

1 **Environmental behaviors of (*E*)-Pyriminobac-methyl in agricultural**  
2 **soils**

3

4 Wenwen Zhou<sup>a</sup>, Haoran Jia<sup>b</sup>, Lang Liu<sup>b</sup>, Baotong Li<sup>b\*</sup>, Yuqi Li<sup>b</sup>, Meizhu Gao<sup>b</sup>

5

6 <sup>a</sup> College of Food Science and Engineering, Jiangxi Agricultural University, Nanchang 330045, China

7 <sup>b</sup> College of Land Resources and Environment, Jiangxi Agricultural University, Nanchang 330045, China

8

9

10

11 \*Corresponding Author: Baotong Li, Tel.: 86-791-83813420, E-mail: btli666@163.com

12

13

14

15

16

17

18

19

20 **Abstract**

21 (*E*)-Pyriminobac-methyl (EPM), a pyrimidine benzoic acid esters herbicide, has a high potential as weedicide;  
22 nevertheless, its environmental behaviors are still not well understood. In this study, we systematically  
23 investigated for the first time the adsorption–desorption, degradation, and leaching behaviors of EPM in  
24 agricultural soils from five exemplar sites in China (Phaeozem: S1, Anthrosol: S2, Ferralsol: S3, Alisol: S4, and  
25 Plinthosol: S5) through laboratory simulation experiments. Our results show that the EPM adsorption–desorption  
26 results were well fitted by the Freundlich model ( $R^2 > 0.9999$ ). In the analyzed soils, the Freundlich adsorption  
27 (i.e.,  $K_{f-ads}$ ) and desorption (i.e.,  $K_{f-des}$ ) coefficients of EPM varied between 0.85–32.22  $\text{mg}^{1-1/n} \text{L}^{1/n} \text{kg}^{-1}$  and  
28 between 0.78–5.02  $\text{mg}^{1-1/n} \text{L}^{1/n} \text{kg}^{-1}$ , respectively. The mobility of EPM in the soils S1–S5 was categorized as  
29 immobile, slightly mobile, highly mobile, slightly mobile, and slightly mobile, respectively. Moreover, the  
30 degradation of EPM reflected first-order kinetics: its half-life ranged between 37.46–66.00 d depending on the  
31 environmental conditions, and abiotic degradation was predominant in the degradation of this compound. Overall,  
32 the high leaching ability and desorption capacity of EPM were accompanied by a low adsorption capacity and  
33 there were no significant relationships between pH and the leaching rate of EPM in the five types of soils. In  
34 contrast, the organic matter content, cation exchange capacity, and soil clay content were the main responsible for  
35 the observed leaching rates. We found that EPM degrades easily, has a high adsorption affinity and a low mobility  
36 in S1, which result in a low contamination risk for groundwater systems. On the contrary, this compound degrades  
37 slowly in S2, S3, S4, and S5, due to a low adsorption affinity and moderate mobility, which result in a high  
38 contamination risk for groundwater systems. Therefore, our results may serve as a reference for evaluating the  
39 risks involved in the increasingly wide application of this compound.

40 **Keywords:** (*E*)-pyriminobac-methyl, herbicide, soil organic matter,  $K_{OC}$ , risk assessment

## 41 **1. Introduction**

42 Herbicides are usually applied to chemically control the growth of weeds associated with different types of crops,  
43 both in China and worldwide (Barchanska et al., 2021; Brillas, 2021). Unfortunately, with the applications of  
44 weedicides, they have been detected outside of their original application sites, meaning that they contribute to  
45 environmental contamination and food safety problems (Jiang et al., 2018; Perotti et al., 2020; Marvin and  
46 Bouzembrak, 2020). Therefore, the Guidelines for good herbicide application (Ny/T, 2011) and the National food  
47 safety standard -- Maximum residue limits for pesticides in food have been established in China (Gb, 2021), which  
48 contain the maximum residual limit (MRL) and acceptable daily intakes (ADI) of 548 commonly used pesticides,  
49 for example, the MRL of pyriminobac-methyl (PM) in paddy rice and brown rice is 0.2 and 0.1 ppm respectively,  
50 and the ADI of PM is 0.02 ppm. Most studies have reported that with the increasing use of glyphosate (a non-  
51 selective herbicide), especially in tea plantations (the detected MRL of glyphosate is 4.12 ppm much bigger than  
52 the limited value 1 ppm) and aquatic systems, the problem of excessive residues of glyphosate has attracted more  
53 and more attention, raising potential environmental threats and public health concerns (Liu et al., 2021a; Luo et  
54 al., 2019; Huang et al., 2016). Importantly, the environmental fate of herbicides in soil mainly depends on the  
55 adsorption–desorption, degradation, and leaching processes. In fact, herbicides can be transferred from soil to  
56 groundwater through surface runoff or leaching, resulting in groundwater pollution (Cueff et al., 2020; Gawel et  
57 al., 2020). Furthermore, the adsorption–desorption rate and the degradation capability of herbicides regulate the  
58 migration of herbicides: the groundwater ubiquity score (GUS) can be used to evaluate their ecological and  
59 environmental safety (Acharya et al., 2020; Liu et al., 2021b). However, few scholars have assessed the effects of  
60 soil properties on the adsorption–desorption, degradation, and leaching behaviors of weedicide, especially the  
61 environmental consequences of these changes.

62 PM [methyl-2-(4,6-dimethoxy-2-pyrimidinylloxy)-6-(1-methoxyiminoethyl) benzoate] (Fig. S1), is composed of  
63 a mixture of its (*E*) - isomer (I) and (*Z*) - isomer (II) as the active ingredient due to its chemical structure contain  
64 oxime(Song et al., 2010), a mixture of two isomers (I and II) in a > 9:1 (major/minor) ratio which was developed  
65 from sulfonyleurea by Kumiai Chemical Industry Co., Ltd. In 1996 (Tokyo, Japan)(Tamaru and Saito, 1996).  
66 Tamaru et al. (1997) reported that (*E*) - isomer (I) has been confirmed to restrain the plant enzyme  
67 acetolactate synthase (ALS) and prevent branched chain amino acid biosynthesis, and the (*E*) - pyriminobac-  
68 methyl (EPM) showed stronger soil adsorption and weaker hydrophilic properties than (*Z*) - pyriminobac-methyl  
69 (ZPM), thus EPM was selected as the best compound to develop a commercial weedicide, which is commonly  
70 used to control the growth of sedges and both gramineous and annual weeds. The chemistry of EPM is well  
71 understood; the octanol-water partition coefficient is 2.31 (low) at pH 7, 20 °C, the solubility - in water is  
72 9.25 mg L<sup>-1</sup> (low) at 20 °C, and the vapour pressure is just 3.1×10<sup>-5</sup> Pa (low) at 20 °C (Lewis et al., 2016). A  
73 distinct advantage of EPM as a weedicide is that, this compound has an herbicidal activity 1.5–2 times higher  
74 and requires an application rate 1/5–1/10 lower than bensulfuron-methyl (a broad-spectrum herbicide) on  
75 *Echinochloa crusgalli* and *Leptochloa chinensis* (Iwakami et al., 2015; Shibayama, 2001; Song et al., 2010).  
76 Notably, EPM can prevent the growth of *E. crusgalli* and *L. chinensis* populations and suppress them effectively  
77 over long periods, while being non-toxic, and eventually increasing the yield of paddy rice and subsequent crops  
78 (e.g., rape, cabbage, *Astragalus smicus*, wheat, and potato) (Iwafune et al., 2010; Qin et al., 2017; Tang et al.,  
79 2010; Yoshii et al., 2020). Nevertheless, few studies have lucubrated the environmental behaviors of EPM after it  
80 was widely used as herbicide in the farming industry.

81 Most former investigations on EPM as a weedicide mainly focused on the photo-transformation in water and low  
82 temperature storage stability in paddy rice. Inao et al. (2009) demonstrated that the photoconversion of PM in

83 water is the main fate, and the main process is EPM / ZPM reached approximately equilibrium after 4.5 h,  
84 furthermore, the EPM / ZPM ratio is about 1/1.35. Another researcher found that even if proper water management  
85 to prevent EPM surface runoff from paddy fields was practiced, a significant amount of EPM components were  
86 discharged into drainage channels through percolation (Sudo et al., 2018). Indeed, the harm of weedicide leaching  
87 have been frequently reported in groundwaters. Several studies have indicated that the leaching risk potential of  
88 herbicides to groundwater is positively correlated with its mobility in soil (Chen et al., 2021; Wang et al., 2019;  
89 Silva et al., 2019; Kaur et al., 2021; Willett et al., 2020). Guimares et al. (2019), who found that hexazinone  
90 (herbicide) proved to be a potential contaminant of groundwater and metribuzin (herbicide) presented high  
91 leaching in the soil profile. As well as metribuzin, atrazine was found to be accumulated in algal cells, which  
92 indicates that herbicide pollution might eventually affect the marine food web and even threaten the seafood safety  
93 of human beings (Yang et al., 2019). On the other hand, Kolakowski et al. (2020) and Mehdizadeh et al. (2021)  
94 reported that the residue levels of herbicides which were uptake by plants and the risk to consumers depends on  
95 the application technique, the environmental conditions, the stage of growth of plants, the volume of use, water  
96 quality and the use of coadjuvants. EPM is also proved to be safe in rice. Jia et al. (2020) showed that the detected  
97 MRL of EPM in paddy rice is 0.0092 ppm far less than the limited value 0.2 ppm. Hence, previous knowledge of  
98 the physico-chemical properties of soils cultivated with crops is essential to recommend the use of these herbicides  
99 in weed management.

100 In the paddy rice field, the half-life of EPM calculated from 4.0 to 19.3 days (half-life  $\leq$  30 day, easily  
101 degradable) (Gb, 2014c) monitored in the Lake Biwa basin, Japan (Iwafune et al., 2010), the sorption constants  
102 of the OC ( $K_{oc}$ ) values ranged from 372 to 741 (  $200 < K_{oc} \leq 1000$ , sub-difficultly adsorbed compound)(Gb,  
103 2014a) conducted with Habikino and Ushiku soils in Japan, indicating that EPM is low-persistence herbicide,

104 which result in a low contamination risk for groundwater systems(Inao et al., 2009). The Japanese Environment  
105 Agency sets limits for residues in paddy rice discharge water by allowing for a 10-fold dilution in river water and  
106 applying the drinking-water limit of EPM is  $200 \mu\text{g L}^{-1}$  (Hamilton et al., 2003). In China, EPM has been registered  
107 to control grassy weeds in paddy rice and brown rice fields at present (Gb, 2021). Nevertheless, the effects of soil  
108 properties on the adsorption–desorption, degradation, and leaching behaviors of EPM have rarely been reported.

109 A number of researchers have reported that the soil matrix is a highly complicated system, in which environmental  
110 processes (e.g., the sorption–desorption and leaching of herbicides) are affected by multiple factors, including the  
111 soil organic matter (OM) content, pH, cation exchange capacity (CEC), microbial or chemical degradation,  
112 chemical type, environmental conditions (e.g., temperature, humidity, and rainfall), and texture (Alonso et al.,  
113 2011; Rao et al., 2020; Xie et al., 2020; Zhou et al., 2019a). Nevertheless, soil organic or inorganic colloids  
114 and pH ( $\text{pH} < pK_a$  neutral state and  $\text{pH} > pK_a$  negative charge) can influence soil–herbicide interactions. In this  
115 context, the leaching of anionic compounds is likely (Pérez-Lucas et al., 2020). Moreover, the leaching of  
116 herbicides in soil and the associated risk of water pollution are both affected by sorption and desorption (Xie et  
117 al., 2020).

118 Until present, the environmental fate of EPM in soils has not been studied in detail. Clarifying the adsorption and  
119 transport of EPM in soil is very important for the protection of surface water and groundwater from EPM pollution.  
120 Hence, this study aimed at: 1) gaining an essential understanding of the adsorption–desorption, degradation, and  
121 leaching behaviors of EPM in agricultural soils through laboratory simulation experiments; 2) determining the  
122 effects of soil properties on the above behaviors in agricultural soils; and 3) conducting a basic evaluation of the  
123 safety and applicability of EPM in the environment. Overall, our results provide a scientific basis for the  
124 prevention or, at least, minimization of the possible effects of EPM on groundwater, as well as for modeling the

125 fate of EPM in the environment and the potentially associated risks.

## 126 **2. Materials and Methods**

### 127 *2.1. Chemicals*

128 EPM (99.0%; chemical formula:  $C_{17}H_{19}N_3O_6$ ; structure shown in Fig. S1) was obtained from ZZBIO Co., Ltd.  
129 (Shanghai, China). Moreover, we used only organic solvents of chromatographic grade (Sigma-Aldrich, Germany).

130 EPM was dissolved in acetonitrile, obtaining a  $1000\text{ mg L}^{-1}$  test mother liquor. Moreover, a standard EPM working  
131 solution ( $0.01\text{--}5.00\text{ mg L}^{-1}$ ) was prepared by diluting the stock solution with a  $\text{CaCl}_2$  solution ( $0.01\text{ mol L}^{-1}$ ),  
132 which was used as an electrolyte to maintain a constant ionic strength and reduce the cationic exchange.

133 In March 2020, five different soils were sampled from the surface layer (0–20 cm) of paddy fields located in five  
134 Chinese provinces: Phaeozem (S1, from Heilongjiang), Anthrosol (S2, from Zhejiang), Ferralsol (S3, from  
135 Jiangxi), Alisol (S4, from Hubei), and Plinthosol (S5, from Hainan). The soil samples were all air-dried, ground,  
136 and passed through a 2-mm sieve before being used. Afterward, standard soil testing methods were applied to  
137 define the basic physicochemical properties of the soils (Table S1) (Gee, 1986; Jackson, 1958; Nelson, 1985),  
138 which were then classified based on the system of the World Reference Base for Soil Resources (WRB) (L'huillier,  
139 1998). Interestingly, the EPM residues in the analyzed soils were always below the detection limit.

### 140 *2.2. Soils samples*

141 The batch equilibration method suggested by the GB 31270.4-2014 guidelines: Adsorption/Desorption in Soils  
142 for these soils (Gb, 2014a) was applied to conduct adsorption–desorption experiments. First, for the adsorption  
143 kinetics tests, each soil sample (2.0 g) was introduced in a centrifuge tube containing 10 mL of a EPM aqueous  
144 solution ( $1\text{ mg L}^{-1}$ ). For each of these tubes, we also analyzed a blank tube (which contained no herbicide) and a

145 control tube (which contained no soil). All the tubes were then shaken by an oscillator at  $25\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$  for different  
146 time intervals of 0.5, 1, 2, 4, 6, 8, 12, 16, 20, and 24 h.

147 The desorption kinetics were analyzed instead by taking 5 mL of supernatant from each tube after adsorption  
148 equilibration and by replacing them with an equal volume of  $\text{CaCl}_2$  solution (which contained no EPM). A  
149 microvortex mixer was used to thoroughly mix the resulting solution and an oscillator was used to shake it at  
150  $25\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$  for several time intervals: 0.5, 1, 2, 4, 6, 8, 12, and 24 h. Finally, for the high-performance liquid  
151 chromatography-mass spectrometry (UPLC-MS/MS) analyses, the samples were centrifuged for 10 min at  
152  $2,400\times g$  and the supernatants were filtered through  $0.22\text{-}\mu\text{m}$  mixed-cellulose ester filter membranes.

153 The adsorption–desorption equilibrium time of EPM in the five soils was 24 h (Fig. 1); moreover, the initial EPM  
154 concentrations adopted for these experiments were 0.01, 0.10, 0.50, 1.00, and  $5.00\text{ mg L}^{-1}$ . The concentration of  
155 EPM in the supernatant was determined after centrifugation. Then, the amount of adsorbed–desorbed EPM in  
156 each soil was calculated based on the concentration of EPM in the solution before and after the adsorption–  
157 desorption process. The supernatant removed after the adsorption experiments was replaced with 5 mL of  $\text{CaCl}_2$   
158 containing no EPM; then, the tubes were shaken for 24 h and centrifuged. Finally, the EPM concentration was  
159 determined based on the supernatant collected after this procedure. Considering the results of preliminary  
160 experiments and with the aim of desorbing the majority of the adsorbed EPM, we decided to repeat the desorption  
161 process for at least three times.

### 162 *2.3. Degradation experiments*

163 By following the GB 31270.1-2014 guidelines (Gb, 2014c), we performed a series of EPM soil degradation  
164 experiments. To ensure aerobic conditions, 20 g of each type of agricultural soil were weighed and introduced



165 in 250-mL Erlenmeyer flasks (in three replicates). Ultrapure water was added during the subsequent cultivation  
166 process in order to maintain the soil water content at 60% of the maximum water holding capacity. We then  
167 spiked each soil sample with 400  $\mu\text{L}$  of the 100  $\text{mg L}^{-1}$  EPM working solution (achieving an initial concentration  
168 of 2  $\text{mg kg}^{-1}$  in the soil: the water-soluble, organic solvent volume was  $\leq 1\%$ ) and then cultured in the dark in an  
169 incubator kept at  $25 \pm 1$   $^{\circ}\text{C}$ . Subsequently, we collected three parallel sub-samples on 0, 1, 2, 4, 6, 10, 15, 30, 45,  
170 60, 90, and 120 day, and the EPM content was determined by UPLC-MS/MS on the respective days of collection.  
171 The amount of water in the Erlenmeyer flasks was periodically adjusted during the culturing process with the  
172 aim of retaining the original water-holding state. Each treatment was done in triplicate, totalizing 60 samples per  
173 treatment (5 soil samples per treatment per sampling day; 12 sampling days in total), The following experiment  
174 was done in the same way.

175 Another set of experiments was conducted under anaerobic conditions. In this case, we first cultured the soil  
176 samples for 30 days and then added a 2 cm-thick water layer to each of them. To maintain the desired conditions,  
177  $\text{N}_2$  was continuously introduced into the culture system. The soil samples were subsequently moved into an  
178 incubator and cultivated in the dark at  $25 \pm 1$   $^{\circ}\text{C}$ . Finally, three parallel sub-samples were collected on 0, 1, 2, 4,  
179 6, 10, 15, 30, 45, 60, 90, and 120 day, and the EPM content was determined by UPLC-MS/MS on the respective  
180 days of collection.

181 A set of degradation experiments was performed under sterilized conditions. With this objective, the sterilized  
182 soils (20 g each) were weighed and introduced in 250-mL Erlenmeyer flasks in three replicates. Notably, in order  
183 to keep the soil water content at 60% of the maximum water holding capacity, sterile water was added during the  
184 cultivation process. Then, each soil sample was spiked with 400  $\mu\text{L}$  of the 100  $\text{mg L}^{-1}$  EPM working solution,  
185 achieving an initial concentration of 2  $\text{mg kg}^{-1}$  (the water-soluble, organic solvent volume was  $\leq 1\%$ ). The samples

186 were hence moved into an incubator and cultured in the dark at  $25 \pm 1$  °C. Three parallel sub-samples were  
187 collected on 0, 1, 2, 4, 6, 10, 15, 30, 45, 60, 90, and 120 day, and the EPM content was determined by UPLC-  
188 MS/MS on the respective days of collection.

189 These experiments were done under different soil moisture conditions and aerobic conditions, at a EPM  
190 fortification level of  $2 \text{ mg kg}^{-1}$ . After adjusting their moisture by adding water (water percentage = 40%, 60%,  
191 and 80% of the total volume), the soils were incubated in the dark at  $25 \pm 11$  °C. During this last phase, we  
192 regularly added ultrapure water to keep the moisture at 40%, 60%, and 80%.

#### 193 *2.4. Leaching experiments*

194 The herbicide leaching process was investigated by following the GB 31270.5-2014 guidelines (Gb, 2014b). PVC  
195 columns (length = 35 cm, internal diameter = 4.5 cm), each hand-packed with 600–800 g of one soil type, were  
196 used to observe the downward movement of the herbicide. Notably, the top 3 cm and the bottom 2 cm were filled  
197 with quartz sand (for minimizing soil disturbance) and glass wool + sea sand (for avoiding soil loss). After packing  
198 each column, we removed any air still present in the column by adding  $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$ ; moreover, the excess  
199 water was eliminated by gravity. The pore volume (PV) was determined by subtracting the volume of water  
200 leached from that of the water added. Subsequently, 1 mL of acetonitrile solution containing  $200 \text{ } \mu\text{g mL}^{-1}$  of the  
201 herbicide (spiking level =  $1 \text{ } \mu\text{g g}^{-1}$ ) was added to the top of each column. afterward, the adsorption equilibrium  
202 was achieved by infiltrating  $700 \text{ } \mu\text{L}$  of  $100 \text{ mg L}^{-1}$  EPM solution into soil surface and leaving it to rest for 24 h.  
203 To simulate rainfall leaching,  $2,000 \text{ mL}$  of  $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$  solution ( $21 \text{ mL h}^{-1}$ ) were added into the soil column  
204 at a peristaltic pump speed of  $250 \text{ mL } 12 \text{ h}^{-1}$ . The leachate was collected every 8 h with a conical flask.  
205 Subsequently, each soil column was extracted, cut into three parts (length = 10 cm), and analyzed by UPLC-  
206 MS/MS on the same day. The total mass of the leachate and soil fractions along the soil column was determined,

207 together with the EPM and water contents within each of them.

## 208 *2.5. Extraction and final analyses*

209 The soil samples were transferred to centrifuge tubes and 10 mL of acetonitrile (containing 0.1% of ammonia  
210 water) were added to each of them for extracting EPM. After vortexing the tubes for 5 min, we added 2 g of NaCl  
211 and 3 g of MgSO<sub>4</sub>. Then, the tubes were capped and vortexed again for 1 min and centrifuged at 2,400 × g for 5  
212 min. The supernatant (1.5 mL) was transferred into a 2.5-mL single-use centrifuge tube that was already containing  
213 the sorbent (50 mg C<sub>18</sub> + 150 mg MgSO<sub>4</sub>). Afterward, all the samples were vortexed again for 1 min and  
214 centrifuged at 5,000 rpm for 5 min (Jia et al., 2019b). Finally, the resulting supernatant was extracted with a sterile  
215 syringe, passed through a 0.22-μm organic membrane filter, and poured into vials for UPLC system (1260 series,  
216 Agilent Technologies, USA) equipped with a triple quadrupole mass spectrometer (6460C series, Agilent  
217 Technologies) using positive ion mode in multiple reaction monitoring (MRM) mode analysis. The instrument  
218 parameters for Agilent 6460C QQQ UPLC-MS/MS analysis are as follows: The flow rate was maintained at 0.2  
219 mL min<sup>-1</sup>, and the column (Agilent ZORBAX Eclipse XDB-C18, length 150 mm, inner diameter = 4.6 mm, 5μm  
220 coating) was heated to 35°C. The mobile phase A was water which consisted of 0.1% formate and mobile phase  
221 B was acetonitrile. Gradient condition was: 0.0-0.5 min, 20% B; 0.5-1.0 min, 20%-80% B; 1.0-4.0 min, 80% B;  
222 4.0-5.0 min, 20% B. The mass spectrometer was operated in electrospray ionization positive with MRM scanning  
223 mode, dry gas temperature at 500 °C, Ion source temperature at 150 °C, desolvation gas flow at 1000 L h<sup>-1</sup>;  
224 capillary voltage at 2500 V; cone voltage at 18 V and collision gas was argon, dwell time at 50 ms, collision  
225 pressure at 58 eV. *The detail information of the determination parameters of the chromatographic method, i.e.,  
226 repeatability, reproducibility, recovery, measurement uncertainty, detection limit and limit of quantification were  
227 shown in the supplementary material (Fig. S2-S4 and Table S2-S4).*

228 The efficiency of the EPM extraction during the adsorption–desorption, degradation, and leaching experiments  
229 was evaluated based on the results of recovery experiments. The average recovery rates of EPM in the adsorption–  
230 desorption experiments, at initial spiked concentrations of 0.1 and 1.0 mg kg<sup>-1</sup> in the soils, varied between 94.3–  
231 102.4% (RSD = 1.1–3.8%). Meanwhile, the average recovery rates of EPM in soil in the degradation experiments,  
232 at initial spiked concentrations of 0.01, 0.2, and 2.0 mg kg<sup>-1</sup> in the soils, ranged between 92.6–106.0% (RSD =  
233 1.1–2.9%). Furthermore, the average recovery rates of EPM at initial spiked concentrations of 0.0001, 0.01, and  
234 0.1 mg L<sup>-1</sup> in the supernatant of soils were 88.7–107.9% (RSD = 1.7–4.9%). Furthermore, the average recovery  
235 rates of EPM in the leaching experiments at initial spiked concentrations of 0.05 and 1.0 mg kg<sup>-1</sup> in the soils were  
236 95.8–109% (RSD = 1.6–4.4%).

## 237 2.6. Data analysis

238 The relationship between the concentrations of EPM sorbed in the soil and in the aqueous solution during the  
239 sorption–desorption equilibrium was described through the linear [Eq. (1)] and Freundlich [Eq. (2)] models  
240 (Azizian et al., 2007; Yang et al., 2021):

$$241 \text{ Linear model: } C_s = KC_e + C \quad (1)$$

$$242 \text{ Freundlich model: } C_s = K_f C_e^{1/n} \quad (2)$$

243 where  $C_s$  (mg kg<sup>-1</sup>) indicates the adsorption of EPM in the soil,  $C_e$  (mg L<sup>-1</sup>) the EPM concentration in the solution  
244 during the adsorption equilibrium,  $C$  (mg kg<sup>-1</sup>) the amount of soil adsorption when the EPM concentration was 0  
245 during the adsorption equilibrium,  $K$  (mL g<sup>-1</sup>) and  $K_f$  (mg<sup>1-1/n</sup> L<sup>1/n</sup> kg<sup>-1</sup>) the adsorption–desorption constants of the  
246 linear and Freundlich models, respectively ( $K_{f-ads}/K_{f-des}$  in the adsorption–desorption process), and  $1/n$  the  
247 adsorption empirical constant (which provides information about the non-uniformity of the adsorbent surface).

248 For the isothermal sorption tests, the amount of EPM adsorbed in the soil was estimated using the subtractive  
249 method [Eq. (3)]:

$$250 \quad C_S = \frac{(C_0 - C_e) \times V}{m} \quad (3)$$

251 where  $C_0$  ( $\text{mg L}^{-1}$ ) is the amount of soil adsorption when the concentration of EPM was 0 during the adsorption  
252 equilibrium,  $m$  the soil mass (2.0 g), and  $V$  the solution volume (10 mL).

253 The amount of EPM retained by the soil after desorption was obtained instead by using [Eq. (4)], while the  
254 hysteresis index ( $H$ ) was estimated by applying [Eq. (5)] (Fan et al., 2021; Zhang et al., 2020b):

$$255 \quad C_{sj} = \frac{C_0 \times V}{m} - \frac{C_{ej} \times V}{2m} - \frac{V}{m} \sum_{n=1}^j C_e (j - 1) \quad (4)$$

$$256 \quad H = \frac{1/n_{F-des}}{1/n_{F-ads}} \quad (5)$$

257 where  $C_{sj}$  ( $\text{mg kg}^{-1}$ ) is the concentration of EPM adsorbed by the soil after the  $j$ -th desorption ( $i = 1-5$ ),  $C_{ej}$  ( $\text{mg}$   
258  $\text{L}^{-1}$ ) the EPM concentration in the supernatant after the  $j$ -th desorption,  $H$  the hysteresis coefficient, and  $1/n_{ads}$  and  
259  $1/n_{des}$  the empirical adsorption and desorption constants, respectively.

260 The distribution coefficient ( $K_d$ ) was calculated based on the distribution ratio of EPM in the water–soil system  
261 by using [Eq. (6)] (Carballa et al., 2008; Ternes et al., 2004):

$$262 \quad K_d = \frac{C_S}{C_e} \quad (6)$$

263 The sorption constants of the OC ( $K_{OC}$ ) and OM ( $K_{OM}$ ) contents were calculated through [Eqs. (7) and (8)] (Rae  
264 et al., 1998; Zhang et al., 2011), respectively. Moreover, the Gibbs free energy change of sorption ( $\Delta G$ ,  $\text{kJ mol}^{-1}$ )  
265 (Jia et al., 2019a) and the GUS (Gustafson, 1989) were calculated as follows:

266

267 
$$K_{OM} = 100 \times K_{f-ads} / OM\% \quad (7)$$

268 
$$K_{OC} = 100 \times K_d / OC\% \quad (8)$$

269 
$$\Delta G = -RT \ln K_{OM} / 1000 \quad (9)$$

270 
$$GUS = \lg t_{1/2} \times (4 - \lg K_{OC}) \quad (10)$$

271 where *OM* % and *OC* % represent the soil OM and OC contents, respectively, *R* the molar gas constant (8.314 J  
 272 K<sup>-1</sup> mol<sup>-1</sup>), *T*(K) the absolute temperature, and *t*<sub>1/2</sub> the half-life (in days) given by [Eq. (12)]. Organic contaminants  
 273 were categorized into five types: highly adsorbed compounds (*K*<sub>OC</sub> > 20,000), sub-highly adsorbed compounds  
 274 (5,000 < *K*<sub>OC</sub> ≤ 20,000), medium-adsorbed compounds (1,000 < *K*<sub>OC</sub> ≤ 5,000), sub-difficultly adsorbed compounds  
 275 (200 < *K*<sub>OC</sub> ≤ 1,000), and difficultly adsorbed compounds (*K*<sub>OC</sub> ≤ 200)(Gb, 2014a).

276 The degradation data relative to herbicides in soil could be successfully fitted to a first-order kinetic model [Eq.  
 277 (11)], previously used in similar studies (Bailey et al., 1968; Liu et al., 2021b; Ou et al., 2020):

278 
$$C_t = C_0 e^{-kt} \quad (11)$$

279 where *C*<sub>*t*</sub> (mg kg<sup>-1</sup>) and *C*<sub>0</sub> (mg kg<sup>-1</sup>) are the concentrations of EPM in the soil at incubation times *t* (d) and 0 (d),  
 280 respectively, while *k* is the first-order rate constant (d<sup>-1</sup>).

281 The half-life (*t*<sub>1/2</sub>) to be used in above model was calculated through [Eq. (12)] (Yin and Zelenay, 2018):

282 
$$t_{1/2} = 0.693/k \quad (12)$$

283 Four categories of herbicide degradability were defined: easily degradable (*t*<sub>1/2</sub> ≤ 30), moderately degradable  
 284 (30 < *t*<sub>1/2</sub> ≤ 90), slightly degradable (90 < *t*<sub>1/2</sub> ≤ 180), and poorly degradable (*t*<sub>1/2</sub> > 180)(Gb, 2014c).

285 Based on the content of EPM in different sections of the soil columns and in the leachate [Eq. (13)](Gb, 2014b),  
286 we were able to calculate the leaching rate of EPM:

$$287 \quad R_i = \frac{m_i}{m_0} \times 100 \quad (13)$$

288 where  $R_i$  (%) is the ratio of EPM content in each soil section or in the leachate to the total added amount,  $m_i$  (mg)  
289 the mass of EPM in each soil section (where  $i = 1, 2, 3,$  and  $4,$  representing the 0–10 cm, 10–20 cm, and 20–30  
290 cm soil sections and in the leachate, respectively), and  $m_0$  (mg) the total added amount of EPM ( $m_0 = 0.02$  mg).  
291 Regarding the mobility scheme we defined the following  $R_i$  ranges: class 1 (immobile,  $R_1 > 50$  %), class 2 (slightly  
292 mobile,  $R_2 + R_3 + R_4 > 50$  %), class 3 (mobile,  $R_3 + R_4 > 50$  %), and class 4 (highly mobile,  $R_4 > 50$  %)(Gb,  
293 2014b).

294 The data fittings (to the linear and Freundlich models for the adsorption isotherms and to the simple first-order  
295 kinetic model for degradation) were conducted with OriginPro 8.05 (OriginLab Corp., Northampton, USA). All  
296 the values reported here were calculated as the means of three replicates; furthermore, the differences between  
297 these means were statistically analyzed through Duncan's multiple range test, while their reciprocal relationships  
298 were determined through a Spearman's correlation analysis using SPSS Statistics 22.0 (IBM SPSS, Somers, USA).

### 299 **3. Results and discussion**

#### 300 *3.1. Adsorption–desorption kinetics*

301 The adsorption and desorption kinetic curves of EPM in different types of agricultural soils are shown in Fig. 1.  
302 After EPM had been in contact with the soil solution for 1 h, the concentration of EPM exhibited a sharp drop  
303 (from 0 to 95.35, 75.45, 51.57, 77.41 and finally 65.84 % between S1–S5). This event corresponded to the fast  
304 sorption phase. After 2–8 h, the EPM soil system entered the slow adsorption stage and there was a gradual

305 increase in the sorption of EPM. This last process reached an equilibrium state of EPM sorption after 8 h, which  
306 was reflected by stable concentrations of EPM. The sorption of EPM decreased from the Phaeozem (S1, 97.99%)  
307 to the Anthrosol (S2, 79.69%), Alisol (S4, 77.81%), Plinthosol (S5, 72.57%), and Ferralsol (S3, 52.35%) (Fig.  
308 1a). This trend reflected the soils' OM contents. Previous studies have also found that the sorption of organic  
309 chemicals in soils is mainly related to their OM contents (Xu et al., 2021; Zhou et al., 2019b).

310 The desorption equilibration of EPM in soil was slightly slower and a hysteresis effect was observed. The rapid  
311 and slow desorption stages occurred between 0–2 h and 2–12 h, respectively; afterward, the concentration of EPM  
312 remained unchanged, until the desorption process reached its equilibrium state (within 24 h). Based on these data,  
313 we defined 24 h as the period of EPM adsorption-desorption. The desorption value of EPM observed in our  
314 experiments after 24 h increased from the Phaeozem (S1, 8.04%) to the Anthrosol (S2, 12.07%), Alisol (S4,  
315 14.48%), Plinthosol (S5, 17.55%), and Ferralsol (S3, 24.08%) (Fig. 1b).

316 The sorption of OM in soil typically occurs during the rapid reaction and slow equilibrium phases (Calvet, 1989).  
317 The tendency of sorbed hydrophobic organic pollutant to become more strongly bound with increasing organic  
318 matter (OM) contents of the soils is well demonstrated for EPM. This is consistent with previously reported  
319 observations that for sorbents with organic-carbon content greater than 0.1%, a highly significant positively  
320 correlation was found between the adsorption constants of non-polar or weakly polar organic compounds and the  
321 OM of soils (Schwarzenbach and Westall, 1981; Chefetz et al., 2004). The main reason is that the OM of soils has  
322 special binding sites with organic pesticide molecules. With the increase of OM content, the adsorption sites also  
323 increased, thus increasing the herbicide adsorption capacity (Stevenson, 1972; Ahmad et al., 2001; Delle Site,  
324 2001; Chianese et al., 2020). The role of different components of the OM in determining herbicide sorption has  
325 been clearly observed in previous studies. Hartley (1960) had speculated that the 'oily' constituent of the OM



326 might be responsible for uptake of nonionic compounds by soil. The existence of such a lipid phase was supported  
327 by Schnitzer and Khan (1972), who reported the presence of fatty acids and alkanes at the surface of the OM  
328 resulting from long alkyl chains projecting from the surface. They suggested that interactions such as hydrogen  
329 bonding might be important in uptake of nonionic contaminants by this lipid fraction. The hydrophobicity of the  
330 OM has generally been reported to originate from aromatic and alkyl domains of the organic matter component  
331 (Ahmad et al., 2001). Murphy and Zachara (1995) suggested the presence of heterogeneous sorption sites on the  
332 OM and considered the most hydrophobic domains as the most energetic and strong binding sites. Therefore, the  
333 reduction of the EPM content in the solution before and after the experiment was likely due to soil sorption.  
334 According to the above results, the soil sorption rate was inversely proportional to the soil desorption rate toward  
335 EPM.

### 336 3.2. Adsorption–desorption isotherms

337 Non-linear adsorption–desorption isotherms of EPM were observed (Fig. 1). When the concentration of EPM  
338 was low, this compound was preferentially adsorbed by OM (which has a strong adsorption capacity);  
339 meanwhile, soils with higher OM contents (e.g., Phaeozems, S1) desorbed EPM slowly. The positive  
340 relationship between sorption and OM has been reported previously (Hochman et al., 2021; Obregón Alvarez  
341 et al., 2021; Patel et al., 2021). Moreover, the adsorption ability of EPM has been found to be high, similar  
342 to those of other herbicides (e.g., chlorsulfuron, imazamethabenz-methyl, flumetsulam, and bispyribac-  
343 sodium) (Kalsi and Kaur, 2019; Medo et al., 2020; Spadotto et al., 2020). Generally, a low mobility of  
344 herbicides in soil is related to a high sorption constant. Hence, the EPM contained in the soils tested in this  
345 study (excluding the phaeozem, S1) is likely to have been polluting the groundwater and surface water of the  
346 respective areas of origin.

347 OM adsorption in soil is currently explained mainly by partitioning and adsorption-site theories (Martins and  
348 Mermoud, 1998), which are well described by the linear and Freundlich isotherm models, respectively. Our  
349 isothermal sorption and desorption data were thus fitted to these two models: the obtained fitting parameters are  
350 listed in Table 1. The average  $R^2$  value for the linear model (0.9950) was smaller than that for the Freundlich  
351 model (0.9999); moreover, the  $C$  values obtained for the Plinthosol (S5,  $-0.01 \pm 0.06$ ) by fitting the data to the  
352 linear model were negative (Table 1) and did not meet the experimental requirements, indicating that this type of  
353 model was not suitable for this experiment. Meanwhile, the sorption-site theory was found to more accurately  
354 describe the sorption–desorption process: the Freundlich model provided a more accurate description of the EPM  
355 sorption-desorption characteristics observed in this study.

356 Generally, larger  $K_{f-ads}$  values correspond to higher sorption capacities (Carneiro et al., 2020; Khorram et al., 2018;  
357 Silva et al., 2019). Here, the  $K_{f-ads}$  values of EPM ranged between 0.85 (in S4) and 32.22 (in S1) ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{kg}^{-1}$ ),  
358 while the  $1/n_{f-ads}$  values ranged between 0.80 (S1) and 1.06 (S5) (Table 1). In brief, S5 showed an S-type  
359 adsorption isotherm (since  $1/n_{f-ads} > 1$ ), while S1, S2, S3, and S4 showed an L-type adsorption isotherm (since  
360  $1/n_{f-ads} < 1$ ). In this study, the  $H$  values of EPM ranged between 0.013 (Phaeozem, S1) and 0.845 (Ferralsol, S3).  
361 Since the  $H$  values were  $< 0.7$  in S1, S2, S4, and S5, these particular soils showed a positive hysteresis: the  
362 desorption rate of EPM was lower than its sorption rate. Meanwhile, since the  $H$  values in S3 were between 0.7–  
363 1.0, the sorption and desorption rates were in equilibrium: S3 did not exhibit any obvious hysteresis. Similar  
364 results were reported that hysteresis was absent when  $0.7 < H < 1$  (Gao and Jiang, 2010; Yue et al., 2017; Barriuso  
365 et al., 1994).

366 Soil physicochemical properties are important factors influencing herbicide adsorption behaviors (Urach Ferreira  
367 et al., 2020; Wei et al., 2020). We determined the relationship between the Freundlich adsorption–desorption

368 constant and the soil physicochemical (soil pH, CEC, soil clay content, OM content, and OC content) properties  
369 and carried out a linear correlation analysis based on the experimental data fitting (Table S5). The results showed  
370 that the soil pH, CEC, soil clay content, OM content, and OC content were positively correlated with  $K_{f-des}$  and  $K_{f-ads}$   
371 ( $slope > 0$ ). In soils, some polar contents, ionizable groups, and the CEC tend to increase during OM  
372 humification (Calvet, 1989; Meimaroglou and Mouzakis, 2019; Rae et al., 1998). This mechanism possibly  
373 explains the adsorption of EPM in soils high in OM and CEC. Our findings agree with those of Acharya et al.  
374 (2020) and García-Delgado et al. (2020): the soil humic acid and clay fractions (high in OM and CEC and  
375 possessing a high number of active sites) are capable of intense EPM adsorption; in contrast, the soil coarse sand  
376 fraction (low in OM and CEC) is characterized by a weaker EPM adsorption. Notably, the soil with the highest  
377 fumigant adsorption capacity was also possibly that with the highest OM abundance and CEC. For example,  
378 strong linear and positive correlations have been found between the adsorption–desorption of benzobicyclon  
379 hydrolysate and the soil clay content, OC content, OM content, and CEC, while moderate linear and negative  
380 correlations were observed between those processes and the soil pH (Rao et al., 2020).

381 The  $K_{OC}$  value is typically used to indicate the EPM sorption capacity of a soil (Fao, 2000; Xiang, 2019) (see  
382 Table 2). EPM was sub-difficultly adsorbed in S2, S3, S4, and S5: this aspect was reflected by the  $K_{OC}$  values,  
383 which ranged between 200–1,000. However, in S1 the  $K_{OC}$  values ranged between 1,000–5,000, indicating a  
384 medium adsorbance of EPM in this soil. Overall, an increasing trend in the mobility of EPM was observed from  
385 the Phaeozem (S1) to the Anthrosol (S2), Alisol (S4), Plinthosol (S5), and Ferralsol (S3). We hence infer that a  
386 relatively low soil adsorption capacity is linked to a relatively high mobility of EPM in that soil.

387 The degree of spontaneity of the adsorption process can be quantitatively evaluated based on variations in the  $\Delta G$   
388 values: negative  $\Delta G$  values generally indicate that an adsorption process is spontaneous and exothermic (Nandi et

389 al., 2009). Notably, the change of free energy linked to physical adsorption is smaller than that linked to  
390 chemisorption. The former is in the range of  $-20$  to  $0$   $\text{kJ mol}^{-1}$ , while the latter is in the range of  $-80$  to  $-400$   $\text{kJ}$   
391  $\text{mol}^{-1}$  (Bulut and Aydın, 2006; Yu et al., 2004). We found that the  $\Delta G$  values relative to EPM adsorption in all  
392 soils were comprised between  $-16.2242$  and  $-12.5753$   $\text{kJ mol}^{-1}$ . Therefore, the adsorptions we observed in our  
393 experiments can be regarded as typically spontaneous and exothermic physical adsorptions (Table 2).

### 394 3.3. Degradation of EPM in soil

395 To investigate the effects of aerobic and anaerobic microorganisms on EPM degradation, we sterilized the soil  
396 samples or removed all aerobic microorganisms. The soil samples were kept in the dark at  $25$   $^{\circ}\text{C}$ , maintaining a  
397 soil moisture of  $60\%$ . The degradation kinetics of EPM under aerobic, anaerobic, and sterilized conditions are  
398 depicted in Fig. 2, while the fitted parameters are summarized in Table 3. The  $R^2$  values for EPM in the five soils  
399 ranged between  $0.9313$ – $0.9924$ , suggesting that the first-order kinetic model agreed with the correspondent  
400 degradation data. The half-life of EPM ranged between  $37.46$ – $58.25$  d in the aerobic soils, between  $41.75$ – $59.74$   
401 d in the anaerobic soils, and between  $60.87$ – $66.00$  d in the sterilized soils. A moderate degradation ( $30$  d  $< t_{1/2} \leq$   
402  $90$  d) of EPM was observed under aerobic, anaerobic, and sterilized conditions. These results can be partly  
403 explained by aerobic and anaerobic transformations occurring in the soils, which have been described by the GB  
404 31270.1-2014 guidelines for the testing of chemicals (Gb, 2014c). Overall, the half-life of EPM decreased from  
405 the aerobic to the anaerobic and sterilized soils. Understanding the degradation kinetics of herbicides is critical  
406 for predicting their persistence in soil and the soil parameters, which affect regional agronomic and environmental  
407 practices (Buerge et al., 2019; Buttiglieri et al., 2009). Under dark conditions, the degradation of herbicides in soil  
408 mainly results from microbial and abiotic degradation (Marín-Benito et al., 2019). In this study, when EPM was  
409 retained under dark conditions for  $30$  d, its degradation rates in all soils under sterilized conditions ( $35.44$ ,  $36.27$ ,

410 33.27, 32.80, and 34.78%) were a little slower than under anaerobic (48.60, 41.51, 35.92, 35.61, and 38.07%) and  
411 aerobic conditions (53.32, 43.20, 36.73, 35.61, and 39.31%) (Fig. 2). As the degradation rate increased only by  
412 10% compared to that observed under sterilized conditions, degradation under aerobic/anaerobic conditions  
413 appeared to be mainly abiotic degradation. In contrast, other studies have found that anaerobic microorganisms  
414 are predominant contributors in the degradation process and capable of accelerating it. For example, the  
415 degradation rates of phenazine-1-carboxamide (PCN) were much higher under anaerobic than aerobic conditions,  
416 due to its own structural characteristics (Ou et al., 2020). Between 30–120 d, there were no significant differences  
417 in the degradation rates of EPM between sterilized and unsterilized soils, suggesting that EPM degradation was  
418 largely abiotic in this time interval. This might be attributed to a low bioavailability of EPM for microbial  
419 degradation, derived from a high adsorption affinity of this compound under the right OM content and pH  
420 conditions (Liu et al., 2021b; Wang et al., 2020a). Overall, it appears that EPM decomposition in the tested soils  
421 was mainly driven by abiotic degradation.

422 The degradation rate of EPM decreased from S1 to S2, S4, S5, and S3 under both aerobic and anaerobic conditions  
423 (Table 3). A negative correlation was noted between the half-life of EPM and the soil OM content and CEC under  
424 aerobic conditions (slope < 0,  $P < 0.05$ ;  $R^2 = 0.9478$  and  $0.8022$ , respectively); besides, a negative correlation was  
425 observed between the half-life of EPM and the soil OM content under aerobic conditions (slope < 0,  $P < 0.05$ ,  $R^2$   
426 =  $0.8983$ ). Notably, an abundance of OM and high CEC result in an increase of the carbon sources accessible to  
427 microorganisms, effectively stimulating their activity (Xu et al., 2020). In the presence of microorganisms, the  
428 particularly high OM and CEC characterizing S1, resulted in the fastest EPM degradation among those observed  
429 in all soils under aerobic and anaerobic conditions. However, under sterilized conditions, the degradation rate of  
430 EPM decreased from S2 to S4, S1, S5, and S3 (Table 3); moreover, the half-life of EPM and the soil pH exhibited

431 a negative correlation under these same conditions (slope < 0,  $P < 0.05$ ,  $R^2 = 0.8850$ ; Table S6). The rate of EPM  
432 hydrolysis is known to be positively affected by alkaline soil pH. This relationship explains why, in the presence  
433 of elevated hydrolysis and under sterilized conditions, the fastest degradation behavior among all the tested soils  
434 was observed in S2 (which was characterized by the highest pH). Notably, the highest differences in the  
435 degradation rate of EPM were observed under aerobic conditions. In order to comprehensively evaluate the  
436 influence of various factors on this degradation rate, we hence focused on the analysis of data collected under  
437 aerobic conditions.

438 The data regarding the degradation behavior of EPM in the tested soils (Table 4 and Fig. 2) conform to first-order  
439 kinetics ( $R^2 > 0.8769$ ). The half-life of EPM varied depending on the moisture conditions: it diminished from soils  
440 with a 60% moisture to those with moisture of 80% and 40%. Additionally, after 120 days, the degradation rates  
441 of EPM in soils with a 40% moisture (74.59, 73.93, 69.98, 73.21, and 71.25 for S1–S5, respectively) were  
442 obviously lower than those in soils with 80% (77.55, 75.38, 72.79, 75.44, and 73.62 for S1–S5, respectively) and  
443 60% (80.04, 77.31, 75.43, 77.78, and 75.77% for S1–S5, respectively) moistures (Table 4 and Fig. 2d, e). These  
444 results show that, when the soil moisture increased from 40% to 60%, the decay rate of EPM accelerated, possibly  
445 due to the stimulation of a degradation pathway (e.g., through aerobic microorganisms and chemical hydrolysis)  
446 linked to the increase in soil moisture (Wang et al., 2014; Liu et al., 2021b). Conversely, EPM showed a slower  
447 decay when the soil moisture increased from 60% to 80%. This phenomenon might have been caused by an  
448 increase in sorption, which would have made EPM less bioavailable. This effect was more or less important  
449 according to the predominance of different biotic pathways of degradation (Bento et al., 2016; García-Valcárcel  
450 and Tadeo, 1999).

#### 451 3.4. Leaching potential

452 The correspondent results are shown in Fig. 3. It was found that the fluidity of EPM was lower in S<sub>1</sub> than in S<sub>2</sub>,  
453 S<sub>3</sub>, S<sub>4</sub>, or S<sub>5</sub>. Furthermore, the R<sub>i</sub> values of this compound in S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>, S<sub>4</sub>, and S<sub>5</sub> were R<sub>1</sub> = 99 %, R<sub>2</sub> + R<sub>3</sub> + R<sub>4</sub> =  
454 55.5 %, R<sub>4</sub> = 71.95 %, R<sub>2</sub> + R<sub>3</sub> + R<sub>4</sub> = 76 %, and R<sub>2</sub> + R<sub>3</sub> + R<sub>4</sub> = 74 %, respectively. Based on the Test guidelines  
455 on environmental safety assessment for chemical pesticide-Part 5: Leaching in soil (Gb, 2014b), the mobility of  
456 EPM in the soils S<sub>1</sub>–S<sub>5</sub> was categorized as immobile, slightly mobile, highly mobile, slightly mobile, and slightly  
457 mobile, respectively. The soil OM content was found to be the most important soil property influencing the  
458 mobility of molecular herbicides, followed by the clay content and the CEC. A lower clay content is usually  
459 associated with a higher sand content, a higher proportion of large pores, a smaller specific surface area per soil  
460 unit volume, and a lower adsorption affinity for herbicides, which, overall, result in a greater herbicide mobility  
461 (Boyd et al., 1988; De Matos et al., 2001; Kulshrestha et al., 2004; Temminghoff et al., 1997). We found that a  
462 lower soil OM content corresponded to a weaker adsorption affinity, a weaker tendency of EPM to pass from the  
463 soil solution to the solid phase, a higher availability of EPM for leaching, and a stronger mobility of this same  
464 compound. Notably, the OM content increased from the Ferralsol (S<sub>3</sub>) to the Plinthosol (S<sub>5</sub>), Alisol (S<sub>4</sub>),  
465 Anthrosol (S<sub>2</sub>), and Phaeozems (S<sub>1</sub>), while the mobility of EPM increased from the Phaeozem (S<sub>1</sub>) to the  
466 Anthrosol (S<sub>2</sub>), Alisol (S<sub>4</sub>), Plinthosol (S<sub>5</sub>), and Ferralsol (S<sub>3</sub>). This mobility tendency is the opposite compared  
467 to the adsorption affinity tendency of EPM in the five soils. As a matter of fact, it is generally known that the  
468 mobility of EPM in soil increases as its adsorption affinity decreases. Similar conclusions were reached through  
469 the study of other herbicides (Acharya et al., 2020; Zhang et al., 2020a).

470 Here, the GUS was also used to estimate both the leaching potential of chemicals and the risk of contaminants  
471 into groundwater. The GUS values of EPM in S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>, S<sub>4</sub>, and S<sub>5</sub> were 0.9765, 2.0402, 2.7160, 2.3755, and  
472 2.6765, respectively (Table 2). The GUS value in S<sub>1</sub> was considerably lower than 1.8, EPM should have little

473 leaching potential in this soil (Gustafson, 1989; Wang et al., 2020b); meanwhile, since the GUS values in the S2,  
474 S3, S4, and S5 soils were between 1.8–2.8, EPM has a considerable leaching potential there and, possibly, the  
475 ability to pollute groundwater (Huang, 2019; Martins et al., 2018). Overall, we can infer that the risk of  
476 groundwater contamination by EPM is low in Phaeozem (S1), due to the low mobility of this compound; however,  
477 the risk is much higher when the same compound is contained in Anthrosol (S2), Ferralsol (S3), Alisol (S4), and  
478 Plinthosol (S5).

#### 479 **4. Conclusions**

480 In this study, we found that EPM degrades easily, has a high adsorption affinity and a low mobility in Phaeozem  
481 (S1), which result in a low contamination risk for groundwater systems. On the contrary, this compound degrades  
482 slowly in Anthrosol (S2), Ferralsol (S3), Alisol (S4), and Plinthosol (S5), due to a low adsorption affinity and  
483 moderate mobility, which result in a high contamination risk for groundwater systems. The adsorption–desorption,  
484 degradation, and leaching of EPM were systematically explored in five agricultural soils. We noticed that physical  
485 adsorption was the main mode of EPM adsorption. The effects of soil physicochemical properties on the  
486 adsorption and desorption of this compound were quantified by linear regression analysis. In this regard, the  
487 Freundlich adsorption ( $K_{f-ads}$ ) and desorption ( $K_{f-des}$ ) constants were linearly and positively correlated with the soil  
488 OC content, OM content, and CEC, while nonsignificant correlations were observed among the above constants  
489 and the soil pH and clay content.

490 The dissipation of EPM depended mainly on soil conditions (i.e., moisture, pH, and soil type). EPM degradation  
491 was most likely derived from abiotic degradation mechanisms; furthermore, the leaching ability of EPM increased  
492 from the Phaeozem (S1) to the Anthrosol (S2), Alisol (S4), Plinthosol (S5), and Ferralsol (S3). Overall, the high  
493 leaching ability and desorption capacity of EPM were accompanied by a low adsorption capacity and there were



494 no significant relationships between pH and the leaching rate of EPM in the five types of soils. In contrast, the  
495 OM content, CEC, and soil clay content were the main responsible for the observed leaching rates.

496 To completely understand the fate of EPM in the environment, it is necessary to perform additional studies on the  
497 microbial community structures and functional diversities of other types of soil besides those analyzed here. As a  
498 matter of fact, there are still only a few studies on the environmental fate of EPM; therefore, our results may serve  
499 as a reference for evaluating the risks involved in the increasingly wide application of this compound.

### 500 **Declaration of Competing Interest**

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

### 503 **Acknowledgements**

504 This work is financially supported by the National Key Research and Development Plan of China  
505 (2017YFD0301604).

### 506 **References**

- 507 Acharya, S. P., Johnson, J., and Weidhaas, J.: Adsorption kinetics of the herbicide safeners, benoxacor and  
508 furilazole, to activated carbon and agricultural soils, *Journal of Environmental Sciences*, 89, 23-34,  
509 <https://doi.org/10.1016/j.jes.2019.09.022>, 2020.
- 510 Ahmad, R., Kookana, R. S., Alston, A. M., and Skjemstad, J. O.: *The Nature of Soil Organic Matter Affects Sorption*  
511 *of Pesticides. 1. Relationships with Carbon Chemistry as Determined by <sup>13</sup>C CPMAS NMR Spectroscopy*,  
512 *Environmental Science & Technology*, 35, 878-884, [10.1021/es001446i](https://doi.org/10.1021/es001446i), 2001.
- 513 Alonso, D. G., Koskinen, W. C., Oliveira, R. S., Constantin, J., and Mislankar, S.: Sorption–Desorption of Indaziflam  
514 in Selected Agricultural Soils, *J Agric Food Chem*, 59, 13096-13101, [10.1021/jf203014g](https://doi.org/10.1021/jf203014g), 2011.
- 515 Azizian, S., Haerifar, M., and Basiri-Parsa, J.: Extended geometric method: A simple approach to derive adsorption  
516 rate constants of Langmuir–Freundlich kinetics, *Chemosphere*, 68, 2040-2046,  
517 <https://doi.org/10.1016/j.chemosphere.2007.02.042>, 2007.
- 518 Bailey, G. W., White, J. L., and Rothberg, T.: Adsorption of Organic Herbicides by Montmorillonite: Role of pH and  
519 Chemical Character of Adsorbate, 32, 222-234, <https://doi.org/10.2136/sssaj1968.03615995003200020021x>,  
520 1968.

521 Barchanska, H., Tang, J., Fang, X., Danek, M., Płonka, J., and Sajdak, M.: Profiling and fingerprinting strategies to  
522 assess exposure of edible plants to herbicides, *Food Chemistry*, 335, 127658,  
523 <https://doi.org/10.1016/j.foodchem.2020.127658>, 2021.

524 Barriuso, E., Laird, D., Koskinen, W., and Dowdy, R.: Atrazine Desorption From Smectites, *Soil Science Society of  
525 America Journal - SSSAJ*, 58, 10.2136/sssaj1994.03615995005800060008x, 1994.

526 Bento, C. P. M., Yang, X., Gort, G., Xue, S., van Dam, R., Zomer, P., Mol, H. G. J., Ritsema, C. J., and Geissen, V.:  
527 Persistence of glyphosate and aminomethylphosphonic acid in loess soil under different combinations of  
528 temperature, soil moisture and light/darkness, *Science of The Total Environment*, 572, 301-311,  
529 <https://doi.org/10.1016/j.scitotenv.2016.07.215>, 2016.

530 Boyd, S. A., Lee, J.-F., and Mortland, M. M.: Attenuating organic contaminant mobility by soil modification, *Nature*,  
531 333, 345-347, 10.1038/333345a0, 1988.

532 Brillas, E.: Recent development of electrochemical advanced oxidation of herbicides. A review on its application  
533 to wastewater treatment and soil remediation, *Journal of Cleaner Production*, 290, 125841,  
534 <https://doi.org/10.1016/j.jclepro.2021.125841>, 2021.

535 Buerge, I. J., Bächli, A., Kasteel, R., Portmann, R., López-Cabeza, R., Schwab, L. F., and Poiger, T.: Behavior of the  
536 Chiral Herbicide Imazamox in Soils: pH-Dependent, Enantioselective Degradation, Formation and Degradation of  
537 Several Chiral Metabolites, *Environmental Science & Technology*, 53, 5725-5732, 10.1021/acs.est.8b07209, 2019.

538 Bulut, Y. and Aydın, H.: A kinetics and thermodynamics study of methylene blue adsorption on wheat shells,  
539 *Desalination*, 194, 259-267, <https://doi.org/10.1016/j.desal.2005.10.032>, 2006.

540 Buttiglieri, G., Peschka, M., Frömel, T., Müller, J., Malpei, F., Seel, P., and Knepper, T. P.: Environmental occurrence  
541 and degradation of the herbicide n-chloridazon, *Water Research*, 43, 2865-2873,  
542 <https://doi.org/10.1016/j.watres.2009.03.035>, 2009.

543 Calvet, R.: Adsorption of Organic Chemicals in Soils, *Environmental Health Perspectives*, 83, 145-177,  
544 10.2307/3430653, 1989.

545 Carballa, M., Fink, G., Omil, F., Lema, J. M., and Ternes, T.: Determination of the solid–water distribution  
546 coefficient (Kd) for pharmaceuticals, estrogens and musk fragrances in digested sludge, *Water Research*, 42, 287-  
547 295, <https://doi.org/10.1016/j.watres.2007.07.012>, 2008.

548 Carneiro, G. D. O. P., Souza, M. d. F., Lins, H. A., Chagas, P. S. F. d., Silva, T. S., Teófilo, T. M. d. S., Pavão, Q. S.,  
549 Grangeiro, L. C., and Silva, D. V.: Herbicide mixtures affect adsorption processes in soils under sugarcane  
550 cultivation, *Geoderma*, 379, 114626, <https://doi.org/10.1016/j.geoderma.2020.114626>, 2020.

551 **Chefetz, B., Bilkis, Y. I., and Polubesova, T.: Sorption–desorption behavior of triazine and phenylurea herbicides  
552 in Kishon river sediments, *Water Research*, 38, 4383-4394, <https://doi.org/10.1016/j.watres.2004.08.023>, 2004.**

553 **Chen, Y., Han, J., Chen, D., Liu, Z., Zhang, K., and Hu, D.: Persistence, mobility, and leaching risk of flumioxazin in  
554 four Chinese soils, *Journal of Soils and Sediments*, 21, 1743-1754, 10.1007/s11368-021-02904-3, 2021.**

555 **Chianese, S., Fenti, A., Iovino, P., Musmarra, D., and Salvestrini, S.: Sorption of Organic Pollutants by Humic Acids:  
556 A Review, 25, 918, 2020.**

557 Cueff, S., Alletto, L., Dumény, V., Benoit, P., and Pot, V.: Adsorption and degradation of the herbicide nicosulfuron  
558 in a stagnic Luvisol and Vermic Umbrisol cultivated under conventional or conservation agriculture,  
559 *Environmental Science and Pollution Research*, 10.1007/s11356-020-11772-2, 2020.

560 de Matos, A. T., Fontes, M. P. F., da Costa, L. M., and Martinez, M. A.: Mobility of heavy metals as related to soil  
561 chemical and mineralogical characteristics of Brazilian soils, *Environmental Pollution*, 111, 429-435,  
562 [https://doi.org/10.1016/S0269-7491\(00\)00088-9](https://doi.org/10.1016/S0269-7491(00)00088-9), 2001.

563 **Delle Site, A.: Factors Affecting Sorption of Organic Compounds in Natural Sorbent/Water Systems and Sorption**

564 Coefficients for Selected Pollutants. A Review, *Journal of Physical and Chemical Reference Data*, 30, 187-439,  
565 [10.1063/1.1347984](https://doi.org/10.1063/1.1347984), 2001.

566 Fan, X., Zou, Y., Geng, N., Liu, J., Hou, J., Li, D., Yang, C., and Li, Y.: Investigation on the adsorption and desorption  
567 behaviors of antibiotics by degradable MPs with or without UV ageing process, *Journal of Hazardous Materials*,  
568 401, 123363, <https://doi.org/10.1016/j.jhazmat.2020.123363>, 2021.

569 FAO: Assessing soil contamination A reference manual, Parameters of pesticides that influence processes in the  
570 soil, FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS Rome, Rome2000.

571 Gao, H.-J. and Jiang, X.: Effect of Initial Concentration on Adsorption-Desorption Characteristics and Desorption  
572 Hysteresis of Hexachlorobenzene in Soils, *Pedosphere*, 20, 104-110, [https://doi.org/10.1016/S1002-](https://doi.org/10.1016/S1002-0160(09)60289-7)  
573 [0160\(09\)60289-7](https://doi.org/10.1016/S1002-0160(09)60289-7), 2010.

574 García-Delgado, C., Marín-Benito, J. M., Sánchez-Martín, M. J., and Rodríguez-Cruz, M. S.: Organic carbon nature  
575 determines the capacity of organic amendments to adsorb pesticides in soil, *Journal of Hazardous Materials*, 390,  
576 122162, <https://doi.org/10.1016/j.jhazmat.2020.122162>, 2020.

577 García-Valcárcel, A. I. and Tadeo, J. L.: Influence of Soil Moisture on Sorption and Degradation of Hexazinone and  
578 Simazine in Soil, *J Agric Food Chem*, 47, 3895-3900, 10.1021/jf981326i, 1999.

579 Gawel, A., Seiwert, B., Sühnholz, S., Schmitt-Jansen, M., and Mackenzie, K.: In-situ treatment of herbicide-  
580 contaminated groundwater—Feasibility study for the cases atrazine and bromacil using two novel  
581 nanoremediation-type materials, *Journal of Hazardous Materials*, 393, 122470,  
582 <https://doi.org/10.1016/j.jhazmat.2020.122470>, 2020.

583 GB: Test Guidelines of the Environmental Safety Assessment for Chemical Pesticides-Part 4:  
584 Adsorption/Desorption in Soils, 2014a.

585 GB: Test Guidelines on Environmental Safety Assessment for Chemical Pesticides: Part 5: Leaching in soil, 2014b.

586 GB: Test Guidelines of the Environmental Safety Assessment for Chemical Pesticides-Part 1 (Transformation in  
587 Soils) 2014c.

588 GB: National food safety standard — Maximum residue limits for pesticides in food, 2021.

589 Gee, G. W., and Bauder, J. W. : 'Particle-size analysis' in *Methods of soil analysis, part-I. Physical and mineralogical*  
590 *methods*, Madison, WI: American Society of Agronomy and Soil Science Society of America, 1986.

591 Guimares, A., Mendes, K. F., Campion, T. F., Christoffoleti, P. J., and Tornisiello, V. L.: Leaching of Herbicides  
592 Commonly Applied to Sugarcane in Five Agricultural Soils, *Planta Daninha*, 37, e019181505, 2019.

593 Gustafson, D. I.: Groundwater ubiquity score: A simple method for assessing pesticide leachability, *Environmental*  
594 *Toxicology and Chemistry*, 8, 339-357, 10.1002/etc.5620080411, 1989.

595 Hamilton, D. J., Ambrus, Á., Dieterle, R. M., Felsot, A. S., Harris, C. A., Holland, P. T., Katayama, A., Kurihara, N.,  
596 Linders, J., Unsworth, J., and Wong, S.-S.: Regulatory limits for pesticide residues in water (IUPAC Technical Report)  
597 *Pure and Applied Chemistry*, 75, 1123-1155, doi:10.1351/pac200375081123, 2003.

598 Hartley, G. S.: *In Herbicides and the Soil*; Woodford, Blackwell Scientific Publishing Company, Oxford1960.

599 Hochman, D., Dor, M., and Mishaël, Y.: Diverse effects of wetting and drying cycles on soil aggregation:  
600 Implications on pesticide leaching, *Chemosphere*, 263, 127910,  
601 <https://doi.org/10.1016/j.chemosphere.2020.127910>, 2021.

602 Huang, B., Yan, D. D., Wang, X. N., Wang, X. L., Fang, W.S., Zhang, D. Q., Ouyang, C. B., Wang, Qi. X., Cao, A. C.:  
603 Soil fumigation alters adsorption and degradation behavior of pesticides in soil, *Environmental Pollution*, 246,  
604 264-273, <https://doi.org/10.1016/j.envpol.2018.12.003>, 2019.

605 Huang, J. L., Xiu-Ying, L. I., Lin, S. Y., Guo, X. D., and Quality: Determination of glyphosate residues in tea by ion  
606 chromatography, *Journal of Food Safety and Quality*, 2016.

607 Inao, K., Mizutani, H., Yogo, Y., and Ikeda, M.: Improved PADDY model including photoisomerization and  
608 metabolic pathways for predicting pesticide behavior in paddy fields: Application to the herbicide pyriminobac-  
609 methyl, *Journal of Pesticide Science*, advpub, 0909190094-0909190094, 10.1584/jpestics.G09-20, 2009.

610 Iwafune, T., Inao, K., Horio, T., Iwasaki, N., Yokoyama, A., and Nagai, T.: Behavior of paddy pesticides and major  
611 metabolites in the Sakura River, Ibaraki, Japan, *Journal of Pesticide Science*, advpub, 1001130109-1001130109,  
612 10.1584/jpestics.G09-49, 2010.

613 Iwakami, S., Hashimoto, M., Matsushima, K.-i., Watanabe, H., Hamamura, K., and Uchino, A.: Multiple-herbicide  
614 resistance in *Echinochloa crus-galli* var. *formosensis*, an allohexaploid weed species, in dry-seeded rice, *Pesticide*  
615 *Biochemistry and Physiology*, 119, 1-8, <https://doi.org/10.1016/j.pestbp.2015.02.007>, 2015.

616 Jackson, M.: *Soil Chemical Analysis*, prentice Hall. Inc, Englewood Cliffs, NJ, 1958.

617 Jia, C.-S., Zhang, L.-H., Peng, X.-L., Luo, J.-X., Zhao, Y.-L., Liu, J.-Y., Guo, J.-J., and Tang, L.-D.: Prediction of entropy  
618 and Gibbs free energy for nitrogen, *Chemical Engineering Science*, 202, 70-74,  
619 <https://doi.org/10.1016/j.ces.2019.03.033>, 2019a.

620 Jia, H. R., Zhang, Y., Li, W., and Li, B. T.: HPLC- tandem Mass Spectrometry Method for the Determination of  
621 Pyriminobac- methyl 10% WP, *Agrochemicals*, 58, 106-108, 2019b.

622 Jia, H. R., Zhang, Y., Li, W., Li, B. T., and Zhou, W. W.: Residue dynamics and dietary risk assessment of pyriminobac-  
623 methyl in rice, *Acta Scientiae Circumstantiae*, 4, 1491-1499, 2020.

624 Jiang, R., Wang, M., Chen, W., and Li, X.: Ecological risk evaluation of combined pollution of herbicide siduron  
625 and heavy metals in soils, *Science of The Total Environment*, 626, 1047-1056,  
626 <https://doi.org/10.1016/j.scitotenv.2018.01.135>, 2018.

627 Kalsi, N. K. and Kaur, P.: Dissipation of bispyribac sodium in aridisols: Impact of soil type, moisture and  
628 temperature, *Ecotoxicology and Environmental Safety*, 170, 375-382,  
629 <https://doi.org/10.1016/j.ecoenv.2018.12.005>, 2019.

630 Kaur, P., Kaur, H., Kaur Kalsi, N., and Bhullar, M. S.: Evaluation of leaching potential of penoxsulam and bispyribac  
631 sodium in Punjab soils under laboratory conditions, *International Journal of Environmental Analytical Chemistry*,  
632 1-19, 10.1080/03067319.2021.1970148, 2021.

633 Khorram, M. S., Sarmah, A. K., and Yu, Y.: The Effects of Biochar Properties on Fomesafen Adsorption-Desorption  
634 Capacity of Biochar-Amended Soil, *Water, Air, & Soil Pollution*, 229, 60, 10.1007/s11270-017-3603-2, 2018.

635 Kolakowski, B. M., Miller, L., Murray, A., Leclair, A., and Riet, J. M. V. D.: Analysis of Glyphosate Residues in Foods  
636 on the Canadian Retail Market between 2015-2017, *J Agric Food Chem*, 10.1021/acs.jafc.9b07819, 2020.

637 Kulshrestha, P., Giese, R. F., and Aga, D. S.: Investigating the Molecular Interactions of Oxytetracycline in Clay and  
638 Organic Matter: Insights on Factors Affecting Its Mobility in Soil, *Environmental Science & Technology*, 38, 4097-  
639 4105, 10.1021/es034856q, 2004.

640 L'Huillier, L., Dupont, S., Dubus, I., Becquer, T., Bourdon, E.: Carence et fixation du phosphore dans les sols  
641 ferrallitiques ferritiques de Nouvelle-Caledonie, XVIe Congres Mondial de Science du Sol, Montpellier, France,  
642 20-26 1998.

643 Lewis, K. A., Tzilivakis, J., Warner, D. J., and Green, A.: An international database for pesticide risk assessments  
644 and management, *Human and Ecological Risk Assessment: An International Journal*, 22, 1050-1064,  
645 10.1080/10807039.2015.1133242, 2016.

646 Liu, J., Dong, C., Zhai, Z., Tang, L., and Wang, L.: Glyphosate-induced lipid metabolism disorder contributes to  
647 hepatotoxicity in juvenile common carp, *Environmental Pollution*, 269, 116186, 2021a.

648 Liu, J., Zhou, J. H., Guo, Q. N., Ma, L. Y., and Yang, H.: Physiochemical assessment of environmental behaviors of  
649 herbicide atrazine in soils associated with its degradation and bioavailability to weeds, *Chemosphere*, 262,

650 127830, <https://doi.org/10.1016/j.chemosphere.2020.127830>, 2021b.

651 Luo, F. M., Wu, X. D., and liu, X. Y.: Determination of Pu'er Tea by High Performance Liquid Chromatography  
652 Tandem Mass Spectrometry Uncertainty Evaluation of Glyphosate Residues, *Analysis and Testing*, 144-148, 2019.

653 Marín-Benito, J. M., Carpio, M. J., Sánchez-Martín, M. J., and Rodríguez-Cruz, M. S.: Previous degradation study  
654 of two herbicides to simulate their fate in a sandy loam soil: Effect of the temperature and the organic  
655 amendments, *Science of The Total Environment*, 653, 1301-1310,  
656 <https://doi.org/10.1016/j.scitotenv.2018.11.015>, 2019.

657 Martins, E. C., de Freitas Melo, V., Bohone, J. B., and Abate, G.: Sorption and desorption of atrazine on soils: The  
658 effect of different soil fractions, *Geoderma*, 322, 131-139, <https://doi.org/10.1016/j.geoderma.2018.02.028>,  
659 2018.

660 Martins, J. M. and Mermoud, A.: Sorption and degradation of four nitroaromatic herbicides in mono and multi-  
661 solute saturated/unsaturated soil batch systems, *J Contam Hydrol*, 33, 187-210, [https://doi.org/10.1016/S0169-  
662 7722\(98\)00070-9](https://doi.org/10.1016/S0169-7722(98)00070-9), 1998.

663 Marvin, H. J. P. and Bouzembrak, Y.: A system approach towards prediction of food safety hazards: Impact of  
664 climate and agrichemical use on the occurrence of food safety hazards, *Agricultural Systems*, 178, 102760,  
665 <https://doi.org/10.1016/j.agsy.2019.102760>, 2020.

666 Medo, J., Hricáková, N., Maková, J., Medová, J., Omelka, R., and Javoreková, S.: Effects of sulfonylurea herbicides  
667 chlorsulfuron and sulfosulfuron on enzymatic activities and microbial communities in two agricultural soils,  
668 *Environmental Science and Pollution Research*, 27, 41265-41278, 10.1007/s11356-020-10063-0, 2020.

669 Mehdizadeh, M., Mushtaq, W., Anusha Siddiqui, S., Ayadi, S., Kaur, P., Yeboah, S., Mazraedoost, S., K.A.Al-Taey,  
670 D., and Tampubolon, K.: Herbicide Residues in Agroecosystems: Fate, Detection, and Effect on Non-Target Plants,  
671 *Reviews in Agricultural Science*, 9, 157-167, 10.7831/ras.9.0\_157, 2021.

672 Meimaroglou, N. and Mouzakis, C.: Cation Exchange Capacity (CEC), texture, consistency and organic matter in  
673 soil assessment for earth construction: The case of earth mortars, *Construction and Building Materials*, 221, 27-  
674 39, <https://doi.org/10.1016/j.conbuildmat.2019.06.036>, 2019.

675 Murphy, E. M. and Zachara, J. M.: The role of sorbed humic substances on the distribution of organic and  
676 inorganic contaminants in groundwater, *Geoderma*, 67, 103-124, [https://doi.org/10.1016/0016-7061\(94\)00055-  
677 F](https://doi.org/10.1016/0016-7061(94)00055-F), 1995.

678 Nandi, B. K., Goswami, A., and Purkait, M. K.: Adsorption characteristics of brilliant green dye on kaolin, *Journal*  
679 *of Hazardous Materials*, 161, 387-395, <https://doi.org/10.1016/j.jhazmat.2008.03.110>, 2009.

680 Nelson, D., Sommers, L. : Total carbon, organic carbon and organic matter. , In *Methods of Soil Analysis*, American  
681 Society of Agronomy, USA1985.

682 *NY/T: Guidelines for good herbicide application*, 2011.

683 Obregón Alvarez, D., Mendes, K. F., Tosi, M., Fonseca de Souza, L., Campos Cedano, J. C., de Souza Falcão, N. P.,  
684 Dunfield, K., Tsai, S. M., and Tornisielo, V. L.: Sorption-desorption and biodegradation of sulfometuron-methyl  
685 and its effects on the bacterial communities in Amazonian soils amended with aged biochar, *Ecotoxicology and*  
686 *Environmental Safety*, 207, 111222, <https://doi.org/10.1016/j.ecoenv.2020.111222>, 2021.

687 Ou, J., Li, H., Ou, X., Yang, Z., Chen, M., Liu, K., Teng, Y., and Xing, B.: Degradation, adsorption and leaching of  
688 phenazine-1-carboxamide in agricultural soils, *Ecotoxicology and Environmental Safety*, 205, 111374,  
689 <https://doi.org/10.1016/j.ecoenv.2020.111374>, 2020.

690 Patel, K. F., Tejnecký, V., Ohno, T., Bailey, V. L., Sleighter, R. L., and Hatcher, P. G.: Reactive oxygen species alter  
691 chemical composition and adsorptive fractionation of soil-derived organic matter, *Geoderma*, 384, 114805,  
692 <https://doi.org/10.1016/j.geoderma.2020.114805>, 2021.

693 Pérez-Lucas, G., Gambín, M., and Navarro, S.: Leaching behaviour appraisal of eight persistent herbicides on a  
694 loam soil amended with different composted organic wastes using screening indices, *Journal of Environmental*  
695 *Management*, 273, 111179, <https://doi.org/10.1016/j.jenvman.2020.111179>, 2020.

696 Perotti, V. E., Larran, A. S., Palmieri, V. E., Martinatto, A. K., and Permingeat, H. R.: Herbicide resistant weeds: A  
697 call to integrate conventional agricultural practices, molecular biology knowledge and new technologies, *Plant*  
698 *Science*, 290, 110255, <https://doi.org/10.1016/j.plantsci.2019.110255>, 2020.

699 Qin, M., Chai, S., Ma, Y., Gao, H., Zhang, H., and He, Q.: Determination of pyriminobac-methyl and bispyribac-  
700 sodium residues in rice by liquid chromatography-tandem mass spectrometry based on QuEChERS, *Se pu =*  
701 *Chinese journal of chromatography*, 35, 719-723, 10.3724/sp.J.1123.2017.02032, 2017.

702 Rae, J. E., Cooper, C. S., Parker, A., and Peters, A.: Pesticide sorption onto aquifer sediments, *Journal of*  
703 *Geochemical Exploration*, 64, 263-276, [https://doi.org/10.1016/S0375-6742\(98\)00037-5](https://doi.org/10.1016/S0375-6742(98)00037-5), 1998.

704 Rao, L., Luo, J., Zhou, W., Zou, Z., Tang, L., and Li, B.: Adsorption-desorption behavior of benzobicyclon  
705 hydrolysate in different agricultural soils in China, *Ecotoxicology and Environmental Safety*, 202, 110915,  
706 <https://doi.org/10.1016/j.ecoenv.2020.110915>, 2020.

707 Schnitzer, M. and Khan, S. U.: *In Humic Substances in the Environment*, Marcel Dekker Inc, New York 1972.

708 Schwarzenbach, R. P. and Westall, J.: Transport of nonpolar organic compounds from surface water to  
709 groundwater. Laboratory sorption studies, *Environmental Science & Technology*, 15, 1360-1367,  
710 10.1021/es00093a009, 1981.

711 Shibayama, H.: Weeds and weed management in rice production in Japan, *Weed Biology and Management*, 1,  
712 53-60, <https://doi.org/10.1046/j.1445-6664.2001.00004.x>, 2001.

713 Silva, T. S., de Freitas Souza, M., Maria da Silva Teófilo, T., Silva dos Santos, M., Formiga Porto, M. A., Martins  
714 Souza, C. M., Barbosa dos Santos, J., and Silva, D. V.: Use of neural networks to estimate the sorption and  
715 desorption coefficients of herbicides: A case study of diuron, hexazinone, and sulfometuron-methyl in Brazil,  
716 *Chemosphere*, 236, 124333, <https://doi.org/10.1016/j.chemosphere.2019.07.064>, 2019.

717 Song, H., Mao, H., and Shi, D.: Synthesis and Herbicidal Activity of  $\alpha$ -Hydroxy Phosphonate Derivatives Containing  
718 Pyrimidine Moiety, 28, 2020-2024, <https://doi.org/10.1002/cjoc.201090337>, 2010.

719 Spadotto, C. A., Locke, M. A., Bingner, R. L., and Mingoti, R.: Estimating sorption of monovalent acidic herbicides  
720 at different pH levels using a single sorption coefficient, *Pest Management Science*, 76, 2693-2698,  
721 <https://doi.org/10.1002/ps.5815>, 2020.

722 Stevenson, F. J.: Organic Matter Reactions Involving Herbicides in Soil, *Journal of Environmental Quality*, 1, 333-  
723 343, <https://doi.org/10.2134/jeq1972.00472425000100040001x>, 1972.

724 Sudo, M., Goto, Y., Iwama, K., and Hida, Y.: Herbicide discharge from rice paddy fields by surface runoff and  
725 percolation flow: A case study in paddy fields in the Lake Biwa basin, Japan, *Journal of Pesticide Science*, 43, 24-  
726 32, 10.1584/jpestics.D17-061, 2018.

727 Tamaru, M. and Saito, Y.: Studies of the New Herbicide KIH-6127. Part I. Novel Synthesis of Methyl 6-  
728 Acetylsalicylate as a Key Synthetic Intermediate for the Preparation of 6-Acetyl Pyrimidin-2-yl Salicylates and  
729 Analogues, *Pesticide Science*, 47, 125-130, [https://doi.org/10.1002/\(SICI\)1096-9063\(199606\)47:2<125::AID-PS394>3.0.CO;2-X](https://doi.org/10.1002/(SICI)1096-9063(199606)47:2<125::AID-PS394>3.0.CO;2-X), 1996.

731 Tamaru, M., Masuyama, N., Sato, M., Takabe, F., Inoue, J., and Hanai, R.: Studies of the New Herbicide KIH-6127.  
732 Part III. Synthesis and Structure-Activity Studies of Analogues of KIH-6127 against Barnyard Grass (*Echinochloa*  
733 *oryzicola*)\*, *Pesticide Science*, 49, 76-84, [https://doi.org/10.1002/\(SICI\)1096-9063\(199701\)49:1<76::AID-PS491>3.0.CO;2-E](https://doi.org/10.1002/(SICI)1096-9063(199701)49:1<76::AID-PS491>3.0.CO;2-E), 1997.

734 Tang, W., Yu, Z.-H., and Shi, D.-Q.: Synthesis, crystal structure, and herbicidal activity of pyrimidinyl benzylamine



736 analogues containing a phosphonyl group, *Heteroatom Chemistry*, 21, 148-155,  
737 <https://doi.org/10.1002/hc.20589>, 2010.

738 Temminghoff, E. J. M., Van der Zee, S. E. A. T. M., and de Haan, F. A. M.: Copper Mobility in a Copper-Contaminated  
739 Sandy Soil as Affected by pH and Solid and Dissolved Organic Matter, *Environmental Science & Technology*, 31,  
740 1109-1115, 10.1021/es9606236, 1997.

741 Ternes, T. A., Herrmann, N., Bonerz, M., Knacker, T., Siegrist, H., and Joss, A.: A rapid method to measure the  
742 solid–water distribution coefficient (Kd) for pharmaceuticals and musk fragrances in sewage sludge, *Water*  
743 *Research*, 38, 4075-4084, <https://doi.org/10.1016/j.watres.2004.07.015>, 2004.

744 Urach Ferreira, P. H., Ferguson, J. C., Reynolds, D. B., Kruger, G. R., and Irby, J. T.: Droplet size and physicochemical  
745 property effects on herbicide efficacy of pre-emergence herbicides in soybean (*Glycine max* (L.) Merr), 76, 737-  
746 746, <https://doi.org/10.1002/ps.5573>, 2020.

747 Wang, H. Z., Zuo, H. G., Ding, Y. J., Miao, S. S., Jiang, C., and Yang, H.: Biotic and abiotic degradation of pesticide  
748 Dufulin in soils, *Environmental Science and Pollution Research*, 21, 4331-4342, 10.1007/s11356-013-2380-8,  
749 2014.

750 Wang, Q., Fu, Y., Zhang, L., Ling, S., and Wu, Y.: Determination of pyriminobac-methyl isomers in paddy and its  
751 storage stability, *Journal of Food Safety and Quality*, 20, 7429-7435, 2020a.

752 Wang, W., Liang, Y., Yang, J., Tang, G., Zhou, Z., Tang, R., Dong, H., Li, J., and Cao, Y.: Ionic Liquid Forms of  
753 Mesotrione with Enhanced Stability and Reduced Leaching Risk, *ACS Sustainable Chemistry & Engineering*, 7,  
754 16620-16628, 10.1021/acssuschemeng.9b03948, 2019.

755 Wang, Z., Yang, L., Cheng, P., Yu, Y., Zhang, Z., and Li, H.: Adsorption, degradation and leaching migration  
756 characteristics of chlorothalonil in different soils, *European Journal of Remote Sensing*, 1-10,  
757 10.1080/22797254.2020.1771216, 2020b.

758 Wei, L., Huang, Y., Huang, L., Li, Y., Huang, Q., Xu, G., Müller, K., Wang, H., Ok, Y. S., and Liu, Z.: The ratio of H/C is  
759 a useful parameter to predict adsorption of the herbicide metolachlor to biochars, *Environmental Research*, 184,  
760 109324, <https://doi.org/10.1016/j.envres.2020.109324>, 2020.

761 Willett, C. D., Grantz, E. M., Sena, M. G., Lee, J. A., Brye, K. R., and Clarke, J. A.: Soil sorption characteristics of  
762 benzbicyclon hydrolysate and estimated leaching risk in soils used for rice production, *Environmental Chemistry*,  
763 17, 445-456, <https://doi.org/10.1071/EN19189>, 2020.

764 Xiang, L., Wang, X. D., Chen, X. H., Mo, C. H., Li, Y. W., Li, H., Cai, Q. Y., Zhou, D. M., Wong, M. H., Li, Q. X.: Sorption  
765 Mechanism, Kinetics, and Isotherms of Di-n-butyl Phthalate to Different Soil Particle-Size Fractions, *J Agric Food*  
766 *Chem*, 67, 4734-4745, 10.1021/acs.jafc.8b06357, 2019.

767 Xie, G., Li, B., Tang, L., Rao, L., and Dong, Z.: Adsorption-desorption and leaching behaviors of broflanilide in four  
768 texturally different agricultural soils from China, *Journal of Soils and Sediments*, 10.1007/s11368-020-02831-9,  
769 2020.

770 Xu, Y., Yu, X., Xu, B., Peng, D., and Guo, X.: Sorption of pharmaceuticals and personal care products on soil and  
771 soil components: Influencing factors and mechanisms, *Science of The Total Environment*, 753, 141891,  
772 <https://doi.org/10.1016/j.scitotenv.2020.141891>, 2021.

773 Xu, Y., Liu, J., Cai, W., Feng, J., Lu, Z., Wang, H., Franks, A. E., Tang, C., He, Y., and Xu, J.: Dynamic processes in  
774 conjunction with microbial response to disclose the biochar effect on pentachlorophenol degradation under both  
775 aerobic and anaerobic conditions, *Journal of Hazardous Materials*, 384, 121503,  
776 <https://doi.org/10.1016/j.jhazmat.2019.121503>, 2020.

777 Yang, L., Li, H., Zhang, Y., and Jiao, N.: Environmental risk assessment of triazine herbicides in the Bohai Sea and  
778 the Yellow Sea and their toxicity to phytoplankton at environmental concentrations, *Environment International*,

779 133, 105175, <https://doi.org/10.1016/j.envint.2019.105175>, 2019.

780 Yang, R., Jia, A., He, S., Hu, Q., Sun, M., Dong, T., Hou, Y., and Zhou, S.: Experimental investigation of water vapor  
781 adsorption isotherm on gas-producing Longmaxi shale: Mathematical modeling and implication for water  
782 distribution in shale reservoirs, *Chemical Engineering Journal*, 406, 125982,  
783 <https://doi.org/10.1016/j.cej.2020.125982>, 2021.

784 Yin, X. and Zelenay, P.: (Invited) Kinetic Models for the Degradation Mechanisms of PGM-Free ORR Catalysts, *ECS*  
785 *Transactions*, 85, 1239-1250, 10.1149/08513.1239ecst, 2018.

786 Yoshii, K., Okada, M., Tsumura, Y., Nakamura, Y., Ishimtsu, S., and Tonogai, Y.: Supercritical Fluid Extraction of Ten  
787 Chloracetanilide Pesticides and Pyriminobac-Methyl in Crops: Comparison with the Japanese Bulletin Method,  
788 *Journal of AOAC INTERNATIONAL*, 82, 1239-1245, 10.1093/jaoac/82.5.1239 %J *Journal of AOAC INTERNATIONAL*,  
789 2020.

790 Yu, Y., Zhuang, Y.-Y., Wang, Z.-H., and Qiu, M.-Q.: Adsorption of water-soluble dyes onto modified resin,  
791 *Chemosphere*, 54, 425-430, [https://doi.org/10.1016/S0045-6535\(03\)00654-4](https://doi.org/10.1016/S0045-6535(03)00654-4), 2004.

792 Yue, L., Ge, C., Feng, D., Yu, H., Deng, H., and Fu, B.: Adsorption-desorption behavior of atrazine on agricultural  
793 soils in China, *Journal of Environmental Sciences*, 7, 180-189, 2017.

794 Zhang, C.-L., Qiao, G.-L., Zhao, F., and Wang, Y.: Thermodynamic and kinetic parameters of ciprofloxacin  
795 adsorption onto modified coal fly ash from aqueous solution, *Journal of Molecular Liquids*, 163, 53-56,  
796 <https://doi.org/10.1016/j.molliq.2011.07.005>, 2011.

797 Zhang, S., Han, B., Sun, Y., and Wang, F.: Microplastics influence the adsorption and desorption characteristics of  
798 Cd in an agricultural soil, *Journal of Hazardous Materials*, 388, 121775,  
799 <https://doi.org/10.1016/j.jhazmat.2019.121775>, 2020a.

800 Zhang, Y., Li, W., Zhou, W., Jia, H., and Li, B.: Adsorption-desorption characteristics of pyraclonil in eight  
801 agricultural soils, *Journal of Soils and Sediments*, 20, 1404-1412, 10.1007/s11368-019-02471-8, 2020b.

802 Zhou, W., Zhang, Y., Li, W., Jia, H., Huang, H., and Li, B.: Adsorption isotherms, degradation kinetics, and leaching  
803 behaviors of cyanogen and hydrogen cyanide in eight texturally different agricultural soils from China,  
804 *Ecotoxicology and Environmental Safety*, 185, 109704, <https://doi.org/10.1016/j.ecoenv.2019.109704>, 2019a.

805 Zhou, Z., Yan, T., Zhu, Q., Bu, X., Chen, B., Xue, J., and Wu, Y.: Bacterial community structure shifts induced by  
806 biochar amendment to karst calcareous soil in southwestern areas of China, *Journal of Soils and Sediments*, 19,  
807 356-365, 10.1007/s11368-018-2035-y, 2019b.



808 **Table 1**

809 Comparison between the results of the linear and Freundlich models for the adsorption–desorption of EPM in five agricultural soils.

Soil sample	Soil type	Adsorption						Desorption					
		Linear model			Freundlich model			Linear model		Freundlich model			
		$K$ (mL g <sup>-1</sup> ) <sup>a</sup>	$C_0$ (mg kg <sup>-1</sup> ) <sup>a</sup>	$R^2$	$K_{f-ads}$ (mg <sup>1-1/n</sup> L <sup>1/n</sup> kg <sup>-1</sup> ) <sup>a</sup>	$1/n_{ads}$ <sup>a</sup>	$R^2$	$K$ (mL g <sup>-1</sup> ) <sup>a</sup>	$R^2$	$K_{f-des}$ (mg <sup>1-1/n</sup> L <sup>1/n</sup> kg <sup>-1</sup> ) <sup>a</sup>	$1/n_{des}$ <sup>a</sup>	$R^2$	$H$
S1	Phaeozem	56.21 ± 3.56	0.17 ± 0.01	0.9841	32.22 ± 4.55	0.80 ± 0.07	0.9999	0.80 ± 0.24	0.8384	5.02 ± 0.02	0.01 ± 33.53	0.9999	0.013
S2	Anthrosol	2.78 ± 0.06	0.13 ± 0.04	0.9982	2.95 ± 0.04	0.88 ± 0.03	0.9999	0.27 ± 0.03	0.9823	2.27 ± 0.01	0.71 ± 0.28	0.9999	0.807
S3	Ferralsol	2.43 ± 0.07	0.16 ± 0.05	0.9975	2.65 ± 0.03	0.84 ± 0.03	0.9999	0.82 ± 0.19	0.8988	1.73 ± 0.05	0.11 ± 1.43	0.9999	0.131
S4	Alisol	0.79 ± 0.01	0.05 ± 0.01	0.9990	0.85 ± 0.02	0.95 ± 0.03	0.9999	0.53 ± 0.05	0.9834	0.78 ± 0.01	0.12 ± 0.01	1.0000	0.126
S5	Plinthosol	2.03 ± 0.07	-0.01 ± 0.06	0.9951	1.99 ± 0.05	1.06 ± 0.04	0.9999	2.53 ± 0.18	0.9905	1.38 ± 0.08	0.19 ± 0.56	0.9999	0.179

810 <sup>a</sup> The values represent means ± standard error (SE, n = 3).

811 **Table 2**

812 Empirical constants, Gibbs free energy, and groundwater ubiquity score (GUS) for the adsorption of EPM  
813 in five agricultural soils.

Soil sample	Soil type	K	C <sub>e</sub> /C <sub>0</sub>	K <sub>f-ads</sub> (mg <sup>1-1/n</sup> L <sup>1/n</sup> kg <sup>-1</sup> )	K <sub>OC</sub>	K <sub>OM</sub>	ΔG (kJ mol <sup>-1</sup> )	GUS
S1	Phaeozem	64.4821	0.0117	32.2230	2395.8435	695.6897	-16.2242	0.9765
S2	Anthrosol	3.0971	0.2441	2.9540	606.7513	335.2273	-14.4143	2.0402
S3	Ferralsol	2.7861	0.2641	2.6530	289.3500	159.6386	-12.5753	2.7160
S4	Alisol	0.8393	0.5437	0.8520	413.3906	242.8571	-13.6153	2.3755
S5	Plinthosol	2.0172	0.3314	1.9950	289.8034	165.8333	-12.6696	2.6765

814

815

816

817

818

819

820

821

822

823

824

825

826

827

828

829

830

831 **Table 3**

832 Degradation kinetic models and parameters of EPM under different conditions.

Soil sample	Soil type	Aerobic			Anaerobic			Sterilized		
		First-order kinetic model	Half-life $t_{1/2}$ (d)	$R^2$	First-order kinetic model	Half- life $t_{1/2}$ (d)	$R^2$	First-order kinetic model	Half- life $t_{1/2}$ (d)	$R^2$
S1	Phaeozem	$C_t = 1.5338e^{-0.0185t}$	37.46	0.9473	$C_t = 1.7792e^{-0.0166t}$	41.75	0.9579	$C_t = 1.8467e^{-0.0111t}$	62.43	0.9800
S2	Anthrosol	$C_t = 1.6419e^{-0.0146t}$	47.47	0.9707	$C_t = 1.8599e^{-0.0139t}$	49.85	0.9696	$C_t = 1.7543e^{-0.0113t}$	60.87	0.9551
S3	Ferralsol	$C_t = 1.9363e^{-0.0119t}$	58.25	0.9843	$C_t = 1.9968e^{-0.0116t}$	59.74	0.9878	$C_t = 1.9349e^{-0.0105t}$	66.00	0.9775
S4	Alisol	$C_t = 1.9476e^{-0.0133t}$	52.10	0.9924	$C_t = 1.9477e^{-0.0133t}$	52.11	0.9924	$C_t = 1.7086e^{-0.0112t}$	61.88	0.9313
S5	Plinthosol	$C_t = 1.7864e^{-0.0126t}$	55.00	0.9655	$C_t = 1.9725e^{-0.0121t}$	57.27	0.9923	$C_t = 1.8638e^{-0.0109t}$	63.58	0.9761

833

834

835

836

837

838

839

840

841 **Table 4**

842 Degradation kinetic models and parameters of EPM in soil under different moisture conditions.

Soil sample	Soil type <sup>a</sup>	Saturation moisture capacity (40%)			Saturation moisture capacity (60%)			Saturation moisture capacity (80%)		
		First-order kinetic model	Half-life $t_{1/2}$ (d)	$R^2$	First-order kinetic model	Half-life $t_{1/2}$ (d)	$R^2$	First-order kinetic model	Half-life $t_{1/2}$ (d)	$R^2$
S1	Phaeozem	$C_t = 1.7324e^{-0.0141t}$	49.15	0.9582	$C_t = 1.5338e^{-0.0185t}$	37.46	0.9473	$C_t = 1.7792e^{-0.0166t}$	41.75	0.9579
S2	Anthrosol	$C_t = 1.6551e^{-0.0133t}$	52.11	0.8769	$C_t = 1.6419e^{-0.0146t}$	47.47	0.9707	$C_t = 1.8599e^{-0.0139t}$	49.87	0.9696
S3	Ferralsol	$C_t = 1.8659e^{-0.0110t}$	62.77	0.9884	$C_t = 1.9363e^{-0.0119t}$	58.25	0.9843	$C_t = 1.9968e^{-0.0116t}$	59.74	0.9878
S4	Alisol	$C_t = 1.8428e^{-0.0116t}$	59.74	0.9742	$C_t = 1.9476e^{-0.0133t}$	52.10	0.9924	$C_t = 1.7076e^{-0.0121t}$	57.27	0.9849
S5	Plinthosol	$C_t = 1.7637e^{-0.0104t}$	66.63	0.9650	$C_t = 1.7864e^{-0.0126t}$	55.00	0.9655	$C_t = 1.9725e^{-0.0121t}$	57.27	0.9923

843

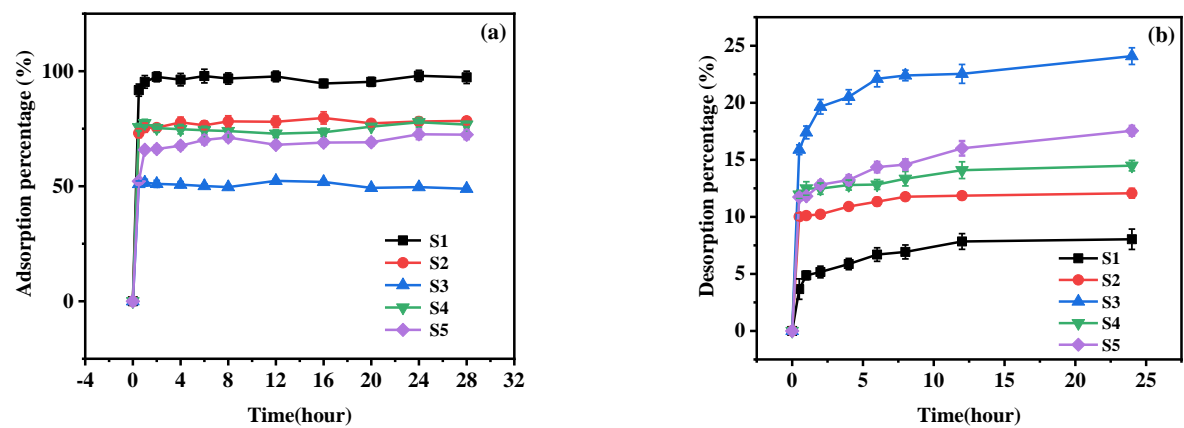
844

845

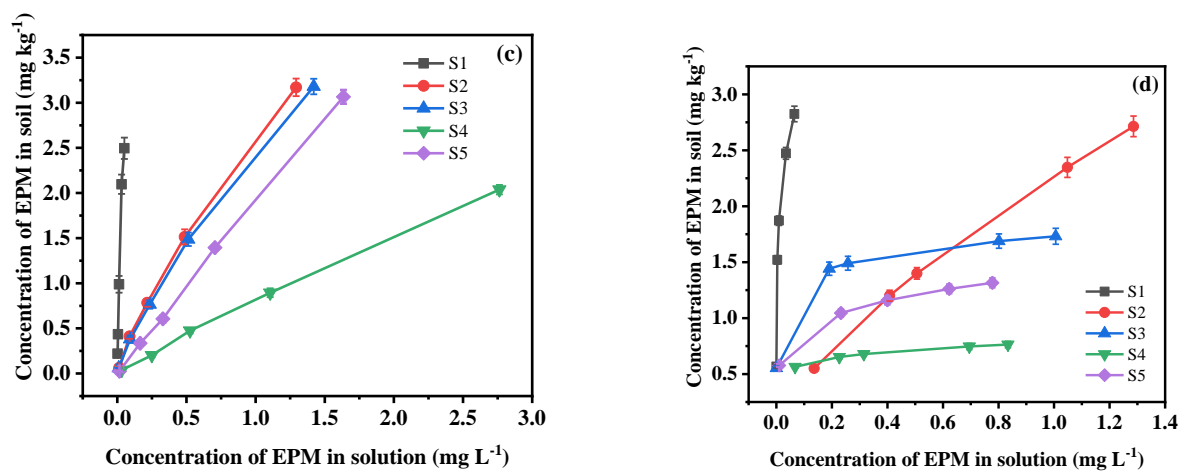
846

847

848



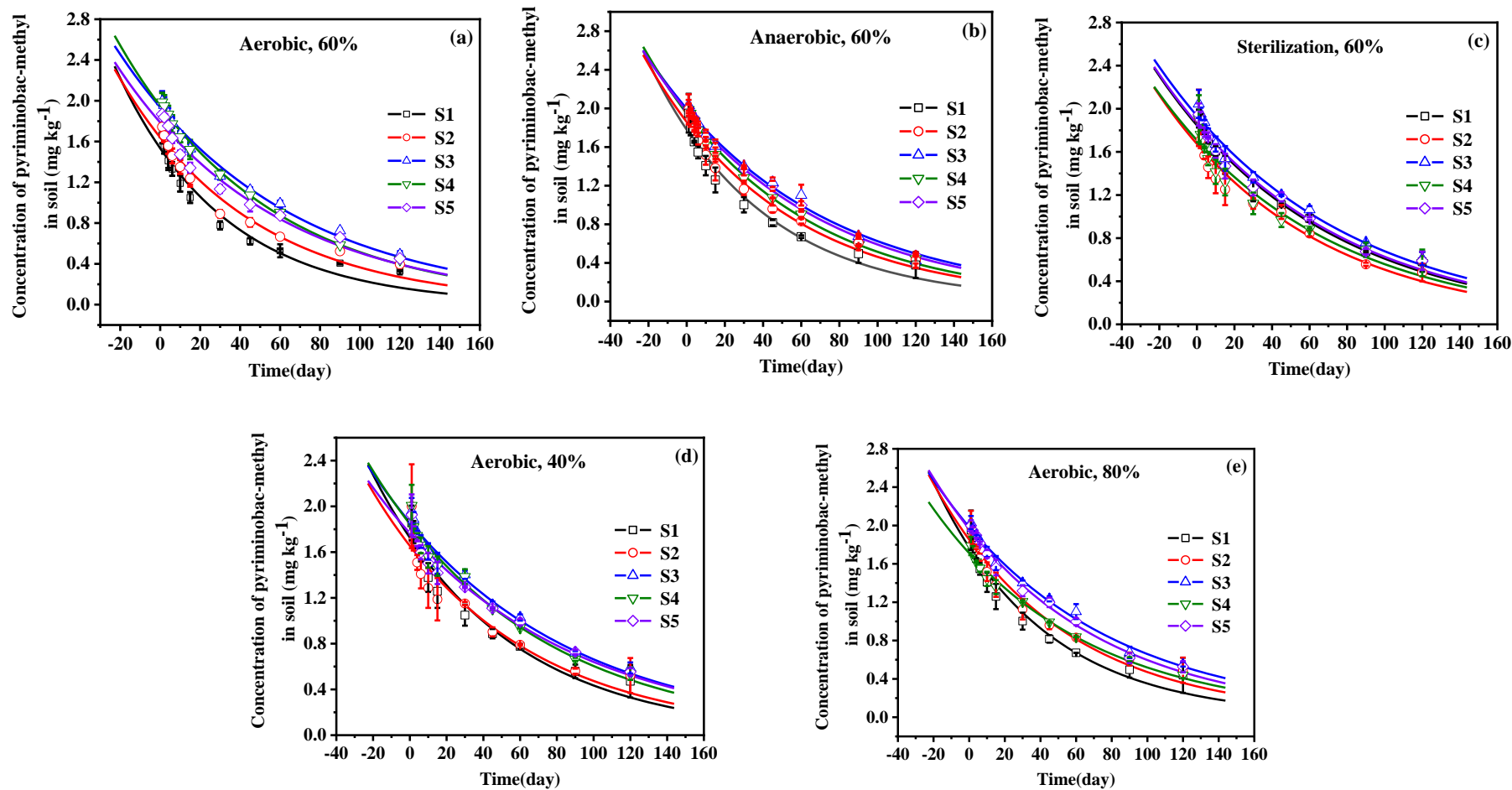
849



850

851

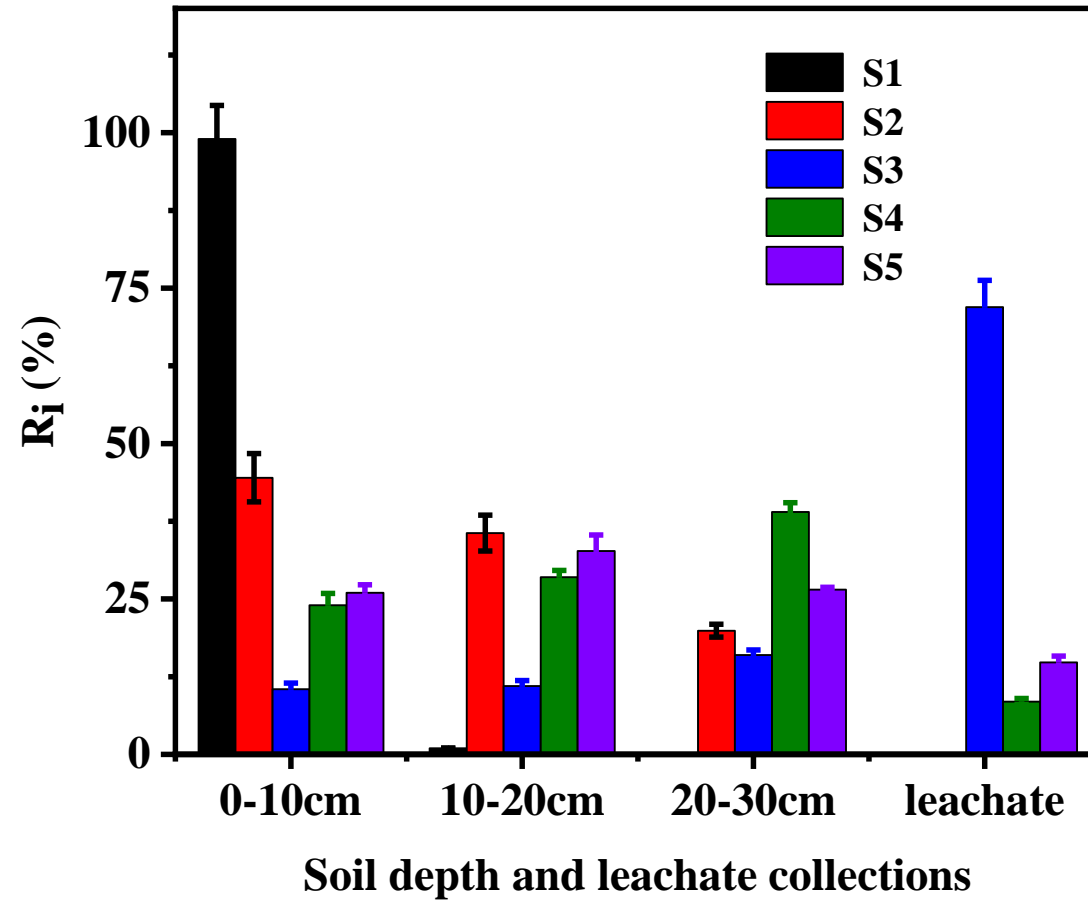
**Fig. 1** Adsorption (a) and desorption (b) kinetic curves and Adsorption (c) and desorption (d) isothermal curves of EPM in five different agricultural soils (S1 to S5 are defined in Table 1). Values are the means  $\pm$  standard error (n=3).



852

853

854 **Fig. 2** Degradation kinetics of EPM under aerobic (a), anaerobic (b), sterilization (c) conditions with 60% moisture, under aerobic conditions with 40% moisture(d) and with  
 855 80% moisture(e)in five different agricultural soils (S1 to S5 are defined in [Table 1](#)). Values are the means  $\pm$  standard error (n=3).



856

857

**Fig. 3** Distribution of EPM in soil column and leachate of five different agricultural soils (S1 to S5 are defined in [Table 1](#))