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

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Abstract

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

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

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

Introduction

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

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

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

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

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

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

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

Materials and methods

Chemicals

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

Soil characteristics and experimental design

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

fertilizers at an annual rate of 50 and 90 kg N ha^{-1}, respectively. For this study, samples were collected from the replicated plots that had also received eight years (2002-2009) of annual mono ammonium phosphate (MAP) applications at rates of 80 kg P ha^{-1}, as well as from control plots that did not receive MAP application during these years. [36] The rotation was continued from 2010 to 2013 but after 2010 no phosphate was applied. In each plot, composite soil samples were collected using a Dutch auger with ten samples per plot and the auger was cleaned in between plots. Samples were air-dried and sieved (<2mm) prior to use in batch equilibrium experiments. Available phosphate was determined by the Olsen (0.5N $NaHCO_3$, pH 8.5) phosphorus test (Olsen P). [37] Olsen P concentrations ranged from 81 to 99 mg kg^{-1} in soil from the 80P plots that had received MAP applications and from 13 to 20 mg kg^{-1} in soil from the 0P plots that had received no phosphate fertilizers. The soil is classified as an Orthic Black Chernozem based on the Canadian System of Soil Classification, which is approximately equivalent to the Udic Boroll subgroup in the U.S. Soil Taxonomy. [38] Key soil properties are listed Table 1.

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

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

2). For treatments *n,n,n* and *n,n,P,* a 0.01M KCl solution (8 mL) was added to soil at 0h and no phosphate was added. For treatments *P,n,n* and *P,n,P,* the added 0.01M KCl solution also contained phosphate while, for treatment *n,P,P,* the phosphate was added to the herbicide and antibiotic solutions. Radiolabelled glyphosate, MCPA or tetracycline in 0.01M KCl (2 mL) was always added at 24h. Radiolabelled chemical solutions contained 1 mg L^{-1} analytical-grade glyphosate, MCPA or tetracycline, with 6.67×10^5 Bq L^{-1} ^{14}C-labelled glyphosate, 3.83×10^5 Bq L^{-1} ^{14}C-labelled MCPA or 4.17×10^5 Bq L^{-1} ^{3}H-labelled tetracycline, respectively. The concentration 1 mg L^{-1} represented environmentally-relevant concentrations of herbicides and antibiotics detected in agricultural soils [45] or animal manure. [46] Phosphate was added as potassium dihydrogen phosphate and always at a rate of 44 mg P kg^{-1}, corresponding to a concentration of 11 mg L^{-1} in the added solution. This rate is equivalent to an estimated 80 P kg ha^{-1} when assuming the fertilizer is being incorporated in the top 15 cm layer of a soil with a bulk density of 1,200 kg m^{-3}.

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

radioactivity in the initial solution and the equilibrium solution. The soil organic carbon coefficient, Koc (L kg^{-1}) of glyphosate, MCPA or tetracycline was calculated by dividing the Kd value by 0.0281 which was the fraction of soil organic carbon in soil.

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

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

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 6.67×10^5 Bq L^{-1} ^{14}C-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^{o}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 6.67×10^5 Bq L^{-1} ^{14}C-labelled glyphosate, 2.08×10^5 Bq L^{-1} ^{14}C-labelled MCPA and

193 5.00×10^5 Bq L^{-1} ^{3}H-labelled tetracycline, respectively. Soil slurries were again rotated for
194 24h, then centrifuged and subsampled as described above to calculate Kd 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} ^{14}C-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 ^{14}C-labelled glyphosate.

211

212 ***Statistical analysis***

213

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

Results

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

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

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 Kd values by 8-13% and MCPA Kd 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 Kd 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 Kd 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 Kd 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 Kd 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 ($H_2PO_4^{-1}$) occupies are positively charged
317 Fe/Al-oxides. When phosphate ($H_2PO_4^{-1}$) 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 competed 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.

Conclusion

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

Acknowledgements

388 The authors acknowledge the Natural Sciences and Engineering Research Council of
389 Canada (NSERC) (#216906) for providing research funding. We also thank the University
390 of Manitoba and the Government of the Province of Manitoba for granting Ms. Sirajum
391 Munira the University of Manitoba Graduate Fellowship (UMGF) and the Manitoba
392 Graduate Scholarship (MGS), respectively. In addition, the authors acknowledge Ms.
393 Hannah Polaczek and Mr. Rob Ellis for their assistance with the laboratory experiments,
394 as well as Dr. Francis Zvomuya for his valuable advice on finalizing the statistical analyses.

395

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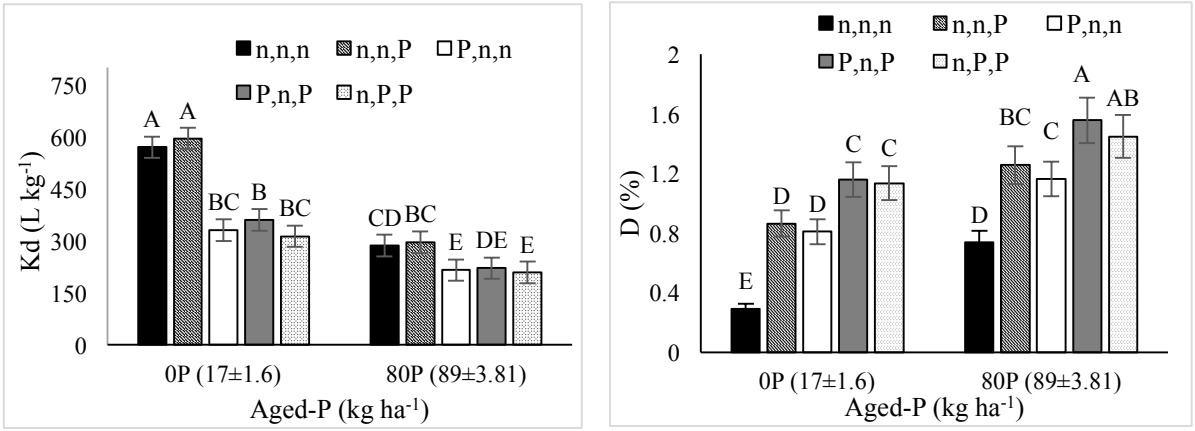
FIGURE CAPTIONS

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

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

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



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615 Fig. 1

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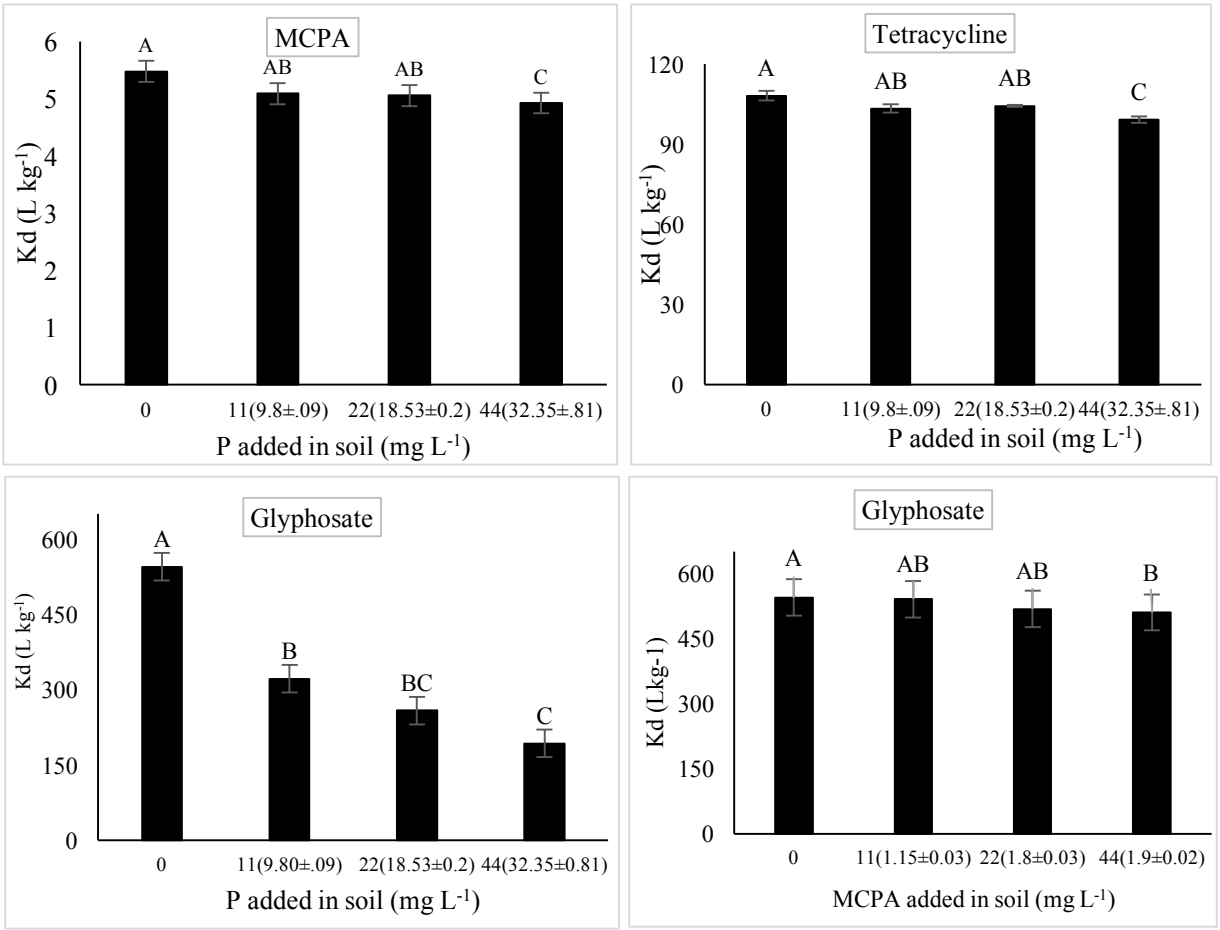

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618 Fig. 2

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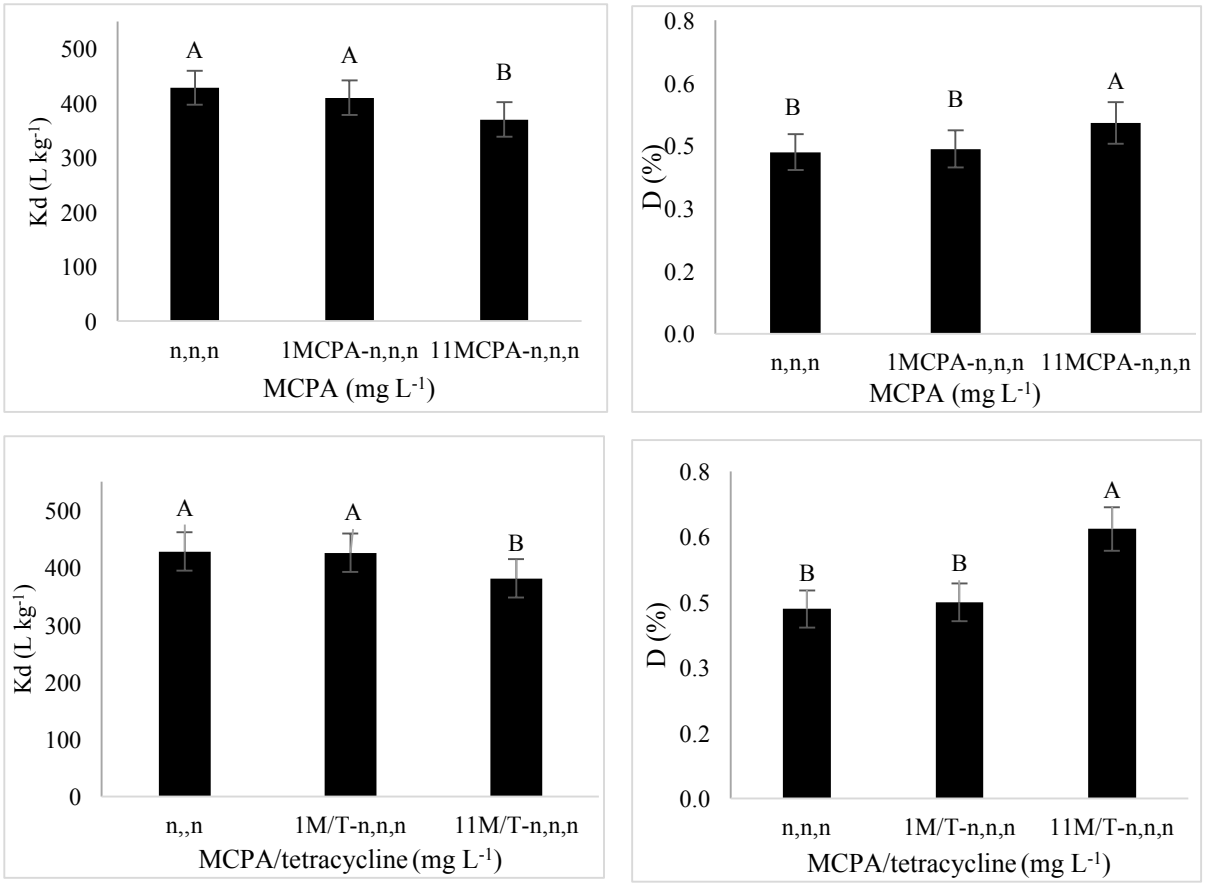

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622 Fig. 3

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

Organic Carbon [a] (%)	pH[b]	Fe_2O_3[c] (mg kg^{-1})	Al_2O_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 $CaCl_2$
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 $CaCl_2$, [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 (%)	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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667 **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
Retained-P	**Glyphosate, Kd**			
	3	9	71.14	<.0001
	MCPA, Kd			
	3	9	5.72	0.0180
	Tetracycline, Kd			
	3	9	9.20	0.0042
Retained-MCPA	**Glyphosate, Kd**			
	3	9	5.03	0.0257

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