



Navigating limitations and opportunities of soil phosphorus fractionation

Chunhao Gu · Andrew J. Margenot 

Received: 19 March 2020 / Accepted: 28 April 2020 / Published online: 25 May 2020
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Keywords Sequential chemical extractions (SCEs) · Fractionation · Phosphorus · XANES

In “The soil phosphate fractionation fallacy”, Barrow et al. (2020) provide valuable insight to the accuracy of soil phosphorus (P) fractionation. They synthesized two types of P-bearing goethite and aluminum oxide to which P was adsorbed or penetrated, without iron phosphate or aluminum phosphate precipitates generated. These P-bearing minerals were then subjected to the fractionations described in Chang and Jackson (1957) and Zhang and Kovar (2009). Iron bound P (Fe-P), aluminum bound P (Al-P) and calcium bound P (Ca-P) were falsely detected by the sequential extraction solutions of NH_4F , NaOH and H_2SO_4 , respectively, as none of these P species were present in the P-bearing minerals. One of the interpretations drawn from these results is that “fractionation procedures designed to measure chemically specified phosphate fractions in soil are fallacious and should be abandoned”.

Responsible Editor: Hans Lambers.

C. Gu (✉) · A. J. Margenot (✉)
Department of Crop Sciences, University of Illinois
Urbana-Champaign, Urbana, IL 61801, USA
e-mail: chunhaogu.biogeo@gmail.com
e-mail: chunhao@illinois.edu
e-mail: margenot@illinois.edu

We agree that the false detection of P in the H_2SO_4 fraction of these laboratory-synthesized P compounds indicates a risk of false detection in the common interpretation of this and other acid-extractable fractions (e.g., HCl) as Ca-P for soil P studies. This is an important finding that builds on past and recent identification of false detection of certain P forms by specific fractions (Bromfield 1967; Gu et al. 2020a; Williams and Walker 1969). However, we argue that the conclusion by Barrow et al. that “fractionations are fallacious and should be abandoned” is overstated. More broadly, we believe this showcases underlying methodological and epistemological challenges in the study of soil P cycling. To offer points of navigation in the discussions on limitations and opportunities of soil P fractionation, we propose how and why the implications of Barrow et al. could and should be more constructively and realistically discussed.

1. The misperception or misunderstanding of what fractionations can and cannot deliver is to a large extent an issue with how scientists interpret the results of an operational technique such as fractionation. We agree with Barrow et al. that the discrete P theory was likely influenced if not inherited from the compartmentalization of P ‘pools’ by fractionations, but we think fractionations have value even if the discrete P theory is incorrect. Assuming that certain fractions correspond to specific P compounds or phases is a symptom of a greater underlying problem in *how* fractionations – but also other P data – are interpreted with respect to soil P *in situ*.

For example, it is conceivable that a scientist could also misinterpret P K-edge X-Ray absorption near-edge structure (XANES) spectroscopy as delivering information on discrete P phases. Indeed, Barrow et al. point to XANES spectroscopy as one of three lines of what they argue are incorrect evidence for the discrete P theory. Yet this too is an issue of interpretation, as XANES spectroscopy uses specific P compounds (e.g., adsorbed, precipitated P forms) as references for linear combination fitting to estimate the proportion of atomic P that has similar local coordination environment (e.g., coordinated with same metal cations), which does not necessarily entail the existence of discrete P compounds in situ.

2. The sweeping claim in the opening line that “many scientists” believe in the discrete P theory does not seem intellectually charitable (nor does there appear to be sufficient data to support or reject this claim). That fractionations falsely detect P forms simply not present in a sample has been the subject of study and much discussion (e.g., review by Condon and Newman 2011) and it may not be fair to characterize “most scientists” as believing in this “myth”. As Barrow et al. note, Hedley et al. (1982) reported the results of fractionation as fractions (e.g., resin-P) instead of inferring discrete P compounds extracted, likely in part because the intent of the Hedley fractionation was not chemical speciation but plant availability (Hedley et al. 1982). To be fair, it is true that some fractions in fractionations are often misinterpreted in the literature as representing certain discrete P compounds. We align with Barrow et al. in the need to disabuse the notion that fractions necessarily represent specific P compounds.
3. Not all P fractionations are the same, and so their shortcomings differ. The first fractionation was developed by Chang and Jackson (1957), though the later developed Hedley fractionation (Hedley et al. 1982) and its modified version (Tiessen and Moir 1993) are today commonly used, as reviewed in Cross and Schlesinger (1995); Negassa and Leinweber (2009); Tamburini et al. (2014). These methods largely differ in whether NH_4F is used to differentiate Al-P from Fe-P. The sequential extraction step employing NH_4F in the Chang and Jackson (1957) and the related version of Zhang and Kovar (2009) methods to separate Al-P from Fe-P are based on the assumed selective reaction of Al but not Fe with fluoride ion. This NH_4F extraction step was not adopted in the well-known method of Hedley et al. (1982) nor its modified version (Tiessen and Moir 1993) because of its recognized unreliability in distinguishing Al-P and Fe-P (Bromfield 1967; Williams and Walker 1969). Thus, these fractionation protocols do not separate Al-P and Fe-P, which are instead approximated as the summed fraction of (Al + Fe)-P using only NaOH solution (Condon and Newman 2011; Hedley et al. 1982; Hieltjes and Lijklema 1980). The demonstrated false differentiation of Al-P and Fe-P by Barrow et al. (2020) is thus not necessarily applicable to other fractionation protocols that do not differentiate these P species using NH_4F extractant.
4. Using synthesized compounds with adsorbed or penetrated P is effective in testing how to interpret – and not interpret – specific fractions, but does not capture the full diversity of P compounds in soils. It is true that 0.25 M H_2SO_4 (or 1 M HCl) can extract not only Ca-P but also significant amounts of Fe-P as demonstrated by Barrow et al. (2020) using laboratory-synthesized P compounds or by Gu et al. (2020a) using soils. The laboratory-synthesized P compounds used by Barrow et al. only represent certain types of P compounds in soils (i.e., adsorbed or penetrated). Evidence suggests that P can exist in soils as a mixture of adsorbed and precipitated as discrete forms on mineral surfaces, with their relative proportions depending on the ratio of soluble P concentration to mineral (Wang et al. 2017, 2019). This could explain why reported flaws in the widely used Hedley fractionation and its modified version (Hedley et al. 1982; Tiessen and Moir 1993) do not consistently nor predictably manifest in all soils (Gu et al. 2020a).

It could also explain why in some systems fractionations can still deliver useful insights to soil P cycling, such as the Walker and Syers model of P biogeochemistry in humid ecosystems (Walker and Syers 1976), as was later corroborated using XANES spectroscopy (Prietzel et al. 2013). The ability of fractionations to broadly distinguish (Al + Fe)-P versus Ca-P in soils was generally supported (Cross and Schlesinger 1995; Hedley et al. 1982; Negassa and Leinweber 2009; Tamburini et al. 2014; Tiessen and Moir 1993) until recent studies showed that the Ca-P pool can be

substantially misquantified (e.g., 61–65% by fractionation versus 16–37% by XANES), suggesting substantial misquantification of other P pools (Gu et al. 2019; Helfenstein et al. 2018). As revealed by using soils (not laboratory-synthesized P compounds) and XANES spectroscopy, the misquantification of Ca-P and other pools was caused by the dissolution of Fe-P in the 1 M HCl extraction (Gu et al. 2020a) that had been assumed for only Ca-P (Tiessen and Moir 1993). Moreover, the false detection of Fe-P as Ca-P has been found to be soil-specific (Gu et al. 2020a). For example, for some soils, fractionation can still provide measures of P pools based on corroboration of the acid extractable P fraction by XANES spectroscopy (Ajiboye et al. 2007; Gu et al. 2020a; Kar et al. 2011; Kruse and Leinweber 2008; McLaren et al. 2015; Takamoto and Hashimoto 2014). Poorly crystalline Al and Fe minerals, and exchangeable Ca in soils hold promise as predictors of the occurrence and magnitude of these artifacts of fractionation (e.g., over/under-estimating Al-P, Fe-P and Ca-P fractions) (Gu et al. 2020a). However, Gu et al. (2020a) also found that these soil properties were not always sufficient to predict (mis)match between Ca-P estimated by fractionation versus XANES spectroscopy, suggesting the role of additional soil properties in determining artifacts of fractionation.

5. Specific fractions obtained by fractionation may still be useful even when other fractions in the same protocol may be limited. Based on the finding that some individual fractions (Al-P, Fe-P and Ca-P fractions) in two specific fractionation protocols can be misquantified, Barrow et al. (2020) seem to imply that *all* fractions in *all* fractionation protocols are fallacious. However, specific fractions may accurately represent certain P pools, and some fractions may be necessary to complement non-fractionation techniques. For example, the labile P pool of Hedley-type fractionations (the first extraction step using an anion exchange resin and the second one using 0.5 M NaHCO₃) has been used widely in soil science and biogeochemistry (Cross and Schlesinger 1995; Gu et al. 2020b; Hou et al. 2018; Johnson et al. 2003; Negassa and Leinweber 2009) because it is thought to mimic natural P acquisition by plants (Klotzbücher et al. 2019). As demonstrated by Wu et al. (2014), the modified Hedley fractionation (Tiessen and Moir 1993) can better quantify soil labile P than P XANES

spectroscopy, which is better suited to quantify metal-bound P species. Moreover, subsequent studies have demonstrated that for certain soils XANES spectroscopy may not enable reliable differentiation between organic P (P_o) and inorganic P (P_i) adsorbed to a given soil adsorbent under certain soil conditions (Prietz et al. 2016a, b), meaning that measures of P_o afforded by fractionation can be used to complement XANES spectroscopy.

6. Many analytical techniques for soil P characterization carry advantages and disadvantages, meaning that for comprehensive study, no one technique alone is sufficient but also that no method should be completely “abandoned”. For example, ³¹P nuclear magnetic resonance (NMR) spectroscopy and XANES spectroscopy also carry biases (e.g., Cade-Menun and Liu 2014; Turner et al. 2014; Wu et al. 2014). This issue extends beyond the study of P, and we argue reflects the compositional complexity of soils. There is an inherent tension between standardization and the diversity of soils: one-size-fits all techniques are necessary for standardization, but the context-specificity of soils means a blanket approach risks artifacts. Here, philosophers of science can offer insight on how to balance the limitations and utility of P fractionations. The well-known example of “paradigm” coined by the physicist and philosopher Thomas Kuhn in *The Nature of Scientific Revolutions* can be defined as the collective set of “best possible” approaches to study a phenomenon (Kuhn 1962). As argued by more contemporary philosophers of sciences, approaches such as fractionation can be thought of as a heuristic: an “approximation to reality” (Wimsatt and Wimsatt 2007). Operational approaches and the artifacts they often entail is a practical necessity of soil science; P fractions should be recognized as approximations to in situ realities. At its extreme, Barrow et al.’s opening line seems to confound a heuristic with the reality the heuristic is meant to approximate.

What then may be a way forward? Condon and Newman (2011) well-suggested that qualifying what fractionations can and cannot do is key to their use. Additionally, existing fractionation methods could be improved by identifying shortcomings. To this end, we propose that a comprehensive soil P dataset of paired XANES spectroscopy and fractionation measurements across soils with (characterized) diverse properties could

help to (1) identify which soil properties can impact the accuracy of fractionation, and thereby establish guidelines for suitability and interpretation of fractionations for specific soils, (2) reveal mechanisms by which these identified soil properties cause the false detection and/or quantification of P pools inferred from fractions, and (3) guide modification of fractionation methods to mitigate artifacts. This approach stands to constrain uncertainties and increase the accuracy of fractionations as a highly accessible method for the study of soil P cycling.

Acknowledgements This work was supported by Illinois Nutrient Research and Education Council (NREC) award 2018-4-360731-385. We thank the three anonymous reviewers for comments and suggestions helped improve and clarify this manuscript.

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