

Helfenstein et al. propose an interesting article about the turnover of P in the soil solution as estimated by isotope exchange kinetics (IEK) experiments, so called  $K_m$ .

The authors argue that  $K_m$  is one of the keys to understand P plant-availability and the underlying mechanisms. They raise the point that, despite its conceptual definition and its derivation were proposed decades ago, this parameter is barely computed and discussed in the IEK literature. To overcome this, they propose a new way of deriving it from the other parameters obtained by IEK experiments. I agree with them that this demonstration is probably more “universally” accessible in the way it does not require the use of Laplace transforms, as proposed by Fardeau (1996).

Taking advantage of a large compilation of existing IEK data from the upper layer of diverse soils, Helfenstein et al. show that  $K_m$  varies among soil types in a way that is coherent with soil properties that are known to influence P dynamics between the solid and the liquid phases of the soil. Together with the concentration of P ions in the soil solution ( $P_w$ ),  $K_m$  allows a mechanistic understanding of the value of isotopically exchangeable P ( $E_{(t)}$ ) and, beyond that, the P fertility of a given soil. The authors also show that  $K_m$  is rather well correlated with P buffering capacity (PBC) as evaluated on long-term fertilization experiments.

I found particularly appealing the study of the proportion of the variation of  $E_{(t)}$  that can be explained by  $P_w$ ,  $K_m$ , and  $P_{inorg}$  (Fig. 4).

Concerning the impact of microbial activity on the results, as raised by referee 1 (see the public discussion), I agree with the response of the authors. This study has to be placed in the framework of IEK experiments with their inherent assumptions.

Globally, I found this manuscript rather clear and concise. The objectives and hypotheses are well stated and relevant—at the exception of the last hypothesis (see below)— and the results are interestingly presented and discussed. The supplementary material is also relevant. I recommend the publication of this study in *Biogeosciences* without major concerns. I provide some specific and technical comments in the next two sections.

*We thank the reviewer for their positive comments.*

### **Specific comments**

p. 2, l. 5: “concentrations of P in the soil solution...” this term could be misleading for those who are not familiar with IEK experiments, particularly in the introduction. It could be confused with field measurements while it is the concentration in the conditions of the IEK experiment.

*We see the reviewers point. However, we think it would be too specific and would confuse the reader to already talk about IEK experiments in this paragraph. To avoid the confusion, we changed the sentence as follows, “However, concentrations of P in the soil solution are usually small (Brédoire et al., 2016), and in order to meet plant needs P in the soil solution must be replenished continuously (Pierzynski and McDowell, 2005).”*

p. 2, l. 5–7: the progression of ideas is not straightforward, what are these “total P requirements”

(provide some examples)? How  $P_w$  is related with them?

*Our aim was to highlight the inability of the P in the soil solution to supply the plant with sufficient P for growth, which would therefore necessitate the resupply of P to the soil solution. See changes to the sentence as written above.*

p. 3, l. 19–20: as formulated, the last hypothesis seems an evidence. In fact,  $E_{(t)}$  is a function of  $P_w$ , and m and n (see Eq. 4 and 2). Please reformulate. Perhaps you wanted to introduce the work presented in Fig. 4. In that case, a suggestion (do what you want with this): “We hypothesized that the dependence of P availability on  $K_m$  and  $P_w$  evolves with time (, in relation to the different mechanisms involved at different time scales)”. Or maybe you wanted to introduce the idea that  $P_w$  together with  $K_m$  permit to understand P availability (and not  $P_w$  or  $K_m$  alone)...

*This concern was also raised by Reviewer 1. We agree with the reviewers and have revised the third hypothesis to, “Lastly, we hypothesized that the dependence of isotopically exchangeable P on  $P_w$  and  $K_m$  evolves with time.”*

p. 4, section 2.2: besides soil types, could you provide some information (such as simple descriptive statistics) on the types of ecosystems (e.g. cropland, pasture, forest, grassland) represented in your dataset?

*We have added this information to the manuscript (p 4, l 26-29).*

p. 5, l. 18–21: this MM paragraph on the sensitivity analysis is not clear. Some additional information, such as the assumption of a RES of 10% for both m and n, is provided in the description of Fig. 6 but it should also be provided in the MM. In addition, why to abbreviate “relative standard deviation” as “RES” and not “RSD”?

We have provided additional information on the sensitivity analysis and made corrections as suggested by the reviewer (p 6, l 23).

p. 6, l. 8: “The lowest  $K_m$  values were found in Podzols, which are known to have low P-sorbing capacity”, however, there is a huge range of  $K_m$  values for podzols and the median does not seem to be one of the lowest (Fig. 1). Are there some hypotheses to discuss this? Nevertheless, we approach here the limits of this dataset, which contains only a few values for each soil type—despite being representative of most, if not all, the IEK literature published—and we have no insurance that the median obtained with 5–29 points is truly representative of the soil type.

*Though the mean is not the lowest, the lowest  $K_m$  values were from soils belonging to the Podzols group. We agree with the reviewer that with only few samples per soil group one should be cautious to make interpretations about soil groups, which are any way extremely broad and often contain soils whose properties overlap with other soil groups. We made minor changes (p 6, l 15), and added a cautionary sentence, “small sample sizes per soil group and large spans in soil properties even within soil groups mean that group-specific  $K_m$  values should not be over-interpreted” (p 6, l 27).*

p. 6, l. 28: remind briefly your second hypothesis.

*Corrected.*

p. 6, l. 30: what does “P status” mean? Rephrase.

*Changed to “heavily fertilized”.*

p. 6, l. 30–31: there is no need to repeat what was written two lines before.

*Corrected.*

p. 7, l. 5–7: “the range of calculated  $E_{(t)}$ ”, this is not clear at first read... I suggest to start l. 6 by “**Indeed**, while  $P_w$  values...”

*We have revised the sentence to make this clearer.*

p.8,l.26: where in the SI? I did not see it.

*In an earlier version of the manuscript we included additional information in the SI, which we later decided to include in the body text of the manuscript. We have removed reference to the SI.*

p. 8, l. 26: “Relatively large errors...”, which errors are you talking about? Rephrase.

*We have made this clearer in the manuscript.*

p. 8, section 3.6: where do the errors come from? Could something be done to reduce them?

*As previously identified in methods section 2.3, the errors presented in the sensitivity analysis of this study were calculated assuming relative standard deviations of 10% for the  $m$  and  $n$  parameters. We did this to highlight the areas in which there is high  $K_m$  sensitivity, i.e. when  $m$  and or  $n$  is low. Error propagation is much higher in this area for mathematical reasons. We have made no changes to the manuscript.*

Supplementary material: add the lists of the references used in the two compilation datasets?

*In “dataset\_fertilizerexperiments.csv” and “dataset\_soils.csv”, the references can be found in the 2<sup>nd</sup> to last and 4<sup>th</sup> to last column, respectively.*

### **Technical corrections**

p. 5, l. 11: “Eq. 4” instead of “Eq. 5”?

*Corrected.*

p. 5, l. 16–17 & Fig. 1: it seems you do not cite R packages properly in the text. In fact, it is a more common practice to state in the MM something like “Jenks natural break optimization was performed with the R package ‘classInt’ v.0.1-24 (Bivand et al, 2015)” right after you wrote you used R for data analyses (p. 5, l. 22). The way you cite Bivand et et (2015) and Adler (2005) seems to refer to the publications where the methods were presented first. Finally, I’m not sure it is useful to provide a citation to justify what is a violin plot or how you performed it.

*We have made changes to the body text and removed the description of the violin plots.*

p. 7, l. 6: do you mean “when  $t > 100$  min” instead of “when  $t < 100$  min”?

*The original sentence was, “However, the range of calculated  $E_{(t)}$  values decreased with time, particularly when  $t < 1$  min.” We meant that the spread in  $E(t)$  was lower at  $E(1)$  than  $E(0)$  (i.e.  $P_w$ ). Since this seems to be confusing, we removed this sentence fragment.*

p. 7, l. 6: refer here to Fig. 3a

*Corrected.*

p. 7, l. 8: the linear relation is with  $\log_{10}(K_m)$ , not  $K_m$

*Corrected.*

p. 7, l. 13: “catch up to other soils”, rephrase?

*Corrected.*

p. 8, l. 3: replace “predicating” by “predicting”

*Corrected.*

p. 8, l. 7: replace “long-time” by “long-term”?

*Corrected.*

p. 8, l. 8: cite as “Morel et al (2000)”

*Corrected.*

p. 9, l. 9: add a comma: “Prior to this study, little was known...”

*Corrected.*

p. 9, l. 20: “the soil solution is buffered **by** P inputs”

*Corrected.*

p. 10, l. 23 & 32: the references for two R packages “Adler (2005)” and “Bivand et al (2015)” look strange, check if no information is missing.

*We have revised the reference to include the package version, which was previously missing.*

Fig. 2, 3b, and 5: explain what are the black dashed lines (e.g. confidence interval at 95 %).

*Corrected.*

Fig. 4: is labelled “Abbildung 4”

*Corrected.*

Fig. 6: add the values higher than 100 % to the legend. Precise in the title of the legend that it concerns the RES of  $K_m$ . I also suggest to inverse the colour code of the legend (blue/green for small RES and red for high RES). Again, why to abbreviate “relative standard deviation” as “RES” and not “RSD”?

*Corrected.*

Supplementary information, around the end of p. 1: can we say “concentration of radioactivity”?

*Yes, e.g. Bq/ml.*