrough patterns are presented in Figure 1 and Figure S2. In general, an increase
273 of S-Metolachlor concentration was detected already during the rainfall following its application. For
274 the un-amended controls, S-Metolachlor peaked at 0.2 µg/L during the third rainfall event following
275 S-Metolachlor application (R5) then slowly decreased to 0.04 µg/L through the next five rainfall
276 events. A low variability between the replicates was observed. For the sewage sludge, S-Metolachlor
277 peak concentrations were similar to that of the control (0.1 – 0.2 µg/L). However, the shape of the
278 breakthrough curve differed with a peak concentration reached already during the rainfall event
279 following S-Metolachlor application (R3) followed by a very progressive decrease. For the compost-
280 and digestate amended soils, a great variability between the replicates was observed. For the
281 digestate, the peak concentrations were recorded during the first rainfall event following S-
282 Metolachlor spraying (R2) and varied from 0.3 to 12 µg/L (Figure 1). The concentration then
283 progressively dropped towards a concentration of 0.04 µg/L. Replicate C of the digestate treatment
284 was stopped after rain 7 because it fell of the rainfall simulator which disrupted its structure. For the
285 compost-amended soil, the concentration increased rapidly during the rainfall event following
286 spraying and remained high during the entire experimental campaign. Peak concentration varied
287 from 0.08 to 0.76 µg/L.

288 Due to the history of S-Metolachlor application at the study site, low, but detectable concentrations
289 were measured in the leachates collected before its application on the cores (Figure 1).

290 The amount of S-Metolachlor recovered in the leachates ranged between 0.01 and 0.1 % of the
291 applied dose (Table 2). No statistical difference was detected between the treatments ($F(3,8)=1.924$,
292 $p = 0.204$, Fig. S1) despite an average recovered dose for the digestate treatment being an order of
293 magnitude higher than for the other treatments.

294 The S-Metolachlor concentration in the soil profile after the succession of rainfall events are
295 presented in Figure 2. For the control treatments, the analyses were not distinguished with depth
296 and the average concentration ranged between 4.6 and 8.8 $\mu\text{g}/\text{kg}$ in the three replicates, which
297 represents 0.9 – 1.8% of the applied dose (Table 2). We compared these values with the average
298 concentrations for the three other treatments computed as the sum of S-Metolachlor masses in the
299 four core slices divided by the total core dry weight. For the digestate (5.5 – 6.9 $\mu\text{g}/\text{kg}$), the sludge
300 (3.4 – 8.8 $\mu\text{g}/\text{kg}$) and the compost (8.8 – 28.0 $\mu\text{g}/\text{kg}$) treatments these averaged concentrations were
301 not statistically different from those of the un-amended control ($F(3,7) = 2.063$, $p = 0,193$, Fig. S1b).

302 For the sludge treatment, the concentrations in the top 0-4 cm depth layer were high, 6.9 – 27.8
303 $\mu\text{g}/\text{kg}$, and decreased with depth down to 1.3 – 3.8 $\mu\text{g}/\text{kg}$. For the digestate treatment the
304 concentrations in the top layer ranged between 12.6 to 18.7 $\mu\text{g}/\text{kg}$ and progressively dropped to 3.5
305 – 6.2 $\mu\text{g}/\text{kg}$. For the compost treatment, the concentration in the top layer is up to an order of
306 magnitude higher than for the other treatments (23 - 172 $\mu\text{g}/\text{kg}$) and remains relatively high for the B
307 and C replicates in the bottom layers. The amount extracted from the soil at the end of the
308 experimental campaign represents 0.7 to 1.8 % of the applied dose for the digestate and sludge
309 treatments and 1.8 to 5.6 % for the compost treatment. No statistical differences between the
310 treatments were detected ($F(3,7) = 2.076$, $p = 0.192$, Fig. S1cS).

311 The fraction of S-Metolachlor applied recovered in the leachates is similar to that collected in till
312 drains after pesticide spraying on crop fields and subsequent leaching through the soil profile (Tang
313 et al., 2012; Voltz and Louchart, 2001). However, studies investigating the influence of OW
314 amendment on the leaching of pesticides (Cabrera et al., 2007; Fernandes et al., 2006; Marín-Benito

315 et al., 2013, 2021; Si et al., 2009) including S-Metolachlor (Marín-Benito et al., 2013, 2021; Peña et
316 al., 2019; Singh, 2003) reported fractions of the applied dose that were leached through the soil one
317 to two orders of magnitude higher than ours. Those studies were performed with repacked soil
318 columns, and pesticides eluted shortly after spraying under near saturation conditions with large and
319 un-fractionated inflow volumes. Our study highlights the importance of approaching field conditions
320 when designing laboratory experiments. Indeed, soil humidity and the interval between spraying and
321 the first rainfall event, because they control the extent of diffusion and adsorption of the chemicals
322 onto the soil constituents, are key parameters influencing the amount of pesticide leaching (de Jonge
323 et al. 2000, Voltz and Louchart, 2001).

324 The influence of organic amendments on S-Metolachlor leaching was reported to vary with OW type
325 and dose (Peña et al., 2019). Amendments with 2.5 % fresh olive-mill waste slightly increased S-
326 Metolachlor leaching while at higher dose or when composted, this OW tended to decrease S-
327 Metolachlor leaching by up to 3 fold (Peña et al., 2019). Manure, slurry, green compost and
328 pelletised manure were also reported to decrease Metolachlor leaching (Singh, 2003; Marín-Benito
329 et al., 2013, 2021). In our study, despite the soil OC increase of 3 %, 17 % and 32 % following
330 digestate, sludge and compost amendments respectively, we didn't evidence any significant effect of
331 these OW on the amount of S-Metolachlor that leached through the soil cores. This might be related
332 to the limited number of replicates and the great variability inherent to studies performed under
333 realistic conditions. Such studies are difficult to replicate more given the considerable time
334 investment they require.

335 Contrasted hydrological behavior between soil cores may explain, to some extent, the great
336 variability of the breakthrough patterns between replicates for the digestate- and compost-amended
337 soils. All of the soil cores showed evidences of preferential flow and of physical non-equilibrium
338 solute transport. Indeed, the breakthrough of a water tracer (bromide) – introduced as calcium
339 bromide in the top two centimeters of the cores simultaneously with the organic waste – occurred

340 well before one pore-volume (PV) of water had eluted from the columns (Fig. S3). Moreover, the
341 tracer leaching dynamic and its recovery at the end of the experimental campaign (ranging from 39
342 to 76 %) highlights that tracer diffusion towards active flow paths was slower in some cores (control,
343 sludge) than in others (Digestate, Compost) suggesting that the diffusion distances in the former
344 were larger than in the latter cores. The differences in tracer recovery were statistically significant
345 between the compost and both the sludge ($p = 0.002$) and control ($p = 0.001$) treatments and
346 between the digestate and both the sludge ($p = 0.025$) and control ($p = 0.005$) treatments (Fig. S1d).

347 We explored whether these differences could stem from the burrowing activity of earthworms, that
348 were present at the core sampling site and thereby in the cores at the beginning of the experiments.
349 The initial earthworm count couldn't be established because it would have disrupted the soil
350 structure or microbial population of the cores. However, punctual observations about their activity
351 (presence of earthworms and casts at the surface and in the storage collection buckets used in
352 between rainfalls) were recorded. The earthworm's activity was low in the un-amended controls and
353 in the sludge amended cores all along the experiment but was higher in the digestate and compost
354 amendments especially between the third and sixth rainfall events. A weak ($R^2 = 0.55$) but significant
355 ($p = 0.009$, Fig. S4) linear relationship between the final earthworm biomass and bromide recovery
356 suggests that the earthworm presence may have indeed affected the tracer leaching dynamics
357 Earthworm activity may also help understanding qualitatively the variability observed in S-
358 Metolachlor breakthrough patterns between replicates, and from one rainfall to the other in specific
359 cores (e.g.: replicates B and C of the compost treatment, Figures 1 and S2, first row, rightmost
360 column). A more precise identification of the mechanisms involved (earthworm burrowing activity
361 favoring preferential flow or direct transport by ingestion-transport-excretion) and their impact on
362 tracer and herbicide leaching would require dedicated experimental situations and observation
363 techniques such as proposed by Capowiez et al. (2021) or Sammartino et al. (2012) and was out of
364 the scope of this study. Finally, the variability of the breakthrough patterns between replicates may
365 also stem from the intrinsic variability of water infiltration in macropores – a process that is affected

366 by multiples factors, including the location of macropore flow initiation (soil surface vs. soil profile),
367 macropore density and soil matrix initial water content – as documented by others both on an
368 experimental and modeling point of view (see Weiler, 2005 and references herein).

369 The maximum concentration regulatory value for pesticides and metabolites in groundwater
370 intended for human consumption in Europe is 0.1 µg/L. This threshold was exceeded for all the
371 treatments including the un-amended controls. This might threaten groundwater quality, although S-
372 Metolachlor can be retained, to a lesser extent, in the vadose zone substratum and further diluted in
373 the groundwater (Baran and Gourcy, 2013; Sidoli et al., 2020). In the following section, we explore
374 the possible contribution of DOC and colloidal particles as vectors of S-Metolachlor in the columns.

375

376 **3.2. S-Metolachlor carrier-phases**

377 Colloids and DOC are generally considered to act as vectors facilitating the transport of pesticides in
378 soils (Bolan et al., 2011; de Jonge et al., 2000, 2004; McGechan and Lewis, 2002). The colloids
379 concentration and DOC content evolution through the successive rainfall events are described in
380 Figure 3 for the different treatments.

381 Colloid concentration was maximal at the beginning of each rainfall event (≈ 10 g/L), then it
382 decreased rapidly until it reached a baseline around 0.05 g/L. This behavior was reported in a large
383 number of studies and highlights the importance of wetting and drying cycles on colloid mobilization
384 (Michel et al., 2010, 2014; Mohanty et al., 2016). Overall, the colloids concentration range did not
385 vary much across the treatments although the baseline and peak concentrations were slightly higher
386 for the composted sludge and digestate amended cores compared to the control and sewage sludge
387 amended cores. Accordingly, the cumulative mass of colloids that leached during the whole
388 experimental campaign (0.97 ± 0.48 g; 1.73 ± 1.00 g; 1.88 ± 0.85 g, 2.83 ± 0.88 g for control, sludge,
389 composted sludge and digestate, respectively) were not statistically different across the treatments
390 ($F(3,8) = 2.575$, $p = 0.127$, Fig. S1e). Colloid leaching was very variable among the replicates of each

391 treatment. The higher colloid and S-Metolachlor leaching observed for example in the D-A and CS-C
392 cores is consistent with a hydrodynamic behavior dominated by preferential macropore flow as
393 suggested by Mohanty et al. (2016), who observed that higher flow path permeability lead to higher
394 colloid leaching.

395 Despite the extent of the colloid concentration range within the rainfall events, no linear correlation
396 was found between the colloids and S-Metolachlor concentrations in the leachates ($R^2 < 0.01$). The
397 colloidal transport of S-Metolachlor seems to be limited. This might be explained by the generally
398 weak affinity of S-Metolachlor for soil particles (PPDB, 2018).

399 The DOC concentration in the un-amended control soils ranged between 8 and 17 mg/L with a
400 decreasing trend observed through the succession of rainfall events. The amendments resulted in an
401 increased DOC concentration during the first two rainfall events compared to the controls. During
402 these rainfalls, concentrations were up to three times higher than in the controls for the digestate
403 and sewage sludge and up to ten times higher for the compost amendment. These concentrations
404 were variable between the replicates of a given treatment with up to a four-fold difference for the
405 composted sludge. From the third rainfall event on, a steady concentration seems to have been
406 reached, and DOC concentrations were similar for the control, digestate and sludge treatments. This
407 suggests that for these events, the DOC released originated mainly from the SOM. The compost
408 amended cores had a different behavior. Indeed, DOC concentration remained higher than the
409 control until the end of the experimental campaign. This suggests that compost released DOC during
410 the whole experimental campaign although with a lower concentration than during the first two
411 rainfalls. The cumulated DOC amounts after S-Metolachlor application (R3 to R10) ranked the highest
412 for the composted sludge with 63 ± 6 mg, then 41 ± 6 mg for the controls, 39 ± 2 mg for the sludge
413 and 30 ± 3 mg for the digestate. The cumulated DOC for the compost treatment was significantly
414 higher than that of the other treatments ($p \leq 0.001$).

415 In a long term field experiment, Cambier et al., (2014) measured similar DOC concentration ranges at
416 45 cm depth for an agricultural soil amended with a compost of sewage sludge and green waste.
417 They found that the DOC concentration was greater for this compost than for manure-amended or
418 un-amended soils. They also monitored a decrease in DOC concentration over time for all of the
419 organic-amended soils. The decrease of DOC over time after organic amendments were also
420 reported by Marín-Benito et al. (2013) who measured significantly higher DOC concentration for soils
421 incubated with a variety of OW during one month than during 12 months. They explained the lower
422 DOC after extended incubation by the stabilization of the soil organic matter.

423 Digestate is a liquid OW and a fraction of it percolated through the core during spreading. This
424 fraction was 2 and 3 fold higher for the A replicate than for the B and C replicates, respectively. This
425 explains why DOC was lower in the A replicate during the first rainfall event, as a significant fraction
426 of the applied digestate had already percolated through the core. It is also a further evidence of the
427 different hydrological functioning of the different cores. The fractions collected during digestate
428 spreading were not analysed for DOC because of low volumes but their brownish color suggests that
429 they were highly loaded with DOC. This DOC peak during spreading is not represented in Figure 3 and
430 occurred before S-Metolachlor application.

431 DOC is a well-known vector of hydrophobic pesticides in soil (Bolan et al., 2011; Tang et al., 2012).
432 However, under the present experimental conditions, DOC concentrations were similar for the
433 control, sludge and digestate treatments after S-Metolachlor spraying (Figure 3) and thereby
434 probably did not impact the herbicide transport. Under field condition, OW are amended several
435 weeks before crop establishment and weeding to allow the degradation of the organic matter and
436 the bioavailability of nutrients for the crops. The high initial DOC release following OW amendment
437 should generally be over at the time of pesticide spraying on the crops. In this respect, the interval
438 between OW amendment and pesticide application is probably a key factor controlling pesticide fate
439 in OW amended soils.

440 DOC came back to the level of the control soil one month (or 1/3 pore volume) after OW amendment
441 for the sludge and digestate amendments and remained higher for the compost. This tailed DOC
442 release after compost amendment was insufficient to significantly increase S-Metolachlor leaching.

443

444 **3.3. Degradation and fate of metabolites**

445 Over 83 % of the applied S-Metolachlor dose was not recovered neither in the leachates nor in the
446 soils (Table 2). To assess the contribution of degradation to this loss of S-Metolachlor, we monitored
447 its two major metabolites, MET-ESA and MET-OA (PPDB, 2018; Torabi et al., 2020; Zemolin et al.,
448 2014).

449 The transport patterns of the two metabolites differed among the treatments (Figure 1). Overall, the
450 detection of both metabolites in the eluted fractions occurred already during the rainfall event
451 following S-Metolachlor application. The MET-OA peak was generally slightly delayed compared to S-
452 Metolachlor and the MET-ESA peak was more delayed than the MET-OA peak. Peak concentration of
453 MET-OA reached 22.4, 44.9, 73.6 and 75.1, µg/L and those of MET-ESA 82.9, 45.9, 40.5, 34.5 µg/L for
454 the control, digestate, sludge and composted-sludge treatments, respectively.

455 A greater proportion of MET-OA (51-100 %) was detected in the eluted fraction than in the soils
456 while MET-ESA was proportionally more detected in the soil (51 – 67%) except for the control (35%)
457 (Table 3). MET-ESA concentration in the soil profiles were generally higher than those of MET-OA,
458 except on the top 4 cm for the control, sludge and composted sludge (Figure 2).

459 All OW amendments stimulated the formation of MET-OA over MET-ESA compared to the control (p
460 < 0.001). However, the proportion of the two metabolites varied greatly among the treatments. MET-
461 OA represented 8 %, 27 %, 45 % and 54 % of the total metabolites (MET-OA + MET-ESA in soil +
462 leachates) recovered in the control, digestate, sludge treatments and compost, respectively. This

463 proportion of MET-OA over MET-ESA was statistically different between all treatments (p value <
464 0.02) except between the sludge and compost (Fig. S1g).

465 Considering that MET-OA and MET-ESA stem from distinct degradation pathways, we hypothesized
466 that one mole of metabolite, either MET-OA or MET-ESA, was generated by the degradation of one
467 mole of S-Metolachlor (Maillard et al., 2016). The term degradation refers hereafter to the total
468 number of MET-ESA and MET-OA moles recovered in the leachates and extracted from the soil
469 divided by the S-Metolachlor moles applied. The degradation contributed to 6.1 ± 0.8 % for the
470 controls, 6.0 ± 0.3 % for the sludge treatment, 6.1 ± 2.0 % for the digestate treatment and 8.6 ± 2.2 %
471 for the compost treatment (Table 2). Despite the higher average degradation rate in the compost
472 treatments, no statistical differences were evidenced ($F(3,7) = 2.113$, $p = 0.187$). This is due to the
473 high variability between the replicates (Fig. S1h).

474

475 The higher concentration of MET-ESA than MET-OA in the soil profiles is in accordance with the
476 greater aqueous solubility (PPDB, 2018) and the lower soil sorption coefficient of MET-OA than MET-
477 ESA (Baran and Gourcy, 2013). The quick detection of MET-OA and MET-ESA in the leachates
478 following S-Metolachlor application evidences a rapid degradation of S-Metolachlor probably favored
479 by the history of application on the studied soils. The concentration of both metabolites greatly
480 exceeded the European regulatory limit of $0.1 \mu\text{g/L}$ for ground water used for human consumption.
481 Therefore, the very high peak concentration under the tilled horizon can be a threat to groundwater
482 quality given the reported low retention of both metabolites and their persistence in the vadose
483 zone (Baran and Gourcy, 2013). MET-OA in particular has been reported to be a skin sensitizer and an
484 eye irritant (Cai et al., 2007; PPDB, 2018).

485

486 The degradation wasn't significantly boosted by any OW amendment. Even the 32% increase in SOC
487 after compost amendment didn't significantly increase the S-Metolachlor degradation rate. However,

488 OW amendments influenced the metabolic pathways of S-Metolachlor. All three OW had contrasted
489 physico-chemical properties such as pH or OC (Table 1) which might have boosted different soil
490 bacterial communities. In addition, these OW were characterized by different bacterial populations
491 themselves. The compost, in particular, contains 42 strains from the genus *Bacillus* (Aigle et al.,
492 2021). Many species from this genus are known to be involved in the degradation of
493 chloroacetamide herbicides (Wang et al., 2008; Zemolin et al., 2014). *Bacillus* species represented
494 6.2% of the total bacterial biomass for the compost and only 0.1% for the digestate and sewage
495 sludge. The composted sludge was also enriched in Actinobacteria compared to the raw-sludge (28%,
496 7% and 0.2% of the biomass for the compost, sludge and digestate respectively (Aigle et al., 2021).
497 Actinobacteria were found to be associated with a higher proportion of MET-OA vs MET-ESA
498 metabolite during microcosm degradation studies of S-Metolachlor in an agricultural soil (Torabi et
499 al., 2020). Whether actinobacteria led to the increasing proportion of MET-OA observed in the
500 digestate, sludge and composted sludge in our study remains to be determined. The knowledge on
501 the S-Metolachlor metabolic pathways is still erratic and the factors favoring a metabolic pathway
502 over another remain to be identified (Torabi et al., 2020).

503

504 A large fraction (83 – 94%) of the applied S-Metolachlor was neither recovered in the eluted fraction
505 or the soil nor transformed into MET-OA or MET-ESA. Given the very quick appearance of both
506 metabolites, complete mineralization may have occurred. For field soils having an history of S-
507 Metolachlor application comparable to the soil studied here and containing cover crop residues,
508 Alletto et al. (2013) reported mineralization rates ranging from 0.8 to 28 %. Similar mineralization
509 ranges were reported by Baran and Gourcy, (2013). Although MET-OA and MET-ESA have been
510 reported to be the major transformation products, other metabolites of S-Metolachlor have been
511 identified (Kiefer et al., 2019; PPDB, 2018; Reemtsma et al., 2013). It is thereby possible that the
512 transformation into secondary metabolites, that were not monitored, explains part of the

513 unrecovered S-Metolachlor. Finally, the formation of non-extractible residues (NER) generally
514 accounts for 10 to 80 % of active molecule losses (Briceño et al., 2007; Fernandes et al., 2006; Li et
515 al., 2015; Marín-Benito et al., 2013). NER formation might thereby be responsible for a consequent
516 fraction of the unrecovered S-Metolachlor in our study.

517

518 **4. Conclusion**

519 This study examined the fate of S-Metolachlor, a chloroacetamide herbicide, under the widespread
520 practice of organic waste recycling in agriculture. The experimental design used was closer to field
521 conditions (undisturbed soil cores, alternating rainy and dry periods, duration long enough to allow
522 for the transformation of organic matter, presence of soil fauna) than most of those reported so far.
523 This experimental setup yielded key results to improve our understanding of the herbicide fate in this
524 context:

525 • The amount of S-Metolachlor that leached through the cores was low and not significantly
526 affected by OW amendments. Moreover, colloid and DOC facilitated transport were not major
527 mechanisms affecting this herbicide's fate. However, for all treatments, the groundwater quality
528 threshold was exceeded during several rainfall events, potentially threatening groundwater quality.
529 These high S-Metolachlor concentrations were probably the consequence of soil hydraulic behavior
530 dominated by preferential macropore flow. Future studies should aim at clarifying the role of
531 earthworms on contaminant transport via the modification of the macroporal network.

532 • The metabolic pathways were impacted by all OW amendments that stimulated MET-OA
533 over MET-ESA formation compared to the un-amended soil. The concentrations of both metabolites
534 in the leachates were more than two orders of magnitude higher than the European regulatory limit
535 of 0.1 µg/L for groundwater used for human consumption in all of the treatments including the un-
536 amended controls. Because of the low retention of these metabolites in the vadose zone and their
537 persistence, this constitutes a threat to groundwater quality.

538 • Less than 12 % of the S-Metolachlor applied was recovered in the soil, the leachates or
539 transformed into MET-OA and MET-ESA. This indicates that other mechanisms occurred such as the
540 transformation into other metabolites, mineralization or the formation of non-extractible residues.
541 Our experimental design doesn't enable to distinguish the relative role of these mechanisms. Future
542 studies with experimental designs using ¹⁴C labeled S-Metolachlor could clarify this aspect.

543 Although it's effect is not statistically significant in our study, composted sludge tends to increase S-
544 Metolachlor availability and transformation into more mobile and persistent metabolites. This
545 deserves to be studied further in depths in future studies.

546

547

548 **5. Declarations**

549 **Availability of data and materials**

550 The datasets used and/or analysed during the current study are available from the corresponding
551 author on reasonable request.

552

553 **Competing interests**

554 The authors declare that they have no known competing financial interests or personal relationships
555 that could have appeared to influence the work reported in this paper.

556

557 **Authors' contributions**

558 JD performed the experiments and coordinated the writing of the manuscript. EM and VP
559 contributed to the experimental design and to the writing of the manuscript. MBD supervised the

560 pesticide analyses and contributed to the writing of the manuscript. VS, NB and GD contributed to
561 the pesticide analyses. MM performed the DOC analyses and contributed to the writing of the
562 manuscript. LC performed the bromide analyses.

563

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567

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569 Not applicable

570

571 **Consent to Participate**

572 Not applicable

573

574 **Consent to Publish**

575 Not applicable

576

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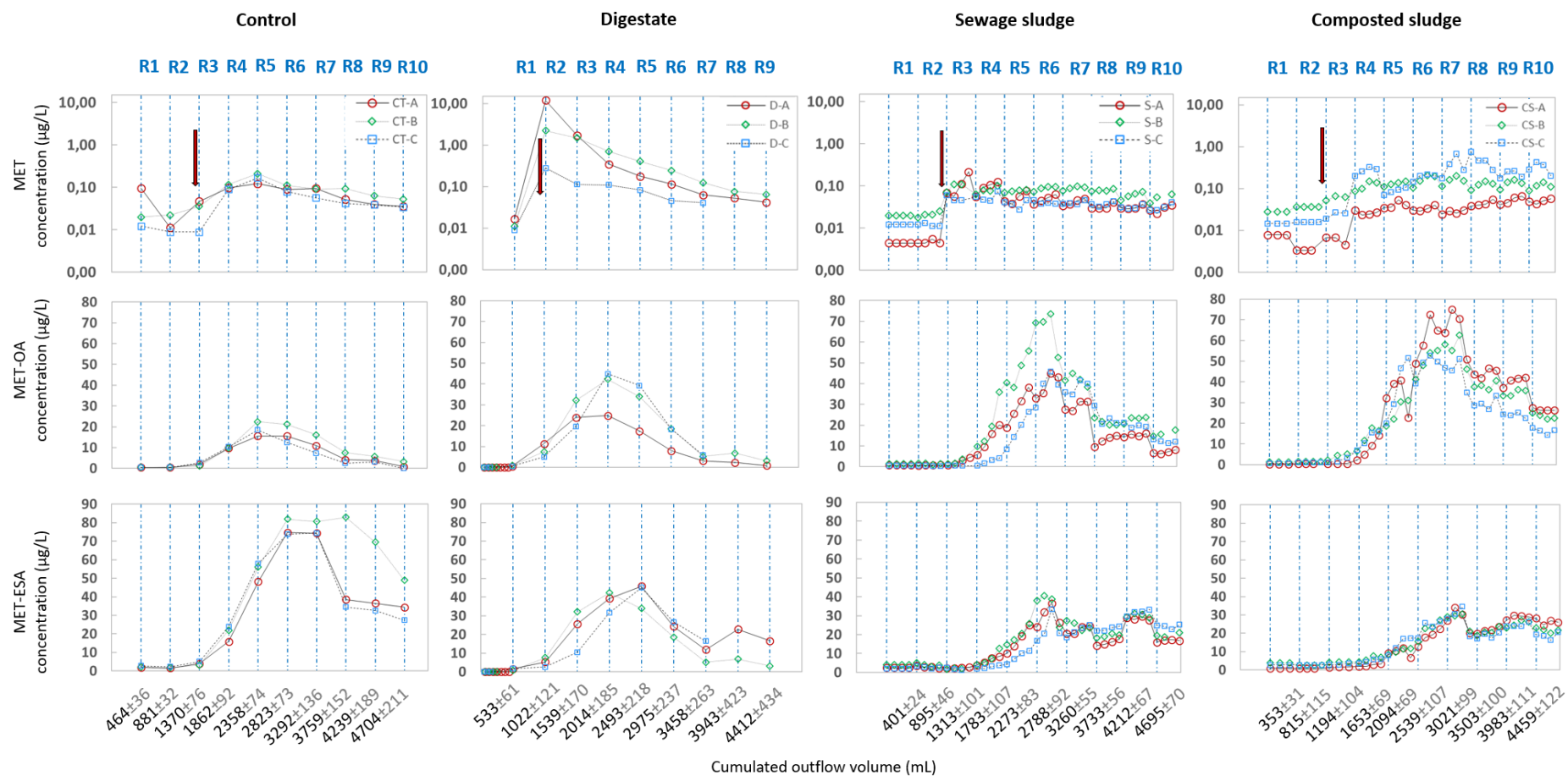
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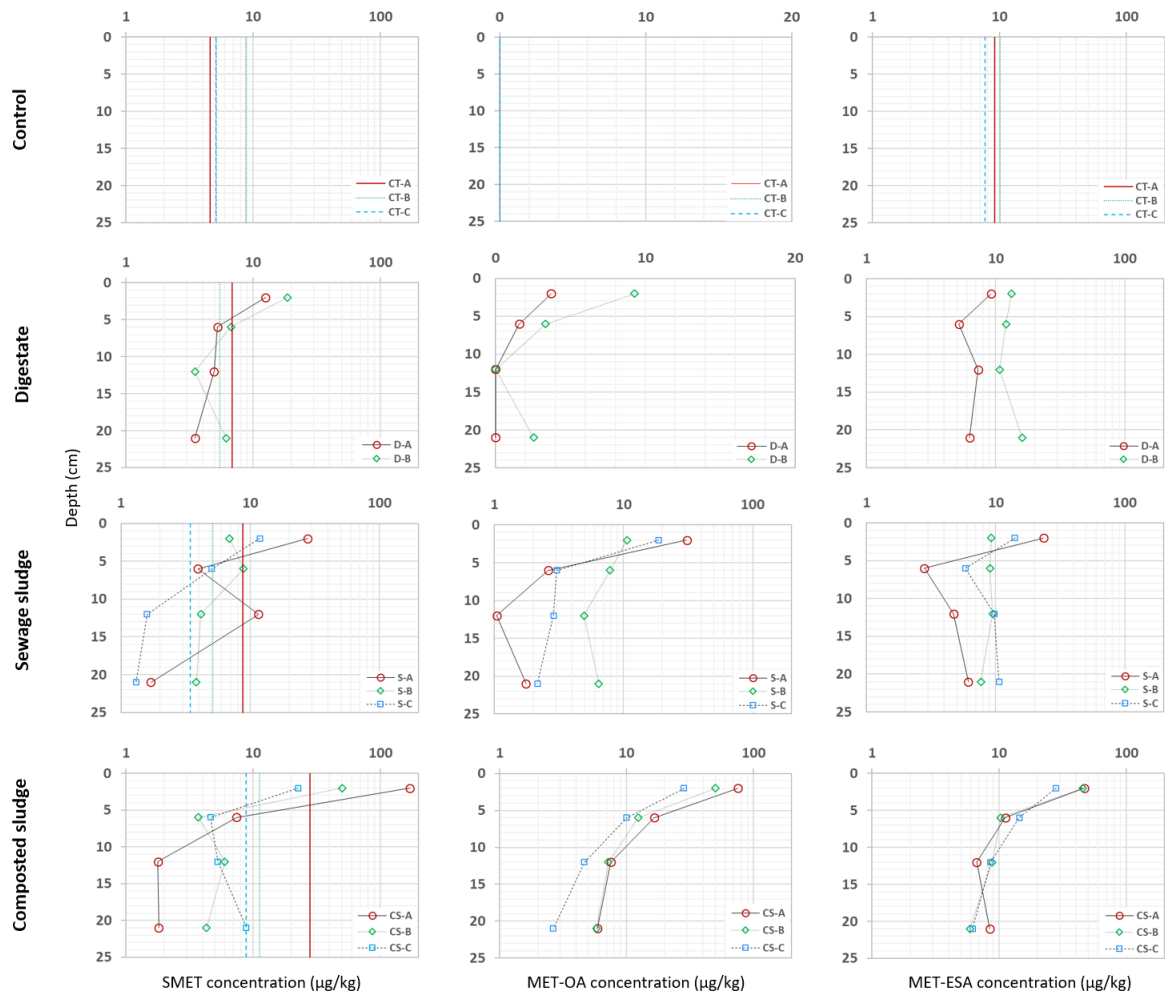
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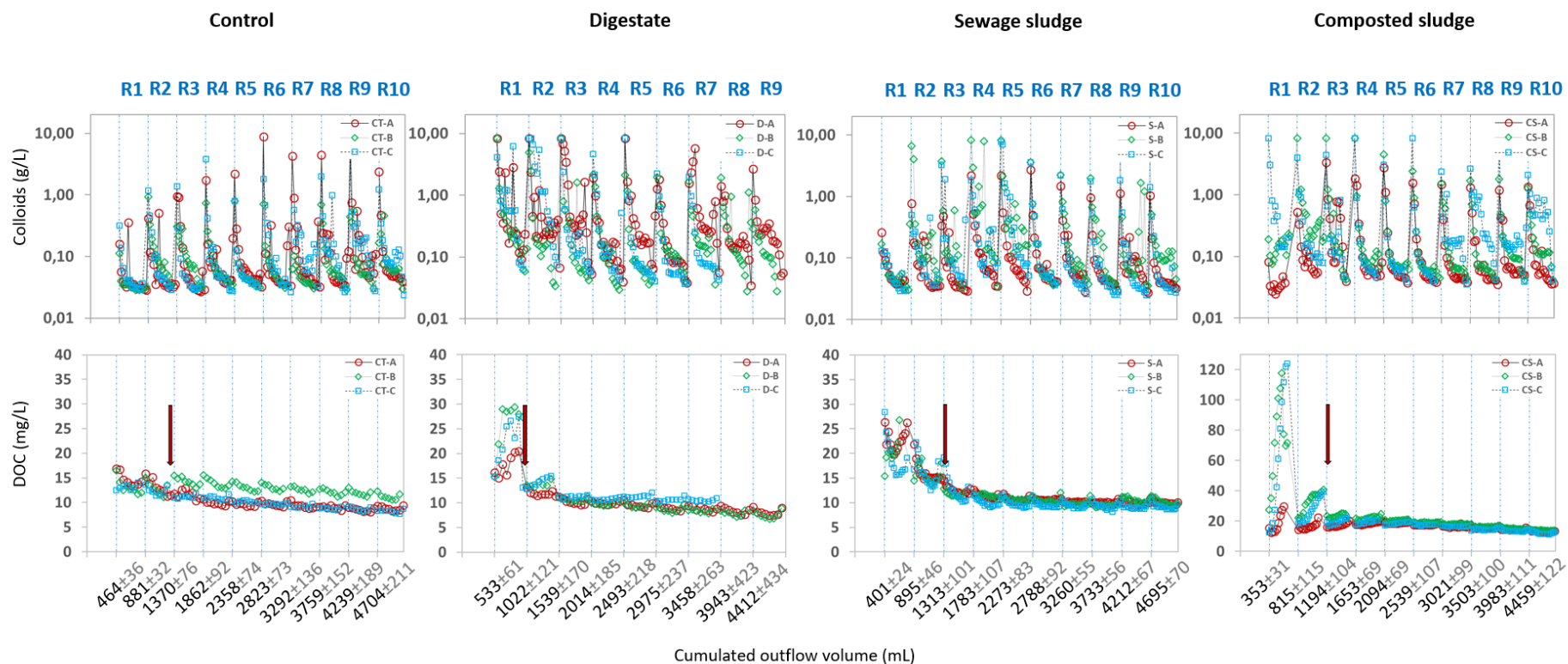
811 **Figure 1: Breachthrough curves of S-Metolachlor and its two main metabolites, SMET-OA and SMET-ESA, under the tilled horizon.** The red arrows
 812 represent the application of S-Metolachlor on top of the cores. A, B and C are the 3 replicates established for each treatment; control (CT); composted
 813 sludge (CS); digestate (D) and sewage sludge (S). The rainfall events are separated by vertical dashed lines. The cumulated outflow volume was different for

814 each replicate. To facilitate the lecture of this figure, we have represented the concentrations of S-Metholachlor and metabolite according to the
815 chronological order of collection of the eluted fractions. The cumulated outflow volume after each rainfall averaged over the three replicates and the
816 standard deviation of this volume is indicated on the horizontal axis. Figure S1 shows the same data represented as a function of cumulated outflow volume.



817

818 **Figure 2: Concentration profiles of S-Metolachlor and its two main metabolites, MET-OA and MET-**
 819 **ESA in the soil. A, B and C are the 3 replicates established for each treatment; control (CT);**
 820 **composted sludge (CS); digestate (D) and sewage sludge (S). The vertical lines represent the average**
 821 **concentration over the entire profile. SMET-OA was not detected in some (digestate) or all (control)**
 822 **depths, and are represented with linear concentration axes. For the control soil, the dashed lines are**
 823 **super-imposed with the y axis. Replicate C of the digestate treatment is not represented here**
 824 **because it fell off the fraction collector after rainfall n# 7 which disrupted its structure. The**
 825 **experiment was thereby terminated earlier for that specific core.**



827

828 **Figure 3: Colloids and DOC concentration in the eluted fractions.** A, B and C are the 3 replicates established for each treatment; control (CT); composted
 829 sludge (CS); digestate (D) and sewage sludge (S). The red arrows represent the application of S-Metolachlor on top of the cores. The rainfall events are
 830 represented by the vertical dashed lines. The cumulated outflow volume after each rainfall event is averaged over the three replicates and the standard
 831 deviation is indicated in grey.

832

833 **Tables**

834

835 **Table 1: Properties of the organic wastes**

Organic waste	Dry matter %	Total nitrogen %	Total carbon %	Organic matter %	pH	Electrical conductivity mS/cm	COD gO ₂ /l*
Digestate (D)	3	3.47	38.07	64.62	9.03	18.51	32.9
Sludge (S)	18	8.22	47.52	79.45	5.90	nd	203.1
Compost (CS)	65	3.06	31.23	54.26	7.01	nd	0.9*

836 The electrical conductivity was measured only for the liquid OW. The chemical oxygen demand was
 837 measure directly on the liquid fraction (after centrifugation) for the digestate and sewage sludge and
 838 after extraction with a 10 mM CaCl₂ solution for the composted sludge. (*) The value for CS is given
 839 as gO₂/g_{OW (DW)}.

840

841

842 **Table 2: Mass balance of S-Metolachlor**

Treatment	SMET eluted %	SMET in soil %	Metabolite formation %	NER/mineralization %
Control (CT)	0.01 ± 0.002	1.25 ± 0.47	6.14 ± 0.84	92.60 ± 1.29
Digestate (D)	0.10 ± 0.11	1.25 ± 0.18	6.13 ± 2.04	92.52 ± 4.59
Sludge (S)	0.01 ± 0.002	1.17 ± 0.56	6.02 ± 0.28	92.80 ± 0.38
Compost (CS)	0.01 ± 0.01	3.30 ± 2.18	8.63 ± 2.22	88.06 ± 4.38

843

844 *The Metolachlor eluted and remaining in soil after the rainfall events are expressed as a fraction of*
 845 *Metolachlor applied. The metabolites formed is the sum of ESA and OA. Metabolite formation is also*
 846 *expressed as the percentage of Metolachlor applied with the hypothesis that 1 mole of metabolite,*
 847 *were generated by the degradation of 1 mole of Metolachlor. The NER/mineralization is the resultant*
 848 *of the mass balance.*

849

850 **Table 3: Metolachlor metabolites in the lixiviates and in the soils**

Treatment	lixiviates		soils	
	MET-OA mole	MET-ESA mole	MET-OA mole	MET-ESA mole
Control (CT)	1.19 10 ⁻⁷ ± 2.2 10 ⁻⁸	5.32 10 ⁻⁷ ± 7.0 10 ⁻⁸	0.0 ± 0.0	8.28 10 ⁻⁷ ± 3.8 10 ⁻⁸
Digestate (D)	2.17 10 ⁻⁷ ± 3.8 10 ⁻⁸	2.56 10 ⁻⁷ ± 4.8 10 ⁻⁸	1.04 10 ⁻⁷ ± 1.3 10 ⁻⁸	6.14 10 ⁻⁷ ± 5.0 10 ⁻⁸
Sludge (S)	3.12 10 ⁻⁷ ± 9.4 10 ⁻⁸	2.18 10 ⁻⁷ ± 2.1 10 ⁻⁸	5.16 10 ⁻⁷ ± 3.4 10 ⁻⁸	7.97 10 ⁻⁷ ± 3.4 10 ⁻⁸
Compost (CS)	4.11 10 ⁻⁷ ± 6.9 10 ⁻⁸	1.99 10 ⁻⁷ ± 9.7 10 ⁻⁹	1.24 10 ⁻⁶ ± 9.2 10 ⁻⁸	1.20 10 ⁻⁶ ± 5.4 10 ⁻⁸

