soil systems

Review

Accessing Legacy Phosphorus in Soils

Sarah Doydora [1], Luciano Gatiboni [1], Khara Grieger [2], Dean Hesterberg [1], Jacob L. Jones [3], Eric S. McLamore [4], Rachel Peters [5], Rosangela Sozzani [5], Lisa Van den Broeck [5] and Owen W. Duckworth [1,*]

[1] Department of Crop and Soil Sciences, North Carolina State University, Raleigh, NC 27695, USA; sadoydor@ncsu.edu (S.D.); luke_gatiboni@ncsu.edu (L.G.); sscdlh@ncsu.edu (D.H.)
[2] Department of Applied Ecology, North Carolina State University, Raleigh, NC 27695, USA; kdgriege@ncsu.edu
[3] Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA; JacobJones@ncsu.edu
[4] Department of Agricultural Sciences, Clemson University, Clemson, SC 29634, USA; emclamo@clemson.edu
[5] Department of Plant and Microbial Biology, North Carolina State University, Raleigh, NC 27695, USA; rsozzan@ncsu.edu (R.S.); rmpeter4@ncsu.edu (R.P.); lfvanden@ncsu.edu (L.V.d.B.)
* Correspondence: owduckwo@ncsu.edu

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Abstract: Repeated applications of phosphorus (P) fertilizers result in the buildup of P in soil (commonly known as legacy P), a large fraction of which is not immediately available for plant use. Long-term applications and accumulations of soil P is an inefficient use of dwindling P supplies and can result in nutrient runoff, often leading to eutrophication of water bodies. Although soil legacy P is problematic in some regards, it conversely may serve as a source of P for crop use and could potentially decrease dependence on external P fertilizer inputs. This paper reviews the (1) current knowledge on the occurrence and bioaccessibility of different chemical forms of P in soil, (2) legacy P transformations with mineral and organic fertilizer applications in relation to their potential bioaccessibility, and (3) approaches and associated challenges for accessing native soil P that could be used to harness soil legacy P for crop production. We highlight how the occurrence and potential bioaccessibility of different forms of soil inorganic and organic P vary depending on soil properties, such as soil pH and organic matter content. We also found that accumulation of inorganic legacy P forms changes more than organic P species with fertilizer applications and cessations. We also discuss progress and challenges with current approaches for accessing native soil P that could be used for accessing legacy P, including natural and genetically modified plant-based strategies, the use of P-solubilizing microorganisms, and immobilized organic P-hydrolyzing enzymes. It is foreseeable that accessing legacy P will require multidisciplinary approaches to address these limitations.

Keywords: legacy phosphorus; speciation; transformation; accessibility

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1. Introduction

Phosphorus (P) is essential to life on Earth. It plays critical roles in core biological systems associated with energy storage, cell replication, and protein synthesis [1]. Among essential macronutrients, it is often the concentration of bioaccessible P, or dissolved inorganic P, in soil that limits plant growth [2]. This fact makes the utilization of P, a finite resource that is mined from specific locations worldwide [3], a critical component of the global food system that aims to feed a growing population [4]. When inorganic fertilizers are added to soil to ameliorate deficiencies, P undergoes sorption, precipitation, and organic matter complexation reactions that render it unavailable for plant uptake [5]. Consequently, large quantities of fertilizers (globally, 16.5 million metric tons P y^{-1} [4]) are added to maintain soil solution P levels that are optimal for plant growth [6]. With only 10–36% of added P taken up by most crops in the year of application [7,8], long-term P fertilization has led to the buildup of residual P in soil (at a rate of ≈10 million metric tons P y^{-1} globally [9]) that is not immediately accessible to plants, and is commonly known as legacy P. Legacy P can be categorized as inorganic and organic legacy P, referring to excess, unassimilated inorganic and organic P, respectively, from added inorganic and/or organic fertilizers in the year of application.

Long-term accumulation of soil P is undesirable from agricultural, economic, and environmental perspectives. Apart from simply being an inefficient use of a finite resource, the buildup of legacy P, such as in European and U.S. soils under long-term P fertilizer applications [10], also presents environmental challenges. Excessive legacy soil P can result in its loss from soil by leaching and erosion to surrounding water bodies. For instance, it is estimated that freshwater ecosystems have had a 75% increase in total P as compared to their pre-industrial revolution state [9]; estuaries and other waterbodies may also be impacted [11]. These increased loadings of P can lead to elevated concentrations and widespread eutrophication of water bodies [12]. For example, 40% of U.S. lakes contain excess P, and ≈80% of states reported the annual occurrence of harmful algal blooms in fresh waterbodies [13,14]. At the same time, legacy P has drawn interest as a potential resource that may be harnessed to reduce use of P fertilizers. Worldwide, soil P is estimated to be five times greater than minable P [15], represented graphically in Figure 1, making the enhancement of legacy P for plant use potentially transformative to the global food system.

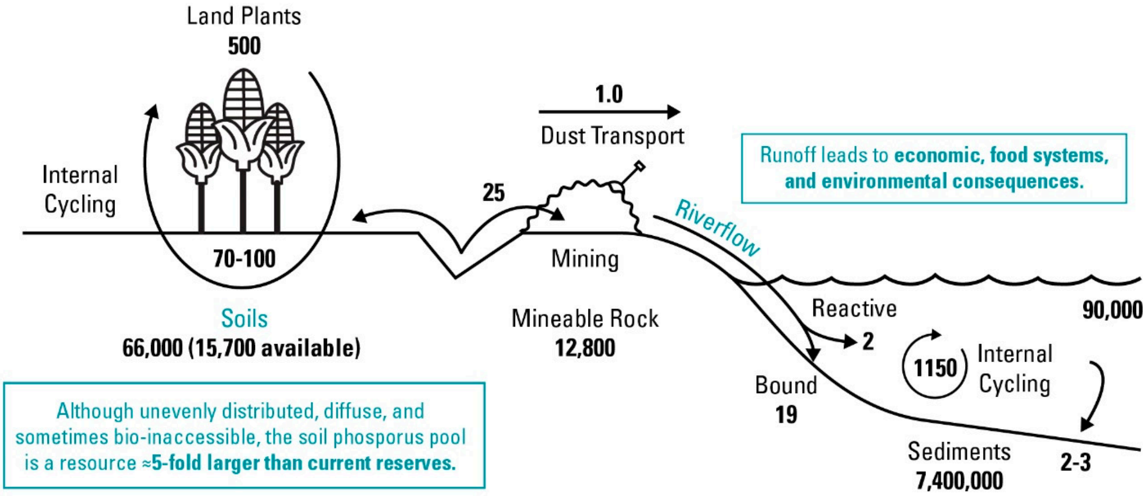

Figure 1. Global phosphorus flows with flux shown in units of 10^{12} g P/year. Recreated from [15].

Currently, there are significant technological and societal challenges associated with accessing legacy soil P as a resource for agriculture. First, legacy P naturally becomes available for plant use. For example, highly P-enriched soils in North Carolina, USA, are estimated to support 50–250 years of crop growth without P application [16]. However, actual crop recoveries of this residual P are highly variable across soils, with 4 to >100 years after last fertilizer application needed to recover up to 80% of added P [7,17,18]. Secondly, controlling and increasing soil P solubilization of inorganic legacy P or mineralization of organic legacy P for plant use requires a detailed understanding of the occurrence and reactivity of different soil chemical P forms. Most soil P is bound in bioinaccessible forms with iron, aluminum, or calcium minerals, and organic matter [10,19]. Therefore, with more than 20,000 different soil types mapped across the U.S. alone [20], determining the relative importance of these soil P chemical forms in relation to edaphic factors is a challenge for developing effective management strategies. Third, understanding the dynamic processes associated with P transformation from mineral and animal waste fertilizers into these soil P chemical forms is necessary to maximize the contributions of legacy P as a complement or substitute for externally added P fertilizers. Finally, technologies and strategies for potentially enhancing the capacity to dissolve inorganic legacy P or hydrolyze organic legacy P, herein referred to as bioaccessibility, that are feasible on a large scale are not yet available.

In light of these challenges, this paper aims to review (1) the chemical forms of P in soil and their variation with chemically relevant soil properties (Section 2), (2) the transformation of P into different proportions of various chemical species after mineral and organic P fertilizer applications (Section 3), and (3) different plant- and microbial-based approaches for accessing native soil P and potentially legacy P and associated challenges (Section 4). We conclude with an overall outlook on legacy P as a currently untapped resource that could potentially decrease the dependence on external fertilizer applications in the future as research and technology advances, particularly with the generation of plant cultivars with more efficient P mobilization and utilization processes/capabilities, and with the use of P-solubilizing microorganisms (Section 5).

2. Occurrence and Bioaccessibility of Different Chemical Forms of Soil Legacy P

Inorganic P typically accounts for the bulk of total P in mineral soils [21]. Phosphorus is predominantly taken up by plant roots via dissolved inorganic forms, *viz.* soluble orthophosphate and its protonated forms. However, concentrations of soluble or bioaccessible phosphate in soils are typically too low for optimal plant growth (ranging from 0.1 to 1 μmol P L^{-1} soil solution [22]). This low dissolved concentration stems from the strong association of inorganic P with a myriad of minerals. Kizewski et al. [19] compiled a list of the most commonly identified inorganic P species in soils by spectroscopic techniques, which include the calcium phosphate minerals hydroxyapatite and octacalcium phosphate, and phosphate adsorbed on Fe- or Al-oxide minerals.

Unlike inorganic P wherein solubilization equals bioaccessibility, organic P becomes bioaccessible only after mineralization, a biological degradation process catalyzed by specific phosphatase enzymes. Orthophosphate monoesters and diesters are the most common classes of organic P, with monoesters typically comprising 50–70% of organic soil P [23,24]. Among monoester compounds, either the inositol hexakisphosates (IHPs) or humic P constitute the predominant portion of this class [25–29]. These species have differing behaviors in soils, and thus understanding organic speciation of soil P is also critical.

Building off of this knowledge, the following section focuses on the relationship between different P forms and bioaccessibility as influenced by relevant soil properties—a topic that is critical to understanding legacy P accumulation and the potential for legacy P utilization.

2.1. Inorganic P Forms and Bioaccessibility

Among edaphic factors, soil pH largely governs the speciation and bioaccessibility of inorganic P species. In general, acidic pH ($pH < 7$) favors P association with Al and Fe whereas alkaline pH ($pH > 7$) favors association with Ca [5]. For instance, in slightly acidic agricultural soils (pH 5.5–6.0), bulk sample P-XANES (X-ray absorption near edge structure) spectroscopy analysis showed 46–56% of total P adsorbed to Fe, 31–42% as Al phosphate mineral, 8–15% as apatite, and 0–12% as organic P [30]. In alkaline, calcareous soils (pH 7.6–7.9), 54–74% of total P existed as hydroxyapatite and/or dicalcium phosphate dihydrate, 25–35% adsorbed to Fe mineral (goethite), and 0–19% organic P [31].

Under acidic soil conditions, Fe- or Al-adsorbed and precipitated P forms control soil solution P (Figure 2a–c). For adsorbed species, composition and phase impact their bioaccessibility. For example, P adsorbed to goethite (α-FeOOH) desorbs similarly to gibbsite ($Al(OH)_3$) and alumina (Al_2O_3) (within 10% difference) at pH $\approx$6 under similar experimental conditions [32]. In fact, plant P uptake by ryegrass has been demonstrated with goethite- and poorly crystalline $Al(OH)_3$-adsorbed P at near sorption capacity as lone P sources, demonstrating the potential bioaccessibility of adsorbed P species [33]. However, specific soil mineralogies can strongly impact P extractability and potentially bioaccessibility. Phosphorus adsorbed to amorphous Fe (hydr)oxide phases (i.e., ferrihydrite and $Fe(OH)_3$) is 400–500 times less desorbable than P adsorbed to goethite and amorphous $Al(OH)_3$, with negligible desorption when Fe to Al ratios are increased in amorphous Fe/$Al(OH)_3$ mixtures [34]. It is worth noting that current analytical capabilities, including spectroscopic techniques, such as P K-edge XANES, are limited in their ability to distinguish between P species lacking in distinct spectral features [35], emphasizing that identifying the key adsorbent species in soils is not always straightforward. Thus, functionally defined extractions have been designed to estimate the concentration of poorly crystalline Fe and Al minerals and the P associated with them [36]. Derived from these measurements, the degree of P saturation, defined as the ratio of oxalate-extractable P to the sum of oxalate extractable Fe and Al [37], is an estimate of how much of the P binding capacity of these minerals is occupied, and may serve as a useful tool in assessing the relatively bioaccessible P stocks of legacy P, particularly for acidic soils [38].

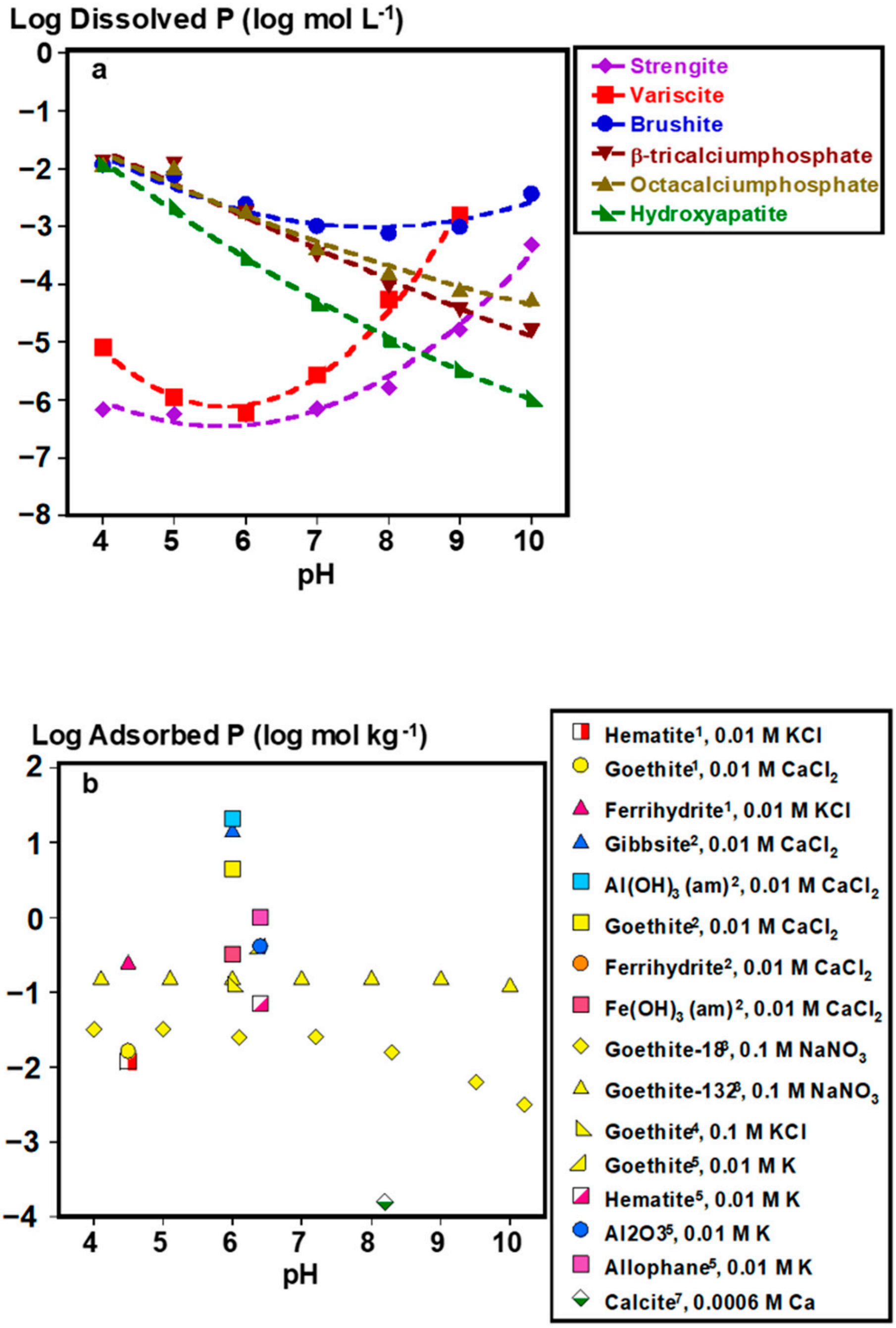

Figure 2. *Cont.*

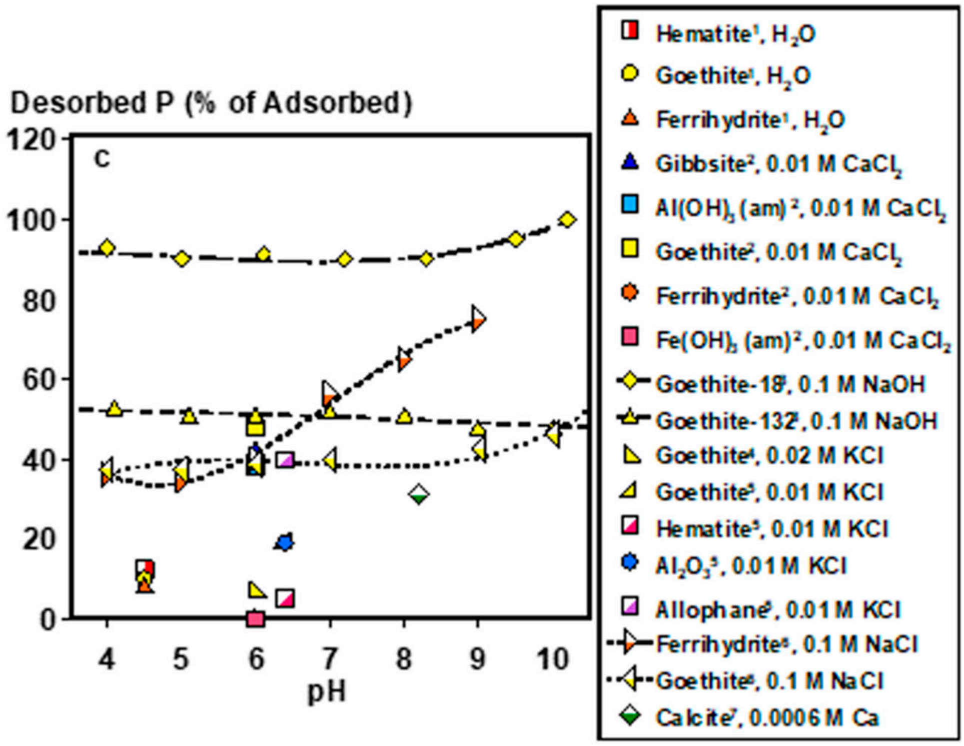

Figure 2. Soil solution pH controls: (**a**) dissolved phosphate concentrations in equilibrium with major phosphate minerals, (**b**) adsorbed P concentrations on to various soil minerals, and (**c**) desorbed P from different soil minerals as fractions of adsorbed concentrations. *Plotted data points were calculated by Visual MINTEQ Ver. 3.1 at 0.001 KCl and excess concentrations of each mineral (2 g L^{-1}). Adsorption and desorption data were computed from the following works: [1] [39], [2] [34], [3] [40], [4] [41], [5] [32], [6] [42], [7] [43]. Lines are meant to guide the eye and do not represent model fits.

In alkaline soils, bioaccessibility of inorganic precipitated P is controlled by the following Ca phosphate minerals of decreasing solubility: brushite ($CaHPO_4 \bullet 2H_2O$) > β-tricalcium phosphate ($Ca_3(PO_4)_2$) > octacalcium phosphate ($Ca_8H_2(PO_4)_6 \bullet 5H_2O$) > hydroxyapatite ($Ca_5(PO4)_3(OH)$) (Figure 2a). In addition to brushite, calcite-adsorbed P can be another source of labile P, particularly for calcareous alkaline soils (Figure 2). Although P adsorption to Fe (hydr)oxide minerals still occurs under alkaline pH [40], fractions of desorbed P could be similar or greater from these Fe adsorbents than from calcite at pH 8.2 (Figure 2b,c). This suggests that Fe adsorbents could still be controlling more of solution P even in alkaline conditions. However, there is a lack of data on the plant uptake of P from Fe or Al adsorbents under alkaline conditions.

In soils, P is often categorized into labile or non-labile pools, but this concept is rather arbitrary with unclear molecular boundaries [44]. For instance, the use of Hedley sequential extraction method could lead to chemical P redistributions in the course of the extraction process, overestimating Ca-bound P species (i.e., hydroxyapatite), particularly for soils high in exchangeable Ca [45]. Similarly, agronomic soil P tests using various types of chemical solutions (e.g., Bray 1 [46], Mehlich-3 [47], Olsen [48], or Morgan [49] extractants), measure labile P, but the extractable P does not equate to P molecules that plants access in soil. Hence, these tests are agronomically useful only when correlated and calibrated with actual crop response [50]. The use of anion exchange resin membranes may offer a more direct alternative index for bioaccessible fractions of soil legacy P by simulating root surfaces in removing dissolved P at native soil pH, thus providing a better approach for predicting bioavailable P [51–53]. However, use of resins can be laborious, time-consuming, and likely incompatible with commercial soil test laboratories where the farmers require quick soil diagnostic tests. Moreover, when well calibrated, soil test extraction methods (e.g., Mehlich-3, Bray, Olsen, and other tests [54]) can determine the fertilizer needs for crops. Consequently, despite being a better method to measure soil bioavailable P, the current use of the anion exchange method is largely limited to research purposes and has low adoption by commercial soil test laboratories. It is worth noting that neither the soil test nor other commonly used labile P extractions, anion resin P measurements, or any field sensing tools can distinguish the individual P species contributing to dissolved inorganic P in soil solution.

2.2. Organic P Forms and Bioaccessibility

Soil pH has been shown to influence occurrence of total organic P and specific organic P species differently. At higher pH in tropical rainforest soils, total organic P concentrations were found to be greater (pH 3.3–7; $R^2 = 0.89$), but this relationship appears to be reversed in temperate agricultural grasslands (pH 5.3–6.7; $R^2 = -0.60$) [55,56]. A more comprehensive regional study by Hou et al. [57] showed generally uniform concentrations of total organic P with pH in tropical, subtropical, and temperate forest soils. This agrees with total organic P concentrations remaining constant across soil pH gradients (pH 3.7–7.8) along the arable Hoosfield strip at Rothamsted Research Station, UK [58]. In terms of specific organic P species, Turner and Blackwell [58] found that non-IHP phosphomonoesters constituted the bulk of soil organic P (51–67%) and did not vary considerably across the Hoosfield pH gradient. However, concentrations of IHPs (myo- and scyllo-isomers), DNA, and phosphonates increased for pH ≤ 5 from relatively uniform concentrations (for IHP) or undetected presence (for DNA and phosphonates) at higher pH (pH 5–8) [58]. The degradation of IHP may be limited by lower enzymatic hydrolysis (breakdown) by phytase enzyme at higher pH, as its activity is mostly optimum between pH 2 and 6.5 with fewer characterized phytases showing optimum activities between pH 7 and 8 [59–63]. In contrast, phosphodiesterase activities decrease at lower soil pH [64]. Additionally, greater accumulation of IHPs and DNAs at highly acidic pH may arise from their stronger associations with clay surfaces at low pH [65,66], with presumably decreased microbial activity under these conditions.

Soil organic P is positively related with soil organic C in natural ecosystems and cultivated grassland soils [57,67–69]. No relationships have been drawn between IHPs and organic C, but mixed relationships have been reported between DNA and organic C in non-agricultural and cropland soils [67,70]. In arable soils, humic P has been highly correlated with soil organic C [70]. Positive associations with organic C, however, do not necessitate equal rates of turnover for organic P. In a meta-analysis of 80 topsoils in different countries, Spohn [71] found no changes in organic P concentrations in bulk soils or clay-size fractions in comparison to the significant reductions in organic C concentrations due to land-use change (i.e., native woodlands to croplands). Although different organic P species were not distinguished in the meta-analysis, this analysis suggests that organic P forms are likely more persistent than organic C, or their degradation is limited by factors independent of those of bulk organic C.

Among commonly identifiable organic P compounds, simple non-IHP phosphomonesters enzymatically degrade the fastest, followed by phosphodiester, with IHP being most resistant [72]. The relatively rapid degradation of non-IHP monoesters could either be due to greater enzymatic efficiencies of non-IHP phosphomonesterases [73,74] or to the longer persistence of these enzymes in soils relative to phosphodiesterases or phytases [75,76]. Although sustained activities have been reported for adsorbed non-IHP phosphomonoesterase [77] and adsorbed phytase [78], it is not clear how much of these immobilized enzyme activities constitute in their activities in field soils. Moreover, although many laboratory experiments imply limited IHP mineralization, when added in the field, IHP has been reported to degrade rapidly, with 12–18% remaining in calcareous soils after 13 weeks [79,80]. However, it has also been recognized that freshly added IHP may be different from residual IHP that has aged in field soils under much longer periods [78]. Dissolved organic P (<0.2 µm, molybdate-unreactive) in soil water extracts hydrolyzed between 0 and 61% of molybdate-unreactive P in the presence of added enzymes with highly variable fractions of hydrolyzed P class or species [81,82]. Similarly, organic P in soil leachate from soils receiving inorganic fertilizer and dairy effluent hydrolyzed 36–54% of malachite-green unreactive P (another measure for organic P) using enzyme additions [83,84]. However, Toor et al. [84] reported 10–21% of unreactive P inherently hydrolyzed in the leachate in the absence of phosphatase enzymes. These studies suggest that organic P could mineralize during transport in water, but their field hydrolysis may be less than laboratory measurements considering the optimized conditions used in added phosphatase assays [85].

As for humic P, information is currently limited regarding its potential mineralization. Jarosch et al. [86] reported highly significant correlation between enzyme-stable P and high molecular weight unhydrolyzed organic P, consistent with humic P bearing monoester P linkages [87]. Collectively, these studies not only show a gradient chemical stability of organic P but also suggest that humic P might be the most recalcitrant form of organic P, thereby presenting a challenge towards mineralizing this pool of soil organic legacy P for plant use.

3. Legacy P Transformations with Mineral and Organic Fertilizer Applications

As noted above, legacy P accumulates in soil with repeated additions of excess P fertilizers. In the USA, inorganic P fertilizer is applied approximately 10 times more than organic fertilizers (by mass; Table 1). This section reviews particularly how legacy inorganic P transforms into various species with mineral and organic fertilizer applications as it relates to its overall speciation and potential bioaccessibility in soils. We also review studies on impacts of fertilizer application and cessation on implied transformations of specific organic legacy P. This section focuses on soil P species transformation studies before and after fertilizer applications as probed by spectroscopic techniques (i.e., P-XANES for inorganic P and solution P-NMR (nuclear magnetic resonance) for organic P). Considering the analytical limitations of these techniques in distinguishing between fertilizer-derived versus native parent material-derived inorganic P in soil, we consider existing soil inorganic P largely as fertilizer-derived or legacy inorganic P throughout this section.

Table 1. Types and annual usage of phosphate fertilizers in the USA (the year 2015). Data are from the United States Department of Agriculture Economic Research Service (https://www.ers.usda.gov/data-products/fertilizer-use-and-price.aspx).

Inorganic P Fertilizers			
Superphosphates	Diammonium phosphate (DAP) (18-46-0)	Monoammonium phosphate (MAP) (11-(51-55)-0)	Other nitrogen–phosphate grades
metric tons of material			
651,162	2,236,864	2,458,331	1,723,509
Organic P Fertilizers			
Compost	Dried manure	Sewage sludge	Other organic materials
metric tons of material			
101,062	86,900	192,101	196,800

3.1. Soil Inorganic Legacy P Transformations

Different types of P fertilizers have been shown to transform inorganic legacy P species of contacted soils depending on soil properties, fertilizer placement, and incubation time. For instance, addition of granular monoammonium phosphate (MAP; $(NH_4)H_2PO_4$) or liquid ammonium polyphosphate (APP) changes P speciation from predominantly Al-adsorbed P (>90%) to Fe-adsorbed (>70%) within 7.5 mm around the point of application. These shifts towards Fe-adsorbed species also yielded the greatest resin P extractability with MAP in acidic Oxisol (pH 3.9) and APP in Andisol (pH 5.9) [88]. Khatiwada et al. [51] also reported predominantly Fe- and Al-adsorbed P (63%) and greater resin-extractable P from liquid MAP than granular MAP (≈50%) when both fertilizers were deep-banded (at 10 cm below the soil surface) and the soils were sampled at 7.5–10 cm depth. Incorporating single superphosphate (monocalcium phosphate) with or without hog manure in bulk soil (0–20 cm) in an acidic soil (pH 5.87–6.13), increased the proportion of Fe-adsorbed P (at 43 or 47%, respectively), and produced Ca-adsorbed P (31.5%) while consuming 100% of apatite in an unfertilized control after 21 years of fertilization [89]. For the same soils, NPK (nitrogen–phosphorus–potassium) addition more than tripled Olsen-extractable P to 10.4

and 38.2 mg kg^{-1} for surface and subsurface layers, respectively; however, NPK application coupled with hog manure increased extractable P up to nine times relative to unfertilized control soils (11.4 to 99.4 and 9.6 to 43.4 mg kg^{-1} for surface and subsurface soils, respectively) [89]. Positive association suggested by these studies between soluble P and adsorbed P forms from additions of synthetic and organic P fertilizers may indicate greater contribution of adsorbed P forms over precipitated P minerals in supplying dissolved P in soils. However, although liquid MAP remained mostly adsorbed (≈80%) even after 6 months of field application, resin-P extractability decreased by as much as two thirds [51]. This highlights the need to couple molecular-scale P speciation studies with macroscale measurements evaluating soluble P (i.e., resin-P extractability), as well as experiments that address in-field kinetics of P solubilization from identified P forms, ideally throughout the growing season and in the long term (i.e., between years of production), when developing P fertility regimes.

Transformations of legacy P have also been shown to differ in alkaline soils upon additions of inorganic P fertilizers. For example, Lou et al. [89] observed a slight increase in hydroxyapatite (71–78% from 67–72%) with concomitant decreases in proportions of P adsorbed to goethite and alumina from NPK additions to a calcareous soil (pH 8.1–8.4). However, to a non-calcareous alkaline soil (pH 7.4–8), the same NPK applications (i.e., P as diammonium phosphate) shifted P speciation from predominantly hydroxyapatite-P in unfertilized soil (52–57%) to brushite-P (44–63%), with a slight increase in goethite- or alumina-bound P [89]. Inorganic P fertilizer applications generally increased Olsen-P from 11 to 19% for calcareous or 9 to 41% for the non-calcareous surface soils, respectively [89]. On the other hand, Kar et al. [90] reported that most soil P (55–90% of total P) precipitated as hydroxyapatite after the addition of MAP coupled with urea, with the rest being adsorbed in a non-calcareous alkaline soil (pH 7.9) from 0–20 cm away from the point of application. However, 27 years of urea-based fertilization with or without P led to >50% reduction of hydroxyapatite species and enrichment of $FePO_4$ for an acidified alkaline Mollisol (originally pH 7.6 to 5.7) [91]. Together, these studies demonstrate how both soil and fertilizer types influence predominant soil legacy P forms in the short and the long term.

Contrary to purely mineral fertilizations, adding manure alone or in combination with inorganic fertilizers tends to show more consistent outcomes in diminishing proportions of more stable legacy P species in alkaline soils. For example, applying hog manure with NPK promoted transformation of hydroxyapatite into brushite (39–50%) on both non-calcareous and calcareous surface soils examined by Lou et al. [89]. This agrees with the findings of Kar et al. [90] who showed that addition of solid cattle manure to a calcareous alkaline soil (pH 7.8) also led to dominant precipitation of brushite (60%), particularly at the point of application (i.e., center of the band). However, for both MAP- and manure-fertilized soils, resin-extractable P decreased with increasing distance away from the point of subsurface band application. Nevertheless, resin-P fractions were 10 times greater in manured compared to MAP-fertilized soils [90]. Under laboratory conditions, Ajiboye et al. [92] also reported decreased hydroxyapatite precipitation and altered distributions among more soluble P species (i.e., β-tricalcium phosphate or calcite-adsorbed P) when different organic amendments were incorporated with calcareous alkaline soils. Increased fractions of soluble P observed in manured alkaline soils has been attributed to organic acids inhibiting precipitation of sparingly soluble Ca phosphate minerals and to the lower Ca to P ratios in manure-amended relative to MAP-amended soils [90]. Together these speciation studies suggest that manure enhances transformation of inorganic legacy P into more soluble chemical forms, confirming their lability in resin P extractions. Management strategies or technological advances that catalyze the solubilization from these pools would be necessary for legacy P to either substitute, if not eliminate, mineral P fertilizers for crop needs.

Overall, results of reviewed literature in this section show that inorganic legacy P could convert to more soluble forms with appropriate fertilizer management (i.e., fertilizer type and placement), but these effects are soil-specific and vary with space and time. For example, formation of insoluble soil P species was decreased in an Andisol (pH 5.9) with a liquid synthetic APP fertilizer, but decreased with a granular fertilizer (MAP) in an Oxisol (pH 3.9) [88]. Additionally, although subsurface banding of some inorganic and manure fertilizers enhanced more soluble inorganic legacy P speciation (e.g., brushite and adsorbed P forms) along with increased resin-extractable P, these effects were diminished farther away from the point and time of application [51]. These results suggest that, depending on long-term P application rates, placement, and soil type, fertilization-enhanced solubilization of inorganic legacy P may be time-sensitive and likely microscopic in scale, which may not necessarily impact the bulk soils in the rooting zone. This observation is consistent with the findings of Weyers et al. [31] and Koch et al. [30], who reported insignificant effects of 3 to 16 years of mineral or manure fertilizer applications on inorganic legacy P speciation of bulk soils. Moreover, the reviewed studies suggest that manure applications may offer a benefit for enhancing the solubilization of soil legacy P (i.e., hydroxyapatite), particularly for alkaline soils, and thus combining inorganic and organic P fertilizer applications may be a simple management strategy for decreasing dependence for mineral P fertilizers. However, it should also be mentioned that hydroxyapatite has also been detected as the main P species in acid soils (pH 4.2–5.9) with a long history of receiving higher rates of poultry litter [93,94]. Therefore, the relationships between application, solubilization, and ultimately crop utilization of manure-driven legacy P requires additional long-term evaluation both for acid and alkaline soils. To further enrich our understanding on legacy P transformations, we review organic legacy P transformations with fertilizer applications and cessations in the succeeding section.

3.2. Soil Organic P Transformations

Existing soil organic P does not seem to be impacted by P fertilizer applications [95], suggesting that organic legacy P may not be actively accumulating in organically P-fertilized soils. However, unlike those of inorganic soil legacy P, many P fertilization studies evaluating organic legacy P transformations are limited in investigating other specific fertilization variables (i.e., changes in organic legacy P speciation as affected by fertilizer application in space and time). For example, in a field study on bulk soils (0–20 cm) by Annaheim et al. [96], no significant changes were observed in concentrations of different organic P forms receiving organic fertilizers relative to unfertilized controls, despite stark differences in contents of organic P species in applied organic fertilizers (i.e., dairy manure, compost, dry sewage sludge). By comparing the expected concentrations of what could have been accumulated after 62 years of additions, they also demonstrated the limited accumulation for all forms of added organic P species, including IHPs, nucleic acids, and unidentified monoesters. Similarly, Dou et al. [29] reported negligible IHP accumulation in farm soils receiving different types of manure for 8–10 years, despite an estimated 30 kg P ha^{-1} annual additions from manure-derived IHPs. These long-term studies suggested organic P mineralization that may have released and supplied inorganic P for plant uptake, although they did not exclude transport losses (i.e., leaching and runoff). Although the fate of organic P species was not determined, these studies suggest that organic fertilizers are not likely to build up organic legacy P in mineral soils in a matter of years or decades. Moreover, their results indicate that inherent or native soil organic P species in bulk soils are relatively more stable against mineralization (and/or transport) in comparison to newly added organic P forms that appeared to be rapidly transformed to inorganic P in the soil.

Indeed, native organic P has been found stable in soils even after cessation of external P additions. For inorganically P-fertilized soils in Canada without history of manure additions, halting chemical P fertilization for 15 years increased organic P and orthophosphate diesters and decreased most of the IHP isomers including myo-IHP, although total IHP remained unchanged relative to continuously P-fertilized soils [23]. Build-up of organic P when inorganic P decreased has been attributed to drawdown or crop utilization of inorganic legacy P [95] from 28 years of prior inorganic fertilizations before stopping P inputs [23]. Although Liu et al. [23] demonstrated crop utilization of inorganic legacy P from soils, mineralization and consequently crop utilization of organic P appeared to be limited in these soils. In another experiment in Northern Ireland, Cade-Menum et al. [97] reported similar findings when orthophosphate decreased, but neither total organic P nor specific organic P forms changed between various P-fertilized treatments from zero-P controls 5 years after P fertilizations had stopped. Liu et al. [91] also found similar levels of accumulated organic P for both P-fertilized and non-P-fertilized soils in China after 27 years of cropping relative to baseline soils, except that phosphodiesters considerably accumulated more in P-fertilized soils. Liu et al. [91] suggested that P deficits induced degradation of phosphodiesters in soils not receiving P. Taken together, these studies suggest that native organic P forms are not likely to mineralize or contribute to bioaccessible P for soils with prolonged inorganic P fertilization history when soil test P is still sufficient.

Based on the reviewed studies above, organic P may be constituting a minor portion of legacy P. Moreover, existing non-fertilizer-derived soil organic P may contribute less to plant uptake than inorganic P in soils highly enriched with inorganic legacy P (i.e., soil test P above optimum) (Figure 3). Organic P mineralization by microorganisms or plant roots may not be promoted when sufficient levels of bioaccessible inorganic P exists. Conversely, mineralization of organic P into inorganic P may occur to a greater extent than desorption and solubilization of inorganic P when bioaccessible inorganic P is deficient (i.e., soil test P is below optimum). This is consistent with the work of Recena et al. [98], who observed greater contribution of organic P to actual plant P uptake more in low-P than in high-P soils. Mineralization of organic P forms under deficient soil P conditions could arise from stimulation of microbial growth when C and N levels are not limiting [99,100], meaning when sufficient C supply is present and soil C/N ratios are lower. Hence, balanced nutrient and organic matter management may be required for releasing bound orthophosphates from natural organic P reserves in P-deficient soils. More work is needed to better track the transformations of added organic P compounds from organic P fertilizers under different fertilizer management scenarios and field conditions over different periods of time. Building off this knowledge, the following section reviews the current literature on potential plant, microbial, and biochemical strategies for accessing soil legacy P.

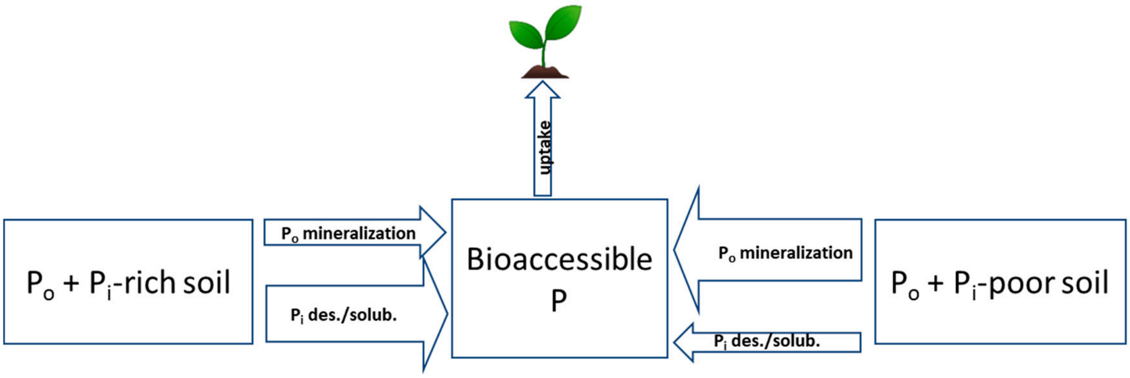

Figure 3. Conceptual representation of organic and inorganic P transformations towards releasing dissolved P and their expected magnitude of occurrence when legacy P is higher and largely dominated by bioaccessible inorganic P (P_o + P_i-rich soil) versus when legacy P is lower and deficient of bioaccessible inorganic P (P_o + P_i-poor soil), assuming equal concentrations of organic P. Arrow size indicates the relative magnitude of fluxes. Legend: P_o, soil organic P; P_i, soil inorganic P; des/solub, desorption and dissolution.

4. Approaches for Accessing Native Soil P and Associated Challenges

4.1. Plant-Based Strategies

Plants can possibly utilize soil legacy P through naturally evolved strategies, such as induction of root architectural changes and exudation of organic acids and enzymes, as well as possibly through scientific pursuits for improving internal P use efficiency (i.e., plant yield per unit P uptake) [101,102]. Another way that plants can thrive on legacy P is through facilitation of symbiotic and beneficial fungi and other soil microbes. However, the role of microorganisms will be discussed separately in the ensuing section.

Root architectural response is a well-recognized plant mechanism for alleviating soil conditions of low bioaccessible soil P [103], making it likely adaptable for extracting legacy P. Examples of efficient root configurational changes include highly branched root systems, increased production and length of lateral roots, proliferation of root hairs, and formation of cluster roots among various crops [101,104–109]. However, these adaptations vary among crop species and genetic varieties [110–113]. Moreover, most of root architectural studies have been performed on seedlings, which do not necessary correspond to root architecture of mature plants grown in the field [114,115]. With limited field measurements in this area [116], soil factors, particularly those associated with low soil P availability (i.e., soil pH), could potentially restrict efficient root architectural responses in field settings. For instance, foraging traits of maize cultivars characterized by greater root surface correlated well with improved P uptake in neutral field soil, but not in alkaline soil [117]. Furthermore, root architecture has been found to vary depending on the chemical forms and supply patterns of P [118], highlighting the importance for understanding soil legacy P speciation and likely distributions across agricultural soils. Interestingly, genotypes of common bean bearing more adaptive root architectures effectively grew in an unfertilized low-P Ultisol, showing comparable P uptake with P-fertilized commercial varieties [111]. Together these studies emphasize that, while efficient root systems can potentially mine soil legacy P, there is a need for a field-based approach for identifying and matching efficient root systems with soil legacy P and other soil conditions. Moreover, soil properties need to be considered in breeding programs aiming for plants with high P uptake efficiencies.

Another plant adaptive means for potentially exploiting soil legacy P is root exudation of organic acids and phosphatases. Organic acids are known to increase dissolved P by rhizosphere acidification, competition for P adsorption sites, complexation of P-precipitating metals, and provision of C source for P-mobilizing microorganisms [119–123]. However, organic acid production is highly specific to certain plant species [121]. For instance, legumes are known to produce more root exudates than grasses [2,22,124,125], which could be advantageous for P acquisition when legumes are intercropped with cereals. However, increasing evidence exists regarding the minor role of organic acids on actual plant P uptake compared to phosphatase activities or root architectural changes. For instance, legacy P uptake was positively correlated with rhizosphere acid phosphatases, but not with organic anions, with wheat (*Triticum aestivum*), oat (*Avena sativa*), potato (*Solanum tuberosum*), and canola (*Brassica napus*) in low bioaccessible P soils [126]. Using statistical redundancy analysis, Sun et al. [127] also found that P uptake of field-grown maize and alfalfa was explained more by root architectural changes (58–87%) than total organic anion concentrations (<0.2–24%). This observation emphasizes the importance of root architecture in acquiring P as compared to other mechanisms (e.g., strategic placement of organic acids [128]), although experimental variables also present challenges in understanding organic anions effects [120]. Nevertheless, these studies suggest that enhanced root exudation could effectively allow plants to utilize soil legacy P when combined with highly adaptive root systems.

Apart from natural plant adaptations, genetic engineering can also be used to increase plant uptake capacity and internal use efficiency of soil legacy P. Efforts related to this field have included increasing P uptake by overexpressing P transporters responsible for root P uptake and P transport to shoots, driving crop resilience to P deficiency [129]. For example, overexpression of transporter TaPht1.4 in wheat promoted growth and P accumulation [130]. Similarly, modulating the expression of OsPHT1 transporters in rice has shown to directly impact P uptake [131–136]. Phosphorus transporters are regulated by genes and transcription factors, which are altogether induced under P-deficient conditions [129,137]. Phosphorus-related genes have already been identified in major agronomic crops, such as rice (*Oryza sativa*), maize (*Zea mays*), and soybean (*Glycine max*) [138–141]. Candidate gene overexpression is a powerful approach to enhance nutrient uptake under conditions of low P availability. It is also foreseeable that a combination of both increased uptake capacity and internal P-use efficiency will be equally desirable for crops that have adapted and developed better P uptake and efficiency use strategies.

Whereas natural plant adaptations (i.e., root architectural changes and root exudation) to mobilize legacy P can be highly specific to plant species or varieties as noted above, genetic engineering can increase legacy P acquisition and internal use efficiency for any desired crops. However, this work continues to be a long-term research trajectory. Consequently, much is still unknown as to whether genetically engineered plants may successfully utilize soil legacy P and reduce, if not eliminate, dependence of mineral P fertilizers. As with natural adaptative plant mechanisms, there is an added uncertainty that these plants could address other soil stresses associated with low bioaccessible P (i.e., Al toxicity in highly acidic soils). To this end, material science, microelectronics, and nanotechnology should develop and deploy several sensor platforms (chemical, electromagnetic, optical, and genetic) for detecting real-time below-ground root development and plasticity response to bioaccessible legacy P. Genetic and genomics approaches should complement this sensor approach and will hone in on the identification of the genes regulating P uptake, use efficiency, and tolerance to other soil conditions. For example, the systems level understanding of the many genes, and their regulation, associated with phosphate deficiency once unveiled would allow for predictive and prescriptive interventions. It would be foreseeable to use genome editing technologies, such as CRISPR (clustered regularly interspaced short palindromic repeats) technologies [142,143], to genetically test the functional relevance of known (e.g., OsPSTOL1, AVP1, PHO1 and OsPHT1;6) [141,144–146] and unknown genes identified in molecular studies. At the same time, it will be important to consider and incorporate stakeholder perceptions and socio-economic considerations of genetically engineered crops for increased legacy P mobilization and crop utilization to ensure adoption by end-users.

4.2. Phosphate-Solubilizing Microorganisms

A diverse genera of microorganisms including bacteria, fungi, actinomycetes, and cyanobacteria have been reported to solubilize native soil P [147], making them potentially capable of solubilizing legacy P. Phosphate-solubilizing microorganisms (PSM) dissolve or mineralize soil P largely through the production of organic acids and phosphatases [148], and recent reviews have reported generally increased crop growth and yield from the use of PSMs [147,149–151]. In general, most studies in this field have focused on effects of PSMs on crop performance, but information is lacking on how PSMs transform legacy P species during or after plant growth, Hence, in the following studies reviewed below, we discuss PSM effects mostly on plant P uptake and growth and suggest research directions for ascertaining the roles of PSMs in impacting legacy P.

Mycorrhizal fungi are perhaps the longest known microorganisms capable of accessing native soil P owing to their capacity for symbiotic associations with 72% of vascular plant roots that began 450 million years ago [152] and could likely be used to access legacy P. Arbuscular mycorrhiza (AM) scavenge greater soil volumes than plant roots for soluble P and rapidly transport acquired P to roots via arbuscules, thereby minimizing the impact of naturally slow replenishment of dissolved P in soil solution [153]. However, AM fungi are diverse; different taxa do not produce the same response from the same plant species, and that the same fungus does not yield the same effects across different plant species or varieties [154]. These effects could range from positive to negative with unknown reasons for these inconsistencies, although elevated C expense by the plant to maintain the symbiotic relationship has been suggested as being detrimental [126,155]. This suggests that compatibility between the plant host and colonizing AM are required for a beneficial outcome of the symbiosis. However, interspecific compatibility between the host plant and the fungi may also vary depending on soil chemical conditions such as soil pH and associated occurrence of different forms of legacy P. Research is therefore needed in understanding t legacy P speciation impacts symbiotic mycorrhizal associations, and vice-versa.

Inoculation of other PSMs to soils has also shown inconsistent effects on plant P uptake and production. For instance, maize increased P uptake by 10% without P addition after 28 d on acidic soil (pH 5.6) with *Enterobacter radicincitans* DSM 16,656 and *Pseudomonas fluorescens* DR54 inoculations [156]. However, the observed increase in P uptake had no effect on plant growth. In contrast, *Bacillus mucilaginosus* inoculation to acidic soil (pH 5.2) did not improve shoot P uptake in maize [157], but *Aspergillus* FS9 and *Bacillus* FS-3 increased strawberry (*Fragaria x ananasa* cv. Fern) yield by 7% and 30%, respectively, in a calcareous soil (pH 7.6) without added P [158]. Although PSM inoculations have been shown to increase water- and resin-extractable P [156], future research needs to focus on how PSMs transform actual soil legacy P species. Direct information on solubilization or mineralization of soil legacy P forms could serve as a tool in matching appropriate PSMs for the a given soil. Moreover, these data are needed both in the short- and the long-term to explore sustainability issues with the use of PSMs in the context of potentially minimizing mineral P fertilizer applications.

PSMs may not thrive on soil legacy P alone and thus may not completely eliminate dependence to external P inputs. The need for supplemental P with PSMs is expected, considering that microorganisms also need bioaccessible P and other essential nutrients for their metabolic processes to establish and sustain microbial activity in soil. Supplementing PSMs with P fertilizers has improved shoot production [156], increased P uptake [157], or exceeded yield of plants from uninoculated P-fertilized control soils by 54–71% [158]. However, inoculating PSM with co-added P not improving plant P uptake and yield has also been reported. This has been observed with *Pseudomonas fluorescens* Pf153 inoculations to soils (pH 4.8 to pH 6.6) after 8 weeks of maize growth compared to uninoculated controls, despite supplemental rock phosphate [159]. In this respect, future research needs to evaluate compatibilities between supplemental P fertilizers and individual or combinations of various PSM species for a given soil. Considering how mineral and organic fertilizers transform soil legacy P (Section 3.1), co-adding mineral and manure with PSM inoculations may enhance utilization of existing P in soils. On one hand, supplementing PSMs with inorganic P may provide for the immediate nutrient need of both the microorganisms and the plants during PSM establishment in soil. On the other hand, supplementing PSMs with organic P fertilizers may alter legacy P speciation into predominantly less sparingly soluble forms. However, given that external P inputs may unavoidably add more to soil legacy P stocks, more work is needed in finding the right balance between minimizing supplemental P additions while maximizing solubilization/mineralization and consequently crop utilization of existing soil legacy P. Moreover, additional research is needed in evaluating any potential combination among PSM species capable of solubilizing P exclusively outside the roots with those capable of solubilizing P within the roots (e.g., endophytic bacteria [160]) with particular application to agricultural crops. Finally, PSM studies involving inoculations to actual test soils require molecular investigation of mechanisms of action to ascertain utilization of legacy P.

4.3. Immobilized Organic P Hydrolyzing Enzymes

Loading organic P-hydrolyzing enzymes onto clay or nanoclay supports has also been explored as a potential biofertilization strategy to mineralize organic P that could likely be applied to hydrolyze organic legacy P. Menezes-Blackburn et al. [161] loaded phytases to either montmorillonite or allophane, found that phytases produced by different microbial species differed in their activities. In their study, phytase activity derived from *Escherichia coli* showed peak activity at pH 5 in water, representing roughly 85% of free phytase activity at the same pH. However, phytase from *Aspergillus niger* showed considerably reduced phytase activity at pH below 5.5 with the tested nanoclay supports [161]. Contrary to decreased activities of immobilized enzymes compared to their freely dissolved forms, Calabi-Floody et al. [162] reported increased activities of up to 48% with allophane-immobilized compared to freely dissolved acid phosphatases. Using the Michaelis–Menten equation to describe degradation of p-nitrophenolphosphate as model organic P substrate, maximum rate of substrate degradation by the enzymes reportedly increased from 33 to 38% with the allophanic compared to montmorillonitic support. However, when composted cattle dung was used as the organic P source, none of the immobilized or the free acid phosphatase showed significant differences from the unamended dung in increasing dissolved inorganic P, which they attributed to high inorganic P concentrations contained in the dung. In contrast, Menezes-Blackburn et al. [163] treated cattle manure with phytases stabilized in allophanic nanoclays and found a significant increase in NaOH-EDTA P (commonly used to extract organic P) and Olsen-extractable inorganic P in soil. However, they did not observe significant hydrolysis of freshly added phytate with soil or manure amended with the immobilized phytases. The stability of these nanoclay-supported enzymes in soils is also of concern, as greatly reduced enzyme activity was also observed after merely 2 h of exposure to high temperature and after 1 d of exposure to protein degradation [161]. Overall, while immobilizing enzymes inside in carrier materials are promising under laboratory conditions, this approach appears to be challenged by limited accessibility of substrates and the interference of other dissolved compounds in the soil solution. Moreover, with a short lifespan, the capacity of nanoclay-immobilized enzymes to release organically bound legacy P in soils and sustain crop P needs would be highly challenged. Future research needs to focus on finding new approaches to adding these enzymes using other carrier materials [164] without negatively affecting their activities when added to soil or when combined with organic fertilizers.

5. Conclusions

Repeated P fertilizer applications over time has led to build-up of soil legacy P, which theoretically could be utilized to substitute for, if not eliminate dependence on, mineral P fertilizers. However, crop recovery of legacy P varies considerably across soils and duration. This paper reviewed (1) the occurrence and factors controlling bioaccessibility of different soil P forms, (2) transformation of different legacy P species with P fertilizer additions, and (3) currently studied strategies that could possibly be used for exploiting soil legacy P for crop use. We found that soil legacy P exists predominantly as inorganic P in either adsorbed or precipitated forms, and secondarily as organic P, mainly as monoester or diester forms. Bioaccessibility of different chemical P forms is predominantly controlled by soil pH either directly (e.g., desorption/dissolution of inorganic P species) or indirectly (e.g., enzymatic degradation of organic P). We also found that inorganic legacy P could transform into more bioaccessible forms with fertilizer applications, but this effect is highly specific to soil and fertilizer type and may diminish away from the point and time of fertilizer application. In contrast, transformation of native soil organic P forms does not appear to be impacted by fertilizer applications and cessations, suggesting lesser accumulation of organic legacy P in soils, as well as lower potential for crop utilization of native organic P in soil particularly when bioaccessible inorganic legacy P is sufficient.

Most currently pursued approaches for possibly increasing crop utility of legacy P are biological in nature. These range from natural to genetically engineered plant adaptations for enhanced soil P uptake and use efficiencies to the use of symbiotic or beneficial P-solubilizing microorganisms and immobilized organic P-hydrolyzing enzymes. However, plant- or microorganism-based strategies are limited by the high specificity of acquired adaptation mechanisms capable of solubilizing soil P, whereas immobilized enzyme efficacy is mainly limited by physical and chemical constraints. Moreover, studies investigating these approaches typically do not elucidate the mechanism of actions for utilization of soil legacy P largely due to lack of molecular soil P speciation component.

As scarcity of P resources becomes a more pressing global issue, mining legacy P from soils may emerge as a more pressing societal need. Harnessing this resource will require not only development of new and existing technologies for improved legacy P utilization but also holistic management strategies that incorporate multiple approaches tailored to specific soil environments. Overall, enhancing our ability to access soil legacy P for croplands will require a multidisciplinary approach to establish soil and crop management systems that enhance complementary use of the different chemical forms, spatial variability, and temporal changes of legacy P. A systems approach should integrate many of the strategies identified above, as well as future technologies, for accessing native soil P. As multidisciplinary advances, for example in genetic engineering and material sciences, are combined with molecular soil P speciation tools in addressing each approach's limitations, it is foreseeable that prospects for widespread utilization of legacy P as a partial or complete substitute for mineral P fertilizer may increase in the future.

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