

1 **EVALUATION OF TWO LANGMUIR MODELS FOR PHOSPHORUS SORPTION OF**
2 **P-ENRICHED SOILS IN NEW YORK FOR ENVIRONMENTAL APPLICATIONS**

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27 **Abstract**

28 The phosphorus (P) sorption isotherm experiment is a widely used tool in environmental
29 applications for assessing soil's vulnerability to P loss to runoff or drainage. The sorbed legacy
30 P (S_0) (i.e. the P retained in soils from previous P applications) participates in sorption processes,
31 but cannot readily be determined in a sorption experiment. Thus, it is important to accurately
32 estimate S_0 for P-enriched soils (e.g. the soils that heavily receive fertilizer, manure, farm
33 wastewater, or sewage sludge). Two curve-fitting procedures (i.e. one-step method and two-step
34 method) with Langmuir models have been used to estimate S_0 and other sorption parameters,
35 including the P sorption maxima (S_{max}), the bonding energy constant (k), and the zero-sorption
36 equilibrium concentration (EPC_0). This study evaluated these two methods on sixteen samples
37 of Langford, Volusia, and Mardin channery silt loam soils at surface (0-8 cm) and subsurface
38 (61-91 cm) in New York. The results indicate that the two methods agreed well in estimating
39 S_{max} , and the estimates of k were close. The S_0 estimates by the two methods had a good
40 agreement for surface soils, but a poor agreement for subsurface soils, which may be of little
41 concern because of small S_0 of subsurface soils. Although the one-step method yielded greater
42 EPC_0 estimates, the EPC_0 estimates by the two methods had an excellent linear correlation for P-

43 enriched surface soils, suggesting that both methods could work equally if only the relative
44 magnitudes of EPC_0 among soils are needed. Overall, both methods are acceptable to fit the
45 Langmuir isotherms.

46 Keywords: phosphorus, sorption isotherm, Langmuir model

47 **Introduction**

48 Phosphorus (P), although an essential element for all life forms, is considered in many
49 cases a limiting mineral nutrient for freshwater lakes, reservoirs, streams, and headwaters of
50 estuarine systems (Correll, 1998). Over-enrichment of P in these waters usually leads to
51 eutrophication, resulting in algal or cyanobacterial blooms, anoxia, and fish kills. Phosphorus
52 export from agricultural production sources contributes significantly to the P accumulation in
53 surface waters (Carpenter et al., 1998). After field applications of chemical P fertilizer, manure,
54 farm wastewaters, or sewage sludge, the P transport through landscape is largely dependent on
55 soil's P sorption properties. Soils accumulate P when receiving P in excess of vegetation
56 removal (Kao and Blanchar, 1973; Sui and Thompson, 2000; Siddique and Robinson, 2003).
57 One portion of the accumulated P from previous P applications readily takes part in P sorption
58 processes between soil and solution (Zhou et al., 2005), thus is prone to the loss to runoff or
59 drainage. This labile pool of the soil P is termed as the sorbed legacy P (S_0) here. Its magnitude
60 is often significant in P-enriched soils, which is of little concern in agronomic applications, but is
61 far more important in environmental applications regarding soil P loss.

62 Phosphorus sorption properties of soils are mainly studied by sorption isotherm
63 experiments, which were historically initiated in agronomy for evaluating the P availability for
64 crop uptake (Olsen and Watanabe, 1957; Holford, 1979), but have become popular for assessing
65 the soil P mobility in environmental applications (Gale et al., 1994; Vadas and Sims, 1999; Sui

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66 and Thompson, 2000; Siddique and Robinson, 2003). Phosphorus sorption isotherms have been
67 quantitatively described by the Langmuir, Freundlich, and Tempkin models (Graetz and Nair,
68 2000; Villapando and Graetz, 2001; Barrow, 2008). The Langmuir model has the advantage
69 over the Freundlich and Tempkin models in environmental applications because the soil's
70 maximum capacity to sorb P (i.e. the P sorption maxima, S_{\max}) and the P bonding energy
71 constant (k) can be determined (Graetz and Nair, 2000; Villapando and Graetz, 2001). These
72 two parameters have been used to evaluate the soil P loss potential: the soil P saturation degree
73 (S_0/S_{\max}) and the maximum P buffering capacity index ($S_{\max}k$) (Holford, 1979; Sharpley, 1995;
74 Sui and Thompson, 2000; Sims et al., 2002; Zhang et al., 2005; Bolster and Hornberger, 2007).
75 In addition, the zero-sorption equilibrium concentration (i.e. the P concentration in soil water that
76 causes neither P sorption nor desorption, EPC_0) has also been employed to assess the soil P loss
77 potential (Vadas and Sims, 1999; Graetz and Nair, 2000; Zhou et al., 2005).

78 In a P sorption isotherm experiment, the difference of P between the initial sorption
79 solution and the final sorption solution is the amount of P sorbed by soils, referred herein as the
80 apparent soil P sorption (S'). The apparent soil P sorption does not include the sorbed legacy P
81 (S_0). Ignoring S_0 could be problematic in environmental applications that utilize P sorption
82 isotherms for P-enriched soils, as a result of erroneous estimates of sorption parameters and
83 consequent misevaluation of the soil P loss potential. Thus, many researchers have put
84 considerable effort in estimating S_0 .

85 In the past, two types of methods have been used to estimate the sorbed legacy P (S_0),
86 namely, the extraction methods and the curve-fitting methods. In the extraction methods, S_0 was
87 estimated using experimental measurements from an extraction method, including the Olsen-
88 extractable P (Siddique and Robinson, 2003), the Mehlich-1 or Mehlich-3 extractable P (Sallade

89 and Sims, 1997; Brock et al., 2007), the Morgan-extractable P (Brock et al., 2007), the
90 isotopically exchangeable P (Olsen and Watanabe, 1957), and the anion-exchange resin-
91 impregnated membrane extractable P (Villapando and Graetz, 2001). In the curve-fitting
92 methods, S_0 was estimated by two curve-fitting procedures associated with the Langmuir
93 isotherm equation (Gale et al., 1994; Reddy et al., 1998; Graetz and Nair, 2000; Pant and Reddy,
94 2001; Zhou et al., 2005), referred here as the two-step method and the one-step method, as
95 explained in detail in the following model section. The curve-fitting methods have advantages
96 over the extraction methods, because the extraction methods usually use an extractant with
97 different chemistry from that of sorption solutions, thus the tested soil P does not necessarily
98 agree with S_0 . Villapando and Graetz (2001) had to use a correction factor to compensate this
99 discrepancy. The curve-fitting methods avoid this problem since S_0 is estimated from the
100 sorption isotherms. Currently, it is not known how well these two curve-fitting methods agree
101 with each other in estimating S_0 and other sorption parameters, including S_{\max} , k , and EPC_0 .

102 Therefore, the objective of this study was to evaluate the two Langmuir curve-fitting
103 methods, the two-step method and the one-step method, in estimating P sorption parameters (i.e.
104 S_0 , S_{\max} , k , and EPC_0) of three soil series in New York. In addition, we applied the one-step and
105 two-step methods to the Freundlich model and examined the model's suitability for P-enriched
106 soils. The results of this study will help researchers better utilize the P sorption model in P
107 sorption studies.

108 **P Sorption Models**

109 The Langmuir model is extensively used in the contemporary environment-related P
110 sorption study. The model is somewhat theoretically based and allows one to estimate the P
111 sorption maxima (Olsen and Watanabe, 1957; Villapando and Graetz, 2001; Essington, 2004;

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112 Bolster and Hornberger, 2007; Bolster, 2008), although the use of the model was challenged for
113 heterogeneous surface of soils (Sparks, 2003). Pant and Reddy (2001) argued that every P
114 compound in soils is independently equilibrated with P in solution, and the heterogeneous soil
115 systems behave as a mixture of homogeneous surfaces.

116 The total amount of P sorbed in soils per unit soil mass, S (mg kg^{-1}), and the equilibrium
117 P concentration, C (mg L^{-1}), in solution follow the Langmuir model as:

$$118 \quad S = \frac{S_{\max} kC}{1 + kC} \quad (1)$$

119 where S_{\max} (mg kg^{-1}) is the maximum of P that can be sorbed on unit soil mass, and k (L mg^{-1}) is
120 the bonding energy constant.

121 Isotherms are usually determined with batch experiments in which flasks are shaken for a
122 predetermined time period (typically 24 hours). In these flasks, M (g) of dry soil and V (mL) of
123 aqueous solution with P concentration of C_i (mg L^{-1}) are added. At the end of experiments, the
124 aqueous P concentration is C . The amount of P removed from solution (i.e. adsorbed to the soil
125 particles) per unit soil mass, S' (mg kg^{-1}), can be expressed as:

$$126 \quad S' = \frac{(C_i - C)V}{M} \quad (2)$$

127 The total amount of P sorbed in the soil (S) is defined as the sum of the sorbed legacy P,
128 S_0 (mg kg^{-1}), before the solution is added and the new amount that is sorbed from solution (S'):

$$129 \quad S = S' + S_0 \quad (3)$$

130 Generally the value of S_0 is unknown and needs to be determined. It can be neglected if
131 it is small (Olsen and Watanabe, 1957). In cases where S_0 is significant (e.g. P-enriched soils),
132 two-curve fitting methods, the two-step method and the one-step method, have been developed
133 to determine S_0 .

134 The two-step method proposed by Gale et al. (1994) has been popular due to its
 135 simplicity (Reddy et al., 1998; Graetz and Nair, 2000; Pant and Reddy, 2001). It assumes a
 136 linear sorption isotherm at low concentrations as:

$$137 \quad S' = KC - S_0 \quad (4)$$

138 where K ($L \text{ kg}^{-1}$) is the partition coefficient.

139 In the two-step method, the apparent isotherm (S' versus C) at low concentrations is first
 140 fitted with eq. 4 to obtain S_0 . Adding S_0 to S' (eq. 3) yields the total sorbed P (S) in soils. The
 141 entire isotherm (S versus C) is then fitted with the Langmuir model (eq. 1) to estimate S_{\max} and k .

142 The one-step method developed by Zhou et al. (2005) assumes that the Langmuir model
 143 is also valid for low concentrations. Combining eqs. 1, 2, and 3 produces:

$$144 \quad \frac{(C_i - C)V}{M} = \frac{S_{\max} kC}{1 + kC} - S_0 \quad (5)$$

145 For soils in P-free initial solutions ($C_i=0$), the equilibrium P concentration (C) in solution
 146 is C_0 (mg L^{-1}). From eq. 5, S_0 can be expressed as:

$$147 \quad S_0 = \frac{S_{\max} kC_0}{1 + kC_0} + \frac{C_0 V}{M} \quad (6)$$

148 Combining eqs. 1, 3 and 6, S' can be found as a function of C :

$$149 \quad S' = \frac{S_{\max} kC}{1 + kC} - \left(\frac{S_{\max} kC_0}{1 + kC_0} + \frac{C_0 V}{M} \right) \quad (7)$$

150 In the one-step method, the apparent isotherm (S' versus C) is directly fitted with eq. 7
 151 using a nonlinear least square fitting algorithm to estimate S_{\max} and k , while C_0 is experimentally
 152 measured (Zhou et al., 2005). Then, S_0 is calculated from eq. 6.

153 The zero-sorption equilibrium concentration (EPC_0), an indicator of the potential of P
 154 loss to runoff or drainage, is defined as the aqueous P concentration that dose not cause either P

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155 sorption or desorption (Graetz and Nair, 2000; Vadas and Sims, 1999; Zhou et al., 2005). Hence,
 156 S' is zero. For the two-step method, EPC_0 can be determined as:

$$157 \quad EPC_0 = S_0 / K \quad (8)$$

158 For the one-step method, EPC_0 can be determined as:

$$159 \quad EPC_0 = \frac{S_{\max} k C_0 / (1 + k C_0) + C_0 V / M}{S_{\max} k / (1 + k C_0) - k C_0 V / M} \quad (9)$$

160 Knowing sorption parameters of S_{\max} and k , the maximum buffering capacity (MBC) of
 161 soils, the index of soils' resistance to the change of P concentration in soil solution with adding
 162 or removing P (Holford, 1979; Sui and Thompson, 2000), is derived as:

$$163 \quad MBC = \left(\frac{dS'}{dC} \right)_{C \rightarrow 0} = \left[\frac{S_{\max} k}{(1 + kC)^2} \right]_{C \rightarrow 0} = S_{\max} k \quad (10)$$

164 The values of MBC , also being the slope of isotherms at $C \rightarrow 0$, dictate the steepness of
 165 isotherms at low concentrations. In the case that S_{\max} does not differ as much as k does among
 166 soils, the bonding energy constant (k) determines the shape of isotherms. The soils' MBC values
 167 are also environmentally relevant since soils with larger MBC would in principle have a greater
 168 tendency to maintain their original aqueous P concentration in the event of the inflow of higher P
 169 concentrations.

170 To examine the suitability of the Freundlich model for use on P-enriched soils, we
 171 present this application as well. The traditional Freundlich model is (Barrow, 2008):

$$172 \quad S = K_f C^n \quad (11)$$

173 where K_f ($\text{mg}^{1-n} \text{kg}^{-1} \text{L}^n$) is the Freundlich sorption energy constant, and n is a dimensionless
 174 correction factor. Similar to the Langmuir models, in the Freundlich two-step method S_0 is
 175 estimated by fitting the apparent isotherm (S' versus C) at the low concentrations to eq. 4 and S is

176 calculated by eq. 3. The entire isotherm (S versus C) is then fitted with eq. 11 to obtain K_f and n .
 177 The EPC_0 estimate is determined by eq. 8. In the Freundlich one-step method, the model
 178 equations are (see Appendix for detailed derivation):

$$179 \quad S_0 = K_f C_0^n + \frac{C_0 V}{M} \quad (12)$$

$$180 \quad S' = K_f C^n - \left(K_f C_0^n + \frac{C_0 V}{M} \right) \quad (13)$$

$$181 \quad EPC_0 = \left(C_0^n + \frac{C_0 V}{M K_f} \right)^{1/n} \quad (14)$$

182 The apparent isotherm (S' versus C) is fitted to eq. 13 to estimate K_f and n . Then, S_0 and
 183 EPC_0 are calculated from eq. 12 and 14.

184 **Materials and Methods**

185 *Site Description*

186 The soils in this study were collected from three vegetative treatment areas (VTAs)
 187 located at Tompkins County, Wyoming County and Delaware County in New York. The soil
 188 was classified as a Langford channery silt loam (fine-loamy, mixed, active, mesic Typic
 189 Fragiudepts) at the Tompkins County site, a Volusia channery silt loam (fine-loamy, mixed,
 190 active, mesic Aeric Fragiaquepts) at the Wyoming County site, and a Mardin channery silt loam
 191 (coarse-loamy, mixed, active, mesic Typic Fragiudepts) at the Delaware County site (NRCS,
 192 2008). The three soil series are typical glaciated soils in the northeastern U.S., and have
 193 extensive distributions in New York and northern Pennsylvania.

194 The Tompkins County and Wyoming County VTAs were planted in a mixture of reed
 195 canarygrass (*Phalaris arundinacea*), redtop (*Agrostis alba*), and tall fescue (*Festuca elatior*), and
 196 have received the farm silage bunker runoff by gravity flow since the spring of 2005 and the

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197 summer of 2006, respectively. The Delaware County VTA is located in a pasture primarily used
198 for hay production and receives the intermittent dosing of farm barnyard runoff collected in a
199 storage tank since the summer of 2005. These nutrient-laden wastewaters contained 300 - 2000
200 mg L^{-1} dissolved organic carbon (DOC), 18 - 170 mg L^{-1} ammonium-nitrogen, 13 - 55 mg L^{-1}
201 soluble reactive P (SRP), and 80 - 350 mg L^{-1} dissolved Ca. The annual P application rate at the
202 Tompkins County site was estimated to be 126 kg P ha^{-1} , which is much greater than the P
203 removal rate of 28 kg P ha^{-1} by grass vegetation (Czymmek and Ketterings, 2007).

204 *Soil Sampling and Analyses*

205 Several sets of surface (0-8 cm) and subsurface (61-91 cm) soil pair located down-slope
206 of wastewater surface distribution points were collected at the Tompkins County site, Wyoming
207 County site, and Delaware County site on October 19, 2006, October 10, 2006, and October 18,
208 2007, respectively. Soil samples from the Tompkins County site were denoted as T1S, T1D,
209 T2S, T2D, T4S, and T4D, the ones from the Wyoming County site as W1S, W1D, W2S, W2D,
210 W4S, and W4D, and the ones from the Delaware county site as D1S, D1D, D3S, and D3D (refer
211 to Table 1 for the labeling convention). The soil samples were air-dried, ground, and passed
212 through a 2 mm-sieve. The soil analysis was conducted for air-dried soil samples by the Cornell
213 Nutrient Analysis Laboratory (CNAL), Cornell University, Ithaca, NY. Soil pH was measured
214 in water at 1:1 soil:water ratio. The soil organic matter (OM) was determined by loss on ignition.
215 Soil samples were extracted with sodium acetate solution (0.72 N NaOAc+0.52 N CH_3COOH),
216 known as the Morgan extraction. The extractants were analyzed for P using the ascorbic acid
217 method with a flow analyzer (ALPKEM RFA/2, OI Analytical, College Station, TX) and for
218 cations including Ca, Fe, and Al by inductively coupled plasma atomic emission spectroscopy
219 (ICP-AES) (JY70 TYPEII, Jobin Yvon, Edison, NJ). The above soil analyses followed the

220 methods of NRCS (2004) and Sims and Wolf (1995). The nitric acid-digestion elements,
221 including P, Ca, Fe, and Al, were determined by ICP-AES (SPECTRO-CIROS^{CCD}, SPECTRO
222 Analytical Instruments Inc., Mahwah, NJ) after the microwave-assisted digestion with HNO₃
223 (USEPA, 2007). Selected chemical properties of soils are summarized in Table 1. The soil tests
224 demonstrate a variety of soil chemical properties. The soils had OM ranging from 0.6% to 8.1%
225 and various degree of P-enrichment with the Morgan extractable P ranging from 0.7 to 262 mg
226 kg⁻¹. The higher Morgan extractable P of the surface soils in the Wyoming County site may
227 partially be a result of silage and manure stockpiling on the ground, prior to the VTA
228 construction. The Morgan extractable cations also covered a wide range, with Ca ranging from
229 347 to 4067 mg kg⁻¹, Fe from 1.5 to 48.5 mg kg⁻¹, and Al from 7.9 to 44.2 mg kg⁻¹. The nitric
230 acid-digestion elements showed the similar variability. The soil pH was between 6.2 and 8.1.
231 While the soil series are listed as acidic in the soil survey (NRCS, 2008), liming and the
232 application of dairy manure and dairy farm wastewater could have increased the soil pH, similar
233 to that reported by Barkle et al. (2000) and Cabrera et al. (2009).

234 *Sorption Isotherms*

235 One gram of air-dried soils was placed in the series of 50 mL polypropylene centrifuge
236 tubes and mixed with 20 mL 0.01 M potassium chloride (KCl) solutions spiked with 0, 1, 5, 10,
237 50, 100, and 200 mg/L P as KH₂PO₄. Duplicate tests were carried out for each soil sample. The
238 centrifuge tubes were shaken on a reciprocal shaker at a speed of 180 cycle/min for 24 hours at
239 25 ± 3 °C. The supernatants were filtered through a 0.45 μm mixed cellulose ester membrane
240 (Pall Life Sciences, Ann Arbor, MI). The filtrates were acidified with concentrated hydrochloric
241 acid and stored in the refrigerator at 4 °C before analysis. Filtrate was analyzed for soluble
242 reactive P (SRP) by a flow-injection P analyzer (Flowsystem-3000, OI Analytical, College

243 Station, TX) using the ascorbic colorimetric method (USEPA, 1983). The initial P
244 concentrations were also measured. The difference between the initial concentration and the
245 final concentration was calculated as the apparent sorbed P (S') by eq. 2.

246 Following the procedures in the model section, the averaged isotherms were fitted using
247 both the one-step and two-step methods by the unweighted trust-region nonlinear least square
248 regression algorithm in Matlab (The MathWorks, Inc., Natick, MA). The estimates of S_{\max} , k , S_0 ,
249 and EPC_0 from both methods in the Langmuir models were plotted in 1:1 scatter plots and linear
250 regressions through the origin were performed to examine the agreement between estimates. The
251 Freundlich models were also examined on their goodness-of-fit and the agreement of parameter
252 estimates by the one-step and two-step methods.

253 **Results and Discussion**

254 As mentioned previously, the isotherms were fitted to the Langmuir models by the one-
255 step method and the two-step method to estimate S_{\max} , k , S_0 , EPC_0 , and MBC , which are shown
256 in Table 2 together with the adjusted R^2 , root mean square error (RMSE), and the parameter 95%
257 confidence intervals. The measured and fitted Langmuir isotherms of T2S and T2D are shown in
258 Figure 1 as examples. The apparent isotherms (S' versus C) in Figure 1 were fitted by the one-
259 step method. The linear fitting of the apparent isotherm at low concentrations (eq. 4) in the two-
260 step method is shown in the inset of Figure 1. Both the Langmuir one-step and two-step methods
261 fitted the sorption data satisfactorily. The adjusted R^2 values ranged from 0.90 to 0.99 for both
262 the Langmuir one-step and two-step methods, suggesting a good model fit. The RMSE values
263 were from 15 to 78 mg kg⁻¹ (Table 2), which were in the same range with the RMSE values (7 to
264 90 mg kg⁻¹) calculated from the SSE (i.e. sum of squared error) values reported by Bolster and
265 Hornberger (2007) and Bolster (2008). The 95% confidence interval widths in the Langmuir

266 one-step method were 0.4 ± 0.2 times of the S_{\max} estimates and 2.3 ± 0.7 times of the k estimates,
267 and the similar parameter uncertainties were observed for the Langmuir two-step method. These
268 parameter uncertainties agreed with the reported ones (see Fig. 5 in Bolster and Hornberger,
269 2007). Thus, our Langmuir models offered the satisfactory goodness of fit, at least equivalent to
270 the results of other studies.

271 The Freundlich one-step method produced unrealistically large K_f and S_0 (for brevity,
272 detailed data not shown), while considerable parameters uncertainty were observed for K_f and n
273 (i.e. the 95% confidence interval widths were 2.5 ± 2.2 times of the K_f estimates and 1.9 ± 1.9
274 times of the n estimates). The Freundlich two-step method had similar goodness of fit, compared
275 to that of the Langmuir models, with the adjusted R^2 values ranging from 0.94 to 0.99 and the
276 RMSE values from 19 to 70 mg kg⁻¹. The 95% confidence interval widths were 0.9 ± 0.2 times
277 of the K_f estimates and 0.5 ± 0.1 times of the n estimates. While the EPC_0 estimates by the two
278 Freundlich methods were close, the estimates of K_f , n , and S_0 differed drastically by over 89%.
279 In addition, the Freundlich sorption parameters are less meaningful in evaluating the soil P loss
280 potential, compared to the Langmuir sorption parameters, because the Langmuir sorption
281 parameters can be used to determine the soil P saturation degree (S_0/S_{\max}) and the maximum P
282 buffering capacity index ($S_{\max}k$) (Sharpley, 1995; Graetz and Nair, 2000; Villapando and Graetz,
283 2001; Zhang et al., 2005; Bolster and Hornberger, 2007). Therefore, in the following sections,
284 we focused on the results of the Langmuir models and the Freundlich models were not further
285 considered.

286 Surface and subsurface soils generally showed distinct sorption behavior in that the
287 isotherms of subsurface soils appeared steeper than that of surface soils at low concentrations
288 (e.g. observing the difference between T2S and T2D in Figure 1). This is supported by the fact

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289 that the *MBC* values of subsurface soils are greater than that of surface soils by a factor of 1.4 to
290 6.9 (Table 2), and the isotherm steepness monotonically increases with increasing *MBC* at low
291 concentrations. The steeper isotherms of subsurface soils had a narrow range of isotherm
292 linearity at very low concentrations, which demands additional considerations for the two-step
293 method. Taking T2S and T2D as examples, the concentration range of isotherm linearity ($R^2 =$
294 0.98) was 1.62 - 5.06 mg L⁻¹ for T2S (the inset of Figure 1), which corresponded to the four
295 lowest concentration points with the initial concentration from 0 to 10 mg L⁻¹. For T2D, the
296 concentration range of isotherm linearity ($R^2 = 0.98$) was 0.08 - 0.43 mg L⁻¹ (the inset of Figure
297 1), which corresponded to the three lowest concentration points with the initial concentration
298 from 0 to 5 mg L⁻¹. Graetz and Nair (2000) recommended that the linear isotherm at low
299 concentrations shall have a R^2 value greater than 0.95. This criterion was met for the lowest four
300 concentration points of surface soil isotherms, but only for the lowest three concentration points
301 of subsurface soil isotherms, as shown in the inset of Figure 1. The isotherms of other soils
302 showed similar trends (data not shown).

303 The 1:1 scatter plots of S_{\max} , k , S_0 , and EPC_0 estimated from the Langmuir one-step and
304 two-step methods for surface and subsurface soils are presented in Figure 2 and Figure 3,
305 respectively. The estimates of S_{\max} by both methods agreed very well, with a regression slope of
306 0.97 for surface soil and 0.98 for subsurface soil, and an R^2 of 0.99 for both soil depths (Figure
307 2A and Figure 3A). This good agreement is a result of the dependency of S_{\max} on P sorption at
308 high equilibrium concentrations (Essington, 2004). Thus, the assumption of isotherm linearity at
309 low concentrations in the two-step method should not significantly affect S_{\max} estimates. The
310 estimates of k from both methods were fairly close, with the estimates by the two-step method
311 being 13% and 7% higher on average for surface and subsurface soils, respectively (Figure 2B

312 and Figure 3B). Eliminating a high value in Figure 2B resulted in a slope of 1.04 with a 95%
313 confidence interval of (0.91, 1.15), indicating no significant difference from 1, similar to Figure
314 3B. Thus, the k values estimated by both methods were indeed not significantly different. For
315 the sorbed legacy P (S_0), the results were similar for surface soils (Figure 2C). However, the
316 estimates of S_0 differed by 48% for subsurface soils with the R^2 value of the regression line being
317 0.80 and the slope being significant different with 1 (Figure 3C), implying a poor agreement.
318 Fortunately, the estimation of S_0 for subsurface soils may be less important, considering the
319 small S_0 and Morgan extractable P of subsurface soils (Table 1 and 2). The EPC_0 estimates from
320 both methods correlate with each other well for surface soils ($R^2 = 0.99$, Figure 2D), but exhibit a
321 slightly poorer correlation for subsurface soils ($R^2 = 0.89$, Figure 3D). Even so, the one-step
322 method overestimated EPC_0 over 22% (Figure 2D and Figure 3D). The EPC_0 estimates from the
323 one-step method are determined from the Langmuir isotherm fitting, which is more dependent on
324 P sorption at high concentrations as mentioned before. This dependency in the one-step method
325 causes lower estimated sorption than the observed values at low concentrations, thus a shift of
326 EPC_0 to greater values when the isotherm crosses the zero sorption line (i.e. $S'=0$). The two-step
327 method estimates EPC_0 by fitting a linear isotherm at low concentrations as shown in the inset of
328 Figure 1, which can be considered a more accurate procedure. If only the relative magnitude of
329 EPC_0 among soils is needed for comparison purpose, both methods could work equally for
330 surface soils since their estimates of EPC_0 are linearly correlated (Figure 2D). For subsurface
331 soils, the EPC_0 values ranging from 0.05 to 0.80 mg L⁻¹ are relatively small and not as much
332 concern as that of surface soils (0.54 to 14.1 mg L⁻¹) when considering the P loss (Table 2).
333 Since the EPC_0 value is interpreted as the potential of soil P loss to runoff or drainage (Vadas

334 and Sims, 1999), the greater estimates of EPC_0 from the one-step method could lead to more
335 environmentally conservative management practices.

336 Overall, both the one-step method and the two-step method are acceptable to fit the
337 Langmuir isotherms for P-enriched soils. The two methods work equally well for estimating the
338 P sorption maxima (S_{\max}) and the bonding energy constant (k). Although there was a large
339 difference in the sorbed legacy (S_0) estimates for subsurface soils, it may be neglected
340 considering the small magnitude of S_0 of the subsurface soils. Since the one-step method
341 overestimated EPC_0 , the two-step method could thus be a preferred method if the accurate
342 estimation of EPC_0 is needed.

343 **Conclusions**

344 The accurate estimation of the sorbed legacy P (S_0) is important in a sorption study on P-
345 enriched soils that heavily receive fertilizer, manure, farm wastewater, and sewage sludge.
346 Ignoring S_0 may result in erroneous estimates of Langmuir sorption parameters, including the P
347 sorption maxima (S_{\max}), the bonding energy (k), and the zero-sorption equilibrium concentration
348 (EPC_0), and consequent misevaluation of the potential of soil P loss to runoff or drainage. The
349 two curve-fitting methods in the Langmuir models (i.e. the one-step method and the two-step
350 method) have been used to estimate S_0 . The one-step method differs with the two-step method in
351 that it assumes the Langmuir isotherm at low concentrations, while the latter assumes a linear
352 isotherm. These two methods were compared for their estimates of S_{\max} , k , S_0 , and EPC_0 on
353 three soil series in New York. The S_{\max} estimates by the two methods agreed well, and the
354 results of k were close. The estimates of S_0 by the two methods had a good agreement for
355 surface soils, but a poor agreement for subsurface soils, which may be neglected because of the
356 small magnitude of S_0 of the subsurface soils. Although the one-step method yielded greater

357 EPC_0 estimates, the EPC_0 estimates by the two methods had an excellent linear correlation for P-
 358 enriched soils. In conclusion, both methods are considered acceptable to fit the Langmuir
 359 isotherms for P-enriched soils.

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 362 the US Department of Agriculture (USDA), Natural Resources Conservation Service (NRCS)
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 364 Cornell University.

365 **Appendix**

366 Here we present the derivation of the equations for the Freundlich one-step method. The
 367 traditional Freundlich model is shown in eq. 11. The apparent sorbed P (S') and the total sorbed
 368 P (S) are defined in eqs. 2 and 3. Combining eqs. 11, 2, and 3, we find the equation given by
 369 Barrow (2008) for P-enriched soils:

$$370 \quad S' = \frac{(C_i - C)V}{M} = K_f C^n - S_0 \quad (A1)$$

371 For soils in P-free initial solutions ($C_i = 0$), the aqueous equilibrium P concentration (C)
 372 is C_0 . From eq. A1, we derive eq. 12:

$$373 \quad S_0 = K_f C_0^n + \frac{C_0 V}{M} \quad (A2)$$

374 Further, we substitute eq. A2 (or eq. 12) into eq. A1 and derive eq. 13:

$$375 \quad S' = K_f C^n - \left(K_f C_0^n + \frac{C_0 V}{M} \right) \quad (A3)$$

376 We then set $S' = 0$ (i.e. the P sorption and desorption are equal). From eq. A3 (or eq. 13),
 377 we find the zero-sorption equilibrium concentration (EPC_0) (i.e. eq. 14):

$$EPC_0 = \left(C_0^n + \frac{C_0 V}{MK_f} \right)^{1/n} \quad (A4)$$

379 **References**

- 380 Barkle, G. F., R. Stenger, P. L. Singleton, and D. J. Painter. 2000. Effect of regular irrigation
 381 with dairy farm effluent on soil organic matter and soil microbial biomass. *Aust. J. Soil*
 382 *Res.* 38(6): 1087-1097.
- 383 Barrow, N. J. 2008. The description of sorption curves. *Eur. J. Soil Sci.* 59: 900-910.
- 384 Bolster, C. H., and G. M. Hornberger. 2007. On the use of linearized Langmuir equations. *Soil*
 385 *Sci. Soc. Am. J.* 71(6): 1796-1806.
- 386 Bolster, C. H. 2008. Revisiting a statistical shortcoming when fitting the Langmuir model to
 387 sorption data. *J. Environ. Qual.* 37(5): 1986-1992.
- 388 Brock, E. H., Q. M. Ketterings, and P. J. A. Kleinman. 2007. Measuring and predicting the
 389 phosphorus sorption capacity of manure-amended soils. *Soil Sci.* 172(4): 266-278.
- 390 Cabrera, V. E., L. J. Stavast, T. T. Baker, M. K. Wood, D. S. Cram, R. P. Flynn, and A. L. Ulery.
 391 2009. Soil and runoff response to dairy manure application on New Mexico rangeland.
 392 *Agric. Ecosyst. & Environ.* 131: 255-262.
- 393 Carpenter, S. R., N. F. Caraco, D. L. Correll, R. W. Howarth, A. N. Sharpley, and V. H. Smith.
 394 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecol. Appl.*
 395 8:559-568.
- 396 Czymmek, K. J., and Q. M. Ketterings. 2007. Removal of phosphorus by field crops. Agronomy
 397 Fact Sheet Series No. 28, Department of Crop and Soil Sciences, Cornell University,
 398 Ithaca, NY.

- 399 Correll, D. L. 1998. The role of phosphorus in the eutrophication of receiving waters: A review.
 400 *J. Environ. Qual.* 27: 261–266.
- 401 Essington, M. E. 2004. Soil and water chemistry: An integrative approach. CRC Press. Boca
 402 Raton, FL.
- 403 Gale, P. M., K. R. Reddy, and D. A. Graetz. 1994. Phosphorus retention by wetland soils used
 404 for treated wastewater disposal. *J. Environ. Qual.* 23: 370-377.
- 405 Graetz, D. A., and V. D. Nair. 2000. Phosphorus sorption isotherm determination. In Methods of
 406 phosphorus analysis for soils, sediments, residuals, and waters. G.M. Pierzynski (ed).
 407 Southern Cooperative Series Bulletin No. 396. Manhattan, KS.
- 408 Holford, I. C. R. 1979. Evaluation of soil phosphate buffering indices. *Aust. J. Soil Res.* 17: 495-
 409 504.
- 410 Kao, C. W., and R. W. Blanchar. 1973. Distribution and chemistry of phosphorus in an
 411 Albaqualf soil after 82 years of phosphate fertilization. *J. Environ. Qual.* 2(2): 237-240.
- 412 NRCS. 2004. Soil survey laboratory methods manual. Soil survey investigations report No. 42.
 413 Burt, R. (Ed). National Resources Conservation Service. Washington, DC.
- 414 NRCS. 2008. National cooperative soil survey: web soil survey 2.0. Natural Resources
 415 Conservation Service. Washington, DC. <http://websoilsurvey.nrcs.usda.gov/> accessed on
 416 2/18/2008.
- 417 Olsen, S. R., and F. S. Watanabe. 1957. A method to determine a phosphorus adsorption
 418 maximum of soils as measured by the Langmuir isotherm. *Soil Sci. Soc. Am. J.* 21: 144-
 419 149.
- 420 Pant, H. K. and K. R. Reddy. 2001. Phosphorus sorption characteristics of estuarine sediments
 421 under different redox conditions. *J. Environ. Qual.* 30: 1474-1480.

EVALUATION OF TWO LANGMUIR MODELS FOR P SORPTION

- 422 Reddy, K. R., G. A. O. Conner, and P. M. Gale. 1998. Phosphorus sorption capacities of wetland
423 soils and stream sediments impacted by dairy effluent. *J. Environ. Qual.* 27: 438-447.
- 424 Sallade, Y. E., and J. T. Sims. 1997. Phosphorus transformations in the sediments of Delaware's
425 agricultural drainageways: I. Phosphorus forms and sorption. *J. Environ. Qual.* 26: 1571-
426 1579.
- 427 Sharpley A. N. 1995. Dependence of runoff phosphorus on extractable soil phosphorus. *J.*
428 *Environ. Qual.* 24: 920-926.
- 429 Siddique, M. T. and J. S. Robinson. 2003. Phosphorus sorption and availability in soils amended
430 with animal manures and sewage sludge. *J. Environ. Qual.* 32: 1114-1121.
- 431 Sims, J. T. and A. Wolf. 1995. Recommended Soil Testing Procedures for the Northeastern
432 United States. Northeast Regional Bull. #493. Agricultural Experiment Station,
433 University of Delaware, Newark, DE.
- 434 Sims, J. T., R. O. Maguire, A. B. Leytem, K. L. Gartley, and M. C. Pautler. 2002. Evaluation of
435 Mehlich 3 as an Agri-environmental soil phosphorus test for the Mid-Atlantic United
436 States of America. *Soil Sci. Soc. Am. J.* 66: 2016-2032.
- 437 Sparks, D. L. 2003. Environmental soil chemistry. Academic Press. San Diego, CA.
- 438 Sui, Y. and M. L. Thompson. 2000. Phosphorus sorption, desorption, and buffering capacity in a
439 biosolids-amended mollisol. *Soil Sci. Soc. Am. J.* 64: 164-169.
- 440 USEPA. 1983. Phosphorus, all forms. Method 365.1 (Colorimetric, Automated, Ascorbic Acid).
441 pp.365-1.1-365-1.7. In Methods for Chemical Analysis of Water and Wastes, EPA-600/
442 4-79-020. US Environmental Protection Agency. Cincinnati, OH.
- 443 USEPA. 2007. Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils,
444 and oils. U.S. Environmental Protection Agency. Washington, DC.

- 445 Vadas, P. A. and J. T. Sims. 1999. Phosphorus sorption in manured Atlantic coastal plain soils
446 under flooded and drained conditions. *J. Environ. Qual.* 28: 1870-1877.
- 447 Villapando, R. R. and D. A. Graetz. 2001. Phosphorus sorption and desorption properties of the
448 spodic horizon from selected Florida spodosols. *Soil Sci. Soc. Am. J.* 65: 331-339.
- 449 Zhang, H., J. L. Schroder, J. K. Fuhrman, N. T. Basta, D. E. Storm, and M. E. Payton. 2005. Path
450 and multiple regression analysis of phosphorus sorption capacity. *Soil Sci. Soc. Am. J.* 69:
451 96-106.
- 452 Zhou, A., H. Tang, and D. Wang. 2005. Phosphorus adsorption on natural sediments: Modeling
453 and effects of pH and sediment composition. *Water Res.* 39:1245-1254.

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454 Table 1. Selected chemical properties of soils from three vegetative treatment areas sites at
 455 Tompkins County (T), Wyoming County (W), and Delaware County (D) in New York.

Soils [†]	pH	OM [‡] (%)	Morgan extractable elements (mg kg ⁻¹)				Nitric acid-digestion elements (mg kg ⁻¹)			
			P	Ca	Fe	Al	P	Ca	Fe	Al
T1S	7.5	5.6	40.1	3143	13.1	19.3	1738	4968	26617	37500
T1D	7.6	1.3	2.0	1284	10.0	35.2	494	1741	28406	19626
T2S	7.7	5.4	92.2	3079	5.7	12.8	1783	4524	24048	22361
T2D	7.8	1.1	1.5	1411	4.0	18.3	609	2338	27267	21950
T4S	6.7	5.2	60.1	2274	3.3	9.8	1648	3743	26994	21826
T4D	7.8	0.8	0.7	1312	3.9	26.8	466	2059	29760	18403
W1S	7.4	6.4	259	3619	3.6	8.8	2233	7696	20399	19318
W1D	7.7	2.5	25.2	2127	33.5	21.6	825	4875	21162	15525
W2S	7.4	7.7	262	3526	4.7	8.7	2175	6504	18158	14793
W2D	8.1	1.4	7.9	1412	48.5	22.6	577	2835	26532	20135
W4S	7.1	8.1	236	4067	4.3	7.9	3030	6522	17560	18233
W4D	7.6	1.0	10.5	1167	1.5	15.7	603	2236	23171	18039
D1S	7.2	7.4	79.8	2190	3.4	12.4	611	913	26150	16673
D1D	6.7	0.6	11.1	423	13.0	44.2	376	478	29993	15198
D3S	6.2	5.8	12.8	1422	5.5	40.2	363	1014	27404	13886
D3D	6.6	1.1	4.4	347	16.7	73.2	297	464	27086	13228

456 [†] Soil samples were labeled as: site = Tompkins County site (T), Wyoming County site (W), and Delaware County
 457 site (D); location = a higher number indicates a greater distance down-slope of wastewater surface distribution
 458 points; depth = surface (S) and subsurface (D).

459 [‡] OM = organic matter.

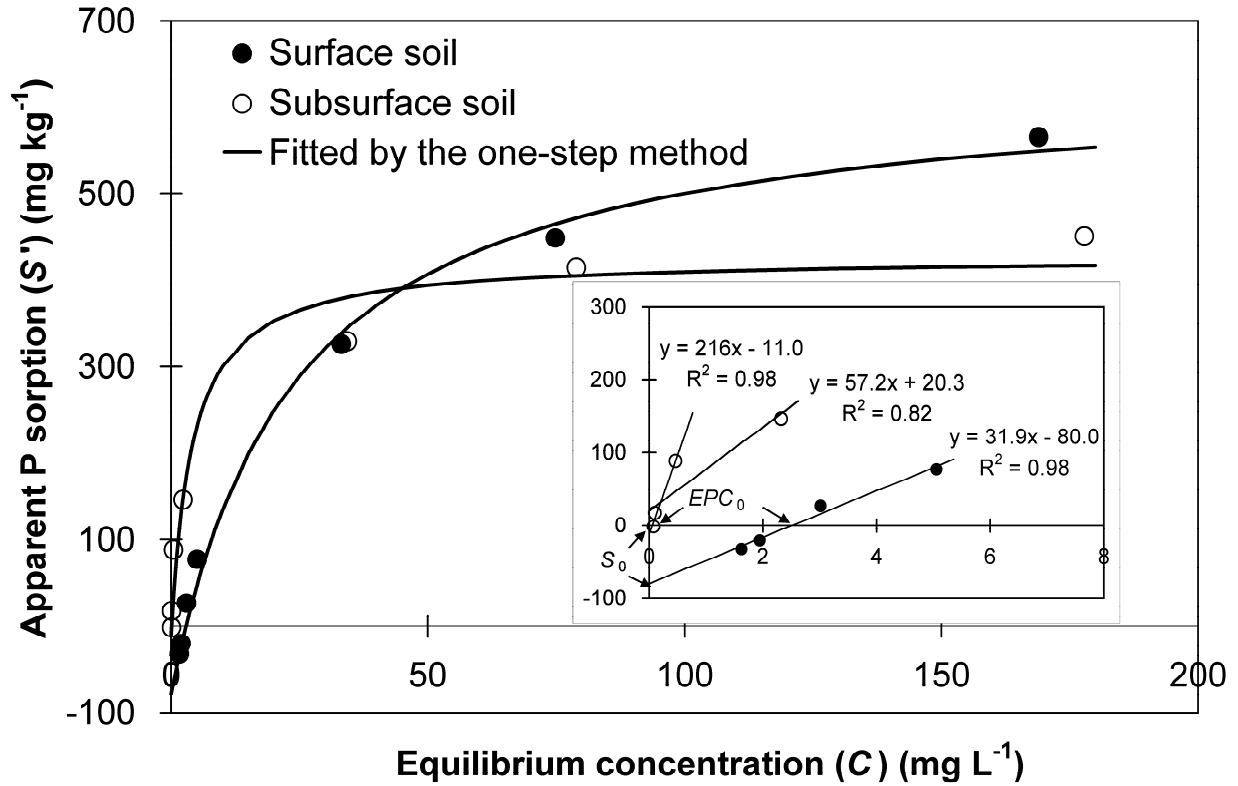
460 Table 2. Estimated sorption parameters by the one-step method and the two-step method in the
 461 Langmuir models.

Methods	Soils	S_{\max}^{\dagger} (mg kg^{-1})	k^{\dagger} (L mg^{-1})	Adjusted R^2	RMSE [†] (mg kg^{-1})	S_0^{\dagger} (mg kg^{-1})	EPC_0^{\dagger} (mg L^{-1})	MBC^{\dagger} (L kg^{-1})
One-step method	T1S	872 (116) [‡]	0.075 (0.058) [‡]	0.98	40	50 [‡]	0.80 [‡]	65 [‡]
	T1D	450 (95)	0.225 (0.324)	0.93	52	9	0.09	101
	T2S	716 (73)	0.042 (0.021)	0.99	21	78	2.91	30
	T2D	437 (66)	0.243 (0.251)	0.96	37	9	0.09	106
	T4S	405 (71)	0.057 (0.069)	0.96	29	80	4.34	23
	T4D	329 (76)	0.403 (0.631)	0.90	47	6	0.05	133
	W1S	613 (128)	0.031 (0.032)	0.97	34	129	8.61	19
	W1D	643 (155)	0.053 (0.061)	0.96	48	26	0.80	34
	W2S	605 (176)	0.023 (0.026)	0.96	37	127	11.7	14
	W2D	562 (122)	0.138 (0.205)	0.94	57	13	0.17	78
	W4S	705 (62)	0.026 (0.012)	0.99	15	187	14.1	18
	W4D	388 (80)	0.241 (0.328)	0.93	46	10	0.23	93
	D1S	1147 (345)	0.012 (0.009)	0.98	35	92	7.00	14
	D1D	314 (86)	0.120 (0.185)	0.90	41	6	0.15	38
D3S	1197 (445)	0.024 (0.027)	0.96	75	16	0.54	29	
D3D	416 (109)	0.164 (0.274)	0.90	56	7	0.14	68	
Two-step method	T1S	851 (112)	0.094 (0.059)	0.98	41	57 (72) [‡]	0.63 [‡]	80
	T1D	448 (96)	0.243 (0.322)	0.93	52	9 (134)	0.04	109
	T2S	704 (70)	0.046 (0.017)	0.99	21	80 (45)	2.51	32
	T2D	436 (68)	0.264 (0.250)	0.96	38	11 (114)	0.05	115
	T4S	398 (82)	0.052 (0.039)	0.96	28	69 (29)	3.90	21
	T4D	327 (77)	0.427 (0.632)	0.90	46	6 (107)	0.02	140
	W1S	602 (125)	0.033 (0.021)	0.97	33	127 (31)	7.26	20
	W1D	614 (133)	0.089 (0.093)	0.95	53	46 (61)	0.58	55
	W2S	580 (148)	0.029 (0.022)	0.96	37	136 (37)	8.68	17
	W2D	556 (115)	0.199 (0.249)	0.94	60	24 (64)	0.13	111
	W4S	694 (61)	0.029 (0.007)	0.99	16	194 (19)	11.3	20
	W4D	385 (82)	0.246 (0.308)	0.93	46	8 (108)	0.05	95
	D1S	1061 (300)	0.016 (0.011)	0.98	42	109 (61)	4.70	17
	D1D	312 (89)	0.108 (0.161)	0.91	40	0 (0)	0.00	34
D3S	1175 (435)	0.027 (0.029)	0.96	78	22 (65)	0.25	32	
D3D	412 (112)	0.157 (0.250)	0.91	55	2 (133)	0.02	65	

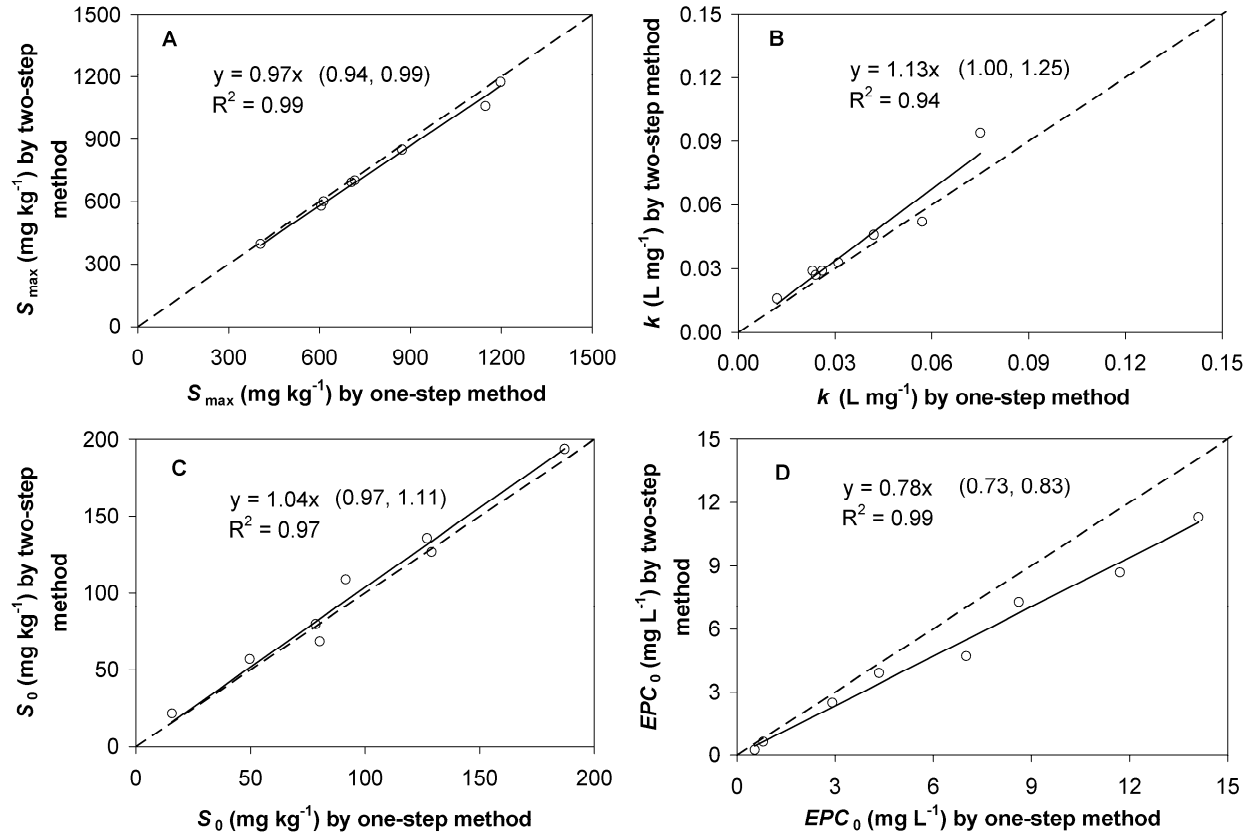
462 [†] S_{\max} = the P sorption maxima; k = the bonding energy constant; RMSE = root mean squared error; S_0 = the sorbed
 463 legacy P; EPC_0 = the zero-sorption equilibrium concentration; MBC = the maximum buffering capacity.

464 [‡] Adding and subtracting the values in the parenthesis on parameter estimates generates the 95% confidence intervals.
 465 For S_{\max} and k , those values were directly obtained from the Langmuir model fitting using the one-step and two-step
 466 methods. For S_0 in the two-step method, the 95% confidence intervals were from the linear isotherm fitting. The S_0
 467 values in the one-step method, the EPC_0 values, and the MBC values were calculated from the fitted parameters,
 468 thus no 95% confidence intervals could be provided.

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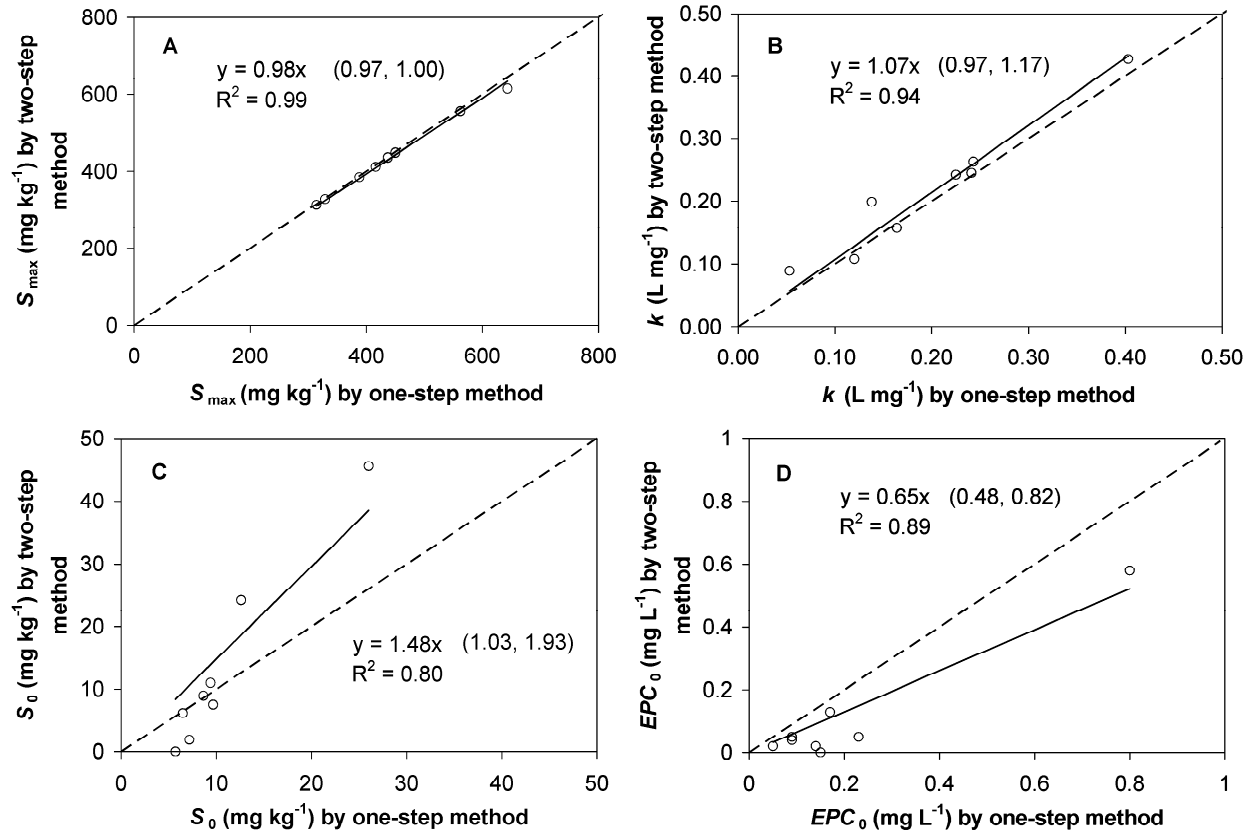
469
 470 Figure 1. Typical observed and fitted Langmuir sorption isotherms of surface
 471 soils (T2S and T2D). The inset showed the estimation of the sorbed legacy P (S_0) and the zero-
 472 sorption equilibrium concentration (EPC_0) by fitting linear isotherms at low concentrations.



473

474 Figure 2. Comparison between sorption parameters estimated by the one-step method and the
 475 two-step method for surface soils: A. the P sorption maxima (S_{\max}); B. the bonding energy
 476 constant (k); C. the sorbed legacy P (S_0); and D. the zero-sorption equilibrium concentration
 477 (EPC_0). The 95% confidence intervals of the slopes are shown in the parenthesis.

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478

479 Figure 3. Comparison between sorption parameters estimated by the one-step method and the
 480 two-step method for subsurface soils: A. the P sorption maxima (S_{\max}); B. the bonding energy
 481 constant (k); C. the sorbed legacy P (S_0); and D. the zero-sorption equilibrium concentration
 482 (EPC_0). The 95% confidence intervals of the slopes are shown in the parenthesis.