

## ***Interactive comment on “Phosphorus transformations as a function of pedogenesis: a synthesis of soil phosphorus data using Hedley fractionation method” by X. Yang and W. M. Post***

**X. Yang and W. M. Post**

yangx2@ornl.gov

Received and published: 15 September 2011

Response to Reviewer 1:

We greatly appreciate the intensive and thorough work reviewer 1 put into her/his review. The detailed comments and suggestions given by the reviewer have lead to valuable improvements in our manuscript, making it more understandable and readable. We respond in detail to the reviewer's comments below (the reviewer's comments are numbered and our responses are given immediately below each comment).

General Comments:

C3109

1. The authors need to very clearly define the different forms of P. I would also suggest the authors restrict the number of terms used. The multiple variations on the different forms of P (e.g., at least 11 different descriptors of P were used) made the manuscript very difficult to follow. I also noticed that the terminology was not always consistent throughout the paper. A table that clearly defines the different definitions would be helpful.

Thanks for the suggestion. In the revised manuscript, we have restricted the number of different forms of P and made the terminology consistent throughout the paper. We revised Table 2 to define the different definitions of P forms used in this study.

2. I would also suggest the authors define how the soil orders were grouped earlier in the paper than the discussion, and possibly show these classifications in the figures. At one point, soils were defined as young rather than lightly weathered and age had not been previously mentioned. The soil classifications should also be consistent throughout the paper.

In the methodology part (section 2.2) we added the description for how the soil orders were grouped in slightly, intermediately, and highly weathered soils. In our original text, the use of young soils rather than slightly weathered soils was misleading since soil age may not reflect the degree of weathering. In the revised text, the discussion is based on soil weathering stages only.

3. Some of the trends the authors describe were not visually apparent in Figure 3.

Please see the 24th in specific comments.

Specific Comments:

Introduction: 1. Page 1, Lines 8-12. The discussion of the different P methodologies could be clarified further. The Hedley fractionation is a sequential extraction of the same soil and is used to determine all of the different forms of P ranging from the most available to the most recalcitrant P. In contrast, the Olsen, Bray, and Mehlich

C3110

extractions are single soil extractions used to evaluate the labile soil P pool only and do not provide information on either the occluded forms of P or total P (e.g., they are equivalent to steps 1-3 in the Hedley Fractionation). You can theoretically establish the proportion of phosphorus held in each form by combining results from different soil extractions (e.g., a strong acid digestion (Total P), Olsen/Bray extraction (Labile P)). The Hedley Fractionation as a whole isn't really comparable to the other methods listed unless you restrict the comparison to the labile forms.

All in all, this paper really focuses on how P fractions vary among soil types over time and does not really evaluate how labile P pools differ depending on methodology. As such, this should really be re-framed to note that there are other measures of labile P outside of what is included in the Hedley Fractionation but this study restricts analysis to Hedley labile P because it is not clear how comparable these measures of P are.

We agree with the reviewer that Hedley fractionation method is not really comparable to the other methods that measure labile fraction of P. We revised the text now following the reviewer's suggestions as

"Although many methods have been devised to measure soil P, such as Olsen bicarbonate method [Olsen, 1954], Bray-I [Bray and Kurtz, 1945], Mehlich-I [Nelson et al., 1953], these methods focus on the labile soil P only and do not provide information on either other forms of P such as occluded P or total P. In recent years, the Hedley sequential fractionation method..."

2. Page 3-4, lines 24-28; lines 1-4, lines 10-15: The discussion of the different forms of P is not clear and should be better defined throughout the paper. For example, the authors use the following terms to discuss the different forms of P in the introduction: mineral P, dissolved P, non-occluded P, labile P, organic P, inorganic P, occluded P, secondary mineral P, available P, plant available P, solution P. A table that defines the different forms of P, including the relevant timeframe could help. The authors might also consider restricting the number of terms used to describe the forms of P so that

C3111

the terminology is more consistent throughout the paper.

The terminology used in the paper is now defined in the revised Table 2.

3. Page 4, line 6: Crews et al. 1995 is another relevant citation. Crews et al., 1995 has been added in the citation here.

4. Page 5, Line 5: It is true that the Total Soil P discussed in these studies includes both occluded and labile forms of P, but as I understand it they don't really include P in parent material. Typically total P is measured in the upper soil horizons using a strong acid digestion, which is basically equivalent to Field 7 in table 1. Perhaps a more appropriate way to frame this point would be a statement to the effect of "Comparing C:N:P ratios using available forms of P, rather than total P, could be a more relevant analysis because x, y, z."

We agree it is misleading using the term of "P in parent material" here. Instead "P in primary mineral particles" should be used here. We also reframed the point here as reviewer suggested as

"Comparing C, N, P ratios using organic P, rather than total P, could be a more relevant analysis since much of total P occurring in primary mineral form, secondary mineral form or occluded form is of limited biological availability while the turnover of organic P comprises a rapid cycle of P in ecosystems, approximately an annual cycle, which likely provide most of P taken up by plants."

5. Page 5, Line 10. It would help if it this were rephrased to "Since nearly all Hedley fractionation method studies also measured soil organic C and N, we were also able to investigate C:N:Po stoichiometry in soils."

Thanks for the suggestion. The text has been revised as suggested.

6. Page 6, Lines 15-19. Which extractions give you Bicarb Pi and Bicarb Po? This is not defined in Table 1. Does this correspond to Field 4 and 5? If so, this should be more clearly labeled.

C3112

Bicarb Pi and Bicarb Po are extracted with 0.5M NaHCO<sub>3</sub> and corresponding to Field 4 and Field 8 in Table 1 respectively. They are now clearly labeled in Table 1.

7. Data Analysis: Need a statement about which soil orders were included in each “weathering stage”.

Thanks for the suggestion. We have now added the following statement in section 2.2:

“Gelisol, Histosol, Andisol, Entisol, and Inceptisol orders are slightly weathered soils. Aridisol, Vertisol, Mollisol, and Alfisol comprise intermediately weathered soils. Spodosol, Ultisol, and Oxisol represent strongly weathered soils.”

8. Page 8, Line 3: Is secondary inorganic P the same as Secondary Pi? On previous page, is secondary mineral P the same as Secondary Pi? The terminology could be more clear and consistent throughout the paper.

Yes, secondary inorganic P is the same as secondary Pi. Secondary mineral P is the same as secondary Pi. It is now termed as secondary mineral Pi throughout the text.

9. Page 8, Line 6: Other than Table 2, this is the first time in the paper that the Apatite P pool is mentioned. This pool should be described earlier in the paper.

Apatite P is now introduced in the introduction section.

10. Section 3.2. I don't see some of the trends that are discussed. See comments on Figure 3. It would be helpful if the classification of each of the soil orders into lightly weathered versus highly weathered was explicitly defined somewhere in the paper.

Regarding the discussion on Figure 3 in section 3.2, please refer to our reply to Reviewer's 24th comment below. The classification of each of the soil orders into lightly weathered versus highly weathered is now explicitly defined in section 2.2 in the revised paper.

11. Page 8, Line 21. In section 2.2 these pools are called bicarbonate Pi and bicarbonate Po not HCO<sub>3</sub>- Pi and Po. Labels for the different P pools should be consistent

C3113

throughout paper.

Bicarbonate Pi and bicarbonate Po are now used throughout the revised text.

12. Page 8, Line 22. This is the first that soil age is mentioned (e.g., young soils versus highly weathered soils). Which soils are young versus lightly weathered versus highly weathered, etc. Because weathering rates differ based on climate, so the age of the soil may not reflect the degree of weathering. This should be clarified.

Thanks for the suggestion. We agree with the reviewer that soil age may not reflect the degree of weathering. In the revised text, we use weathering stages only.

13. Page 8, Line 25-26: This statement needs further clarification. Are you stating that because highly weathered tropical soils have similar labile P relative to lightly weathered systems that the decline in total P is likely due to leaching losses? The logic is not clear to me.

We apologize for the confusion. This statement is not clearly phrased and actually not very related to the discussion here. Therefore we have deleted this statement in the revised text. In any case what we mean by this statement is that labile P is highly correlated with total P indicating that the depletion of total P over time is the dominant reason for low labile P in highly weathered soils, although many other factors may also contribute to low labile P in highly weathered soils, such as strong P sorption on secondary minerals.

14. Page 9, Line 8-9. The analysis really refers to labile P requirement for plants in forested ecosystems. Other terrestrial ecosystems aren't really considered.

We agree. The text has been revised.

15. Page 10, line 5-10. These definitions of lightly to highly weathered should be included in the methods. It would also be helpful if there were some indication of how these soil orders are grouped in the figures, or figure heading.

C3114

The definitions of lightly to highly weathered are now added in the method section (section 2.2). We have added the definition in the figure caption for Figure 5.

16. Discussion Page 11, line 14. The following citations are relevant here: Chacon et al. 2006- Biogeochemistry; Liptzin and Silver 2009-Soil Biology & Biochemistry. These papers discuss the release of Fe-bound P under anaerobic conditions in wet tropical forests.

Thanks for the suggestion. The suggested citations have been added in the revised text.

“P bound in Fe minerals can also be released under anaerobic conditions in wet tropical forests[Chacon et al., 2006; Liptzin and Silver, 2009].”

17. Page 11, Line 25. However, see the citations listed above. In wet forests, Fe can fluctuate between oxidized and reduced forms. During wet conditions, Fe is reduced and releases Fe- bound P. There is also seasonal variability in the available forms of P, which could be related to this process (Chacon et al. 2006, Wood & Lawrence 2008- Plant & Soil).

The discussion regarding the release of Fe-bound P has been added in the revised text.

“these soils usually have enormous P sorption capacities because of their high Al and Fe minerals content[McGroddy et al., 2008] although there is some evidence that Fe-bound P can be released under wet conditions due to Fe reduction;”

18. Page 12, line 26. However, “fertilization” with litterfall in a wet tropical forest in Costa Rica led to a significant increase in forest productivity within 5 months of litter application. This increase in productivity was positively correlated with the total P in the litter, suggesting a strong link between litter P and forest productivity. In the tropics, roots grow within the litter layer. Hence, it could be that the labile P measured in tropical soils does not capture the rapid uptake of P mineralized in the litter layer.

C3115

We assume the reviewer refers to the paper by Wood et al.[2009]. Wood et al. [2009] investigated the response of nutrient cycling and productivity to large-scale litter “fertilization” in rain forest in Costa Rica. They found that the increase in leaf litter production was significantly positively related to the total P that was applied in litter form, suggesting highly efficient cycling of leaf litter nutrients in tropical forest. Although the overall response was positive, in two low soil P sites the response was negative because the combination of large inputs of litter and low soil P might have led to net immobilization of P by microbes. This also highlights the important control of microbial dynamics on soil P availability for plants. Therefore we add the following discussion in section 4.2 the revised text.

“In a litterfall fertilization experiment in a wet tropical forest in Costa Rica, the increase of litterfall and total P inputs led to an average 22% increase in leaf litter production 2-6 months following litter addition, suggesting a strong link between total P input and forest productivity and highly efficient cycling of leaf litter P in P-limited tropical forests. However, the two low P-fertility sites in this experiment demonstrated a net negative response to litter addition, because the large inputs of litter and low soil P led to the net immobilization of P by microbes. “

19. Page 14, Line 10. Higher P resorption rate in plants, not soils.

It is now revised.

20. Page 15. Something to consider: The bray extract is often used to analyze available P in acidic soils rather than a bicarbonate extract (see Cross & Schlesinger). It is therefore possible that the Hedley fractionation is not the most appropriate analysis of the available P fraction in tropical soils.

Thanks for the suggestion. We have added the following discussion regarding this point in section 4.2:

“Previous studies suggested that in highly weathered soils labile P based on Hedley

C3116

method is much higher than that measured using acidic extracting solutions, such as the Bray method, suggesting the choice of different methods for assessing available P lead to different estimates of the size of available P [Cross and Schlesinger, 1995; Johnson et al., 2003]. However the advantage of Hedley fraction method is that it provides the fractions of different P forms that have potential to contribute to available P over a growing season. Furthermore the increasing application of this method in different soils has made it possible to relate the measurement produced by this method with other soil properties such as weathering stages, soil pH, soil organic carbon, providing us great opportunity for better understanding the controls on available P in soils. “

21. Table 1: The fields should match the specific terminology used in the paper. This will help clarify the various definitions of P used in the paper.

The field names have been modified to match those used in the paper.

22. Table 2: The terminology should match the field labels listed in Table 1. This will clarify the definitions of the different P fractions.

The terminology has been revised and is now matched with fields listed in Table 1.

23. Figure 2: It would help if the heading stated that soils are organized from least to most weathered, and also showed how the soils are classified (e.g., lightly vs. intermediately, vs. highly weathered).

It is now shown in the figure that soils are organized from slightly weathered to highly weathered. We added the following statement in figure caption to show how the soils are classified:

“Slightly weathered soils: Andisols, Histosols, Entisols, Inceptisols; Intermediately weathered soils: Aridisols, Vertisols, Mollisols, Alfisols; Highly weathered soils: Ultisols, Spodosol, Oxisols. ”

24. Figure 3: If the soil orders are organized from lightly weathered to highly weathered then the figure doesn't really reflect some of the trends discussed in Results 3.2. For

C3117

example, I don't see the decrease in the % of Apatite with weathering. It works if you start with the Aridisol and work your way to the Oxisol, but not if you look across all soil orders. Even if you exclude the Aridisol, the Andisol and Histosol have less apatite P than the Entisol. Also, the Histosols have a lot of occluded P relative to the other “lightly weathered” soil orders. It is difficult visualize trends in the various forms in this figure.

The soil orders are organized from lightly weathered to highly weathered, but Andisol and Histosol are two special soil orders in USDA soil taxonomy. Histosols, unlike other soils, are characterized by accumulations of a large amount of organic matter. Therefore Histosols have a large fraction of organic P and low fraction of apatite P although they are slightly weathered soils. The high fraction of occluded P in Histosols is associated with highly stable organic materials such as lignin and organometallic complexes. Andisols is considered as a special soil order that have formed in volcanic ash or other volcanic ejecta. Andisols have andic properties – unique chemical and physical properties such as rapid accumulation of organic matter and high P retention due to high levels of Ferrihydrite, Imogolite, Allophane. Therefore Andisols usually has large fractions of P in organic, secondary, occluded form and low fractions of apatite P except in fresh volcanic ash. We have added the following discussion in section 3.2 in the revised text.

“The exceptions to the general patterns here are Andisols and Histosols, the two special soil orders in USDA soil taxonomy. Although they are slightly weathered soils, Histosols have a large fraction of organic P and low fraction of apatite P because Histosols, unlike other soils, are characterized by large surface accumulations of slowly decomposing organic matter. The high fraction of occluded P in Histosols is associated with highly stable organic materials such as lignin and organometallic complexes [Schlichting et al., 2002]. Andisols have andic properties – unique chemical and physical properties such as rapid accumulation of organic matter and high P retention due to high levels of Ferrihydrite, Imogolite, and Allophane. Therefore Andisols has

C3118

large fractions of P in organic, secondary, occluded form and low fractions of apatite P[Satti et al., 2007]. “

25. Technical Corrections: Page 3, Line 2: delete “element”

It is revised

Page 3, Line 6: delete “as”

It is revised

Page 12, Line 10: higher “than” that of

It is revised

Figure 3: Change Oxidosol to Oxisol

It is revised

Reference:

Bray, R., and L. Kurtz (1945), Determination of total, organic, and available forms of phosphorus in soils, *Soil science*, 59(1), 39.

Chacon, N., W. L. Silver, E. A. Dubinsky, and D. F. Cusack (2006), Iron reduction and soil phosphorus solubilization in humid tropical forests soils: the roles of labile carbon pools and an electron shuttle compound, *Biogeochemistry*, 78(1), 67-84.

Cross, A., and W. Schlesinger (1995), A literature review and evaluation of the Hedley fractionation: Applications to the biogeochemical cycle of soil phosphorus in natural ecosystems, *Geoderma*, 64(3-4), 197-214.

Johnson, A. H., J. Frizano, and D. R. Vann (2003), Biogeochemical implications of labile phosphorus in forest soils determined by the Hedley fractionation procedure, *Oecologia*, 135(4), 487-499.

Liptzin, D., and W. L. Silver (2009), Effects of carbon additions on iron reduction and

C3119

phosphorus availability in a humid tropical forest soil, *Soil Biology and Biochemistry*, 41(8), 1696-1702.

McGroddy, M. E., W. L. Silver, R. C. de Oliveira, W. Z. de Mello, and M. Keller (2008), Retention of phosphorus in highly weathered soils under a lowland Amazonian forest ecosystem, *Journal of Geophysical Research*, 113(G4), G04012, doi: 10.1029/2008jg000756. Nelson, W., A. Mehlich, and E. Winters (1953), The development, evaluation, and use of soil tests for phosphorus availability, *Soil and fertilizer phosphorus in crop nutrition*, 153-188.

Olsen, S. (1954), Estimation of available phosphorus in soils by extraction with sodium bicarbonate, US Dept. of Agriculture.

Satti, P., M. Mazzarino, L. Roselli, and P. Crego (2007), Factors affecting soil P dynamics in temperate volcanic soils of southern Argentina, *Geoderma*, 139(1-2), 229-240, doi: 10.1016/j.geoderma.2007.02.005.

Schlichting, A., P. Leinweber, R. Meissner, and M. Altermann (2002), Sequentially extracted phosphorus fractions in peat derived soils, *Journal of Plant Nutrition and Soil Science*, 165(3), 290-298.

Wood, T. E., D. Lawrence, D. A. Clark, and R. L. Chazdon (2009), Rain forest nutrient cycling and productivity in response to large-scale litter manipulation, *Ecology*, 90(1), 109-121.

---

Interactive comment on Biogeosciences Discuss., 8, 5907, 2011.

C3120