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4

5 Comment on "Citrate adsorption can decrease soluble phosphate
6 concentration in soils: Results of theoretical modeling" by Marek
7 Duputel, Nicolas Devau, Michel Brossard, Benoît Jaillard, Davey L.
8 Jones, Philippe Hinsinger and Frédéric Gérard (2013)

9

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11

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21 Gustafsson).

22

23 **1. Introduction**

24 In their recent paper Duputel et al. (2013) predict using a multi-site surface complexation
25 model that citrate can decrease inorganic phosphorus (P) solubility in the presence of
26 common soil minerals. Duputel et al. (2013) even suggest, that "special attention should be
27 given to microbiologically-mediated citrate degradation in order to avoid the risk of
28 obtaining an adverse effect of citrate adsorption on available P". To the present date the
29 general scientific consensus is that citrate enhances soluble P in soil solution. Previous work

30 shows that citrate and some other carboxylic acids decrease P sorption (e.g. Geelhoed et al.
31 1998) and therefore increase solubility. In early work on soil P, citric acid was used as an
32 extractant (Dyer, 1894). The authors suggest that their modelled citrate effect only occurs on
33 soils where adsorption is influenced by phyllosilicate clays. In this comment we report that
34 this conclusion is the result of a series of unfortunate data and modelling errors, which mean
35 that the modelling exercise of Duputel et al. (2013) is completely wrong.

36 The work of Duputel et al. (2013) builds on the modelling approach of Devau et al. (2014).
37 Together these two papers provide the details necessary for us to reproduce their modelling
38 approach and explain the associated errors. To model ion adsorption on mineral surfaces
39 (goethite, kaolinite, illite and montmorillonite) they used the CD-MUSIC (Charge Distribution
40 Multi Site Complexation) model (Hiemstra and van Riemsdijk, 1996). For their soil model
41 they used the soil content of these four mineral surfaces as a model input to simulate
42 adsorption by the whole soil.

43 In our comment we intend to explain why these errors are the result of
44 miscomprehended modelling approach rather than merely simple typographical errors. It is
45 important that the propagation of these mistakes in the scientific literature is arrested
46 because:

- 47 1. Plant breeding programs of research are being conducted that are based on the
48 hypothesis that root exudation of citrate will enable enhanced recovery of soil P
49 reserves.
- 50 2. It is misleading for other modellers working on issues related to soils and water
51 quality.
- 52 3. Understanding P solubility in soils is of global significance to food production.

53 We have found that the model calculations and parameters of Duputel et al. (2013) and
54 those of Devau et al. (2014) contain **three** fundamental errors that make their model
55 calculations invalid. In addition the paper of Duputel et al. (2013) also contains some
56 typographical mistakes concerning the citation of data sources and errors in the tables
57 containing the modeling parameters, the most important of which will be listed.

58 The three fundamental errors are:

- 59 1. The data used to derive model parameters for P adsorption on kaolinite were
60 incorrectly digitized from the cited source reference.

- 61 2. Calculation errors concerning the magnitude of the reported intrinsic surface
62 complexation constants for the formation of bidentate P complexes on kaolinite, illite
63 and montmorillonite.
- 64 3. Errors resulting from an incorrect use of conditional equilibrium constants
65 concerning the formation of bidentate P complexes and the binding of electrolyte
66 ions in the compact part of the double layer.

67 Below we will first describe the three fundamental errors in some detail, and then
68 secondly we will show with illustrated model calculations that by implementing these errors
69 we can reproduce the model output of Duputel et al. (2013) for P adsorption on kaolinite,
70 illite and montmorillonite.

71

72 **2. Errors associated with the optimization of PO_4 adsorption to clay minerals**

73 *2.1. Data for P adsorption on kaolinite*

74 To derive the model parameters for P adsorption by kaolinite, Duputel et al. (2013) report
75 using the P adsorption data published by Ioannou and Dimirkou (1997). However when we
76 were checking our calculations we digitized the adsorption data from both Duputel et al.
77 (2013) and the original source data of Ioannou and Dimirkou (1997) and found a major
78 divergence. We show the data from the two sources in Fig. 1. A similar error also appears in
79 the data shown in Fig. 3 of Devau et al. (2014). This error means that the model parameters
80 derived from fitting the data points shown in Duputel et al. (2013) would make P sorption by
81 kaolinite stronger than it actually is (assuming that all other the parts of model calculation
82 were all performed correctly, which we will show they were not). Furthermore because
83 kaolinite is one of the four mineral surfaces used in their soil model, this error will alter the
84 calculated distribution of adsorbed P on the other mineral surfaces. It would also impact the
85 modelled competitive adsorption between phosphate and citrate on the kaolinite mineral.

86

87 *2.2. Errors resulting from incorrect intrinsic equilibrium constants*

88 Duputel et al. (2013) claim that they need to convert intrinsic equilibrium constants to
89 conditional equilibrium constants for the bidentate P complexes prior to calculations. The
90 first thing we note is that they have made a mistake in this conversion, which will mislead
91 others who try to use their published intrinsic equilibrium constants for modeling P

92 adsorption. They use an equation given by Hiemstra and van Riemsdijk (1996), in which the
93 relationship between the conditional equilibrium constant and an intrinsic constant for a
94 bidentate complex is given by:

95

$$96 \log K_{P-2, \text{cond}} = \log K_{P-2, \text{int}} - \log(\rho AN_s) \quad (1)$$

97

98 where $\log K_{P-2, \text{cond}}$ is the conditional equilibrium constant for a bidentate complex
99 involving phosphate, $\log K_{P-2, \text{int}}$ is the corresponding intrinsic constant, ρ is the suspension
100 density in kg L^{-1} , A is the specific surface area in $\text{m}^2 \text{kg}^{-1}$, and N_s is the adsorption site density
101 in mol m^{-2} . Under these conditions, equation (2) can be simplified to

102

$$103 \log K_{P-2, \text{cond}} = \log K_{P-2, \text{int}} - \log [\equiv\text{SOH}] \quad (2)$$

104

105 where $[\equiv\text{SOH}]$ is the concentration of surface adsorption sites (in mol L^{-1}). This is the
106 equation normally coded in chemical equilibrium software (Wang and Giammar, 2013).

107 The authors used equation (1) to calculate the conversion factor between intrinsic and
108 conditional equilibrium constants (see our Table 1). However, when applying equation (1)
109 they have used incorrect units (i.e. for N_s they used sites nm^{-2} instead of mol m^{-2}). As a
110 result, the conditional equilibrium constants (as shown in Table 1) are actually between five
111 and six orders of magnitude lower than the real ones if one assumes the intrinsic equilibrium
112 constants as shown in Table 1 are correct (which they are not). This numerical error can be
113 easily verified by examination of the conditional equilibrium constants given in Fig. A.1,
114 Supplementary Information, and those for the intrinsic equilibrium constants given in Table
115 A.1, Supplementary Information. For example, consider kaolinite, the $\log K$ (conditional)
116 values for the two bidentate surface complexes are given as 26.5 and 32.0. If one calculates
117 the factor $\log(\rho AN_s)$ from equation (1), using the incorrect units for N_s (i.e. 2.0 sites nm^{-2}) a
118 value of 1.383 is obtained. It can be verified that the value of 1.383 was used in equation (1)
119 to calculate the intrinsic equilibrium constants given in Table A.1 (Supplementary
120 Information). The true value of the factor for kaolinite should have been -4.40 (i.e. $\log(1.0 \times$
121 $12.07 \times 2.0 \times 10^{18}/N_A)$), where N_A is Avogadro's number. The same error has also been
122 repeated for illite and montmorillonite. This error means that the reported intrinsic
123 constants are too large and all wrong. For surface complexation modelling, the intrinsic

124 constants are regarded as the “gold standard” thermodynamic equilibrium constant and are
125 used by other modellers for model input, therefore if others were to use these values it
126 would be impossible to model the original data from which they were derived. Furthermore
127 the authors in their approach will compound this error further because they use the derived
128 intrinsic constants to model their soil data. However, the mineral suspension density(ρ) in
129 the modeled soils is different to that used for the modelling of P sorption on the pure
130 mineral phases. Therefore, the authors require a new conversion ($\log(\rho AN_s)$) factor to
131 change the miscalculated intrinsic $\log K$ values back into conditional values. This obviously
132 introduces another layer of error.

133

134 *2.3. Errors resulting from an incorrect use of conditional equilibrium constants*

135 In their modelling, Duputel et al. (2013) maintain that “conditional” equilibrium constants
136 must be used for certain surface reactions when using the CD-MUSIC model. In particular
137 they used conditional constants for:

- 138 i) the formation of bidentate P surface complexes, and
- 139 ii) the binding of electrolyte ions such as K^+ and Cl^- (e.g. see foot notes in Table A.1 and
140 A.3 in the Supplementary Information section of Duputel et al., 2013).

141 First, Duputel et al. (2013) claim (p. 122) that “conditional values should be used for some
142 equilibrium constants according to the CD-MUSIC model (see Table A, p. 506 in Hiemstra and
143 van Riemsdijk, 1996).” In this case, the authors failed to recognize that the conversion to
144 conditional equilibrium constants takes place inside modern geochemical software codes
145 such as Visual MINTEQ, ORCHESTRA and PHREEQC, which is why, intrinsic equilibrium
146 constants should always be used in the input. The important thing to note is that Duputel
147 and colleagues, because of this error, carried out the conversion to conditional equilibrium
148 constants twice (i.e. first outside and then inside the software), which lead to errors which
149 become serious especially when there are large differences in $[\equiv SOH]$ between the
150 calibration data set and the data set subject to model predictions.

151 In part, the senior author feels that he may have some responsibility for the latter
152 mistake, since it has not been clear in the Visual MINTEQ documentation that the conversion
153 to conditional equilibrium constants for bidentate complexes takes place inside the
154 software. However, again it would have been easy for the authors to test their model on
155 another published data set, and again they would have discovered their mistake.

156 Second, in the paper of Duputel et al. (2013), the authors state on page 122 that:

157 “Conditional log K values were used for the formation of monovalent ions such as Cl⁻ as
158 outersphere surface complexes onto variable-charged surface sites of minerals”

159 In support of their argument, the authors cite Hiemstra and van Riemsdijk (1996), who
160 used conditional equilibrium constants to account for the reactions of a NaNO₃ electrolyte.
161 In the case of NO₃⁻ adsorption to goethite the conditional equilibrium constant can be
162 defined as:

163

$$164 \log K_{\text{NO}_3} = \log K_{\text{NO}_3, \text{int}} + \log [\text{NO}_3^-] \quad (4)$$

165

166 where $\log K_{\text{NO}_3}$ is the conditional equilibrium constant for NO₃⁻ adsorption to goethite,
167 whereas $\log K_{\text{NO}_3, \text{int}}$ is the intrinsic equilibrium constant for NO₃⁻ adsorption to goethite. The
168 reason why Hiemstra and van Riemsdijk (1996) used a version of equation (4) in their
169 modeling was that they did not use Na⁺ or NO₃⁻ as chemical components in the electrolyte
170 ion-binding reactions shown in their table of chemical reactions (this can be seen in their
171 table on p. 506). Therefore only when Na⁺ and NO₃⁻ are not defined as chemical
172 components, should the equilibrium constants be rewritten as conditional equilibrium
173 constants. However, in almost all later applications of the CD-MUSIC model, e.g. Weng et al.
174 (2012), the electrolyte ions have been included as chemical components in the set of
175 reactions, and in such cases the *intrinsic* equilibrium constants should be used.

176 From the text of Duputel et al. (2013), it seems clear that the authors did not understand
177 the reason why Hiemstra and van Riemsdijk (1996) used conditional equilibrium constants
178 for electrolyte ion binding. As a consequence they were misled to believe that conditional
179 equilibrium constants (according to equation 1) should always be used, also when the
180 electrolyte ions are included as chemical components. This error is further supported by our
181 model simulations shown in Fig. 2 as explained below.

182 It would have been easy for the authors to test their model on, for example, published
183 acid-base titration data for goethite. They would then quickly find out that they had entered
184 the wrong path. In fact, this error will strongly affect the simulation of phosphate binding to
185 (hydr)oxide surfaces and is therefore a very serious one. This is because the binding
186 electrolyte ions will strongly affect the potential gradient near the surface.

187

188 **3. Modeling of phosphate and citrate adsorption to clay minerals.**

189 In this section we investigate whether we can replicate the model fits of Duputel et al.
190 (2013) when accounting for the aforementioned errors. For the purpose of this comparison
191 we will accept all the parameters and constants used by the authors. Two model fits are
192 produced by use of Visual MINTEQ ver. 3.0 (Gustafsson, 2012); one “normal” fit using
193 intrinsic constants as reported by the authors, and the other one using the conditional
194 equilibrium constants as used by Duputel et al. (2013) and which include the errors
195 described. Table 1 shows the constants and model parameters considered. To double-check
196 the accuracy of our model simulations we also used ORCHESTRA (Meeussen, 2003), with
197 identical results. The reader is referred to either Lumsdon (2012) or Devau et al. (2014) for
198 definition of the constants used.

199 For all clay minerals our model calculation using the reported intrinsic equilibrium
200 constants (Table A.1, Supplementary Information) from Duputel et al. (2013) grossly
201 overestimated PO₄ adsorption (Fig. 2) whereas when we used the incorrect ‘conditional’
202 equilibrium constants as given by Duputel et al. (2013) we correctly replicated (Fig. 3) the
203 model lines given by Duputel et al. (2013, Fig. A.1, Supplementary Information). This in turn
204 lends support to our conclusion that Duputel and coworkers made the series of mistakes as
205 described earlier. Obviously the large errors in the phosphate parameters will modify the
206 competitive adsorption of citrate and other components.

207 We also made efforts to replicate the model fits for citrate as reported by the authors.
208 However, in this case we were not successful. For this reason we can only state that the
209 given surface complexation parameters simply do not result in the citrate model fits shown
210 in the paper. We tried several different ways to interpret the author’s model parameters,
211 but in no case did the model result in decreased P solubility as a result of increased citrate
212 concentrations. Therefore we question the authors’ claim that the CD-MUSIC model shows
213 that citrate can decrease P availability in certain soils.

214

215 **4. Other miscellaneous errors and related typos**

- 216 • In Table A.1 (Supplementary Information) the values for the Boltzmann factors for Cl⁻
217 are wrong. They are given as (1, 0, 1), but they should be (1, 0, -1).

- 218 • The Boltzmann factors for the K^+ complex are given as (-1, 1, 0). In recent papers in
219 which the CD-MUSIC model has been used (e.g. Weng et al. 2012), the Boltzmann
220 factors for the interaction of a monovalent cation and a surface site is given as (0, 1,
221 0). Also in Table A.3 (Supplementary Information) the reaction information for the
222 formation of the potassium outer sphere complex is incorrect, because there is a
223 proton missing in the reaction product.
- 224 • For Fig. 2 in the Duputel et al. (2013) paper, the reference cited as the source of the
225 data for citrate adsorption on kaolinite and illite does not contain these data. The
226 correct reference is probably to a different paper by Lackovic et al. (i.e. Lackovic et
227 al., 2003).
- 228 • Table A.1 (Supplementary Information) shows that a bidentate and a monodentate
229 citrate complex are used to model citrate adsorption on kaolinite, but in Table A.3
230 (Supplementary Information) two bidentate complexes (with the same log K values
231 as those in Table A.1, Supplementary Information) are given as the reactions needed
232 to model citrate adsorption by kaolinite.
- 233 • In both Table A.1 and Table A.3 the log K value for the $(\equiv\text{SOH}_2)_2^{\text{---}}\text{CitH}^-$ complex,
234 claimed to be important for illite, is suspiciously low (10, implicating that the complex
235 is unimportant at all conditions). Moreover the Boltzmann factors (3, -2, -1) are not
236 reasonable as there are only two surface groups that can protonate.
- 237 • In Table A.1 (Supplementary Information) there are several errors in the stated
238 surface reactions for the interaction of Ca^{2+} with goethite; to be specific the protons
239 in the reaction products do not balance the number of protons in the reactants.
- 240 • The proton stoichiometry for the Ca^{2+} complexes on illite and kaolinite is not
241 balanced.

242

243 **5. Implications for modeling PO_4 adsorption to whole soils.**

244 Further problems of the model approach of Duputel et al. (2013) will become apparent
245 when applying it to soils. We have not attempted a detailed analysis of the errors that would
246 result. However, one fundamental point of concern is that the intrinsic constants for PO_4
247 adsorption to clay minerals were too high since they were incorrectly back-calculated from
248 the 'conditional' equilibrium constants. On the other hand, the intrinsic constants for

249 goethite, as reported by the authors were genuine intrinsic constants obtained from the
250 literature e.g. Weng et al. (2008). As a result PO₄ will be disproportionately more strongly
251 adsorbed to clay minerals than to iron (hydr)oxides.

252 This is probably the reason why Devau et al. (2009, 2011) predicted illite to be the most
253 important sorbent for P in their model for a clay soil, despite the fact that < 30 % of any
254 added P is adsorbed to illite in laboratory systems (Manning and Goldberg, 1996).

255

256 **6. Conclusions.**

257 The issues identified here show that the modelling approach of Duputel et al. (2013) and
258 Devau et al. (2014) leads to meaningless model parameters, because the model parameters
259 in some cases were fitted to incorrect data, and in other cases the model parameters were
260 derived by applying a series of incorrect modelling procedures. Based on our findings we
261 believe that the modelling methodology, equilibrium constants and conclusions of Duputel,
262 Devau and their co-authors in the paper of Duputel et al. (2013) and in a series of previous
263 papers (Devau et al. 2009, 2010a, 2010b, 2011 and 2014) require major reevaluation.

264

265 **Acknowledgements**

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269

270 **References**

271

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314

315

316 **Table 1**

317 CD-MUSIC constants and model parameters according to Duputel *et al.* (2013).

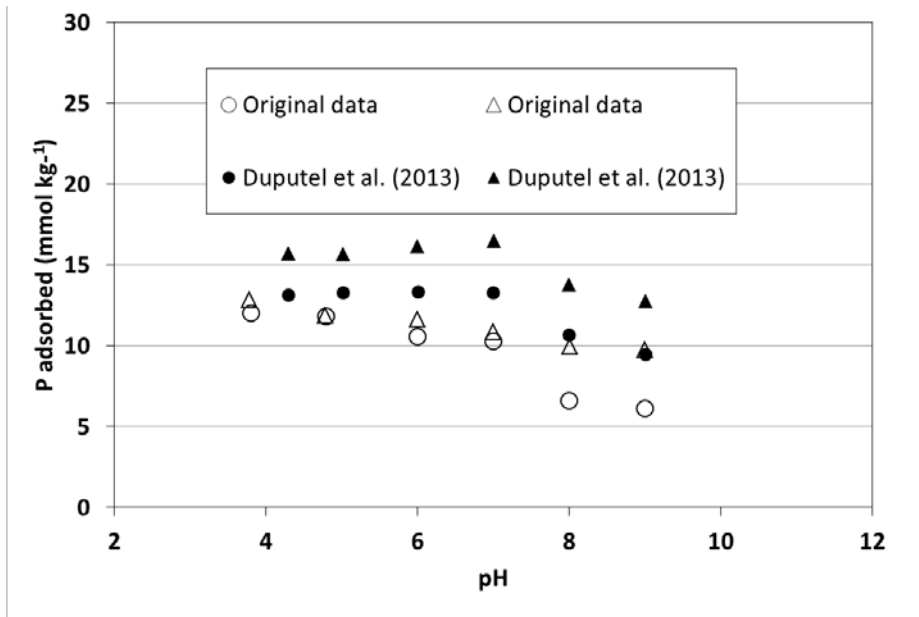
	Kaolinite	Illite	Montmorillonite
Data source	Iannou and Dimirkou (1997)	Manning and Goldberg (1996)	Manning and Goldberg (1996)
$\log K_H$	4.36	3.46	3.46
$\log K_{P-1}$	23.50	18.50	19.30
$\log K_{P-2}$	27.90 ^a / 26.50 ^b	26.50 ^a / 24.80 ^b	27.06 ^a / 25.40 ^b
$\log K_{P-3}$	33.4 ^a / 32.0 ^b	29.50 ^a / 27.80 ^b	28.60 ^a / 26.90 ^b
$\log K_{Na}$	-	-1.6 ^a / -2.6 ^b	-
$\log K_K$	-1.6 ^a / -2.6 ^b	-	-
$\log K_{Cl}$	7.50 ^a / 6.50 ^b	7.50 ^a / 6.50 ^b	7.50 ^a / 6.50 ^b
mineral concentration (g l ⁻¹)	1.0	2.5	2.5
Specific surface area (m ² g ⁻¹)	12.07	24.2	18.6
Site density (sites nm ⁻²)	2.0	0.8	1.0
$\log(\rho AN_s)^c$ (incorrect)	1.383	1.685	1.667
$\log(\rho AN_s)$ (true value)	-4.397	-4.095	-4.112
C_1 (F m ⁻²)	1.5	1.5	1.5
C_2 (F m ⁻²)	5	5	5

318 ^a Intrinsic' log *K* values according to Duputel *et al.* (2013)

319 ^b Conditional' log *K* values according to Duputel *et al.* (2013) and assumed to be valid for the specified data
320 sources only.

321 ^c The use of incorrect and true values of $\log(\rho AN_s)$ is explained in the main text.

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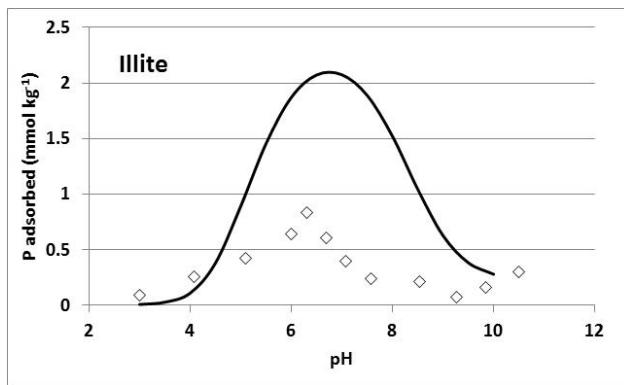
326 **Fig. 1.** Phosphate adsorption by kaolinite (1.0 g dm^{-3}), for total P concentrations of $40.3 \text{ }\mu\text{M}$

327 (circles) and $81 \text{ }\mu\text{M}$ (triangles). Original data (open symbols) were digitized from the source

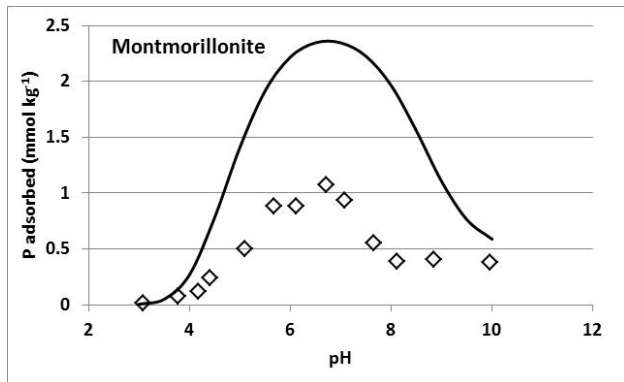
328 reference (Iannou and Dimirkou, 1997). The closed symbols were digitized from Duputel et

329 al. (2013)

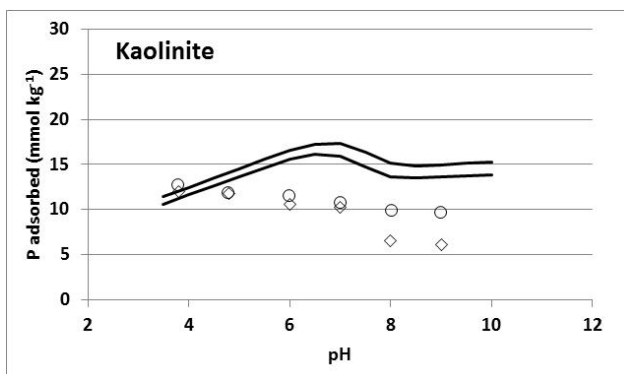
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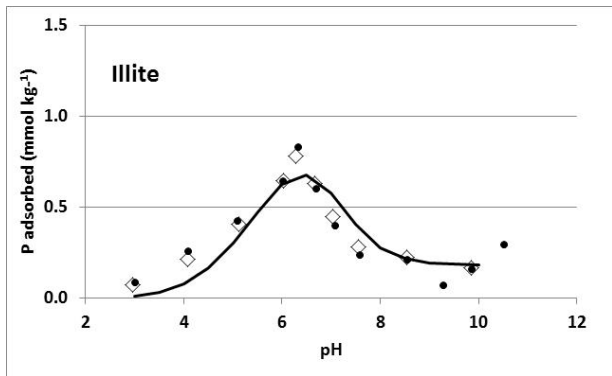


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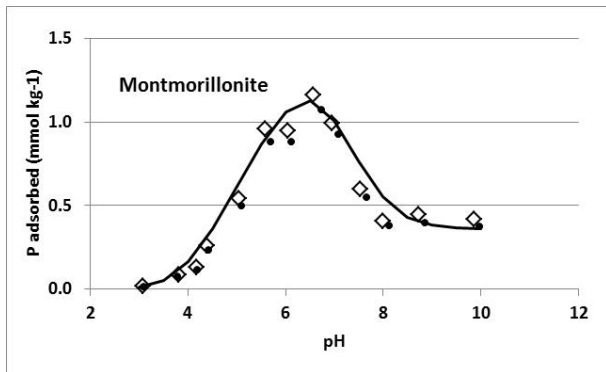
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335 **Fig. 2.** Phosphate adsorption onto illite, montmorillonite and kaolinite. Observations are
 336 shown as points; these data were digitized from the source references (Iannou and
 337 Dimirkou, 1997; Manning and Goldberg, 1996). Solid lines are model fits when the intrinsic
 338 equilibrium constants, as reported by Duputel et al. (2013) are used. The model parameters
 339 required to produce the model fits are given in Table 1.

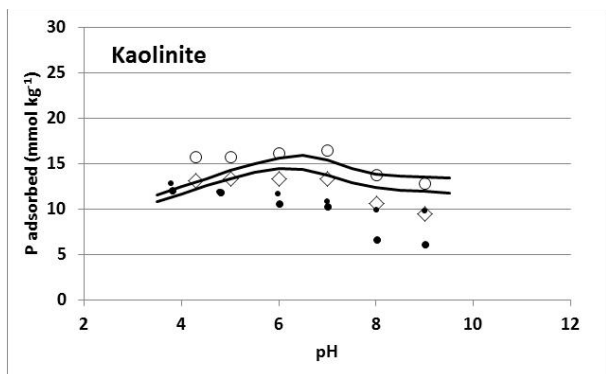
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345 **Fig. 3.** Phosphate adsorption onto illite, montmorillonite and kaolinite. Data points digitized
 346 from Duputel et al. (2013) are shown with open symbols. Data shown as filled circles were
 347 digitized from the source references (Iannou and Dimirkou, 1997; Manning and Goldberg,
 348 1996). Solid lines are model fits when the conditional equilibrium constants as reported by
 349 Duputel et al. (2013) are used.