

In general, this paper presents some very interesting results on soil solution phosphorus (P) turnover, which, as the authors pointed out, is a very important concept in describing the kinetics of bioavailable P.

We thank the reviewer for their positive comments.

However, I do have several concerns about the methodology and interpretations of results.

The major concern I have is the possible impacts of microbial processes on the results. The authors did not clarify the possible impacts of microbial uptake and turnover in the paper, but emphasizing the new insight is about the diffusion-based mechanism. One guess I have is that the authors accept the assumption from isotopic exchange kinetics studies that during the short-term batch experiment (100 minutes), there is only physicochemical exchange but no biological exchange. It will be better if this argument is clearly stated in the beginning of the method section. Moreover, assuming this assumption is taken for granted, there is still recent evidence showing the strong active role of microbes during the short-term batch experiment (Bunemann et al. 2012). It also seems that the microbial inhibitors don't always work as a perfect solution due to various reasons (Bunemann et al. 2015). It would be not only interesting but also necessary to see if any results of microbial impacts could be drawn from the current dataset.

We agree with the reviewer that the role of microbial processes during an IEK experiment needs to be more clearly explained in the manuscript. Please see the 'Interactive comment' published in the online discussion (11/10/2017) for our response related to this comment. We have revised the manuscript to make this clearer (p 2, l 28 and p 4, l 18).

The second concern I have is about the evolution of the equation 2 and also the determination of parameter m in the dataset. As far as I know, there is a simple version, a version without the $r(1)/R$ term, and a full version of the equation from papers in the dataset; and for the parameter m , it is sometimes directly using the value $r(1)/R$ and sometimes a fitted value. How reliable are the results given the huge inconsistency of the dataset, particularly because K_m derives from the full version of the equation and is calculated using m and n values?

The reviewer is correct regarding the use of a 'simple' and a 'full' version of equation 2 (see below).

Simple version:
$$\frac{r(t)}{R} = \frac{r(1)}{R} * t^{-n}$$

Full version:
$$\frac{r(t)}{R} = m * \left(t + m^{\frac{1}{n}}\right)^{-n} + \frac{r(\infty)}{R}$$

From a mathematical point of view, $m = \frac{r(1)}{R}$ if $\frac{r(\infty)}{R}$ approaches 0 and $m^{\frac{1}{n}}$ also approaches 0. Values derived from these terms tend to be small and differences in the $r(1)/R$ and m parameter using both models are minor in most soils (Fardeau et al. 1991). We have made this clearer in the manuscript (p 4, l 29-31). To make sure that using parameters estimated by the simple model does not bias K_m calculation, we tested this assumption with data from our lab. As shown in Fig. 1, we found that there is no systematic difference between K_m calculated using $r(1)/R$ and n from

the simple model or using m and n from the full model. In fact, the difference between the full and the simple model is in the same range as the scatter between replicates of the same soil. We consider this as proof that it is valid to calculate K_m from either parameters estimated by the simple or parameters estimated by the full model.

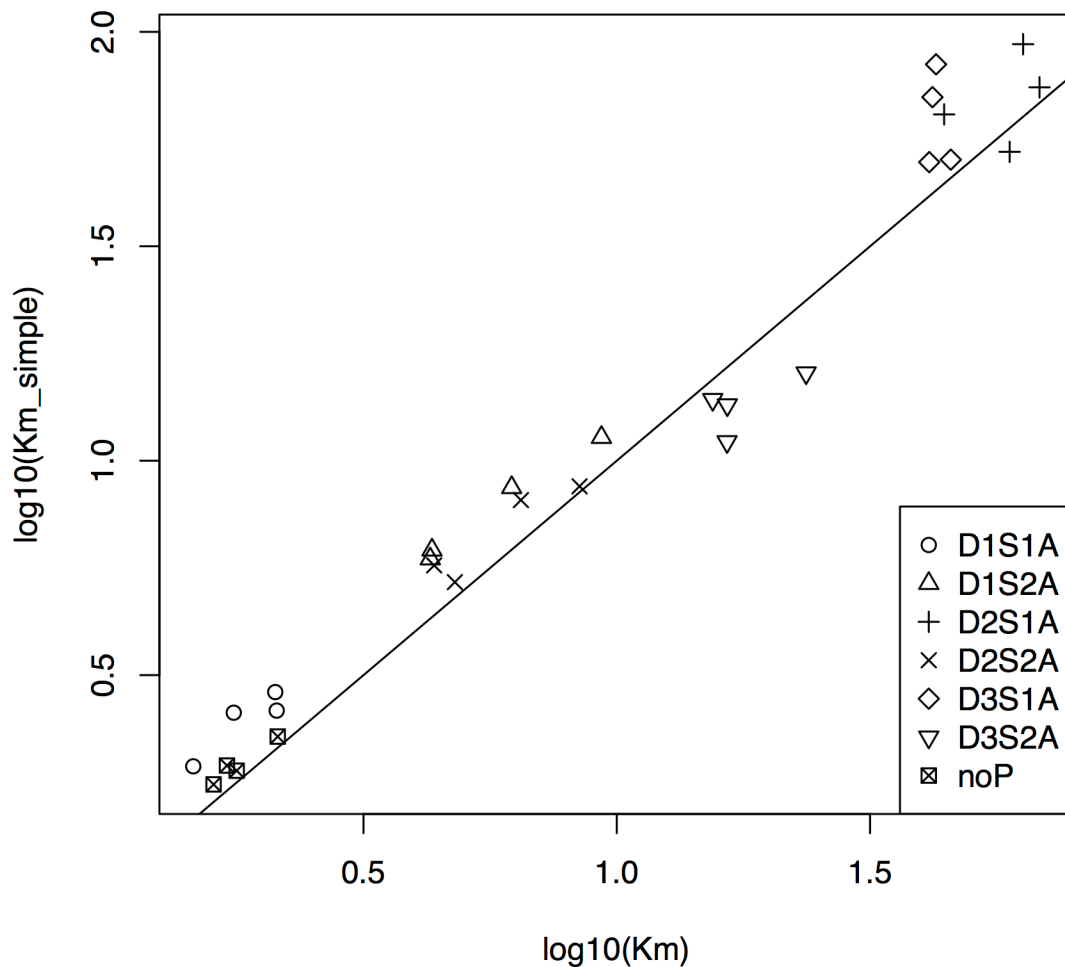


Figure 1. Comparison of K_m calculated from parameters of the full and simple model for seven different soils, with four replicates each. The line denotes the 1:1 line. These seven soils were chosen because the first author performed IEK analyses on these soils, and thus had the full raw data available to fit both models. “noP” is a Cambisol and the other soils are Andosols with strongly varying P exchange dynamics. For more information on these soils, please see “dataset_soils.xlsx”, the supplementary table containing information on all the soils used in the study.

It should be noted that the effect of the two models on calculated parameters/terms is more pronounced over the long-term, which is particularly the case for E -values due to the missing $\frac{r^{(\infty)}}{R}$ term. In this case, E -values tend to be overestimated using the simple model compared to that of the full model. Therefore, we only used the full model when calculating E -values (Fig. 3

and 4) (p 5, l 14-15).

The third concern is that some of the hypothesis and discussion section are seemingly self-verifying. For example, in the third hypothesis, $E(t)$ is mathematically already defined as a function of P_w (Eqn. 4), meaning the authors are only looking at $E(t)$ and K_m ; in section 3.3, the authors concluded that K_m is 'an important predictor of isotopically exchangeable P at exchange times of less than 1 minute', but in fact it is because it is defined/derived in this way mathematically (as shown in SI). I would suggest reconsidering some of the sayings used in the paper, as the authors have already mentioned that many of the terms discussed are calculated by the same parameters.

In regards to the hypothesis: This concern was also raised by Reviewer 2. We have adapted the suggestion by reviewer 2 (see below).

"Lastly, we hypothesized that the dependence of isotopically exchangeable P on P_w and K_m evolves with time."

In regards to Section 3.3: Yes, $E(t)$ is mathematically defined as a function of P_w (Eq. 4). In contrast, an analysis of the dataset revealed that P_w has little predictive power for $E(t)$, particularly for soils with low concentrations of P_w (see Fig. 4a). Our results show that K_m is the main driver of P availability at short time spans (Fig. 3b). In, "an important predictor of isotopically exchangeable P at exchange times of less than 1 minute", we changed "predictor" to "buffer". We were not sure what other sayings the reviewer was concerned about.

Some technical/specific corrections:

P1, L25-30: the sequence of the three points is a bit difficult to follow

Agreed. We have changed the order of the sentences so that the flow is more logical.

P2, L11: PBC should be abbreviated here rather than at L15

Agreed, the term 'Phosphorus buffering capacity' is first used and its abbreviation defined on Page 2, Line 12.

P2, L15: any reference for it?

Yes, a reference has been added.

P2, from L23: from the content of the paper, K_m is the main topic, but this is not mentioned in L10 ('In this study, we investigate. . .'). And it came too late in this paragraph, would be better if it comes earlier and uses an equation, in parallel to PBC.

Yes, agreed. We have changed the sentence in Line 10 accordingly. Also, we changed the paragraph starting at Line 23 to emphasise the importance of K_m in the study, and added the equation for calculating K_m as suggested by the reviewer.

P3 L5: as far as I know, Frossard et al. 2011 is a book chapter which doesn't publish any new

data, maybe cite this in another way?

The reviewer is correct that this reference relates to a book chapter. The reason it is cited here is because it reports K_m values, which are not reported in the original publication of Gallet et al. (2003).

P5 L29: no need for the abbreviation of conc.

Corrected.

P7 L23: misuse of hyphen

Corrected.

P7 L29: loose (typo)

Corrected.

SI: the numbering and alignment of equations

Corrected.

References

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2017-304>, 2017.

*Fardeau, J.-c., C. Morel, and R. Boniface. 1991. Phosphate ion transfer from soil to soil solution: kinetic parameters. Agronomie **11**:787-797.*