

## ***Interactive comment on* “Estimates of mean residence times of phosphorus in commonly-considered inorganic soil phosphorus pools” by Julian Helfenstein et al.**

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Received and published: 4 September 2019

We thank the reviewer for their comments and would like to address the questions raised by the reviewer point by point.

“The short-term isotope exchange data is gained in isotope exchange studies that have been conducted in order to estimate the capacity of the soils to sorb P. The experiments typically last for 90 minutes and during this time the  $^{33}\text{P}$  activity in the soil solution decreases strongly due to sorption to the soil solid phase. Isotope exchange experiments have been used by Frossard et al. and other working groups to learn about the plant availability of different P pools in soil.”

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Isotope exchange kinetic experiments (IEK) were developed to “determine the rate at which phosphate ions in the soil solution are renewed from phosphate ions in the solid phase,” not to measure soil P sorption capacity (Fardeau et al. 1991). Isotopic methods using P radioisotopes date back to the 1940s (McAuliffe et al. 1948). IEK method was then further developed and tested by J.C. Fardeau and colleagues (Fardeau and Marini 1968, Fardeau and Jappe 1988, Fardeau 1985). Unfortunately, these and further key publications validating the IEK method are in French, which explains why they are little known outside of French-speaking regions. IEK experiments are thus based on, and have done much to further, our understanding of exchange mechanisms. This explains why E-values derived from IEK perform much better at predicting crop response than other soil P tests (Frossard et al. 1994), and why E-values are widely accepted as the gold standard for determining P bioavailability (Hamon et al. 2002, Kruse et al. 2015).

“I have doubts about the validity of the approach proposed here for the following reasons. First, the calculation of MRT is based on the assumption of steady state (inputs=outputs). However, it is highly questionable whether this assumption is correct. In the experiments used by the authors, typically 10 g of sieved soil are oversaturated by 100 ml of water and put on a shaker until the end of the experiment. Being oversaturated with water and kept on a shaker is not a natural condition for soils. Thus, very likely the soils move away from steady state during these experiments due to this disturbance. Thus, the assumption of study state is very likely violated in the experiments, on which the calculation is based.”

It is true, as the reviewer pointed out, that the soil/water suspension we use in IEK is not similar to soil natural conditions, however several studies comparing E-values extrapolated from IEK and L-values from pot experiments with plants (so under conditions much closer to “natural”) have shown that these two independent estimations of P exchangeability closely overlap. Fardeau and Jappe (1976), showed that measured L-values and extrapolated E-values were very similar. Morel and Plenchette (1994) showed the same for soybean and barley (measuring E-values on soil suspensions in

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periods from 1 min to several days) and Frossard et al. (1994) for *Agrostis* on several different soil types. Similarly, Sinaj et al., (2004) demonstrated the same for zinc (different nutrient, but same IEK method) on several different soils and plant species. The comparisons between E-values extrapolated from IEK experiments and L-values measured in pot experiments with plants suggest that extrapolated E-values are a good approximation for P exchange between solid phase and soil solution. Although in IEKs soil is suspended in water, the soil/solution transfer is not readily affected, especially compared to other methods using chemical extractions.

“Second, the authors derive MRTs of more than 10,000 years (Fig. 4) from experiments that last only for a much, much shorter period of time, which is problematic since the exchange processes measured over a short period of time are extrapolated by a factor of  $> 1,000,000$ .”

We agree that estimates of longer MRTs (i.e. for the HCl-P pool) are more uncertain because extrapolated E-values can only be validated with incubation data for time spans up to several months due to the short half-life of the P radioisotopes. This limitation is clearly stated in the manuscript (p. 9, l. 19). However, three independent lines of evidence support our estimates even of the very long MRTs of HCl-P. Firstly, the strong correlation (following the 1:1 line) of E-values with sequentially extracted pools, also for P not exchangeable in three months and HCl-P (Fig. 2). This shows that these pools are clearly related even though measured by independent methods. The same correlation was found already by Frossard et al (1996) for a sewage sludge in which the HCl-P pool was composed by sparsely soluble (and therefore slowly exchangeable) Ca-P minerals. Secondly, stable oxygen isotopic ratios of phosphate have been studied in HCl-P pools in soils of known ages, and shown that indeed this pool may remain stable for time spans of years to » millennia, depending on environmental conditions and soil properties (p. 9, l. 23-32). This range fits with our estimates. See (p. 9, l. 23-32). Thirdly, the strong relationship between pH and MRT of HCl-P that we observed in our data is supported by empirical observation, or at least make sense given what

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we know about the composition and stability of HCl-P (p. 8, l. 19-24). Hence, both the order of magnitude and the pattern in our HCl-P estimates make sense given what we know about P species extracted by HCl and their relative stability under different environmental conditions.

“Third, the calculation proposed by the authors (Equation 1) is based on the assumption that the specific activity of the soil solution ( $^{33}\text{P}$  in solution to total inorganic P in solution) is stable during the 90-minute experiment. This assumption is not correct. During 90-minute experiments the specific activity of  $^{33}\text{P}$  decreases exponentially, which means that the ratio of  $^{33}\text{P}$  and total inorganic P decreases, which is mostly due to adsorption of  $^{33}\text{P}$  to the soil solid phase. This change of the specific activity of  $^{33}\text{P}$  is problematic because  $^{33}\text{P}$  is used as a tracer, and the ratio of the tracer to the inorganic P in the soil solution is changing continuously over the course of a short-term experiment. The proposed approach would require that the ratio of  $^{33}\text{P}$  to inorganic P in the solution is stable, but the specific activity of the soil solution approaches a stable value only over longer periods of time.”

We do not understand the reviewer's concern here: equation 1 is not based on the assumption that specific activity of  $^{33}\text{P}$  (or  $^{32}\text{P}$ ) is constant in the soil solution. Rather, the denominator of Eq. 1 specifically describes the change in specific activity. IEK experiments provide insights on P exchange between the soil solution and the solid phase by measuring the decrease of radioisotope activity in the soil solution. This decrease in specific activity is modelled by  $r(t)/R = m(t + m^{1/n})^{-n} + r_{\infty}/R$  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 physicochemical processes, respectively (Fardeau et al. 1991, Frossard et al. 2011).

“In addition (and less importantly), the description of the applied calculation is incomplete, and the calculation of the variables  $n$  and  $m$ , which are derived from short-term experiments is not explained in the present manuscript.”

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We thank the reviewer for pointing out that the description needs to be improved. In the present version we kept the description of Eq. 1 and the meaning of the variables  $m$  and  $n$  minimal because it has been described in detail in previous publications (Fardeau et al. 1991, Frossard et al. 2011, Helfenstein et al. 2018, ...). To address the reviewers concern, we propose to expand the background information on Eq. 1 in the revision.

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Interactive comment on *Biogeosciences Discuss.*, <https://doi.org/10.5194/bg-2019-192>, 2019.

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