

## ***Interactive comment on “Soil phosphorus dynamics on terrestrial natural ecosystems” by Leonardo Deiss et al.***

**Anonymous Referee #1**

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Organic phosphorus (P) cycling in soils is a topic that has received attention in recent years. As more papers are published, meta-analyses that link the data from these papers together to identify trends in organic P cycling become possible, at least in theory, and a paper presenting novel findings could be of interest to readers. However, deriving meaningful interpretations from a meta-analysis of soil P-NMR studies requires a clear understanding of the P-NMR method and its limitations, in order to correct for known artifacts of analysis. This was not done for this manuscript. As such, it cannot be published in its present form, and will require a major revision, including reanalysis of data, to make it publishable.

1. Writing quality: a) The quality of English in the manuscript is poor in many places. If the authors revise this manuscript, I suggest they have it read by someone more

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familiar with English, who also understands the research field. b) Please check that you are using the correct spelling of the names of authors whose papers are cited. For example, “Vincent” is repeatedly cited as “Vicent”, including in the supplemental files. c) Be specific with terminology. The term “P” is an abbreviation for the element for phosphorus. However, the authors use it interchangeably for phosphate, which is incorrect.

2. As P-NMR has become more widely used to characterize soil P forms, enough data has become available to indicate the possibility of using these data in meta-analyses to look at soil factors controlling P forms, especially organic P. However, those of us who use this technique the most also recognize its limitations. Although the use of P-NMR has advanced our understanding of soil organic P cycling more than almost any other method to date, the technique is not perfect. It is important to understand the artifacts of the method. It is also important to separate P-NMR results on a soil extract from the P forms that would have been present in the original soil sample prior to extraction. After all, isn't that the objective of a soil science study? Unfortunately, it isn't clear to me that the authors of this manuscript are familiar enough with the soil P-NMR technique to understand its limitations and address them. This has produced a study that clearly involved a lot of work by the authors, but which ultimately has not produced any new insights with respect to soil P. Some specific areas of concern are:

a) Concentration: It is not possible to determine absolute concentrations of P forms or compound classes using NMR; only relative percentages can be determined, because it is a compositional analysis in which the total must be 100%. Concentrations of P forms are then determined by multiplying by the total extracted P concentration by the percentage of each P form, which is still based on the compositional analysis. This is why the proportions and concentrations of total organic P and total inorganic P (Figs. 2 and 3) show inverse relationships to one another – together they have to add to 100%. This is exactly what would be expected, so it is strange to me that the authors would comment on this (p. 6, lines 13-16). The authors also do not seem

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to understand the relationship between total P in the soils and P extraction in NaOH-EDTA. In natural (non-tilled) samples, P is stratified, such that concentrations are higher at the soil surface and lower with depth. There will also be an increase in organic P at the soil surface from inputs of plant material, which will decrease with depth – especially in forests with limited mixing and with greater fungal activity in mats in the forest floor (as is typical for temperate forests, where the majority of these studies were conducted). This needs to be accounted for somehow.

b) Extraction efficiency and soil pH: It has been very well established that the recovery of total P from soil samples with NaOH-EDTA extraction is never 100%, and is higher from samples with lower pH. The extraction seems to favor samples high in iron and aluminum, with generally poor P recovery from samples high in calcium; the reasons for this are unclear. As such, any meta-analysis comparing across a range of sample depths within the same soil profile or at different points along a soil chronosequence. For example, the recovery of total P in the samples for the Turner et al. (2003) paper ranged from 14-45%, in the Turner et al. (2007) paper 63-91%, and in the McDowell et al. (2007) paper 11-75%. If the purpose of this meta-analysis is to look at factors controlling soil P, then these differences in recovery must be factored in. Is it even possible to compare the results for a soil where only 11% of the total P was extracted to one with 91% extraction? What about the 89% of total P that wasn't extracted? The authors of this manuscript don't even mention this as a factor, let alone correct for it. And that, unfortunately, undermines their results.

c) Degradation: As noted, it is important for any soil study to ensure that the forms discussed, or the ratios of compound classes such as orthophosphate monoesters and diesters, are based on what was in the original soil sample, and not what was produced during extraction and analysis. It is well established that some orthophosphate diesters such as RNA and phospholipids can degrade to the orthophosphate monoesters  $\alpha$ - and  $\beta$ -glycerophosphates (phospholipids) and various monophosphates (RNA) when

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analyzed at the high pH required for good peak separation in P-NMR spectra [e.g. Turner et al. 2003; Doolette et al. 2009; He et al. 2011, Vincent et al. 2013; Schneider et al. 2016. The degree of degradation will vary depending on the length of NMR experiment and other factors [see Cade-Menun and Liu (2014) and Cade-Menun (2015) for more details]. It is essential that these degradation peaks are identified and quantified in order to determine the correct concentrations of orthophosphate monoesters and diesters that were in the original soil sample; doing so improves any comparison of these P forms to other soil properties (e.g. Young et al., 2013; Liu et al. 2013 J. Environ. Qual. 42:1763-1770). Unfortunately, most studies before 2010 did not identify these compounds and correct for degradation. The authors of this manuscript acknowledge that degradation can occur (p. 4), but for some reason have chosen to ignore it, which is a major problem. The issue of degradation MUST be addressed for any study of edaphic and climatic characteristics to have any meaning. If the concentrations of orthophosphate monoesters and diesters were not corrected in the original study, then the authors of this manuscript could have applied some correction factor to compensate. For example, Vincent et al. (2013) note that most non-inositol phosphate monoesters were diester breakdown products (p. 160). The studies used by the authors here all included some measurement of inositol phosphates (at least myo-IHP and scyllo-IHP). As such, the authors could have assumed that those were the only true monoesters, and corrected the remaining proportion of monoesters to diesters. It would have at least been more meaningful that what they did, which was to ignore degradation but then reach the conclusion that the ratio of diesters to monoesters was a significant factor in the study.

3. Selection of studies: The authors indicate in the methods that they were careful in their selection of papers to include in their meta-analysis, such as native vegetation. As such, I am puzzled as to why the Turner et al. 2003 paper was included as the only study from the USA, because it used agricultural soils. And while the abstract and elsewhere in the text indicate a "dataset including 88 sites", these are overwhelmingly biased to sites in New Zealand (59) and Panama (21), which does not cover a range

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of “temporal, edaphic and climatic characteristics”. The sites selected are also mainly from chronosequence studies, which may also have affected the P forms and their relationship to soil properties.

#### 4. Introduction:

a) Please include references for all statements of fact, and make sure those facts are correct. For example, p. 1, lines 24-25: “Once P has been dissolved as free orthophosphate” It isn’t possible for free orthophosphate to exist in the soil solution; it will still be associated with cations, although as more soluble forms.

b) Be careful with terminology. Page 2, line 1: “inorganic and organic P pools are each composed by fractions or functional groups”. No, they are composed of specific P compounds. The term “functional group” is used elsewhere in the introduction. Please indicate what is meant by this term, which isn’t one used for soil P chemistry. And note that fractionation measures operationally-defined P pools, rather than specific P forms.

c) Page 2, line 10: Turner 2007 is not cited in the references.

#### 5. Methods:

a) See comments above about site selection.

b) Page 4, lines 14-23: This discussion about degradation belongs in the Discussion section, not the methods section.

c) The authors have made a lot of assumptions here, particularly for soil classification. Please justify these assumptions in the Discussion section of the manuscript.

6. Results: a) I am puzzled by the phrase “concentration (% of total NaOH EDTA P)”, page 6 line 30. Do you mean % or concentration in mg/kg? They are not the same thing, although they are derived from the same data (% of P forms multiplied by extract concentration).

b) As noted above, any results related to total concentrations or percentages of or-

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thophosphate monoesters, orthophosphate diesters and the diester:monoester ratio are meaningless if not corrected for degradation. The authors must remove all reference to uncorrected concentrations and ratios. They could correct them as suggested above, or they could focus on specific P forms (e.g. DNA or IHP).

7. Discussion: Given the issues noted above, I am not sure there is anything meaningful in the discussion section, which as written is a review of the temporal, edaphic and climatic characteristics affecting P forms in NaOH-EDTA extracts, rather than in the original soils themselves. This is really unfortunate given the amount of work the authors put into this study. I hope the authors will address these issues. When they do, I expect much of the discussion section to change.

#### 8. Figures:

a) The two figures used for Figure 1 were both published elsewhere, and thus are covered by copyright. However, the authors do not indicate anywhere that they have permission to use these figures in their manuscript, which must be obtained from the publishers of the original papers.

b) All figures containing references to total orthophosphate monoesters and diesters, and the diester:monoester ratio (e.g. 3, 5, 7, 8, 9, S4.1, S4.2, S4.3, S4.4) must be corrected for degradation. And all figures will likely change when the authors have normalized the data used in this study for P recovery.

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