

1 **Sorption and desorption of glyphosate, MCPA and tetracycline and their mixtures**
2 **in soil as influenced by phosphate**

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3 **Abstract**

4 Phosphate fertilizers and herbicides such as glyphosate and MCPA are commonly applied
5 to agricultural land, and antibiotics such as tetracycline have been detected in soils
6 following the application of livestock manures and biosolids to agricultural land. Utilizing
7 a range of batch equilibrium experiments, this research examined the competitive sorption
8 interactions of these chemicals in soil. Soil samples (0-15 cm) collected from long-term
9 experimental plots contained Olsen P concentrations in the typical (13 to 20 mg kg⁻¹) and
10 elevated (81 to 99 mg kg⁻¹) range of build-up phosphate in agricultural soils. The elevated
11 Olsen P concentrations in field soils significantly reduced glyphosate sorption up to 50%,
12 but had no significant impact on MCPA and tetracycline sorption. Fresh phosphate
13 additions in the laboratory, introduced to soil prior to, or at the same time with the other
14 chemical applications, had a greater impact on reducing glyphosate sorption (up to 45%)

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16 than on reducing tetracycline (up to 13%) and MCPA (up to 8%) sorption. The impact of
17 fresh phosphate additions on the desorption of these three chemicals was also statistically
18 significant, but numerically very small namely < 1% for glyphosate and tetracycline and
19 3% for MCPA. The presence of MCPA significantly reduced sorption and increased
20 desorption of glyphosate, but only when MCPA was present at concentrations much greater
21 than environmentally relevant and there was no phosphate added to the MCPA solution.
22 Tetracycline addition had no significant effect on glyphosate sorption and desorption in
23 soil. For the four chemicals studied, we conclude that when mixtures of phosphate,
24 herbicides and antibiotics are present in soil, the greatest influence of their competitive
25 interactions is phosphate decreasing glyphosate sorption and the presence of phosphate in
26 solution lessens the potential impact of MCPA on glyphosate sorption. The presence of
27 chemical mixtures in soil solution have an overall greater impact on the sorption than
28 desorption of individual organic chemicals in soil.

29

30 **Keywords:** Glyphosate, MCPA, tetracycline, phosphate, batch equilibrium experiment,
31 competitive effects, sorption, desorption.

32

33 **Introduction**

34

35 The herbicides glyphosate and MCPA are among the top 5 most widely applied pesticides
36 in Canada. Glyphosate half-lives in soil range from 30 to 197 days ^[1,2] and glyphosate is
37 typically strongly retained in soil with the sorption distribution constant, K_d , ranging from

38 108 to 1,140 L kg⁻¹. [2,3] Soil half-lives for MCPA range from 15 to 50 days [4,5] and the
39 herbicide is weakly sorbed in soil with K_d ranging from 0.01 to 9.3 L kg⁻¹. [6-8] MCPA (26-
40 100%) is more readily desorbed than glyphosate (0.6-23.6%) in soil. [6] The antibiotics
41 tetracycline accounts for more than three-quarters of the total sales of antibiotics in USA
42 livestock production. [9] Tetracycline is also registered for human use, for example for the
43 treatment of urinary tract and respiratory diseases. [10,11] Tetracycline is detected in soils
44 following the application of livestock manure and biosolids on agricultural land. [12-14] Soil
45 half-lives for tetracycline range from 23 to 87 days [13,15] and its K_d ranges from 74 to 1,093
46 L kg⁻¹. [13,16] Tetracycline desorption has been shown to only range from 1 to 9%. [17,18]
47 Sorption and desorption are important processes that determine the mobility of glyphosate,
48 MCPA and tetracycline in soils. [19-21] The sorption and desorption of herbicides and
49 antibiotics may be influenced by phosphate concentrations in soil. [14,21,22]

50

51 Batch equilibrium studies [23,24] have demonstrated that long-term applications of
52 phosphate fertilizer significantly reduced glyphosate sorption in soil. Using similar
53 procedures, glyphosate sorption was also reduced when phosphate was added in the
54 laboratory at the same time as glyphosate was added in solution to soils. [22,25] For a clay
55 loam soil, Gimsing et al. (2007) [26] demonstrated that the competition was even stronger
56 when phosphate was added prior to glyphosate additions because the pre-sorbed phosphate
57 increased the net negative charge of the soil colloids and repelled the negatively charged
58 glyphosate molecules. In contrast, in another study [27], the differential timing of phosphate
59 applications, relative to glyphosate additions, produced the same reducing impact on
60 glyphosate sorption in sandy to sandy clay loam soils.

61

62 Fewer studies have examined the impact of phosphate on the sorption of other pesticides
63 or antibiotics in soils. ^[14,21,28] The impact of phosphate on MCPA ^[21] and tetracycline ^[14]
64 sorption was recently examined but both studies utilized phosphate and organic chemical
65 concentrations far exceeding their potential concentrations in agricultural soils ^[21] found
66 that added phosphate reduced MCPA sorption but only in two of the three soils examined.
67 Wang et al. (2010) ^[14] reported that phosphate significantly reduced tetracycline sorption
68 in two soils. The effect of phosphate on MCPA and tetracycline desorption in soil is
69 unknown. However, two studies have examined the impact of phosphate on glyphosate
70 desorption with phosphate being added to soil either two ^[29] or four ^[30] weeks prior to
71 glyphosate addition. In both cases, phosphate additions increased glyphosate desorption,
72 by ~2-10% in Prata et al. (2003) ^[30] and by 6-13% in Laitinen et al. (2008). ^[29]

73

74 Herbicides and antibiotics can be present in agricultural soils as mixtures. Studies have
75 shown that herbicide mixtures in soil can influence the sorption of an individual herbicide.
76 ^[31-34] There have been no studies that examined the impact of antibiotics on herbicide
77 sorption in soil, but it has been reported that the presence of some antibiotics increased
78 pesticide persistence. ^[35]

79

80 Utilizing a range of batch equilibrium experiments, this research examined the competitive
81 sorption of chemicals as mixtures, particularly focusing on the impacts of phosphate
82 concentrations on glyphosate, MCPA and tetracycline sorption and desorption in soil, and

83 on the impact of MCPA and tetracycline and their mixtures, in the presence and absence
84 of phosphate, on glyphosate sorption and desorption.

85

86 **Materials and methods**

87

88 *Chemicals*

89

90 Analytical grade glyphosate (99.9% purity), MCPA (99%), tetracycline (98%) were
91 obtained from Sigma-Aldrich Co., St. Louis, MO; and potassium dihydrogen phosphate
92 (KH_2PO_4) (99% chemical purity) and potassium chloride (100% chemical purity) from
93 Fisher Scientific, Fair Lawn, NJ. Radioactive [phosphonomethyl- ^{14}C] glyphosate (99%
94 radiochemical purity; specific activity 50 mCi/mmol), [2-methyl -4-chlorophenoxyacetic
95 acid ^{14}C] MCPA (98% radiochemical purity; specific activity 55 mCi/mmol) and [7- ^3H
96 (N)] tetracycline (98% radiochemical purity; specific activity 20 Ci/mmol) were obtained
97 from American Radiolabeled Chemicals Inc., St. Louis, MO.

98

99 *Soil characteristics and experimental design*

100

101 Soil samples (0-15 cm) were collected in spring 2013 from experimental plots that were
102 arranged in a randomized complete block design with four replications and were located at
103 the University of Manitoba Carman Field Research Station (49° 29.7' N, 98° 2.4' W),
104 Manitoba, Canada. All plots were under a flax and durum wheat rotation and received urea

105 fertilizers at an annual rate of 50 and 90 kg N ha⁻¹, respectively. For this study, samples
106 were collected from the replicated plots that had also received eight years (2002-2009) of
107 annual mono ammonium phosphate (MAP) applications at rates of 80 kg P ha⁻¹, as well as
108 from control plots that did not receive MAP application during these years. [36] The rotation
109 was continued from 2010 to 2013 but after 2010 no phosphate was applied. In each plot,
110 composite soil samples were collected using a Dutch auger with ten samples per plot and
111 the auger was cleaned in between plots. Samples were air-dried and sieved (<2mm) prior
112 to use in batch equilibrium experiments. Available phosphate was determined by the Olsen
113 (0.5N NaHCO₃, pH 8.5) phosphorus test (Olsen P). [37] Olsen P concentrations ranged from
114 81 to 99 mg kg⁻¹ in soil from the 80P plots that had received MAP applications and from
115 13 to 20 mg kg⁻¹ in soil from the 0P plots that had received no phosphate fertilizers. The
116 soil is classified as an Orthic Black Chernozem based on the Canadian System of Soil
117 Classification, which is approximately equivalent to the Udic Boroll subgroup in the U.S.
118 Soil Taxonomy. [38] Key soil properties are listed Table 1.

119

120 ***Impact of phosphate in solution on herbicides and antibiotic sorption and desorption***

121

122 Batch equilibrium procedures using 50-mL centrifuge Teflon tubes (duplicates) followed
123 the OECD guideline 106 [44] with air-dried soil (2 g) and a soil/solution ratio of 1:5 with
124 0.01M KCl as the background electrolyte. Soil slurries were rotated in the dark at 5°C from
125 0 to 24h (pre-incubation), from 24 to 48h (sorption) and from 48 to 72h (desorption) with
126 phosphate added at 0h, 24h and/or 48h, or never added, depending on the treatment (Table

127 2). For treatments *n,n,n* and *n,n,P*, a 0.01M KCl solution (8 mL) was added to soil at 0h
128 and no phosphate was added. For treatments *P,n,n* and *P,n,P*, the added 0.01M KCl
129 solution also contained phosphate while, for treatment *n,P,P*, the phosphate was added to
130 the herbicide and antibiotic solutions. Radiolabelled glyphosate, MCPA or tetracycline in
131 0.01M KCl (2 mL) was always added at 24h. Radiolabelled chemical solutions contained
132 1 mg L⁻¹ analytical-grade glyphosate, MCPA or tetracycline, with 6.67×10⁵ Bq L⁻¹ ¹⁴C-
133 labelled glyphosate, 3.83×10⁵ Bq L⁻¹ ¹⁴C-labelled MCPA or 4.17×10⁵ Bq L⁻¹ ³H-labelled
134 tetracycline, respectively. The concentration 1 mg L⁻¹ represented environmentally-
135 relevant concentrations of herbicides and antibiotics detected in agricultural soils [45] or
136 animal manure. [46] Phosphate was added as potassium dihydrogen phosphate and always
137 at a rate of 44 mg P kg⁻¹, corresponding to a concentration of 11 mg L⁻¹ in the added
138 solution. This rate is equivalent to an estimated 80 P kg ha⁻¹ when assuming the fertilizer
139 is being incorporated in the top 15 cm layer of a soil with a bulk density of 1,200 kg m⁻³.

140

141 At 48h, tubes were centrifuged at 10,000 rev min⁻¹ for 10 min and subsamples (1 mL) of
142 the supernatant (duplicates) were added to scintillation vials (7 mL) containing 5 mL 30%
143 Scintisafe scintillation cocktail (Fisher Scientific, Fair Lawn, NJ). Radioactivity was
144 quantified by Liquid Scintillation Counting (LSC) with automated quench correction (#H
145 method) (LS 6500 Beckman Instruments, Fullerton, CA). The sorption distribution
146 constant, K_d (L kg⁻¹), of glyphosate, MCPA or tetracycline was quantified by C_s/C_e, where
147 C_s is the concentration of the organic chemical in soil at equilibrium (mg kg⁻¹) and C_e is
148 the concentration of the organic chemical in the equilibrium solution (mg L⁻¹). The
149 concentration of the organic chemical in soil was calculated by the difference between the

150 radioactivity in the initial solution and the equilibrium solution. The soil organic carbon
151 coefficient, K_{oc} ($L\ kg^{-1}$) of glyphosate, MCPA or tetracycline was calculated by dividing
152 the K_d value by 0.0281 which was the fraction of soil organic carbon in soil.

153

154 Following the subsampling (2 mL in total), an additional portion of supernatant (6 ml) was
155 removed so that what was left in the tubes was a “slurry” consisting of soil mixed with the
156 remaining supernatant. Not all supernatant was removed from the tubes to ensure that the
157 same amount of supernatant was removed from each tube (8 mL in total) and replaced by
158 a 0.01M KCl solution (8 mL) with (treatments n,n,P , P,n,P and n,P,P) or without phosphate
159 (treatments n,n,n and P,n,n) in this solution (Table 2). Tubes were again rotated and at 72h,
160 tubes were centrifuged and subsampled as described above to determine radioactivity
161 remaining in solution. The percentage of organic chemical (herbicide or antibiotic)
162 desorbed from soil was quantified by dividing the mass of the organic chemical desorbed
163 from the soil at 72h by the mass of the organic chemical in the soil at 48h and multiplying
164 by 100. The mass of the organic chemical desorbed from the soil at 72h was calculated as
165 the mass of organic chemical in the supernatant at 72h minus the mass of the organic
166 chemical in the 2 mL solution remaining at 48h. ^[44]

167

168 ***Impacts of MCPA and tetracycline in solution on glyphosate sorption and***
169 ***desorption in the presence and absence of fresh phosphate***

170

171 Experiments followed similar protocols as described for *n,n,n*; *n,n,P*; and *P,n,P* in Table 2
172 above and also added to soil (at 0h) were MCPA, tetracycline (Tetra), or their mixtures
173 (M/T). MCPA, Tetra, and M/T were added at concentrations of 1 or 11 mg L⁻¹. Treatments
174 were labeled as *MCPA-n,n,n*; *Tetra- n,n,n*; *M/T- n,n,n*; *MCPA- n,n,P*, etc. There was also
175 a treatment labeled as *n,n,n* in which case neither phosphate nor MCPA, Tetra, or M/T was
176 added. The glyphosate solution was always added at 24h and contained 1 mg L⁻¹ analytical-
177 grade glyphosate with 6.67×10⁵ Bq L⁻¹ ¹⁴C-labelled glyphosate.

178

179 ***Effect of the pre-sorbed phosphate on the sorption of glyphosate, MCPA and***
180 ***tetracycline***

181

182 This batch equilibrium experiment only used the soil samples obtained from the plots that
183 had not received phosphate fertilizer applications. Potassium dihydrogen phosphate
184 solutions were prepared in 0.01M KCl at concentrations of 0, 11, 22, 44 mg P L⁻¹ and added
185 (8 mL) to air-dried soil (2 g) in Teflon tubes. Soil slurries were rotated in the dark at 5°C
186 for 24h and centrifuged at 10,000 revmin⁻¹ for 10 min. Supernatant (8 mL) was removed
187 and the concentrations of phosphate was determined colorimetrically by the molybdate
188 blue method ^[47] to calculate the amount of phosphate retained in soil. 0.01M KCl (8 mL)
189 was added to the soil followed by the addition of radiolabeled glyphosate, MCPA or
190 tetracycline in 0.01M KCl (2 mL). Radiolabelled glyphosate, MCPA or tetracycline
191 solutions contained 1 mg L⁻¹ analytical-grade glyphosate, MCPA or tetracycline, with
192 6.67×10⁵ Bq L⁻¹ ¹⁴C-labelled glyphosate, 2.08×10⁵ Bq L⁻¹ ¹⁴C-labelled MCPA and

193 5.00×10^5 Bq L⁻¹ ³H-labelled tetracycline, respectively. Soil slurries were again rotated for
194 24h, then centrifuged and subsampled as described above to calculate K_d values and
195 determine the effect of the pre-sorbed phosphate concentrations on the sorption of
196 glyphosate, MCPA and tetracycline.

197

198 *Effect of the pre-sorbed MCPA on glyphosate sorption*

199

200 Experiments followed similar protocols as described for the pre-sorbed phosphate above,
201 and thus MCPA was added in 0.01M KCl (8 mL) to soil (2 g) at concentrations of 0, 11,
202 22, 44 mg P L⁻¹. In order to calculate the amount of MCPA sorbed by soil, one subset of
203 samples (duplicated) also contained 2.83×10^3 , 5.83×10^4 , and 1.67×10^5 Bq L⁻¹ ¹⁴C-labelled
204 MCPA to measure the radioactivity in subsamples (1mL) from the supernatant that was
205 removed. The mass of MCPA in the soil at 24h was calculated by the difference between
206 the added radioactivity at 0h and the radioactivity in the supernatant at 24h. For the other
207 subset of samples (duplicated), the supernatant (8 mL) was removed at 24h and then
208 replaced by 0.01M KCl (8 mL) plus radiolabeled glyphosate in 0.01M KCl (2 mL). The
209 glyphosate solution contained 1 mg L⁻¹ analytical-grade glyphosate with 6.67×10^5 Bq L⁻¹
210 ¹⁴C-labelled glyphosate.

211

212 *Statistical analysis*

213

214 Statistical analyses were carried out using SAS software version 9.4 for Windows (SAS
215 Institute Inc. 2002-2012). Prior to each analysis, data sets were checked for outliers, normality
216 of residuals and homogeneity of variances. Residuals were normally distributed and variances were
217 homogeneous. For the K_d values, data were analysed by using normal distribution and for
218 the % desorption by beta distribution. Two-way ANOVA in PROC GLIMMIX was used
219 to quantify the effect of field aged-P (0P, 80P) and fresh-P addition (0, 11 mg L⁻¹) on K_d
220 values and % desorption of MCPA, tetracycline, and glyphosate in soil. One-way ANOVA
221 in PROC GLIMMIX was utilized to determine the effect of retained phosphate in soil on
222 glyphosate, MCPA and tetracycline sorption, and of retained MCPA in soil on glyphosate
223 sorption. Both in the presence and absence of fresh phosphate, two-way ANOVAs in
224 PROC GLIMMIX were carried out to quantify the effect of field aged-P (0P, 80P) and of
225 the concentrations (0, 1, 11 mg L⁻¹) of MCPA, tetracycline, or MCPA-tetracycline mixtures
226 on glyphosate K_d values. For fresh phosphate added at 48h only, or at both 0h and 48h,
227 and in the absence of fresh phosphate, two-way ANOVAs in PROC GLIMMIX were
228 carried out to quantify the effect of field aged-P (0P, 80P) and of the concentration (0, 1,
229 11 mg L⁻¹) of MCPA, tetracycline, or MCPA-tetracycline mixtures on the percent of
230 glyphosate desorbed. For all ANOVAs, the separation of treatment means was performed
231 using the Tukey's test (p<0.05).

232

233 **Results**

234

235 Kd values on average ranged from 209 to 596 L kg⁻¹ for glyphosate (Fig. 1), from 118 to
236 135 L kg⁻¹ for tetracycline, and from 4.99 to 5.37 L kg⁻¹ for MCPA (Table 3). Koc values
237 ranged from 6105 to 25,496 L kg⁻¹ for glyphosate, from 3,928 to 4,901 L kg⁻¹ for
238 tetracycline, and from 156 to 209 L kg⁻¹ for MCPA. These results are within the ranges
239 observed in previous studies of the sorption of glyphosate^[2,29,48], tetracycline^[14,16,18] and
240 MCPA^[7,21,49] in soils. Glyphosate (< 2%) (Fig. 1) and tetracycline (< 1%) desorption was
241 always small but MCPA desorption ranged from 26 to 31 % (Table 3).

242

243 Phosphate significantly reduced glyphosate sorption in soil (Fig. 1). Without laboratory-
244 added phosphate, glyphosate Kd values were 50% smaller in soil containing 81 to 99 mg
245 kg⁻¹ Olsen P than in soil containing 13 to 20 mg kg⁻¹ Olsen P. Regardless of whether
246 MCPA, tetracycline or MCPA/tetracycline mixture were added to soils in the laboratory,
247 field aged-P always significantly reduced glyphosate Kd values (Table 4). When phosphate
248 was added to soil solution at either 0h or 24h, it had the same significant effect on reducing
249 glyphosate sorption with glyphosate Kd values being reduced by 37-45% in field soils
250 containing 13 to 20 mg P kg⁻¹, and by 23-27% in field soils containing 81 to 99 mg P kg⁻¹
251 (Fig. 1). In the pre-sorbed phosphate experiment, the soil retained 9.8, 18.5 and 32.4 mg P
252 kg⁻¹ for the additions of 11, 22, 44 mg P L⁻¹, respectively, and glyphosate sorption was
253 significantly reduced by 41% (11 mg P L⁻¹), 52% (22 mg P L⁻¹) and 65% (44 mg P L⁻¹)
254 (Fig. 2).

255

256 The amount of field aged-P in soil had no significant impact on MCPA and tetracycline
257 sorption in soil (Table 1S). However, fresh phosphate added to soil solution significantly
258 reduced tetracycline K_d values by 8-13% and MCPA K_d values by 7-8% (Table 3). The
259 competitive effect of phosphate on MCPA and tetracycline sorption was not dependent on
260 when the phosphate was added in the laboratory (either 0h or 24h) (Table 3). In the pre-
261 sorbed phosphate experiment, phosphate significantly reduced MCPA sorption by 10% and
262 tetracycline sorption by 8% for the addition of 44 mg P L⁻¹ (Table 5, Table 3S, or Fig. 2).
263 However, there was no impact on MCPA or tetracycline sorption when phosphate additions
264 were 11 or 22 mg P L⁻¹.

265

266 Glyphosate desorption was significantly greater in field soils containing 81 to 99 mg kg⁻¹
267 Olsen P (0.74%) than in soils containing 13 to 20 mg kg⁻¹ Olsen P (0.29%) (Fig. 1, Table
268 1S). Regardless of whether MCPA, tetracycline or MCPA/tetracycline mixture were added
269 to soils in the laboratory, field aged-P always significantly increased glyphosate desorption
270 (Table 2S). Fresh phosphate additions at 0h, 24h or/and 48h to soil solutions in the
271 laboratory also significantly increased glyphosate desorption by 0.52-0.84% in soils
272 containing 13 to 20 mg kg⁻¹ Olsen P and by 0.52-0.82% in field soils containing 81 to 99
273 mg kg⁻¹ Olsen P (Fig. 1). The amount of field aged-P in soil had no significant impact on
274 MCPA and tetracycline desorption in soil, but the addition of fresh phosphate to soil
275 solutions in the laboratory significantly increased desorption of MCPA by 2-3% and
276 tetracycline by 0.18-0.23% (Table 3). The competitive effect of phosphate on MCPA,
277 tetracycline and glyphosate desorption was not dependent when phosphate was added to
278 soil solution (either at 0h, 24h or 48h). The number of times that phosphate was added had

279 no significant effect on MCPA and tetracycline desorption (Table 3). However, glyphosate
280 desorption was greater when phosphate was added twice (*P,n,P*, or *n,P,P*) rather than once
281 (*P,n,n* or *n,n,P*) but glyphosate desorption remained < 2% in all cases (Fig. 1).

282

283 MCPA and MCPA/tetracycline mixtures added at 11 mg L⁻¹ significantly reduced
284 glyphosate K_d values and increased glyphosate desorption, but only when no phosphate
285 was added to the soil solution (Fig. 3, Table 4). MCPA and MCPA/tetracycline mixtures
286 added at 1 mg L⁻¹ had no significant effect on glyphosate sorption and desorption (Table
287 4). Tetracycline had no significant effect on glyphosate K_d values and desorption,
288 regardless of whether it was added to soil at 1 or 11 mg L⁻¹, and whether or not phosphate
289 was added to soil solution (Table 4). Thus, the effect of MCPA/tetracycline mixtures on
290 glyphosate sorption and desorption was due to MCPA. MCPA addition significantly
291 reduced glyphosate K_d values by 14% (Fig. 3) and glyphosate desorption by 0.1% (Fig. 3).
292 In the pre-sorbed MCPA experiment, the addition of 11, 22, 44 mg MCPA L⁻¹ the soil
293 retained 1.2, 1.8 and 1.9 mg MCPA kg⁻¹, respectively. The pre-sorbed MCPA significantly
294 reduced glyphosate sorption by 6% for the addition of MCPA at 44 mg L⁻¹, but there was
295 no impact on glyphosate sorption when additions were at 11 or 22 mg L⁻¹ (Table 5, Table
296 3S, or Fig. 2).

297

298 **Discussion**

299

300 The addition of phosphate at either 0h or 24h yielded the same impact on glyphosate
301 sorption (Fig. 1), in agreement with the findings of Gimsing et al. (2004) ^[27] who also
302 reported that the timing of phosphate additions had no significant effect. Glyphosate and
303 phosphate have shown to compete for the same sorption sites in soil. ^[22,26] Application of
304 phosphate with glyphosate in solution reduced glyphosate sorption because phosphate is
305 preferentially sorbed over glyphosate by available sorption sites. ^[50]

306

307 Glyphosate K_d values were significantly smaller in soils containing elevated Olsen P
308 concentrations than in soils containing typical Olsen P concentrations. This elevated Olsen
309 P concentrations resulted from eight years of annual phosphate application from 2002 to
310 2009, with soils being sampled for this study in 2013. These results indicate that phosphate
311 persists in agricultural soils and occupies sorption sites that otherwise would be available
312 sorption sites for glyphosate. In-addition, in the pre-sorbed phosphate experiment,
313 glyphosate sorption was also reduced with increasing phosphate application to soil thus
314 indicating that phosphate from recently fertilizer applications will also occupy sorption
315 sites otherwise available for glyphosate sorption. Given the moderately acidic conditions
316 (soil pH 5), the sorption sites that phosphate ($\text{H}_2\text{PO}_4^{-1}$) occupies are positively charged
317 Fe/Al-oxides. When phosphate ($\text{H}_2\text{PO}_4^{-1}$) is retained by Fe/Al-oxides, the Fe/Al-oxides
318 will yield a net negative charge, leading to an electrostatic repulsion between the Fe/Al-
319 oxides and glyphosate (H_2G^-) in soil. ^[26,29] However, a portion of glyphosate molecules
320 that were sorbed by available positively charged Fe/Al-oxides. The addition of phosphate
321 after this sorption increased glyphosate desorption (Fig. 1) possibly because phosphate is
322 able to displace glyphosate bound to Fe/Al-oxides as the bonding forces between phosphate

323 and Fe/Al-oxides are stronger than the bonding forces between glyphosate and Fe/Al-
324 oxides. ^[50]

325

326 Under the experimental conditions with the soil slurries being at a pH 5, the molecules of
327 MCPA (pKa = 3.73) ^[3] are predominantly negatively-charged. Given that tetracycline (pKa
328 = 3.3, 7.7 and 9.7) ^[51] is a zwitterion in moderately acidic to neutral soils ^[16,52] part of the
329 tetracycline molecules are also deprotonated. ^[53] Hence, phosphate (H_2PO_4^-), MCPA and
330 tetracycline molecules may compete for positively-charged Fe/Al-oxides in soil. ^[14,21,53]

331 In the pre-sorbed phosphate experiment, an increasing addition of phosphate and sorption
332 in soil increased the portion of Fe-/Al-oxides with a net negative charge. ^[14,21] Of the three
333 phosphate rates used in the pre-sorbed phosphate experiment (11, 22 and 44 mg P L⁻¹),
334 MCPA and tetracycline sorption was only significantly reduced at the highest rate because
335 more Fe/Al-oxides were net negatively charged and repelling MCPA and tetracycline
336 molecules.

337

338 The effect of phosphate on reducing sorption was less for MCPA and tetracycline than for
339 glyphosate. Under moderately acidic conditions, Fe/Al-oxides are the dominant sorption
340 sites for glyphosate and phosphate because both have a phosphonic acid group. ^[22,26,27,54,55]

341 However, MCPA (i.e., carboxyl and phenyl groups) and tetracycline (i.e., tricarbonylamide
342 carbonyl, amine and hydroxyl groups) have other functional groups ^[56-58] and sorption sites
343 for MCPA and tetracycline can include under moderately acidic conditions humic
344 substances and clay minerals in addition to Fe/Al-oxides in soils. ^[14,53,59]

345

346 MCPA had no longer a significant effect on glyphosate sorption when phosphate was added
347 to the soil solution. The molecular size of phosphate (0.25 nm) is smaller than glyphosate
348 (0.43 nm) and MCPA (0.77 nm). ^[60-62] Therefore, it is possible that phosphate is
349 preferentially sorbed over glyphosate and MCPA. ^[50] Thus, when both phosphate and
350 MCPA were added to the soil solution, phosphate occupied the sorption sites that may
351 otherwise be available to MCPA and suppressed the effect of MCPA on glyphosate
352 sorption. In the pre-sorbed experiment, in the absence of phosphate additions, MCPA
353 reduced glyphosate sorption because pre-sorbed MCPA occupied some sorption sites
354 which may otherwise be accessible to glyphosate.

355

356 MCPA was weakly retained with Koc values ranging from 156 to 209 L kg⁻¹ while
357 glyphosate and tetracycline were strongly retained with Koc values ranging from 6,105 to
358 25,496 and 3,928 to 4,901 L kg⁻¹, respectively. It has been reported that organic molecules
359 are considered relatively mobile when Koc value ranges from 150 to 500 L kg⁻¹. ^[63] Thus,
360 given these Koc values, MCPA is relatively mobile in soil because it is only weakly
361 retained ^[6], unlike glyphosate and tetracycline. Thus, glyphosate is very strongly retained
362 in soil and is less likely to be mobile in matrix flow than MCPA, regardless of the amounts
363 of phosphate or MCPA that can compete with glyphosate for sorption sites in soil. In
364 contrast, the presence of recent phosphate applications to agricultural soils may increase
365 the mobility of MCPA to deeper depths but only when applied at relatively large phosphate
366 fertilizer rates.

367

368 **Conclusion**

369

370 Field-aged phosphate had no significant effect on MCPA and tetracycline sorption and
371 desorption but significantly reduced glyphosate sorption up to 50% and increased
372 glyphosate desorption by 0.45%. Pre-sorbed phosphate had a greater impact on reducing
373 glyphosate sorption than on reducing MCPA and tetracycline sorption. The addition of
374 fresh phosphate in the laboratory also significantly decreased glyphosate sorption (up to
375 45%) and increased glyphosate desorption (up to 0.87%) and the impact on reducing
376 MCPA and tetracycline sorption (< 13%) and increasing MCPA and tetracycline
377 desorption (< 3%) was significant but smaller than the impact on glyphosate. Glyphosate
378 and tetracycline were strongly retained in soil with K_d values $> 100 \text{ L kg}^{-1}$ and desorption
379 less than 2%. In contrast, MCPA was weakly retained in soil with K_d values $< 6 \text{ L kg}^{-1}$ and
380 desorption was above 25%. Hence, even in soils with a large phosphate build-up,
381 glyphosate will be less mobile in matrix flow than MCPA. MCPA but not tetracycline
382 additions significantly decreased glyphosate sorption, but only when MCPA was present
383 at concentrations ten times greater than typically detected in agricultural soils and there
384 was no phosphate added to the herbicide solutions.

385

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387

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395

396 **References**

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398 [1] Smith, A.E.; Aubin, A.J. Degradation of ¹⁴C-glyphosate in saskatchewan soils. *Bull.*
399 *Environ. Contam. Toxicol.* **1993**, *50* (4), 499–505.

400 [2] Giesy, J.P.; Dobson, S.; Solomon, K.R. Ecotoxicological risk assessment for
401 Roundup herbicide. *Rev. Environ. Contam. Toxicol.* **2000**, *167*, 35–120.

402 [3] IUPAC. Pesticide properties database <http://sitem.herts.ac.uk/aeru/iupac/atoz.htm>
403 (accessed Jul 20, 2016).

404 [4] Soderquist, C.J.; Crosby, D.G. Dissipation of 4-chloro-2-methylphenoxyacetic acid
405 (MCPA) in a rice field. *Pestic. Sci.* **1975**, *6*, 17–33.

406 [5] Sattar, M.A.; Paasivirta, J. Fate of the herbicide MCPA in soil. Analysis of the
407 residue of MCPA by an internal standard method. *Chemosphere* **1980**, *9*, 365–375.

408 [6] Sørensen, S.R.; Schultz, A.; Jacobsen, O.S.; Aamand, J. Sorption, desorption and
409 mineralisation of the herbicides glyphosate and MCPA in samples from two Danish soil

410 and subsurface profiles. *Environ. Pollut.* **2006**, *141* (1), 184–194.

411 [7] Jacobsen, C.S.; van der Keur, P.; Iversen, B.V.; Rosenberg, P.; Barlebo, H.C.; Torp,
412 S.; Vosgerau, H.; Juhler, R.K.; Ernstsens, V.; Rasmussen, J.; Brinch, U.C.; Jacobsen,
413 O.H. Variation of MCPA, metribuzine, methyltriazine-amine and glyphosate
414 degradation, sorption, mineralization and leaching in different soil horizons. *Environ.*
415 *Pollut.* **2008**, *156* (3), 794–802.

416 [8] Alister, C.A.; Araya, M.A.; Kogan, M. Adsorption and desorption variability of four
417 herbicides used in paddy rice production. *J. Environ. Sci. Heal. Part B* **2010**, *46* (1), 62–
418 68.

419 [9] FDA. Antimicrobials sold or distributed for use in food-producing animals
420 <https://www.fda.gov/downloads/ForIndustry/UserFees/AnimalDrugUserFeeActADUFA>
421 [/UCM476258.pdf](https://www.fda.gov/downloads/ForIndustry/UserFees/AnimalDrugUserFeeActADUFA/UCM476258.pdf) (accessed Apr 20, 2017).

422 [10] De Briyne, N.; Atkinson, J.; Borriello, S.P.; Pokludová, L. Antibiotics used most
423 commonly to treat animals in Europe. *Vet. Rec.* **2014**, *175* (13), 325–325.

424 [11] Lamb, R.; Ozsvári, B.; Lisanti, C.L.; Tanowitz, H.B.; Howell, A.; Martinez-
425 Outschoorn, U.E.; Sotgia, F.; Lisanti, M.P. Antibiotics that target mitochondria
426 effectively eradicate cancer stem cells, across multiple tumor types: Treating cancer like
427 an infectious disease. *Oncotarget* **2015**, *6* (7), 4569–4584.

428 [12] Hamscher, G.; Sczesny, S.; Höper, H.; Nau, H. Determination of persistent
429 tetracycline residues in soil fertilized with liquid manure by high-performance liquid
430 chromatography with electrospray ionization tandem mass spectrometry. *Anal. Chem.*
431 **2002**, *74* (7), 1509–1518.

- 432 [13] Pan, M.; Chu, L.M. Adsorption and degradation of five selected antibiotics in
433 agricultural soil. *Sci. Total Environ.* **2016**, *545–546*, 48–56.
- 434 [14] Wang, Y.J.; Sun, R.J.; Xiao, A.Y.; Wang, S.Q.; Zhou, D.M. Phosphate affects the
435 adsorption of tetracycline on two soils with different characteristics. *Geoderma* **2010**,
436 *156* (3–4), 237–242.
- 437 [15] Aga, D.S.; O'Connor, S.; Ensley, S.; Payero, J.O.; Snow, D.; Tarkalson, D.
438 Determination of the persistence of tetracycline antibiotics and their degradates in
439 manure-amended soil using enzyme-linked immunosorbent assay and liquid
440 chromatography-mass spectrometry. *J. Agric. Food Chem.* **2005**, *53* (18), 7165–7171.
- 441 [16] Bao, Y.; Zhou, Q.; Wang, Y. Adsorption characteristics of tetracycline by two soils:
442 Assessing role of soil organic matter. *Aust. J. Soil Res.* **2009**, *47* (3), 286–295.
- 443 [17] Fernández-Calviño, D.; Bermúdez-Couso, A.; Arias-Estévez, M.; Nóvoa-Muñoz, J.
444 C.; Fernández-Sanjurjo, M. J.; Álvarez-Rodríguez, E.; Núñez-Delgado, A. Kinetics of
445 tetracycline, oxytetracycline, and chlortetracycline adsorption and desorption on two
446 acid soils. *Environ. Sci. Pollut. Res.* **2015**, *22* (1), 425–433.
- 447 [18] Pils, J.R.V.; Laird, D.A. Sorption of Tetracycline and Chlortetracycline on K- and
448 Ca-Saturated Soil Clays, Humic Substances, and Clay–Humic Complexes. *Environ. Sci.*
449 *Technol.* **2007**, *41* (6), 1928–1933.
- 450 [19] Duke, S.O.; Reddy, K. N.; Bu, K.; Cizdziel, J.V. Effects of glyphosate on the
451 mineral content of glyphosate-resistant soybeans (*Glycine max*). *J. Agric. Food Chem.*
452 **2012**, *60*, 6764–6771.
- 453 [20] Zhang, G.; Liu, X.; Sun, K.; Zhao, Y.; Lin, C. Sorption of tetracycline to sediments

454 and soils: Assessing the roles of pH, the presence of cadmium and properties of
455 sediments and soils. *Front. Environ. Sci. Eng. China* **2010**, *4* (4), 421–429.

456 [21] Hiller, E.; Tatarková, V.; Šimonovičová, A.; Bartal', M. Sorption, desorption, and
457 degradation of (4-chloro-2-methylphenoxy)acetic acid in representative soils of the
458 Danubian Lowland, Slovakia. *Chemosphere* **2012**, *87* (5), 437–444.

459 [22] Kanissery, R.G.; Welsh, A.; Sims, G.K. Effect of soil aeration and phosphate
460 addition on the microbial bioavailability of carbon-14-glyphosate. *J. Environ. Qual.*
461 **2015**, *44* (1), 137.

462 [23] de Jonge, H.; de Jonge, L.W.; Jacobsen, O.H.; Yamaguchi, T.; Moldrup, P.
463 Glyphosate sorption in soils of different pH and phosphorus content. *Soil Sci.* **2001**, *166*
464 (4), 230–238.

465 [24] Munira, S.; Farenhorst, A.; Flaten, D.; Grant, C. Phosphate fertilizer impacts on
466 glyphosate sorption by soil. *Chemosphere* **2016**, *153*, 471–477.

467 [25] Cruz, L.H.da.; Santana, H.de.; Zaia, C.T. B.V.; Zaia, D.A.M. Adsorption of
468 glyphosate on clays and soils from Paraná State: effect of pH and competitive adsorption
469 of phosphate. *Brazilian Arch. Biol. Technol.* **2007**, *50* (3), 385–394.

470 [26] Gimsing, A.L.; Szilas, C.; Borggaard, O.K. Sorption of glyphosate and phosphate
471 by variable-charge tropical soils from Tanzania. *Geoderma* **2007**, *138*, 127–132.

472 [27] Gimsing, A.L.; Borggaard, O.K.; Bang, M. Influence of soil composition on
473 adsorption of glyphosate and phosphate by contrasting Danish surface soils. *Eur. J. Soil*
474 *Sci.* **2004**, *55*, 183–191.

475 [28] Vasudevan, D.; Cooper, E.M. 2,4-D Sorption in Iron Oxide-Rich Soils: Role of Soil

476 Phosphate and Exchangeable Al. *Environ. Sci. Technol.* **2004**, *38* (1), 163–170.

477 [29] Laitinen, P.; Siimes, K.; Rämö, S.; Jauhiainen, L.; Eronen, L.; Oinonen, S.;
478 Hartikainen, H. Effects of Soil Phosphorus Status on Environmental Risk Assessment of
479 Glyphosate and Glufosinate-Ammonium. *J. Environ. Qual.* **2008**, *37* (3), 830–838.

480 [30] Prata, F.; Cardinali, V.C.D.B.; Lavorenti, A.; Tornisielo, V.L.; Regitano, J.B.
481 Glyphosate sorption and desorption in soils with distinct phosphorus levels. *Sci. Agric.*
482 **2003**, *60* (1), 175–180.

483 [31] Farenhorst, A.; Bowman, B.T. Competitive sorption of atrazine and metolachlor in
484 soil. *J. Environ. Sci. Heal. B* **1998**, *33* (6), 671–682.

485 [32] Leistra, M.; Matser, A.M. Adsorption, transformation, and bioavailability of the
486 fungicides carbendazim and iprodione in soil, alone and in combination. *J. Environ. Sci. Heal.*
487 *B* **2004**, *39* (1), 1–17.

488 [33] Hernández-Soriano, M.C.; Mingorance, M.D.; Peña, A. Interaction of pesticides
489 with a surfactant-modified soil interface: Effect of soil properties. *Colloids Surfaces A*
490 *Physicochem. Eng. Asp.* **2007**, *306* (1–3), 49–55.

491 [34] De Wilde, T.; Spanoghe, P.; Ryckeboer, J.; Jaeken, P.; Springael, D. Sorption
492 characteristics of pesticides on matrix substrates used in biopurification systems.
493 *Chemosphere* **2009**, *75* (1), 100–108.

494 [35] Nordenholt, R.M.; Goyne, K.W.; Kremer, R.J.; Lin, C.H.; Lerch, R.N.; Veum, K.S.
495 Veterinary antibiotic effects on atrazine degradation and soil microorganisms. *J.*
496 *Environ. Qual.* **2016**, *45* (2), 565.

497 [36] Grant, C.; Flaten, D.; Tenuta, M.; Malhi, S.; Akinremi, W. The effect of rate and Cd

498 concentration of repeated phosphate fertilizer applications on seed Cd concentration
499 varies with crop type and environment. *Plant Soil* **2013**, 372 (1–2), 221–233.

500 [37] Frank, K.; Geegle, D.; Denning, J. Phosphorus. In *Recommended chemical soil test*
501 *procedures for the North Central Region*; Brown, J. R., Ed.; Missouri Agricultural
502 Experiment Station: Missouri, SB. USA, 2011; 21–26.

503 [38] CSSC. *The Canadian System of Soil Classification*, 3rd ed.; Haynes, R. H., Ed.;
504 NRC Research Press: Ottawa, 1998.

505 [39] Nelson, D.W.; Somemers, L.E. Total carbon, organic carbon, and organic matter. In
506 *Methods of soil analysis. Part 3. Chemical methods*; Bigham, J. M., Ed.; American
507 Society of Agronomy Inc. Soil Science Society America Inc.: Madison, WI. USA,
508 1996; 961–1010.

509 [40] Jones Jr, J. B. Soil pH. In *Laboratory guide for conducting soil tests and plant*
510 *analysis*; CRC press: Boca Raton, London, NY. WA. D.C USA, 2001; 7–36.

511 [41] Whitney, D.A. Micronutrients: zinc, iron, manganese and copper. In *Recommended*
512 *chemical soil test procedures for the North Central Region*; Brown, J. R., Ed.; Missouri
513 Agricultural Experiment Station: Missouri, SB. USA, 2011; 41–44.

514 [42] Barnhisel, R.; Bertsch, P.M. Total Aluminium. In *Methods of Soil Analysis. Part 2.*
515 *Chemical and Biological Properties, Agronomy 9*; Page, A. L., Ed.; Madison, WI, USA,
516 1982; 275–300.

517 [43] Warncke, D.; Brown, J.R. Potassium and other basic cations. In *Recommended*
518 *chemical soil test procedures for the North Central Region*; Brown, J. R., Ed.; Missouri
519 Agricultural Experiment Station: Missouri, SB. USA, 2011; 31–33.

- 520 [44] OECD. *OECD guideline for the testing of chemicals. Adsorption-desorption using*
521 *a batch equilibrium method*, 106; **2000**.
- 522 [45] Hu, J.; Yang, T.; Yin, S.; Cao, D. Dissipation and residue of MCPA (4-chloro-2-
523 ethylphenoxyacetate) in wheat and soil. *Environ. Monit. Assess.* **2012**, *184* (8), 5017–
524 5024.
- 525 [46] Karci, A.; Balcioglu, I.A. Investigation of the tetracycline, sulfonamide, and
526 fluoroquinolone antimicrobial compounds in animal manure and agricultural soils in
527 Turkey. *Sci. Total Environ.* **2009**, *407* (16), 4652–4664.
- 528 [47] Murphy, J.; Riley, J.P. A modified single solution method for the determination of
529 phosphate in natural waters. *Anal. Chim. Acta* **1962**, *27*, 31–36.
- 530 [48] Kumari, K.G.I.D.; Moldrup, P.; Paradelo, M.; Elsgaard, L.; de Jonge, L.W. Soil
531 properties control glyphosate sorption in soils amended with birch wood biochar. *Water*
532 *Air Soil Pollut.* **2016**, *227*, 174.
- 533 [49] Shang, C.; Arshad, M.A. Sorption of clopyralid, dicamba and MCPA by two soils
534 with conventional and no-till management. *Can. J. Soil Sci.* **1998**, *78* (1), 181–186.
- 535 [50] Gimsing, A.L.; Borggaard, O.K. Effect of KCl and CaCl₂ as background
536 electrolytes on the competitive adsorption of glyphosate and phosphate on goethite.
537 *Clays Clay Miner.* **2001**, *49* (3), 270–275.
- 538 [51] Tolls, J. Sorption of Veterinary Pharmaceuticals in Soils: A Review. *Environ. Sci.*
539 *Technol.* **2001**, *35* (17), 3397–3406.
- 540 [52] Zhang, Z.; Sun, K.; Gao, B.; Zhang, G.; Liu, X.; Zhao, Y. Adsorption of
541 tetracycline on soil and sediment: Effects of pH and the presence of Cu(II). *J. Hazard.*

542 Mater. **2011**, *190* (1–3), 856–862.

543 [53] Gu, C.; Karthikeyan, K.G. Interaction of tetracycline with aluminum and iron
544 hydrous oxides. *Environ. Sci. Technol.* **2005**, *39* (8), 2660–2667.

545 [54] Barja, B.C.; Afonso, M.D.S. Aminomethylphosphonic acid and glyphosate
546 adsorption onto goethite: A comparative study. *Environ. Sci. Technol.* **2005**, *39* (2),
547 585–592.

548 [55] Sprankle, P.; Meggit, W.F.; Penner, D. Adsorption , mobility , and microbial
549 degradation of glyphosate in the soil. *Weed Sci. Soc. Am.* **1975**, *23* (3), 229–234.

550 [56] Spadotto, C.A.; Hornsby, A.G. Soil Sorption of Acidic Pesticides. *J. Environ. Qual.*
551 **2003**, *32* (3), 949.

552 [57] Sassman, S.A.; Lee, L.S. Sorption of three tetracyclines by several soils: Assessing
553 the role of pH and cation exchange. *Environ. Sci. Technol.* **2005**, *39* (19), 7452–7459.

554 [58] Haberhauer, G.; Pfeiffer, L.; Gerzabek, M.H.; Kirchmann, H.; Aquino, A.J.A.;
555 Tunega, D.; Lischka, H. Response of sorption processes of MCPA to the amount and
556 origin of organic matter in a long-term field experiment. *Eur. J. Soil Sci.* **2001**, *52* (2),
557 279–286.

558 [59] Werner, D.; Garratt, J.A.; Pigott, G. Sorption of 2,4-D and other phenoxy
559 herbicides to soil, organic matter, and minerals. *J. Soils Sediments* **2013**, *13* (1), 129–
560 139.

561 [60] Liu, F.; He, J.; Colombo, C.; Violante, A. Competitive adsorption of sulfate and
562 oxalate on goethite in the absence or presence of phosphate. *Soil Sci.* **1999**, *164* (3),
563 180–189.

564 [61] Martin, M.J.S.; Villa, M.V; Camazano, M.S. Glyphosate-hydrotalcite interaction as
565 influenced by pH. *Clays Clay Miner.* **1999**, *47* (6), 777–783.

566 [62] Tylor, J.S.; Chen, S.S.; Mulford, L.A.; Norris, C.D. *Flat sheet, bench and pilot*
567 *testing for pesticide rremoval using reverse osmosis*; AWWA Research Foundation and
568 American Water Works Association: Orlando, Fl, 2000.

569 [63] Barcelo, D. Pesticides and their degradation products: charateristics, uses and
570 environmental behaviour. In *Trace determination of pesticides and their degradation*
571 *products in water*; Hennion, M.C., Eds.; Elsevier, 1997; 89–94.

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590 **FIGURE CAPTIONS**

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592 **Figure 1.** Effect of phosphate fertilizer on glyphosate sorption and desorption in soil.
593 Potassium dihydrogen phosphate was added prior or during glyphosate addition for the
594 sorption study and prior, during and/or post stage of glyphosate addition for the desorption
595 study (see Table 2 for labels and details).

596

597 **Figure 2.** Effect of pre-sorbed phosphate concentrations on MCPA, tetracycline and
598 glyphosate sorption, and of pre-sorbed MCPA concentrations on glyphosate sorption in
599 soil. Numbers on x-axis in parenthesis refer to mean (+/-standard error) of measured pre-
600 sorbed phosphate and MCPA.

601

602 **Figure 3.** Effect of MCPA and MCPA/tetracycline mixtures on glyphosate sorption and
603 desorption in soil. Potassium dihydrogen phosphate with MCPA or MCPA/tetracycline
604 were added prior glyphosate for the sorption study and prior, or post stage of glyphosate
605 addition for the desorption study: (see Table 2 for labels and details).

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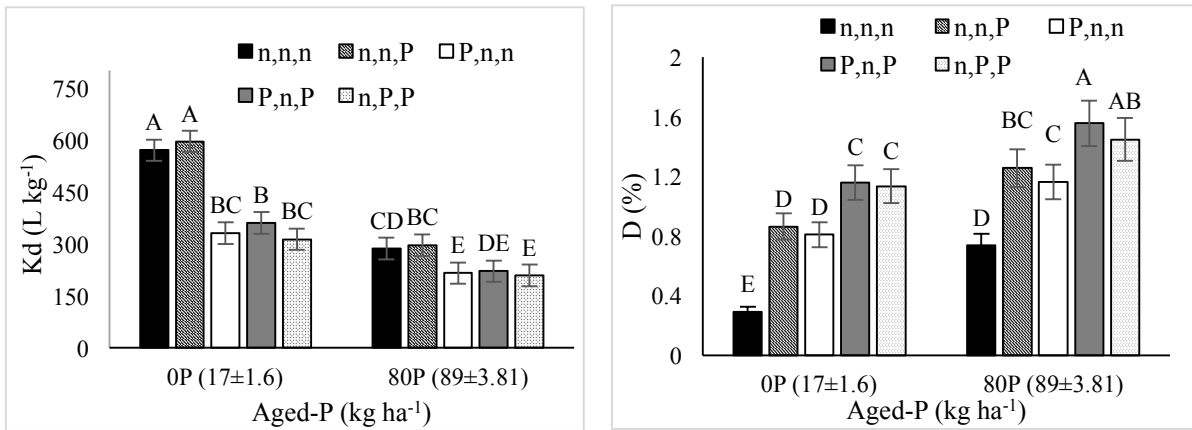
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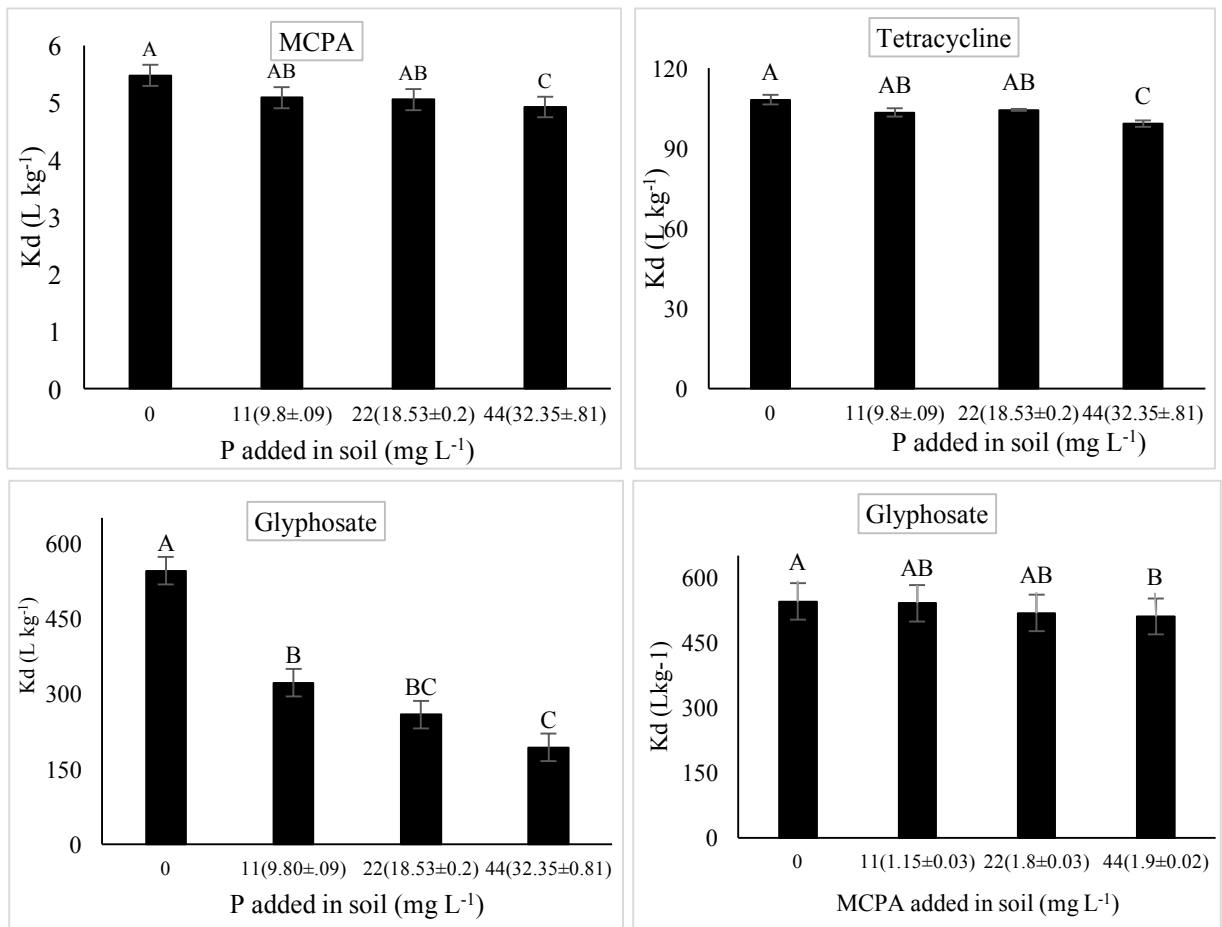
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615 Fig. 1

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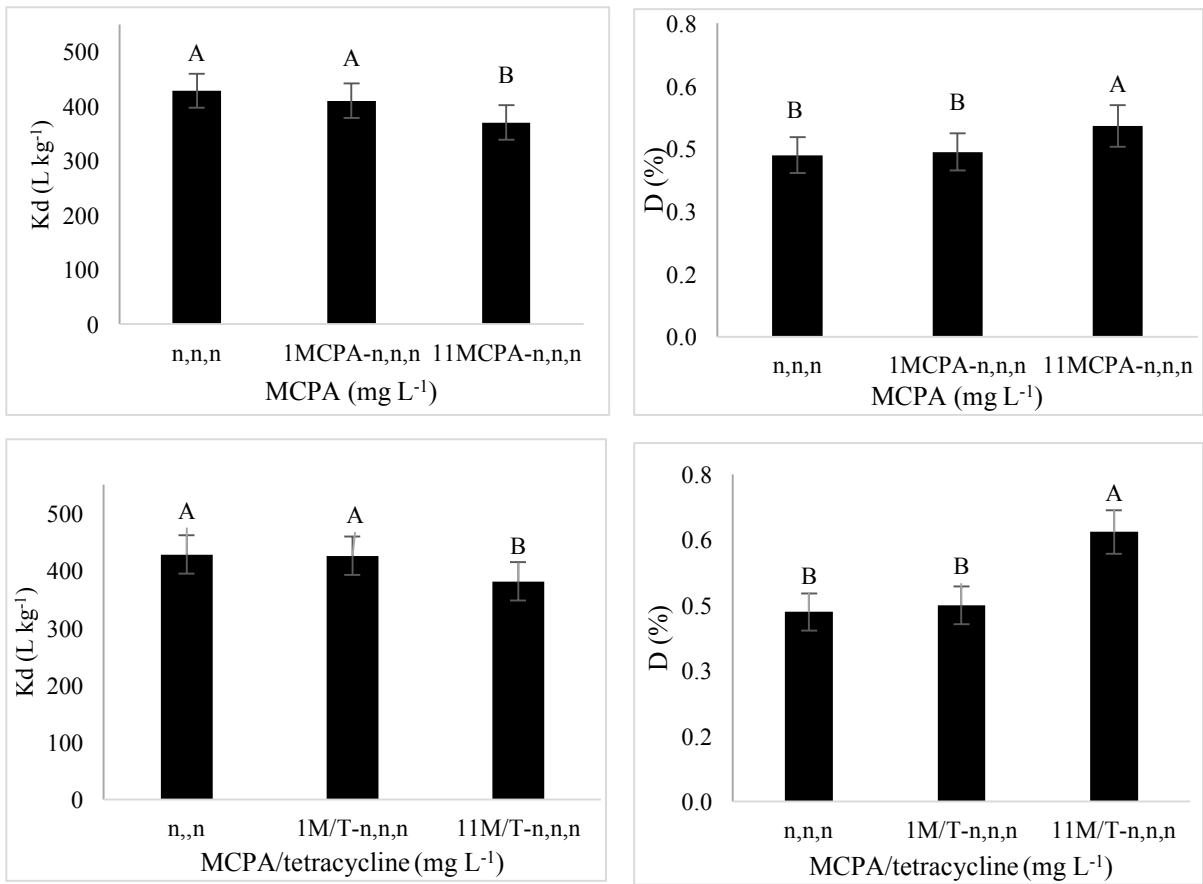


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618 Fig. 2

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Table 1. Selected soil physical and chemical properties as mean with standard error

Organic Carbon ^a (%)	pH ^b	Fe ₂ O ₃ ^c (mg kg ⁻¹)	Al ₂ O ₃ ^c (mg kg ⁻¹)	Ca ^d (mg kg ⁻¹)	Clay ^e %	Silt ^e %	Sand ^e %
2.81 ± 0.04	4.7 ± 0.02	237 ± 7.93	6.41 ± 0.64	2,252 ± 35	20	20	60

633 ^a Soil organic carbon content was determined using combustion technique with a high
634 temperature induction furnace. ^[39] ^b Soil pH was determined using a 10 ml 0.01M CaCl₂
635 solution and 2 g soil solution ratio. ^[40] ^c Extractable Fe and Al were extracted with
636 diethylenetriaminepentaacetic acid (*DTPA*) ^[41] and 0.01M CaCl₂, ^[42] respectively, and
637 extracts were analyzed by *ICP*. ^d Extractable Ca was also measured by *ICP* using
638 ammonium acetate as an extractant ^[43] ^e data adapted from Grant et al. ^[36]

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Table 2. Addition of phosphate during pre-incubation, sorption and desorption steps

Code	Pre-incubation	Sorption	Desorption
	from 0h to 24h	from 24h to 48h	from 48 to 72h
n,n,n	No P added	No P added	No P added
n,n,P	No P added	No P added	P added at 48h
P,n,n	P added at 0h	No P added	No P added
P,n,P	P added at 0h	No P added	P added at 48h
n,P,P	No P added	P added at 24h	P added at 48h

n = no phosphate added during pre-incubation, sorption and/or desorption step; P = phosphate added at time 0h at the start of the pre-incubation step or at time 24h at the start of the sorption step; or at time 48h at the start of the desorption step.

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Table 3. Effect of phosphate fertilizer on MCPA and tetracycline sorption and desorption in soil. See Table 2 for an explanation of the treatment labels.

Treatment	Kd (L kg ⁻¹)		Desorption (%)	
	MCPA	Tetracycline	MCPA	Tetracycline
n,n,n	5.37 A	134.49 A	27.45 B	0.51 B
n,n,P	5.28 A	129.02 A	29.63 A	0.73 A
P,n,n	5.00 B	117.50 B	29.04 A	0.69 A
P,n,P	5.00 B	122.55 B	30.18 A	0.71 A
n,P,P	4.99 B	117.55 B	29.91 A	0.74 A

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Table 4: Effect of MCPA (0, 1, 11 mg L⁻¹), tetracycline (0, 1, 11 mg L⁻¹) and MCPA/tetracycline mixtures (0, 1, 11 mg L⁻¹) on sorption and desorption of glyphosate in soil in the presence and absence of phosphate.

Chemicals	Concentration (mg L ⁻¹)	Kd (Lkg ⁻¹)		D (%)		Kd (Lkg ⁻¹)		D (%)	
		No P		P at 48h		P at 0h and 48h			
MCPA	0	428.48 A	0.52 A	445.99 A	1.10 A	290.80 A	1.38 A		
	1	409.73 A	0.53 A	424.99 A	1.11 A	271.09 A	1.42 A		
	11	370.88 B	0.60 B	382.32 B	1.16 A	278.44 A	1.43 A		
Tetracycline	0	428.48 A	0.52 A	445.99 A	1.10 A	290.80 A	1.38 A		
	1	415.64 A	0.54 A	426.02 A	1.04 A	283.50 A	1.36 A		
	11	415.94 A	0.55 A	426.02 A	1.08 A	271.72 A	1.45 A		
MCPA-tetracycline mixtures	0	428.48 A	0.52 A	445.99 A	1.10 A	290.80 A	1.38 A		
	1	426.02 A	0.48 A	444.58 A	1.12 A	283.50 A	1.39 A		
	11	318.05 B	0.66 B	386.72 B	1.15 A	290.51 A	1.44 A		

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Table 5: Effect of pre-sorbed phosphate (0, 11, 22, 44 mg L⁻¹) on glyphosate, MCPA and tetracycline sorption and pre-sorbed MCPA on glyphosate sorption (L kg⁻¹) in soil

Concentration (mg L ⁻¹)	Glyphosate	MCPA	Tetracycline	Glyphosate
0	544.60 A	5.48 A	108.22 A	544.6 A
11	321.78 B	5.09 AB	103.39 AB	540.8 AB
22	258.49 BC	5.05 AB	104.35 AB	518.25 AB
44	192.96 C	4.93 C	99.32 C	510.25 B

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SUPPORTING INFORMATION

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Table 1S: Effect of fresh-phosphate added at different time (*n,n,n; n,n,P; P,n,n; P,n,P; n,P,P*) and field aged-P (0P, 80P) on sorption and desorption of glyphosate, MCPA and tetracycline in soil

Effect	Num DF	Den DF	F Value	Pr > F	Num DF	Den DF	F Value	Pr > F
MCPA, Kd				MCPA, %D				
Fresh-P	4	27	7.09	0.0005	4	27	8.17	0.0002
Aged-P	1	27	2.11	0.1578	1	27	0.91	0.3475
Fresh-P*Aged-P	4	27	0.39	0.8132	4	27	2.27	0.0874
Tetracycline, Kd				Tetracycline, %D				
Fresh-P	4	27	24.69	<.0001	4	27	6.42	0.009
Aged-P	1	27	4.06	0.0541	1	27	1.28	0.2679
Fresh-P*Aged-P	4	27	0.57	0.6847	4	27	0.33	0.8525
Glyphosate, Kd				Glyphosate, %D				
Fresh-P	4	27	80.78	<.0001	4	27	130.63	<.0001
Aged-P	1	27	461.56	<.0001	1	27	258.28	<.0001
Fresh-P*Aged-P	4	27	22.42	<.0001	4	27	12.40	<.0001

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Table 2S: Effect of MCPA (0, 1, or 11 mg L⁻¹) and field aged-P (0P, 80P); tetracycline (0, 1, or 11 mg L⁻¹) and field-aged-P (0P, 80P) MCPA-tetracycline mixture (0, 1, or 11 mg L⁻¹) and field-aged-P (0P, 80P) on sorption and desorption of glyphosate in soil

Effect	Num DF	Den DF	F Value	Pr > F	Num DF	Den DF	F Value	Pr > F
Glyphosate, Kd				Glyphosate, %D				
MCPA	2	15	10.23	0.0016	2	15	15.06	0.0003
Aged-P	1	15	622.79	<.0001	1	15	1302.94	<.0001
MCPA*Aged-P	2	15	2.33	0.1317	2	15	0.77	0.4792
Tetracycline	2	15	3.14	0.0745	2	15	1.52	0.2512
Aged-P	1	15	820.69	<.0001	1	15	657.45	<.0001
Tetra*Aged-P	2	15	0.47	0.6369	2	15	0.05	0.9558
Mixture	2	15	6.37	0.0100	2	15	11.77	0.0011
Aged-P	1	15	560.14	<.0001	1	15	223.21	<.0001
Mixture*Aged-P	2	15	2.21	0.1442	2	15	1.53	0.2480

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Table 3S. Effect of pre-sorbed phosphate (0, 11, 22, 44 mg L⁻¹) on glyphosate, MCPA and tetracycline sorption and retained MCPA on glyphosate sorption (L kg⁻¹) in soil

Effect	Num DF	Den DF	F Value	Pr > F
			Glyphosate, Kd	
	3	9	71.14	<.0001
			MCPA, Kd	
Retained-P	3	9	5.72	0.0180
			Tetracycline, Kd	
	3	9	9.20	0.0042
			Glyphosate, Kd	
Retained-MCPA	3	9	5.03	0.0257

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