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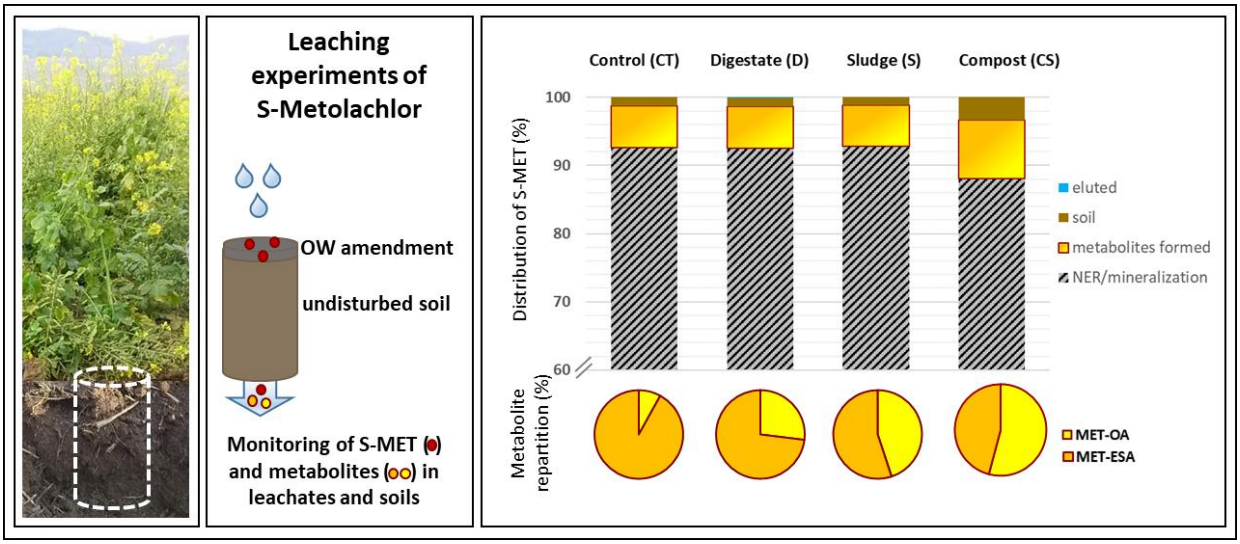
Abstract: Organic waste (OW) reuse in agriculture is a common practice fostered by benefits in terms of waste recycling and crop production. However, OW amendments potentially affect the fate of pesticides spread on fields to protect the crops from pests and weeds. The influence of OW on the sorption,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

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

1. Introduction

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

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

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

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

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

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

succession of rainy (10 mm h^{-1} rainfall events) and dry periods over a cropping season (126 days). We also monitored colloids and DOC, two potential herbicide carrier phases. This experimental design allows to simultaneously assess the balance of the leaching, sorption and degradation mechanisms.

S-Metolachlor was selected for this study because it is a widely used pre-emergent herbicide applied worldwide on a variety of crops including maize and sugar beet (PPDB, 2018). It is classified as moderately mobile due to a low sorption affinity for soils. As a consequence, it has been frequently detected in surface and groundwater in the USA and EU (Baran and Gourcy, 2013; Bexfield et al., 2021; Kupfersberger et al., 2018; Toccalino et al., 2014; Zambito Marsala et al., 2020). The major metabolites of S-Metolachlor are Metolachlor oxanilic acid (MET-OA) and Metolachlor ethane sulfonic acid (MET-ESA). Whether S-Metolachlor's fate is influenced or not by sewage sludge, composted sludge or digestate amendments remains to be characterized.

2. Material and methods

2.1. Soil cores sampling and preparation

The soil cores were taken from an experimental field located in Colmar, France (48.059777, 7.327474) which is part of the SOERE PRO network (SOERE PRO, 2015). This network gathers long term field experimental stations mainly over France where the impacts of organic waste amendments on crop yields, soil and water quality are evaluated. The crop rotation in the Colmar experimental field consists in a succession of wheat, corn, sugar beets and barley. Cover crops are established during the winter seasons. The plots have an history of S-Metolachlor application. The climate at the site is temperate with an average yearly rainfall of 552 mm (INRAE, 2020). The soil of 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

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

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

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

2.2. Organic waste amendments

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

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

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 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.

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).

2.6. Statistical analyses

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.

3. Results and discussion

3.1. S-Metolachlor leaching

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

Due to the history of S-Metolachlor application at the study site, low, but detectable concentrations 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 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

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

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

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

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

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

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

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

3.2. S-Metolachlor carrier-phases

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

Colloid concentration was maximal at the beginning of each rainfall event (≈10 g/L), then it decreased rapidly until it reached a baseline around 0.05 g/L. This behavior was reported in a large number of studies and highlights the importance of wetting and drying cycles on colloid mobilization (Michel et al., 2010, 2014; Mohanty et al., 2016). Overall, the colloids concentration range did not vary much across the treatments although the baseline and peak concentrations were slightly higher for the composted sludge and digestate amended cores compared to the control and sewage sludge amended cores. Accordingly, the cumulative mass of colloids that leached during the whole 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, composted sludge and digestate, respectively) were not statistically different across the treatments ($F(3,8) = 2.575$, $p = 0.127$, 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 ($p \leq 0.001$).

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

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

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

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

3.3. Degradation and fate of metabolites

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

The transport patterns of the two metabolites differed among the treatments (Figure 1). Overall, the detection of both metabolites in the eluted fractions occurred already during the rainfall event following S-Metolachlor application. The MET-OA peak was generally slightly delayed compared to S-Metolachlor and the MET-ESA peak was more delayed than the MET-OA peak. Peak concentration of 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 the control, digestate, sludge and composted-sludge treatments, respectively.

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

All OW amendments stimulated the formation of MET-OA over MET-ESA compared to the control ($p < 0.001$). However, the proportion of the two metabolites varied greatly among the treatments. MET-OA represented 8 %, 27 %, 45 % and 54 % of the total metabolites (MET-OA + MET-ESA in soil + 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 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,

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

A large fraction (83 – 94%) of the applied S-Metolachlor was neither recovered in the eluted fraction or the soil nor transformed into MET-OA or MET-ESA. Given the very quick appearance of both metabolites, complete mineralization may have occurred. For field soils having an history of S-Metolachlor application comparable to the soil studied here and containing cover crop residues, Alletto et al. (2013) reported mineralization rates ranging from 0.8 to 28 %. Similar mineralization ranges were reported by Baran and Gourcy, (2013). Although MET-OA and MET-ESA have been reported to be the major transformation products, other metabolites of S-Metolachlor have been identified (Kiefer et al., 2019; PPDB, 2018; Reemtsma et al., 2013). It is thereby possible that the 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.

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

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

5. Declarations

Availability of data and materials

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

Competing interests

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

Authors' contributions

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

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

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Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

Not applicable

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Figures

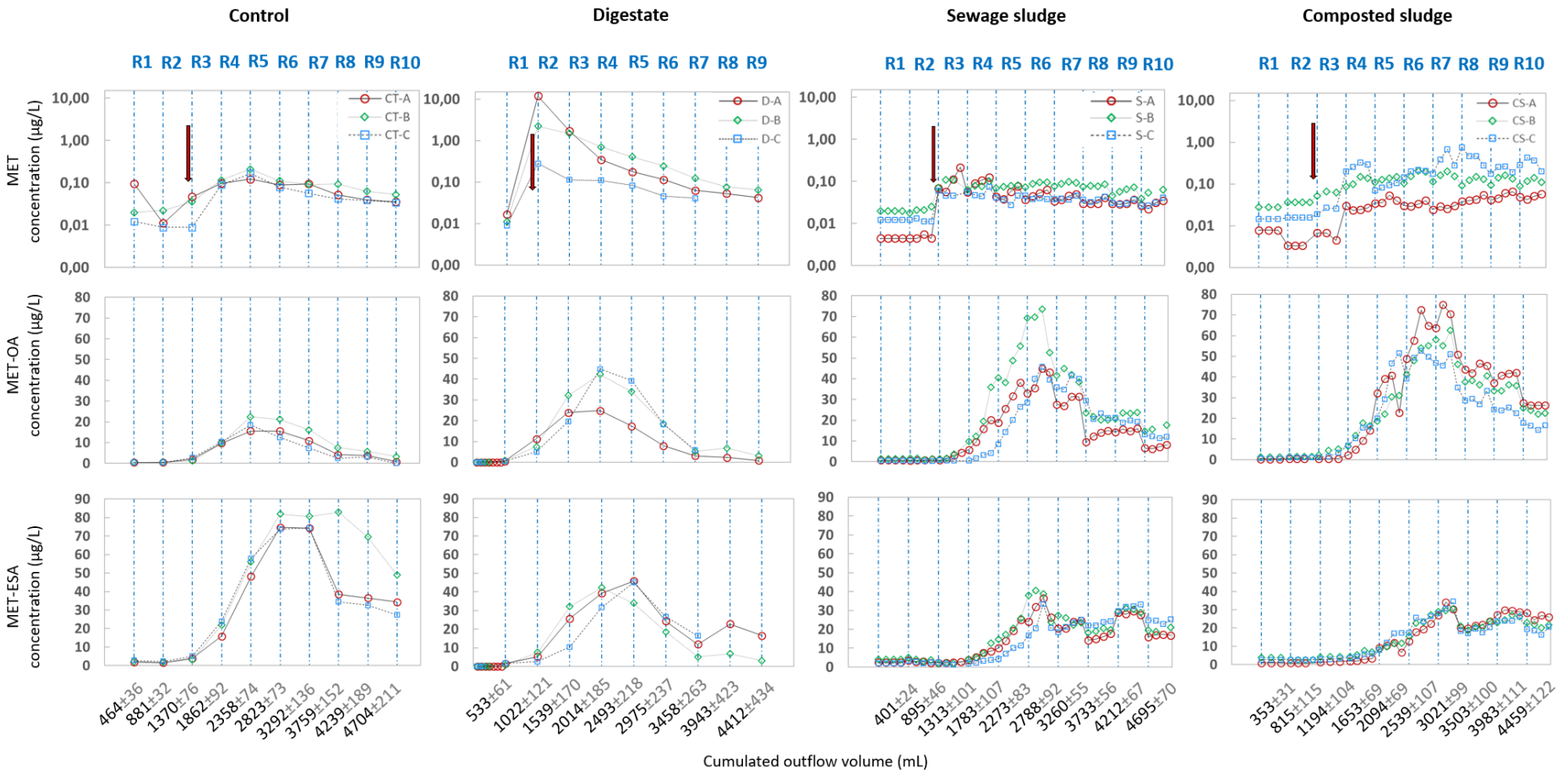
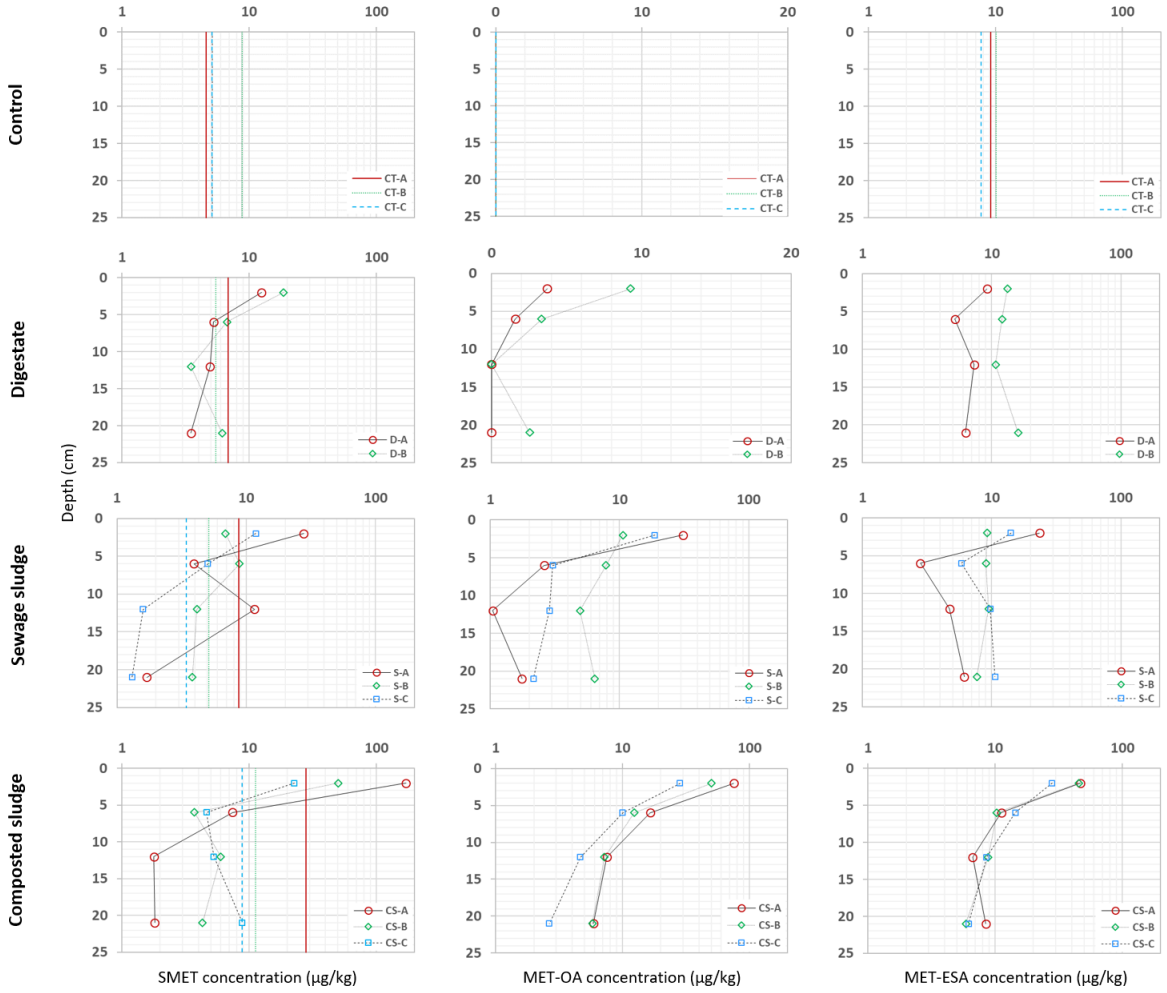


Figure 1: **Breackthrough curves of S-Metolachlor and its two main metabolites, SMET-OA and SMET-ESA, under the tilled horizon**. The red arrows represent the application of S-Metolachlor on top of the cores. A, B and C are the 3 replicates established for each treatment; control (CT); composted sludge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

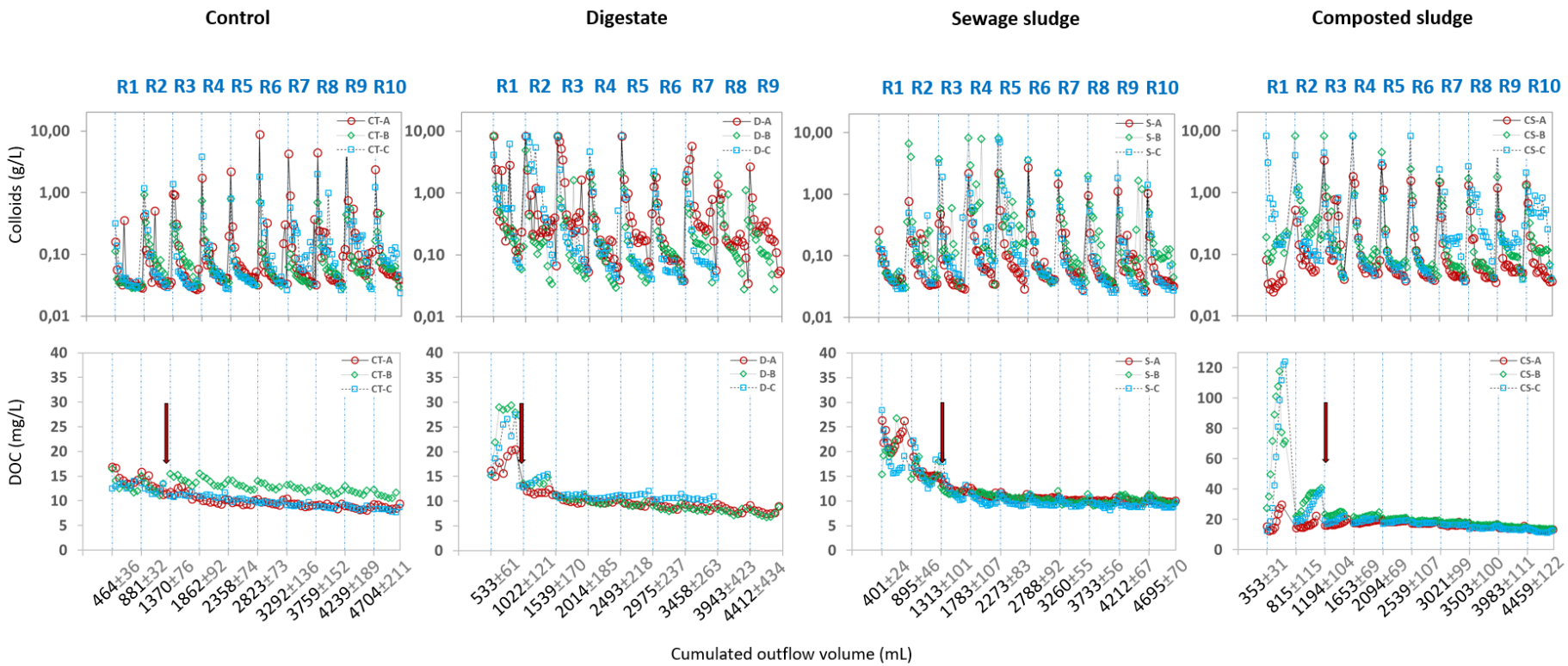
each replicate. To facilitate the lecture of this figure, we have represented the concentrations of S-Metholachlor and metabolite according to the chronological order of collection of the eluted fractions. The cumulated outflow volume after each rainfall averaged over the three replicates and the standard 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.

826



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	COD
	%	*%*	*%*	*%*		*mS/cm*	*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 $CaCl_2$ solution for the composted sludge. (*) The value for CS is given
839 as $gO_2/g_{OW\ (DW)}$.

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	MET-ESA	MET-OA	MET-ESA
	mole	*mole*	*mole*	*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)	$4.11\ 10^{-7} \pm 6.9\ 10^{-8}$	$1.99\ 10^{-7} \pm 9.7\ 10^{-9}$	$1.24\ 10^{-6} \pm 9.2\ 10^{-8}$	$1.20\ 10^{-6} \pm 5.4\ 10^{-8}$

851