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

3 *Jeanne Dollinger*[*1], Marjolaine Bourdat-Deschamps[2], Valérie Pot[2], Valentin Serre[2], Nathalie Bernet[2],*
4 *Ghislaine Deslarue[2], Mélanie Montes[3], Line Capowiez[4], Eric Michel[4]*

5

6 *(1): UMR LISAH, Université Montpellier, INRAE, IRD, Institut Agro, 34060 Montpellier, France*
7 *(2):* Université Paris-Saclay, INRAE, AgroParisTech, UMR ECOSYS, 78850 Thiverval-Grignon, France
8 *(3): UR Recyclage et Risque, CIRAD, Avenue Agropolis 34398 Montpellier, France*
9 *(4): UMR EMMAH, INRAE, Avignon Université, Domaine Saint Paul - Site Agroparc, 84000 Avignon,*
10 *France*
11
12 *(*) Corresponding author: jeanne.dollinger@inrae.fr*
13

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

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

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

Graphical abstract:
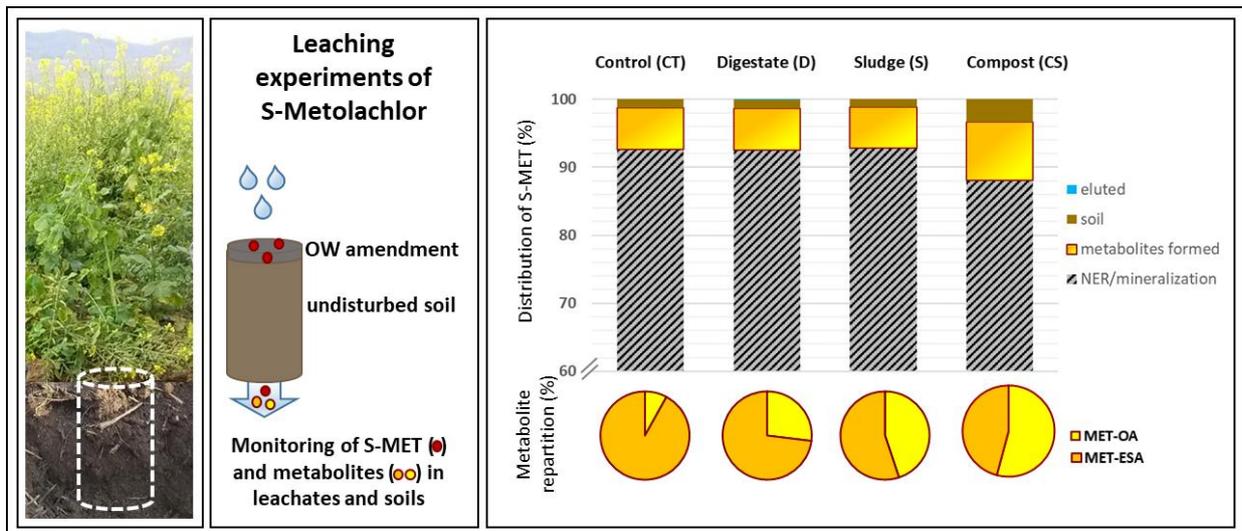
Highlights:

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

2

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

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 (Barłóg 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

4

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 Kd 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.

7

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 Kow = 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 (Koc 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 (Koc 2-63 L/kg for MET-OA and Koc 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 ± 3°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

2.5. Analyses

222

223

    2.5.1.   Analysis of the herbicide carrier-phases

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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 Schimadzu). 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

2.5.2. S-Metolachlor and metabolites

The elution fractions were acidified and analysed by online solid phase extraction and ultra-high-performance-liquid chromatography coupled with triple quadrupole mass spectrometry (online SPE - UHPLC-MS-MS) with the method described for soil and water samples by Bourdat-Deschamps et al., (2014). Soil samples were extracted by ultrasonic extraction, purified using a modified QuEChERS method and analysed by online SPE – UHPLC-MS-MS as described by Ferhi et al. (2016). Mass spectrometrer transitions for the quantification of S-Metolachlor, MET-OA and MET-ESA were 284.3 > 252.3 (positive electrospray ionization), 278.07 > 206.2 (negative electrospray ionization) and 328.16 > 79.95 (negative electrospray ionization), respectively. Other transitions were also used for confirmation of the compounds. The compound concentrations were determined by internal quantification-isotope dilution (polynomial calibration curves; weighting 1/X; coefficients of determination higher than 0.97 and residues below 20%) in order to correct both extraction/purification losses and potential matrix effects in mass spectrometry. Soils and elution fractions were therefore spiked with a solution of (±)-Metolachlor-d_6 (propyl-d_6) from Cluzeau Infor Labo (Sainte-Foy-La-Grande, France).

259

2.6. Statistical analyses

261

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

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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).

12

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 µg/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 µg/kg), the sludge

300   (3.4 – 8.8 µg/kg) and the compost (8.8 – 28.0 µg/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   µg/kg, and decreased with depth down to 1.3 – 3.8 µg/kg. For the digestate treatment the

304   concentrations in the top layer ranged between 12.6 to 18.7 µg/kg and progressively dropped to 3.5

305   – 6.2 µg/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 µg/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

15

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 ($\approx$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

16

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 ($p \le 0.001$).

17

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

19

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 µg/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-extractable 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.

22

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 ^{14}C 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

567

568   **Ethical Approval**

569   Not applicable

570

571   **Consent to Participate**

572   Not applicable

573

574   **Consent to Publish**

575   Not applicable

576

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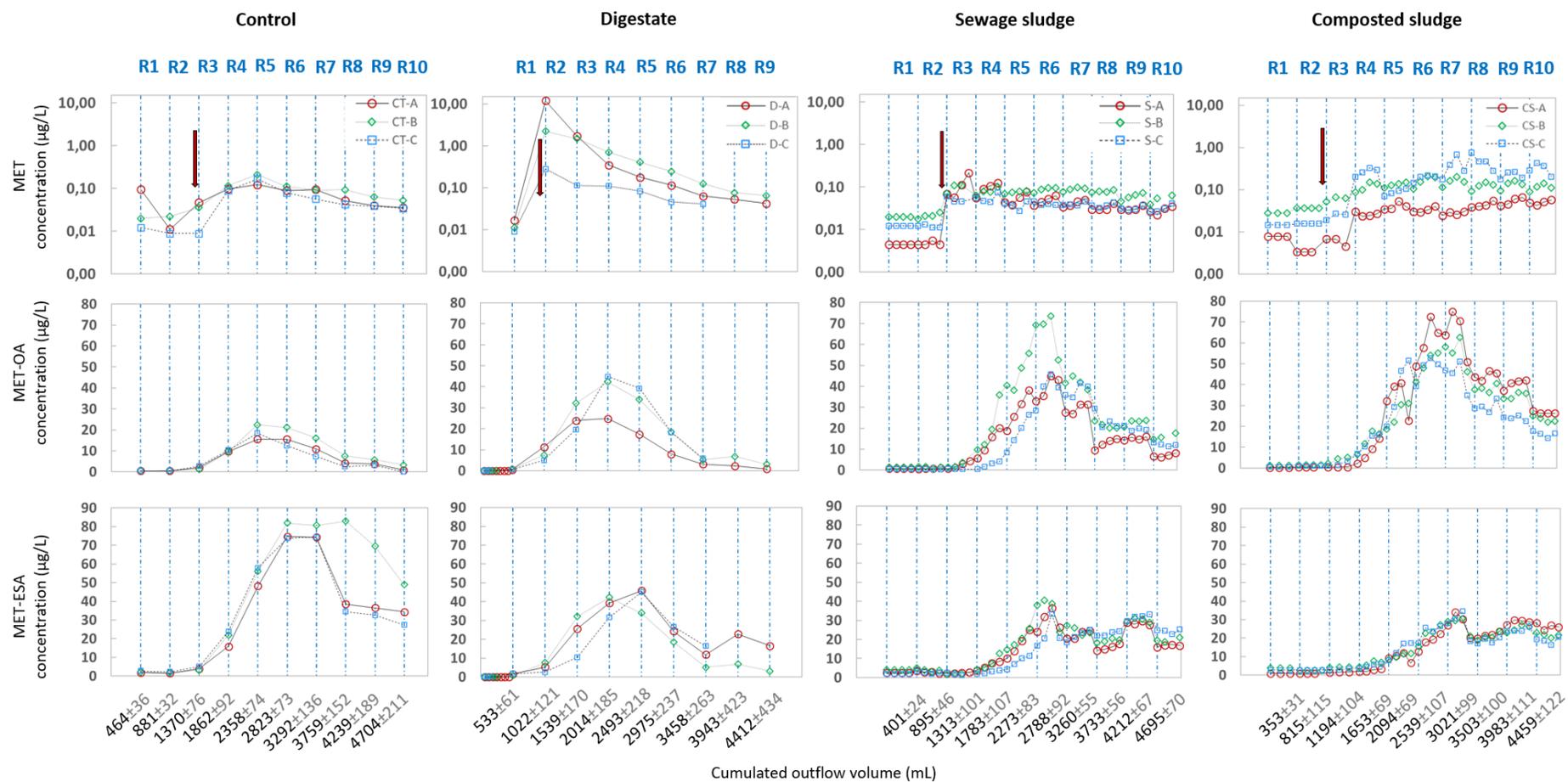
Figures

811 *Figure 1:* **Breackthrough 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.
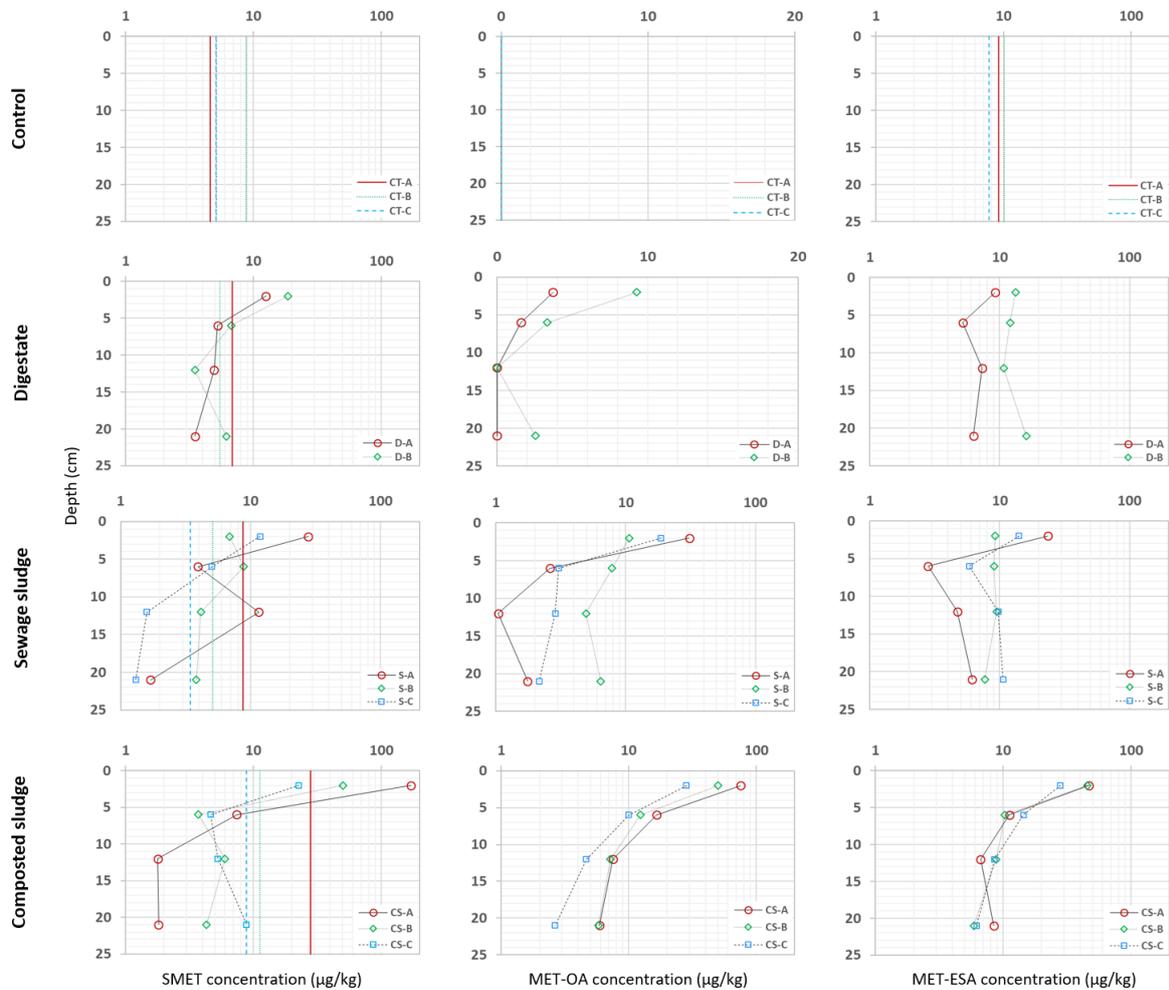
Figure 2: **Concentration profiles of S-Metolachlor and its two main metabolites, MET-OA and MET-ESA in the soil.** A, B and C are the 3 replicates established for each treatment; control (CT); composted sludge (CS); digestate (D) and sewage sludge (S). The vertical lines represent the average concentration over the entire profile. SMET-OA was not detected in some (digestate) or all (control) depths, and are represented with linear concentration axes. For the control soil, the dashed lines are super-imposed with the y axis. Replicate C of the digestate treatment is not represented here because it fell off the fraction collector after rainfall n# 7 which disrupted its structure. The experiment was thereby terminated earlier for that specific core.

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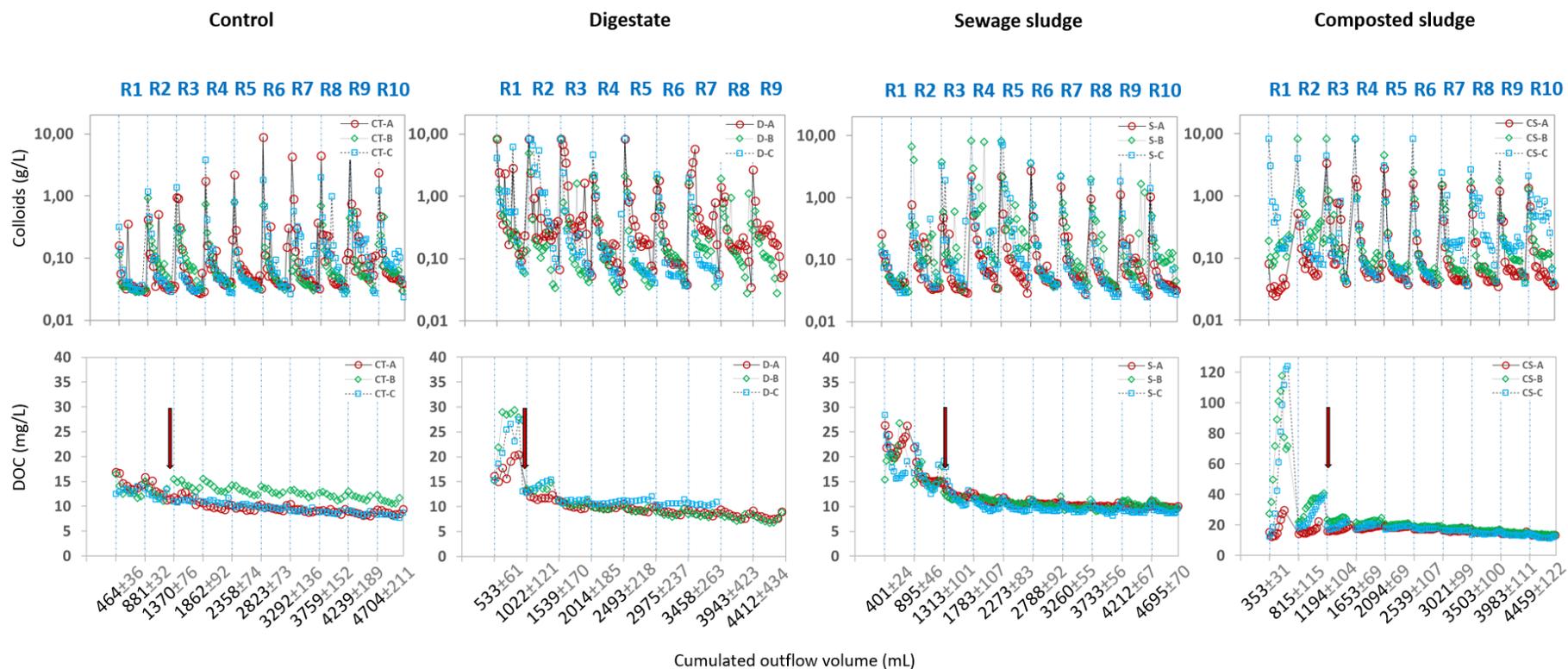
Figure 3: **Colloids and DOC concentration in the eluted fractions**. A, B and C are the 3 replicates established for each treatment; control (CT); composted sludge (CS); digestate (D) and sewage sludge (S). The red arrows represent the application of S-Metolachlor on top of the cores. The rainfall events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

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Tables

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*

The electrical conductivity was measured only for the liquid OW. The chemical oxygen demand was measure directly on the liquid fraction (after centrifugation) for the digestate and sewage sludge and after extraction with a 10 mM CaCl$_2$ solution for the composted sludge. (*) The value for CS is given as $gO_2/g_{OW\,(DW)}$.

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

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

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)	$1.19\ 10^{-7} \pm 2.2\ 10^{-8}$	$5.32\ 10^{-7} \pm 7.0\ 10^{-8}$	0.0 ± 0.0	$8.28\ 10^{-7} \pm 3.8\ 10^{-8}$
Digestate (D)	$2.17\ 10^{-7} \pm 3.8\ 10^{-8}$	$2.56\ 10^{-7} \pm 4.8\ 10^{-8}$	$1.04\ 10^{-7} \pm 1.3\ 10^{-8}$	$6.14\ 10^{-7} \pm 5.0\ 10^{-8}$
Sludge (S)	$3.12\ 10^{-7} \pm 9.4\ 10^{-8}$	$2.18\ 10^{-7} \pm 2.1\ 10^{-8}$	$5.16\ 10^{-7} \pm 3.4\ 10^{-8}$	$7.97\ 10^{-7} \pm 3.4\ 10^{-8}$
Compost (CS)	$4.11\ 10^{-7} \pm 6.9\ 10^{-8}$	$1.99\ 10^{-7} \pm 9.7\ 10^{-9}$	$1.24\ 10^{-6} \pm 9.2\ 10^{-8}$	$1.20\ 10^{-6} \pm 5.4\ 10^{-8}$

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