10.11.2017

Dear Dr. Sönke Zaehle,

Thank you for giving us the opportunity to revise the manuscript with minor revisions. The two reviewers gave us constructive comments that allowed us to improve the text. The concerns by reviewer one showed us where readers could not follow our approach, and we amended the text accordingly and tried to address his/her concerns as best as possible. Reviewer two had more minor/technical comments, which we also implemented. Below, please find our point by point response to both reviewer comments.

Sincerely,

Julian Helfenstein (on behalf of all authors)

Reviewer 1

In general, this paper presents some very interesting results on soil solution phos- phorus (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 physiochemical 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 as- sumption 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.

Please see the 'Interactive comment' published in the online discussion (11/10/2017) for our response related to this comment. Reviewer two agreed with our response from 11/10/2017, saying that "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."

Nevertheless, we agree with reviewer 1 that the role of microbial processes during an IEK experiment needs to be more clearly explained in the manuscript. We have revised the manuscript to state our assumptions and the limitations more clearly (p 2, l 28 and p 4, l 16).

The second concern I have is about the evolution of the equation 2 and also the deter- mination 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 Km derivates 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 27-29). 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.*

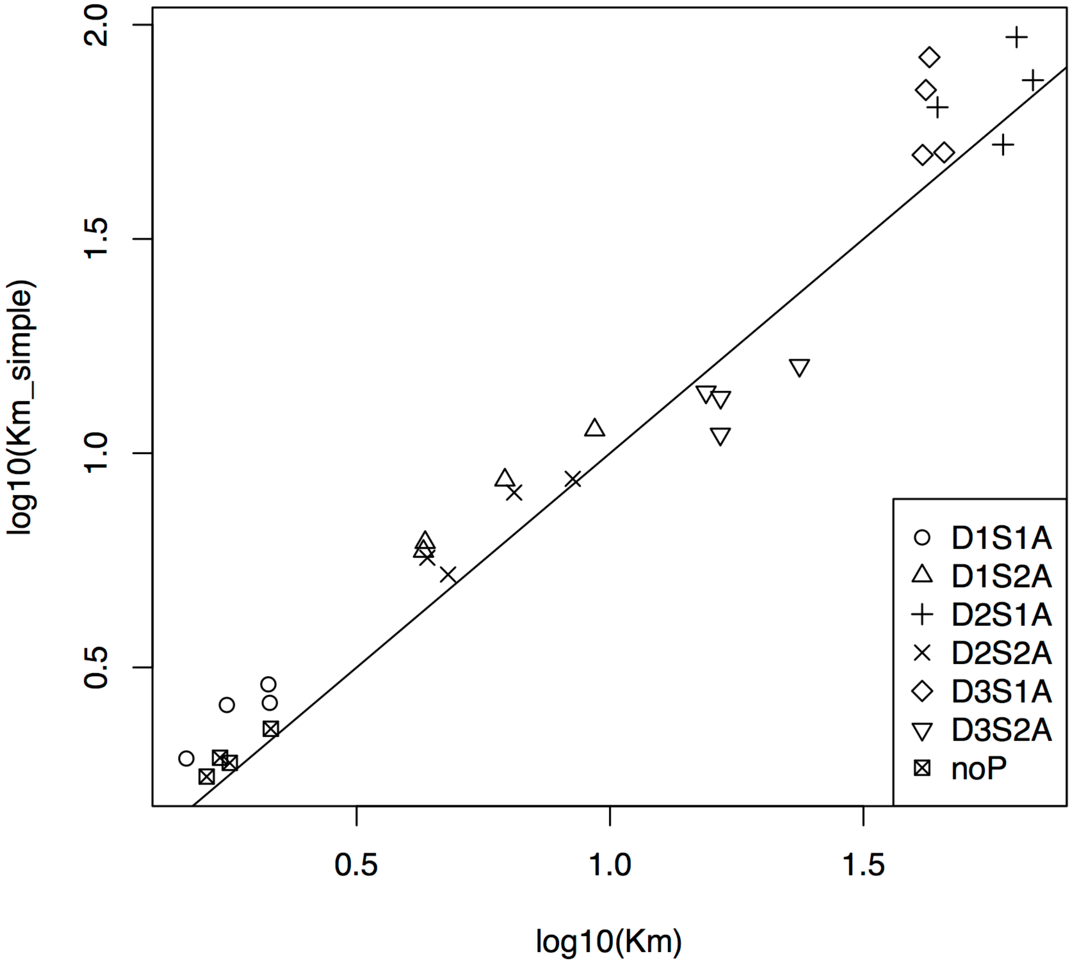

Figure 1. Comparison of Km calculated from parameters of the full and simple model for seven different soils, with four replicates each. The line denotes the 1:1 line. These seven soils were chosen because the first author performed IEK analyses on these soils, and thus had the full raw data available 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 12-13).*

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 de- fined as a function of Pw (Eqn. 4), meaning the authors are only looking at E(t) and Km; in section 3.3, the authors concluded that Km 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, Km is the main topic, but this is not men- tioned 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 Km in the study, and added the equation for calculating Km 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 Km 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.

Reviewer 2

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 hypothe- ses 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 ad- ditional 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 addi- tion, 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 5, 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 Km 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 Km 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 2nd to last and 4th 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. Pw). 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. No changes made.

Soil solution phosphorus turnover: derivation, interpretation, and insights from a global compilation of isotope exchange kinetic studies

Julian Helfenstein[1], Jannes Jegminat[2], Timothy I. McLaren[1], Emmanuel Frossard[1]
[1]Institute of Agricultural Sciences, ETH Zürich, Lindau, 8315, Switzerland
[2]Institute of Neuroinformatics, University of Zürich and ETH Zürich, Zürich, 8057, Switzerland
Correspondence to: Julian Helfenstein (julian.helfenstein@usys.ethz.ch)

Abstract. The exchange rate of inorganic phosphorus (P) between the soil solution and solid phase, also known as soil solution P turnover, is essential for describing the kinetics of bioavailable P. While soil solution P turnover (K_m) can be determined by tracing radioisotopes in a soil-solution system, few studies have done so. We believe that this is due to a lack of understanding on how to derive K_m from isotopic exchange kinetic (IEK) experiments, a widespread form of radioisotope dilution study. Here, we provide a derivation of calculating K_m using parameters obtained from IEK experiments. We then calculated K_m for 217 soils from published IEK experiments in terrestrial ecosystems, and also for that of 18 long-term P fertilizer field experiments. Analysis of the global compilation dataset revealed a negative relationship between concentrations of soil solution P and K_m. Furthermore, K_m buffered isotopically exchangeable P in soils with low concentrations of soil solution P. This finding was supported by an analysis of long-term P fertilizer field experiments, which revealed a negative relationship between K_m and phosphate buffering capacity. Our study highlights the importance of calculating K_m for understanding the kinetics of P between the soil solid and solution phases where it is bioavailable. This also has implications for other environmentally-relevant, and strongly-sorbing elements that can be traced with radioisotopes, such as zinc, cadmium, nickel, arsenic, and uranium.

Deleted: thus highlights the potential of K_m for future studies—not only for P, but also for other environmentally-relevant, strongly-sorbing elements with radioisotopes such as zinc, cadmium, nickel, arsenic, or uranium.

1 Introduction

As an essential but often limiting nutrient, phosphorus (P) plays a central role in food production and more efficient P management is key to improve food security (Tilman et al., 2002;Syers et al., 2008). Phosphorus limitation in agroecosystems is usually overcome by applying P fertilizers to the soil surface. However, excessive applications of fertilizer P to soil can cause ecological, societal and economic problems. First, fertilizer P is largely derived from rock phosphate, which is a non-renewable resource and major deposits are located in only a few countries (Elser and Bennett, 2011;Obersteiner et al., 2013). Second, applications of P fertilizers to soils with a high P sorption capacity can be inefficient because P largely accumulates in the soil as sparingly-soluble forms (Roy et al., 2016). Third, leaching or runoff of fertilizer

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P from agricultural land to aquatic and marine ecosystems contributes to fish die-off and declining water quality (Carpenter et al., 1998). To improve food security while reducing ecosystem pollution, it is essential that we improve our understanding of soil P dynamics, particularly the mechanisms controlling P movement between the soil solid phase and the soil solution where it is bioavailable.

Plants take up P from the soil solution as ionic orthophosphate ($H_2PO_4^-$ or HPO_4^{2-}) via roots or mycorrhizal hyphae (Pierzynski and McDowell, 2005). However, concentrations of P in the soil solution are usually small (Achat et al., 2016), and in order to meet plant needs P in the soil solution must be replenished continuously (Pierzynski and McDowell, 2005). Therefore, P exchange kinetics, or the rate at which the soil solution is replenished by P from the soil solid phase, have important implications for the P requirements of living organisms (Menezes-Blackburn et al., 2016;Fardeau et al., 1991). In this study, we investigate a potential link between two different concepts: phosphorus buffering capacity and soil solution P turnover, by analyzing a dataset of global soils and P fertilizer experiments.

Phosphorus buffering capacity (PBC) is defined as the ability of soil to moderate changes in the concentration of soil solution P (Pypers et al., 2006;Olsen and Khasawneh, 1980;Beckett and White, 1964). Historically, PBC has been calculated using Equation 1.

$$PBC = \frac{\Delta\, conc.\ of\ P\ in\ soil\ solution}{\Delta\, conc.\ of\ P\ in\ the\ soil}, \qquad (1)$$

The traditional approach of determining PBC in soil is by adding various amounts of P to a soil suspension, equilibrating, and then measuring the slope between adsorbed P and P in soil solution (Olsen and Khasawneh, 1980). Alternatively, PBC can be measured by analyzing the change in soil solution P concentration with regard to P budget in field P fertilization experiments (Morel et al., 2000). These approaches have revealed that PBC is influenced by ambient temperature, soil solution pH, and concentrations of P in the soil solution, and is highly variable among soil types (Barrow, 1983). One of the most important factors among soil types is the specific surface area of Fe/Al oxides and clay minerals, which are important sites of P sorption (Gérard, 2016). Whilst the aforementioned approaches are a useful and cost effective way to study soil P dynamics (Bolland and Allen, 2003;Burkitt et al., 2002;Barrow and Debnath, 2014), they are not able to directly determine the turnover of P in the solution.

Mean soil solution P turnover can be calculated from parameters determined in an isotopic exchange kinetic experiment (IEK) (Fardeau et al., 1991;Fardeau, 1985). Isotopic exchange kinetic experiments involve the use of P radioisotopes (^{32}P or ^{33}P) to directly measure the exchange of P between the soil solid and solution phases (Frossard et al., 2011). They are based on the assumption that during the short term experiments usually lasting 100 minutes there is only physicochemical exchange but no biological exchange (Oehl et al., 2001). Measures of isotopically exchangeable P are a more accurate indicator of P bioavailability than that of conventional soil tests based on chemical extraction because the former involve a P radiotracer that can be directly measured and distinguished from all other P ions in the soil (Demaria et al., 2005;Hamon et al., 2002). Previous studies have shown that isotopically exchangeable P is the predominant source of P for most crops (Frossard et al., 1994;Morel and Plenchette, 1994). Though the IEK approach does not consider root-induced

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pH alterations or secretion of organic acids, increased P availability due to root exudates can be quantified by comparing isotopically exchangeable P with radioisotope uptake in plants (Hedley et al., 1982). Isotopic dilution in a soil-solution system is characterized by two statistically fitted parameters, *m* and *n* (Fardeau, 1985), which can be used to calculate soil solution P turnover using Equation 2.

$$K_\mathrm{m} = \frac{n}{m^{\frac{1}{n}}} \qquad (2)$$

The importance of parameters *m* and *n* as well as their relation to physicochemical properties in the soil was recently investigated (Achat et al., 2016).

Despite several decades of using radioisotopes in P research and the potential relevance of soil solution P turnover to understanding agricultural and natural ecosystems, only six studies have published K_m values, and there has been no synthesis of these values (Frossard et al., 2011;Fardeau et al., 1991;Fardeau, 1985, 1993;Oberson et al., 1993;Xiong et al., 2002). We believe that this is because an intuitive derivation of K_m has never been published. Whilst information on soil solution P turnover remains limited, K_m values can easily be calculated using data from previously published IEK experiments.

The first aim of our study was to provide a clear and intuitive derivation of the K_m term. Our second aim was to calculate K_m values from previously published IEK studies, which resulted in a global dataset of over 200 soils. We then tested specific hypotheses related to concentrations of soil solution P and isotopically exchangeable P. Our third aim was to understand the relationship between PBC and K_m. This involved an additional dataset based on long-term P fertilizer field experiments, which have reported IEK results and the fertilizer P budgets. Lastly, we carried out a sensitivity analysis of K_m in order to assist interpretation of future results.

Our first hypothesis was that turnover of soil solution P would differ based on soil group. More specifically, we hypothesized that soil groups known to have higher concentrations of sorption sites (such as Andosols and Ferralsols) would have faster turnover rates. Our second hypothesis was that soils with higher concentrations of soil solution P (P_w) would have lower values of K_m compared to soil with lower concentrations of soil solution P. This is because a high concentration of sorption sites leads to fast adsorption and consequently low concentration of P in the solution. Lastly, we hypothesized that the dependence of isotopically exchangeable P on P_w and K_m evolves with time.

2. Materials and methods

2.1 Derivation of K_m

A given volume of soil can be described as containing inorganic P in one of two states: the soil phase or the soil solution phase. In any given time interval, physicochemical reactions transfer a fraction of P from the soil solution phase into the solid phase. The rate constant of this reaction is solution P turnover K_m [min^{-1}]. Thus, K_m plays a critical role in determining the time and amount of P that is potentially available to plants. At low values of K_m, there is little exchange.

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In equilibrium, an underlying assumption of an IEK experiment, the net flux between the phases is zero because of the balancing effect of the inverse flux, i.e. the flux from the soil phase to the solution phase through desorption and dissolution. In other words, the inverse flux prevents us from measuring K_m directly by fitting the temporal loss of P in soil solution. If radioisotopes (for P, either ^{32}P or ^{33}P) are injected in the soil solution, it becomes possible to experimentally eliminate the inverse flux. Shortly after the injection, the radioisotope is not present in the solid phase and, consequently, there is no inverse flux. Equation 2 has been found to describe the resulting decline of radioisotope in solution (Fardeau et al., 1991;Frossard et al., 2011).

$$\frac{r_{(t)}}{R} = m\left(t + m^{\frac{1}{n}}\right)^{-n} + \frac{r_{(\infty)}}{R} \qquad (3)$$

where $r_{(t)}$ is the radioactivity [Bq] measured at time t [min], R is the total amount of radioactivity added, and m and n are the model parameters that describe the rapid and slow physico-chemical processes respectively. Since K_m is equivalent to the decline rate of the radioisotope in the absence of an inverse flux, we analyze Eq. (3) right after the injection (t = 0) and derive Eq. 2 (for details on the derivation, please see Supporting Information).

K_m is thus calculated in three steps: first, $r_{(t)}/R$ is measured, then n and m are determined by non-linear regression, and finally equation 3 is applied. A limitation of K_m is that it does not take into account an indefinite number of P species each with their own exchange rate (Andersson et al., 2016;Menezes-Blackburn et al., 2016;Gérard, 2016). Also, the IEK method as described above does not consider microbial uptake or mineralization of organic P (Oehl et al., 2001). Therefore, the variable K_m should be considered as the average P exchange rate of the soil solution with an indefinite number of solid inorganic P pools.

2.2 Dataset

We carried out a literature search for IEK studies reporting m, n, and P_w values based on the methodological approach of Fardeau et al. (1991). Only values from topsoil layers (0 – 30 cm layer, if reported) were compiled. The dataset includes all papers cited by Achat et al. (2016) in accordance with our aforementioned selection criteria, plus more recent publications. In addition, data obtained from the published literature were supplemented with unpublished data (7 soils), from studies carried out in the Group of Plant Nutrition (ETH Zurich). This resulted in a final dataset of 217 soils taken from 41 references (see Supporting Information Table S1). The soils represented 19 soil groups across the world reference base (WRB, 2015), 26 countries, and all continents except Antarctica. Eighty-five soils were from cropland, 64 from grassland, and 32 from forest, while for 36 soils land use was not specified. Several studies (58 soils) used a simplified version of Eq. 3. Since the simplified version leads to only minor differences in parameter estimation, we assumed that this would not affect calculation of K_m (Fardeau et al., 1991). To avoid overrepresentation, sample sizes of two articles reporting many samples of similar soils were randomly reduced, from 30 to 10 (Compaoré et al., 2003) and from 48 to 12 (Tran et al., 1988).

In addition, we carried out a literature search for IEK studies on long-term P fertilizer field experiments. We found published data across 18 long-term experiment sites (Oberson et al., 1993;Oberson et al., 1999;Fardeau et al., 1991;Gallet et

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al., 2003;Morel et al., 1994). The soils represented the following soil groups (WRB, 2015): Cambisols, Chernozems, Ferralsols, Fluvisols, Gleysols and Luvisols. In general, the field experiments involved different types of mineral and organic P fertilizers applied at varying rates. The difference in inputs minus outputs led to a range in P budgets from -52 to 125 kg P ha^{-1} yr^{-1}.

2.3 Data analysis

Isotopically exchangeable P (i.e. *E*-values: $E_{(t)}$ [mg kg^{-1}]), the amount of P that can reach the soil solution within a given time frame is calculated using Equation 4 (Hamon et al., 2002;Fardeau, 1996).

$$E_{(t)} = P_w * \frac{R}{r_{(t)}} \tag{4}$$

While IEK experiments only last several minutes, $E_{(t)}$ values can be extrapolated beyond the IEK experiment based on Equations 2 and 4 (Frossard et al., 1994;Morel and Plenchette, 1994;Buehler et al., 2003). Extrapolated $E_{(t)}$ values are highly influenced by concentrations of P_w. One of the main challenges of the IEK experiment is an accurate and precise determination of P_w, particularly in high P-fixing soils (Randriamanantsoa et al., 2013). Analysis involving $E_{(t)}$ could only be performed for studies that reported P_{inorg} in addition to P_w, *m* and *n*.

To examine the relationship between K_m and isotopically exchangeable P, $E_{(t)}$ was calculated for t = 0 to 129,600 min using Eq. 4 (129,600 minutes is equal to 3 months). First, we calculated the difference between $E_{(1)}$ and $E_{(0)}$ as $\log_{10}(E_{(1)}) - \log_{10}(E_{(0)})$. We then tested if K_m was a significant predictor of this difference using linear regression. To determine the timespan over which K_m affected $E_{(t)}$, we performed linear regression between K_m and $E_{(t)}$ at t = 1 to 129,600 min. We also carried out linear regression with P_w and P_{inorg} as predictors of $E_{(t)}$ over the aforementioned time points, respectively. During data analysis, we noticed that different P_w levels were differently sensitive to predictor variables. Therefore, we used Jenks natural breaks optimization to systematically partition the P_w data into three clusters using R package 'classInt' (Bivand et al., 2015).

To show sensitivity of K_m, we assumed relative standard deviations (standard deviation/mean [%]) of 10% for each reported *m* and *n*. Uncertainty was then approximated using the partial derivatives approach for error propagation (Eq. (5)) (Ku, 1966). By assuming independent errors of the two fitted parameters, we obtain an upper bound on the error of K_m (Weiss et al., 2006):

$$s_{K_m} = \sqrt{\left(\frac{\partial K_m}{\partial m}\right)^2 s_m^2 + \left(\frac{\partial K_m}{\partial n}\right)^2 s_n^2} \tag{5}$$

All statistical analyses and graphics were carried out using R (R Core Team, 2017). All model regressions were checked and the model fit determined using significance of fit (p = 0.05) and the regression coefficient (R^2).

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2.4 Analysis of long-term field experiments

The fertilizer P budgets were calculated as the average annual input of fertilizer P minus that of crop offtake (kg P ha^{-1} yr^{-1}). Each site had three to four P treatments, usually one with a negative budget, one with a balanced budget, and one with a positive budget. To determine the effect of P budget on P_w and K_m, we calculated the slope of linear regressions between P budget and P_w. The slope of the line relating P_w to P budget can be taken as a field PBC, since the slope of P_w corresponds to the change in P_w over the change in soil P concentration (Eq. (1)). Next, we investigated if there was a relationship between the thus determined PBC and K_m.

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3. Results and discussion

3.1 Global analysis of P turnover in the soil solution (K_m)

The turnover rate of P in the soil solution ranged nine orders of magnitude from 10^{-2} to 10^{6} min^{-1} across the 217 soils surveyed (Fig. 1). However, approximately half of the soils had a P turnover rate within the range of 10^{0} and 10^{2} min^{-1}. Clear differences in K_m between different soil groups suggest that K_m is related to soil properties governing kinetics of inorganic P in the soil-solution system. Surface soil horizons of Ferralsols had the highest values of K_m, followed by Andosols and Cambisols (Fig. 1). High K_m values of Ferralsols suggest that P in these soils is rapidly adsorbed, i.e. these soils have a high P buffering capacity. The three of the four lowest K_m values were found in Podzols, soils which are known to have low P-sorbing capacity (Chen et al., 2003;Achat et al., 2009).

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Fardeau, Morel, and Boniface (Fardeau et al., 1991) showed that K_m is largest for small values of n and m, and becomes smaller as n approaches 0.5, and m approaches 1, respectively. Values of n and m have often been found to correlate with soil properties (pH, carbonate concentration, oxalate-extractable Al-/Fe, organic matter, etc.) (Tran et al., 1988;Demaria et al., 2013;Frossard et al., 1993;Achat et al., 2013). In a global compilation study, it was shown that low values of n occur for soils with low concentrations of oxalate-extractable Al and Fe, which are indicative of amorphous Al and Fe oxides (Achat et al., 2016). In contrast, low values of m tend to occur for soils with a low ratio of organic C to Al and Fe oxides (Achat et al., 2016). The high K_m values of Ferralsols are due to extremely low m values (Mean = 0.025, SD = 0.012, n = 26), and are consistent with low ratios of organic C to Al and Fe oxides typically reported in these soils (Randriamanantsoa et al., 2013). The Podzols in the dataset, on the other hand, have distinguishably high m values (Mean = 0.50, SD = 0.43, n = 14), which is consistent with the low Al and Fe oxide content of the upper horizon of Podzols (Achat et al., 2009). However, 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.

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3.2 Relationship between soil solution P turnover (K_m) and concentration of soil solution P (P_w)

There was a negative correlation between K_m and P_w, as shown in Fig. (2) and described in Eq. (6):

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$$log10(K_m) = 1.26 - 0.960 * log10(P_w) \qquad (6)$$

with $F = 127$, $p < 10^{-15}$ and an $R^2 = 0.37$. The two variables P_w and K_m are important in governing plant available P, because the former describes the amount of P in solution and the latter describes the rate at which it is exchanged. At $t = 1$ min, the highest values of $E_{(t)}$ occurred for soils with high values of K_m and P_w, whereas the lowest values of $E_{(t)}$ occurred for soils with low values of K_m and P_w (Fig. S1). The relationship was less clear at $t = 1$ day (Fig S1). However, the trend that lowest E-values occurred for soils with a low K_m and low P_w is still apparent at $t = 1$ day.

The negative correlation between K_m *and* P_w confirms our second hypothesis, that soils with high P_w would have low K_m, and is in accordance with findings from other studies using different methodological approaches. For example, it has been observed that sorption is less pronounced on heavily fertilized soils, due to more negative surface charge (Barrow and Debnath, 2014). In our study, high K_m values imply the presence of many potential binding sites, where P may adsorb or precipitate. This leads to a rapid exchange between sorption sites and the soil solution, as solution P quickly binds to a new site. Consequently, P_w is low. On the other hand, slower turnover rates of *P* in the soil solution and high P_w occur when P-binding sites are few or saturated.

3.3 Soil solution P turnover (K_m) as a buffer of isotopically exchangeable P ($E_{(t)}$)

We found that K_m is an important buffer of isotopically exchangeable P. As *t* increases, $E_{(t)}$ values diverge from P_w and eventually approach P_{inorg}. Interestingly, the range of $E_{(t)}$ values decreased with time (Fig 3a). While P_w values ranged almost 4 orders of magnitude, $E_{(1)}$ values only ranged 3 orders of magnitude. Furthermore, differences in *E*-values between soils of low, middle and high P_w decreased with time. We found that the difference between $\log_{10}(E_{(1)})$ and $\log_{10}(E_{(0)})$ was strongly correlated with log10(K_m) ($F = 615$, $p < 10^{-15}$, and $R^2 = 0.79$). Thus, soils with fast rates of K_m had large increases in $E_{(t)}$ compared to soils with slow rates of K_m, which showed little difference in $E_{(t)}$ from $E_{(0)}$ to $E_{(1)}$. Furthermore, soils with the largest increases in $E_{(t)}$ had low concentrations of P_w but high values of K_m (Fig. 3b).

While it is evident that $E_{(t)}$ and K_m would be related since both variables are calculated from the same isotope exchange kinetic parameters, the dependency reveals that many soils with low concentrations of P_w attained *E*-values comparable to other soils due to extremely high soil solution P turnover rates (Fig. 3b). One can thus interpret that a soil with high K_m has a higher PBC and a majority of P applied as fertilizer will be quickly adsorbed. On the other hand, high turnover means that there is a large flux of P ions through the soil solution and phosphate ions in solution are quickly replaced through desorption when plants take up P. If soils with $E_{(1min)}$ value of over 5 mg P kg^{-1} are considered highly P-fertile (Gallet et al., 2003), high P fertility can be found in both soils with high P_w and or soils with low P_w but high K_m (Fig. S1). Soils with low P_w and low K_m, such as most Lixisols, also have low *E*-values. Thus, P "fixing" by soils is reversible and says little about P availability.

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3.4 Timeframe over which K_m buffers isotopically exchangeable P ($E_{(t)}$)

For what time frame is $E_{(t)}$ dependent on K_m? By performing linear regressions between P_w, K_m, and P_{inorg}, respectively, and $E_{(t)}$ for t = 1 min to 3 months, we found that the fits are strongly dependent on P_w class (high, middle, low). Based on Jenks natural breaks optimization, three clusters of P_w were determined: 0.008 – 0.16 mg kg^{-1} (n = 46), 0.16 – 1.9 mg kg^{-1} (n = 94), and 1.9 – 42.5 mg kg^{-1} (n = 77). Calculating the R^2 of the regression as a function of time showed that for the class of high P_w soils, P_w explained 60% of variability in $E_{(t)}$ at 1 min (Fig 4a). However, P_w lost power as a predictor of $E_{(t)}$ rapidly, explaining only 20% of variability by t = 60 min. In contrast, soils with low concentrations of P_w showed no relationship between values of $E_{(t)}$ and P_w even at short time spans. Thus, the concentration of P in the soil solution has a strong legacy on plant P-availability for soils with high P_w at short time spans, but does not indicate P availability in soils with low concentrations of P_w. In these soils, values of $E_{(t)}$ are primarily driven by K_m (Fig 4b). Eventually both K_m and P_w lose predictive power, as $E_{(t)}$ inevitably approaches P_{inorg} (see Eq. (4)) (Fig 4c). However, predictive power of P_{inorg} is again dependent on P_w -class.

$E_{(t)}$ over timespans between 1 min and 3 months were differently related to predictors P_w, K_m, and P_{inorg} depending on concentrations of P_w. The effect of K_m on $E_{(t)}$ is thus strongly dependent on P_w. In P depleted soils the kinetic component is crucial in predicting a soil's P availability. An underestimation of the kinetic components of P availability will lead to overfertilization of P-fixing soils. In more P-rich soils, however, P availability can be relatively accurately assessed with static measures, i.e. the concentration of P in the solution and the total inorganic P in the soil.

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3.5 K_m buffers fertilizer application in long-term fertilizer experiments

There was a positive relationship between P_w and P budget across all 18 long-term P fertilizer experimental sites, which is consistent with the study of Morel et al. (2000). However, the slopes spanned three orders of magnitude, from 0.007 [mg P kg^{-1} soil]/[kg P ha^{-1} yr^{-1}] (Ferralsol, Colombia) (Oberson et al., 1999) to 3.9 [mg P kg^{-1} soil]/[kg P ha^{-1} yr^{-1}] (Chernozem, Canada) (Morel et al., 1994). This shows that soil solution P is more strongly buffered in some soils than others. Results from the fertilizer experiments thus confirm that in high P-sorbing soils, such as Ferralsols, additions of P fertilizers may lead to only incremental increases in solution P concentration (Roy et al., 2016). However, this does not necessarily translate to P availability (Pypers et al., 2006).

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PBC on the field experiments, taken as the slope of P_w increase with increasing P budget, was negatively dependent on K_m (F = 10.8, p = 0.0047, and R^2 = 0.40) (Fig. 5). In other words, soils with higher K_m values were characterized by slower increases in P_w at similar yearly P input-output budgets, and vice-versa. Both PBC and K_m are measures to describe the exchange of P between the soil solution and solid phases (Olsen and Khasawneh, 1980;Fardeau et al., 1991). However, the two have never been directly related. Data from long-term field experiments enabled us to compare K_m to field-scale PBC. The fact that the two are correlated in fertilizer field experiments thus underlines our findings from the global soil investigation that K_m and PBC provide information on the same underlying processes.

3.6 Implications for using K_m

Most previous studies involving isotopic exchange kinetics have focused on analyzing m, n, and E-values (Frossard et al., 1993;Achat et al., 2016;Tran et al., 1988;Brédoire et al., 2016). However, m and n are simply statistical parameters, whereas K_m is a process-based variable (Fardeau et al., 1991). K_m is the mechanism behind PBC and is useful in explaining P availability. However, when using K_m, it is important to be aware of its limitations (as described in the methods section) and K_m's sensitivity to the parameters m and n. (Fig. 6) Depending on the study, a relatively large uncertainty for K_m may be acceptable because differences in K_m between soils or treatments often vary in orders of magnitude (Frossard et al., 2011;Fardeau et al., 1991). However, for low values of m and or n, K_m calculation becomes very sensitive to uncertainty in m and or n, and relative errors may be much higher than 100% (Fig. 6). Future studies should take this into account and conduct appropriate error propagation, or consult Fig. 6 to get an overview of sensitive m and n ranges.

While we focused our analysis on P studies, the derivation of K_m as well as the finding that there is extremely rapid exchange between solid and liquid phases is equally relevant for other nutrients and or pollutants with strongly-sorbing ion species. The isotope exchange kinetic approach has also been successfully applied to study availability of Zn (Sinaj et al., 1999), Cd (Gray et al., 2004;Gérard et al., 2000), Ni (Echevarria et al., 1998), As (Rahman et al., 2017), and U (Clark et al., 2011), and applications are also plausible for other elements with radioisotopes. Isotope exchange kinetic studies with Zn, Cd, and Ni have used the same method as studies on P analyzed here, also modeling the decline in radioactivity using Eq. (2) (Gray et al., 2004;Sinaj et al., 1999;Echevarria et al., 1998). For such studies, the derivation of K_m as it is presented here is directly transferable and might provide additional useful information for understanding soil-solution exchange.

3.7 Environmental implications

Our study provides new insight on the diffusion-based mechanisms of P buffering across a large range of soil types. Prior to this study, little was known about soil solution P turnover rate, as K_m had previously been calculated by only a handful of studies. Our analysis of 217 soils showed that K_m is inversely proportional to P_w and is an important determinant of plant available P. Biological adaptations to P availability have received a lot of attention, as it has been shown that plant communities have different strategies for P nutrition depending on P availability (Lambers et al., 2008). Indeed, biological activity acts as an important buffer of P in many ecosystems, with higher fluxes of biological P often occurring when there are lower fluxes of physicochemical P (Bünemann et al., 2016;Bünemann et al., 2012). Our global compilation of 217 samples demonstrated there is another buffer of soil solution P, which is independent of biological activity and exclusively diffusion-based. Soils with a low concentration of P in the soil solution tend to have a high P turnover rate, thus buffering isotopically exchangeable P values. This does not mean that negative balances of P will improve the availability of soil P for plant uptake, rather it explains why changes in P availability are not as large as suggested by more drastic changes in P_w.

Our findings complement the notion that there are two categories of soils in regard to P dynamics. In many low P_w soils, sorption is extremely high and the soil solution is buffered from P inputs or outputs (Barrow and Debnath, 2014). For

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these soils, the prevalence of sites with fast exchange rates is crucial to assure a steady flux of P to the soil solution (Fig. 3b). In terms of agricultural management, in such a soil, P fertilization has to be higher than P output via crop removal to account for the buffering effect (Roy et al., 2016). However, once a soil reaches a certain P level and binding sites are saturated by phosphate and other anions, P exchange is less important and fertilizer inputs can be lowered to equal crop offtake (Syers et al., 2008). For these soils, additional P inputs will directly reflect in an increase in P in the soil solution and P availability is largely driven by the amount of P in the soil solution (Fig. 4a). A better understanding of P kinetics in soil will allow more effective nutrient management to meet the dual goals of improving agricultural production while reducing fertilizer use and pollution.

Data availability

The global soil as well as the fertilizer field experiments datasets used in this study are available via the supporting online material.

Information about the supplement

The derivation of K_m, a table presenting isotope exchange kinetic properties of soils used in the study, and figures relating E-values to P_w and K_m are available in the supplement.

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Author contributions

The project was conceived and carried out by Julian Helfenstein with support from Emmanuel Frossard, Timothy McLaren and Jannes Jegminat. Jannes Jegminat provided the derivation of K_m. Julian Helfenstein prepared the manuscript with contributions from all co-authors.

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Competing interests

The authors declare that they have no conflict of interest.

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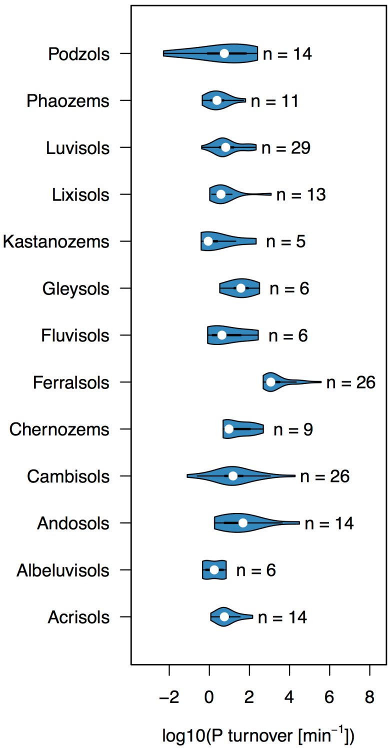

Figure 1: Violin plots of P turnover (K_m) for different world reference base soil groups. Only soil groups with at least five observations were plotted. The number of observations in each violin is written next to the plot. Violin plots were made using the R package 'vioplot' (Adler, 2005).

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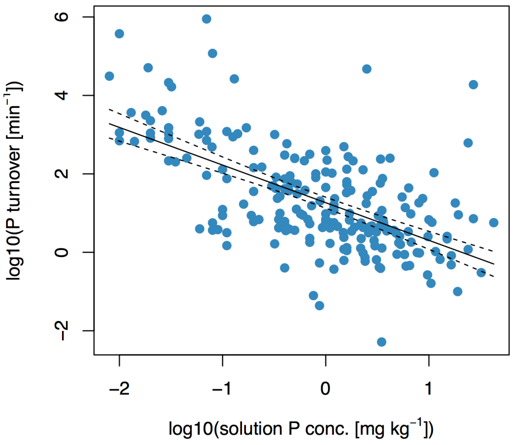

Figure 2: Simple linear regression between soil solution P turnover (K_m) and soil solution P concentration (P_w) for 217 soils. The equation is given by $log10(K_m) = 1.26 - 0.960 * log10(P_w)$ with $F = 127$, $p < 10^{-15}$ and an $R^2 = 0.37$. Dashed lines represent the 95% confidence interval.

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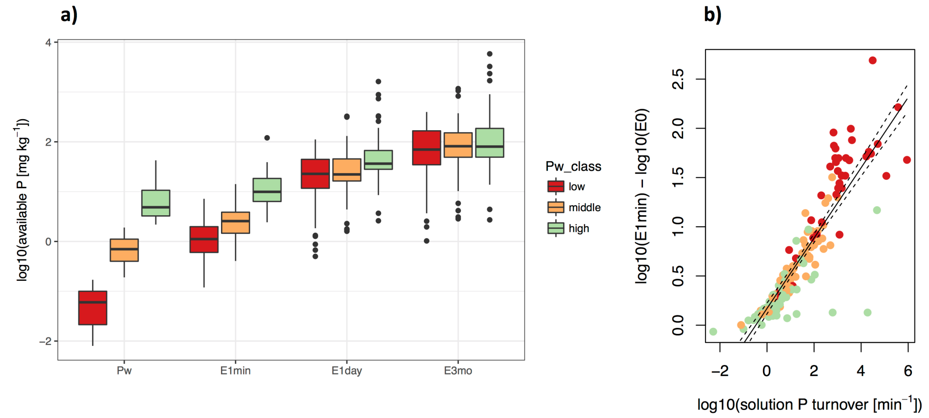

Figure 3: Soil solution P turnover (K_m) as a driver of available P ($E_{(t)}$). While there is a large range in P availability at t = 0 (P_w), this variability becomes smaller and gradually uncoupled from P_w class for longer time frames (t=1, 1440, 129'600 min) (a). The growth in P availability between t=0 and t = 1 is dependent on K_m (b). Simple linear regression between K_m and the difference between $E_{(1)}$ and $E_{(0)}$ is given by $\log 10(E_{(1)}) - log10(E_{(0)}) = 0.170 + 0.357 * log10(K_m)$ with F = 615, p < 10^{-15}, and R^2 = 0.79. n = 170. Red, orange, and green colors refer to low, middle, and high P_w -classes as determined by Jenks natural breaks optimization. In (b), dashed lines represent the 95% confidence interval.

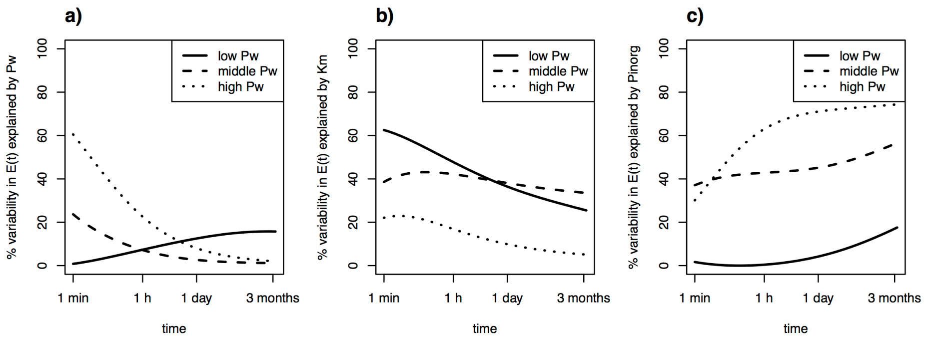

Figure 4: R^2 of simple linear regressions between isotopically exchangeable P ($E_{(t)}$) explained by predictors P_w (a), K_m (b), and P_{inorg} (c) as a function of time. Regressions were fit separately for each class of P_w (low, middle, high), as determined by Jenks natural breaks optimization. Low P_w = 0.008 - 0.16 mg kg^{-1} (n = 46), middle P_w = 0.16 – 1.9 mg kg^{-1} (n = 94), and high P_w = 1.9 – 42.5 mg kg^{-1} (n = 77).

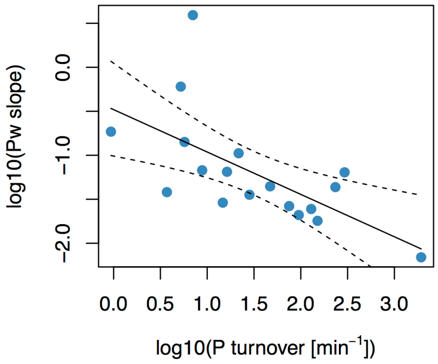

Figure 5: Simple linear regression between phosphorus buffering capacity (PBC) and soil solution P turnover (K_m) for 18 long-term P fertilizer experiments. PBC was calculated as the slope of the regression between P_w and P budget. PBC was found to correlate with K_m, as given by, $log10(PBC) = -0.481 - 0.482 * log10(K_m)$, with an R^2 of 0.40 ($F$ = 10.8, p = 0.0047). Dashed lines represent 95% confidence interval.

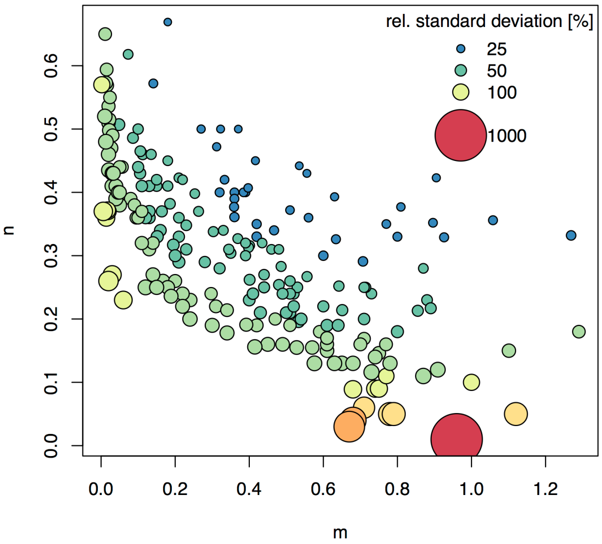

Figure 6: Relative standard deviations (RSD) of K_m after error propagation assuming 10% uncertainty in m and n input parameters, respectively. The plot shows the m and n values from the 217 soils included in this global compilation study. Uncertainty in K_m was approximated using the partial derivatives approach. Bubble size and color relates to the RSD of K_m for the plotted m and n combination.

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