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

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1. Introduction

In their recent paper Duputel et al. (2013) predict using a multi-site surface complexation model that citrate can decrease inorganic phosphorus (P) solubility in the presence of common soil minerals. Duputel et al. (2013) even suggest, that “special attention should be given to microbiologically-mediated citrate degradation in order to avoid the risk of obtaining an adverse effect of citrate adsorption on available P”. To the present date the general scientific consensus is that citrate enhances soluble P in soil solution. Previous work
shows that citrate and some other carboxylic acids decrease P sorption (e.g. Geelhoed et al. 1998) and therefore increase solubility. In early work on soil P, citric acid was used as an extractant (Dyer, 1894). The authors suggest that their modelled citrate effect only occurs on soils where adsorption is influenced by phyllosilicate clays. In this comment we report that this conclusion is the result of a series of unfortunate data and modelling errors, which mean that the modelling exercise of Duputel et al. (2013) is completely wrong.

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

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

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

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

The three fundamental errors are:

1. The data used to derive model parameters for P adsorption on kaolinite were incorrectly digitized from the cited source reference.
2. Calculation errors concerning the magnitude of the reported intrinsic surface complexation constants for the formation of bidentate P complexes on kaolinite, illite and montmorillonite.

3. Errors resulting from an incorrect use of conditional equilibrium constants concerning the formation of bidentate P complexes and the binding of electrolyte ions in the compact part of the double layer.

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

2. Errors associated with the optimization of PO₄ adsorption to clay minerals

2.1. Data for P adsorption on kaolinite

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

2.2. Errors resulting from incorrect intrinsic equilibrium constants

Duputel et al. (2013) claim that they need to convert intrinsic equilibrium constants to conditional equilibrium constants for the bidentate P complexes prior to calculations. The first thing we note is that they have made a mistake in this conversion, which will mislead others who try to use their published intrinsic equilibrium constants for modeling P
adsorption. They use an equation given by Hiemstra and van Riemsdijk (1996), in which the relationship between the conditional equilibrium constant and an intrinsic constant for a bidentate complex is given by:

\[
\log K_{P-2, \text{cond}} = \log K_{P-2, \text{int}} - \log(\rho AN_s) \tag{1}
\]

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

\[
\log K_{P-2, \text{cond}} = \log K_{P-2, \text{int}} - \log [≡SOH] \tag{2}
\]

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

The authors used equation (1) to calculate the conversion factor between intrinsic and conditional equilibrium constants (see our Table 1). However, when applying equation (1) they have used incorrect units (i.e. for \( N_s \) they used sites nm\(^{-2}\) instead of mol m\(^{-2}\)). As a result, the conditional equilibrium constants (as shown in Table 1) are actually between five and six orders of magnitude lower than the real ones if one assumes the intrinsic equilibrium constants as shown in Table 1 are correct (which they are not). This numerical error can be easily verified by examination of the conditional equilibrium constants given in Fig. A.1, Supplementary Information, and those for the intrinsic equilibrium constants given in Table A.1, Supplementary Information. For example, consider kaolinite, the \( \log K \) (conditional) values for the two bidendate surface complexes are given as 26.5 and 32.0. If one calculates the factor \( \log(\rho AN_s) \) from equation (1), using the incorrect units for \( N_s \) (i.e. 2.0 sites nm\(^{-2}\)) a value of 1.383 is obtained. It can be verified that the value of 1.383 was used in equation (1) to calculate the intrinsic equilibrium constants given in Table A.1 (Supplementary Information). The true value of the factor for kaolinite should have been -4.40 (i.e. \( \log(1.0 \times 12.07 \times 2.0 \times 10^{18}/N_a) \)), where \( N_a \) is Avogadro’s number. The same error has also been repeated for illite and montmorillonite. This error means that the reported intrinsic constants are too large and all wrong. For surface complexation modelling, the intrinsic
constants are regarded as the “gold standard” thermodynamic equilibrium constant and are used by other modellers for model input, therefore if others were to use these values it would be impossible to model the original data from which they were derived. Furthermore the authors in their approach will compound this error further because they use the derived intrinsic constants to model their soil data. However, the mineral suspension density ($\rho$) in the modeled soils is different to that used for the modelling of $P$ sorption on the pure mineral phases. Therefore, the authors require a new conversion ($\log(\rho AN_s)$) factor to change the miscalculated intrinsic log $K$ values back into conditional values. This obviously introduces another layer of error.

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

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

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

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

In part, the senior author feels that he may have some responsibility for the latter mistake, since it has not been clear in the Visual MINTEQ documentation that the conversion to conditional equilibrium constants for bidentate complexes takes place inside the software. However, again it would have been easy for the authors to test their model on another published data set, and again they would have discovered their mistake.
Second, in the paper of Duputel et al. (2013), the authors state on page 122 that:

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

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

\[
\log K_{\text{NO}_3} = \log K_{\text{NO}_3, \text{int}} + \log [\text{NO}_3^-]
\]  \hspace{1cm} (4)

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

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

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

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

For all clay minerals our model calculation using the reported intrinsic equilibrium constants (Table A.1, Supplementary Information) from Duputel et al. (2013) grossly overestimated PO$_4$ adsorption (Fig. 2) whereas when we used the incorrect ‘conditional’ equilibrium constants as given by Duputel et al. (2013) we correctly replicated (Fig. 3) the model lines given by Duputel et al. (2013, Fig. A.1, Supplementary Information). This in turn lends support to our conclusion that Duputel and coworkers made the series of mistakes as described earlier. Obviously the large errors in the phosphate parameters will modify the competitive adsorption of citrate and other components.

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

4. Other miscellaneous errors and related typos

- In Table A.1 (Supplementary Information) the values for the Boltzmann factors for Cl$^-$ are wrong. They are given as (1, 0, 1), but they should be (1, 0, -1).
• The Boltzmann factors for the K⁺ complex are given as (-1, 1, 0). In recent papers in which the CD-MUSIC model has been used (e.g. Weng et al. 2012), the Boltzmann factors for the interaction of a monovalent cation and a surface site is given as (0, 1, 0). Also in Table A.3 (Supplementary Information) the reaction information for the formation of the potassium outer sphere complex is incorrect, because there is a proton missing in the reaction product.

• For Fig. 2 in the Duputel et al. (2013) paper, the reference cited as the source of the data for citrate adsorption on kaolinite and illite does not contain these data. The correct reference is probably to a different paper by Lackovic et al. (i.e. Lackovic et al., 2003).

• Table A.1 (Supplementary Information) shows that a bidentate and a monodentate citrate complex are used to model citrate adsorption on kaolinite, but in Table A.3 (Supplementary Information) two bidentate complexes (with the same log $K$ values as those in Table A.1, Supplementary Information) are given as the reactions needed to model citrate adsorption by kaolinite.

• In both Table A.1 and Table A.3 the log $K$ value for the ($≡$SOH$_2$)$_2$−CitH⁺ complex, claimed to be important for illite, is suspiciously low (10, implicating that the complex is unimportant at all conditions). Moreover the Boltzmann factors (3, -2, -1) are not reasonable as there are only two surface groups that can protonate.

• In Table A.1 (Supplementary Information) there are several errors in the stated surface reactions for the interaction of Ca$^{2+}$ with goethite; to be specific the protons in the reaction products do not balance the number of protons in the reactants.

• The proton stoichiometry for the Ca$^{2+}$ complexes on illite and kaolinite is not balanced.

5. Implications for modeling PO$_4$ adsorption to whole soils.

Further problems of the model approach of Duputel et al. (2013) will become apparent when applying it to soils. We have not attempted a detailed analysis of the errors that would result. However, one fundamental point of concern is that the intrinsic constants for PO$_4$ adsorption to clay minerals were too high since they were incorrectly back-calculated from the ‘conditional’ equilibrium constants. On the other hand, the intrinsic constants for
goethite, as reported by the authors were genuine intrinsic constants obtained from the
literature e.g. Weng et al. (2008). As a result PO$_4$ will be disproportionately more strongly
adsorbed to clay minerals than to iron (hydr)oxides. This is probably the reason why Devau et al. (2009, 2011) predicted illite to be the most
important sorbent for P in their model for a clay soil, despite the fact that < 30 % of any
added P is adsorbed to illite in laboratory systems (Manning and Goldberg, 1996).

6. Conclusions.

The issues identified here show that the modelling approach of Duputel et al. (2013) and
Devau et al. (2014) leads to meaningless model parameters, because the model parameters
in some cases were fitted to incorrect data, and in other cases the model parameters were
derived by applying a series of incorrect modelling procedures. Based on our findings we
believe that the modelling methodology, equilibrium constants and conclusions of Duputel,
Devau and their co-authors in the paper of Duputel et al. (2013) and in a series of previous

Acknowledgements

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Services (RESAS) Division (DL).

References

Devau N., Le Cadre E., Hinsinger P., Jaillard B., Gérard F., 2009. Soil pH controls the environmental availability of
availability of phosphorus: Experimental and mechanistic modelling approaches” [Appl. Geochem. 24 (11),
and mechanisms controlling dissolved inorganic phosphorus in soils. Geochim. Cosmochim. Acta 75, 2980-
2996.


Table 1
CD-MUSIC constants and model parameters according to Duputel et al. (2013).

<table>
<thead>
<tr>
<th></th>
<th>Kaolinite</th>
<th>Illite</th>
<th>Montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>log ( K_H )</td>
<td>4.36</td>
<td>3.46</td>
<td>3.46</td>
</tr>
<tr>
<td>log ( K_{P-1} )</td>
<td>23.50</td>
<td>18.50</td>
<td>19.30</td>
</tr>
<tr>
<td>log ( K_{P-2} )</td>
<td>27.90(^a) / 26.50(^b)</td>
<td>26.50(^a) / 24.80(^b)</td>
<td>27.06(^a) / 25.40(^b)</td>
</tr>
<tr>
<td>log ( K_{P-3} )</td>
<td>33.4(^a) / 32.0(^b)</td>
<td>29.50(^a) / 27.80(^b)</td>
<td>28.60(^a) / 26.90(^b)</td>
</tr>
<tr>
<td>log ( K_{Na} )</td>
<td>-</td>
<td>-1.6(^a) / -2.6(^b)</td>
<td>-</td>
</tr>
<tr>
<td>log ( K_{K} )</td>
<td>-1.6(^a) / -2.6(^b)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>log ( K_{Cl} )</td>
<td>7.50(^a) / 6.50(^b)</td>
<td>7.50(^a) / 6.50(^b)</td>
<td>7.50(^a) / 6.50(^b)</td>
</tr>
<tr>
<td>mineral concentration (g l(^{-1}))</td>
<td>1.0</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Specific surface area (m(^2) g(^{-1}))</td>
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<td>24.2</td>
<td>18.6</td>
</tr>
<tr>
<td>Site density (sites nm(^2))</td>
<td>2.0</td>
<td>0.8</td>
<td>1.0</td>
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<tr>
<td>log((\rho AN_s))(^c) (incorrect)</td>
<td>1.383</td>
<td>1.685</td>
<td>1.667</td>
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<tr>
<td>log((\rho AN_s)) (true value)</td>
<td>-4.397</td>
<td>-4.095</td>
<td>-4.112</td>
</tr>
<tr>
<td>( C_1 ) (F m(^{-2}))</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>( C_2 ) (F m(^{-2}))</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

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

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

\(^c\) The use of incorrect and true values of log(\(\rho AN_s\)) is explained in the main text.
Fig. 1. Phosphate adsorption by kaolinite (1.0 g dm$^{-3}$), for total P concentrations of 40.3 µM (circles) and 81 µM (triangles). Original data (open symbols) were digitized from the source reference (Iannou and Dimirkou, 1997). The closed symbols were digitized from Duputel et al. (2013).
Fig. 2. Phosphate adsorption onto illite, montmorillonite and kaolinite. Observations are shown as points; these data were digitized from the source references (Iannou and Dimirkou, 1997; Manning and Goldberg, 1996). Solid lines are model fits when the intrinsic equilibrium constants, as reported by Duputel et al. (2013) are used. The model parameters required to produce the model fits are given in Table 1.
Fig. 3. Phosphate adsorption onto illite, montmorillonite and kaolinite. Data points digitized from Duputel et al. (2013) are shown with open symbols. Data shown as filled circles were digitized from the source references (Iannou and Dimirkou, 1997; Manning and Goldberg, 1996). Solid lines are model fits when the conditional equilibrium constants as reported by Duputel et al. (2013) are used.