

Review

A Critical Review on Soil Chemical Processes that Control How Soil pH Affects Phosphorus Availability to Plants

Chad J. Penn ^{1,*}  and James J. Camberato ² 

¹ USDA-ARS National Soil Erosion Research Laboratory, West Lafayette, IN 47907, USA

² Purdue University, Department of Agronomy, West Lafayette, IN 47907, USA; jcambera@purdue.edu

* Correspondence: chad.penn@ars.usda.gov; Tel.: +01-765-494-0330

Received: 26 April 2019; Accepted: 4 June 2019; Published: 8 June 2019



Abstract: Occasionally, the classic understanding of the effect of pH on P uptake from soils is questioned through the claim that maximum P uptake occurs at a pH much lower than 6.5–7. The purpose of this paper was to thoroughly examine that claim and provide a critical review on soil processes that control how soil pH affects P solubility and availability. We discuss how individual P retention mechanisms are affected by pH in isolation and when combined in soils, and how both real and apparent exceptions to the classic view can occasionally occur due to dynamics between mechanisms, experimental techniques (equilibration time, method of soluble P extraction, and pH adjustment), and plant species that thrive under acidic conditions. While real exceptions to the rule of thumb of maximum P availability at near neutral pH can occur, we conclude that the classic textbook recommendation is generally sound.

Keywords: soil phosphorus solubility; plant available phosphorus; pH

1. Introduction

Soil pH is considered to be the “master variable” of soil chemistry due to its profound impact on countless chemical reactions involving essential plant nutrients, phytotoxic elements, and pollutants. Either directly or indirectly, pH influences the solubility of these elements determining their biological availability and mobility. For a nutrient to be plant-available, it must first dissolve into solution; at that point, it is also mobile and can potentially be lost in leachate or runoff. Thus, pH management is critical for both agronomic and environmental management. For several decades, considerable research focused on the impact of soil properties, especially pH, on the solubility of phosphorus (P). Thanks to the landmark work on basic soil P chemistry by scientists such as M.L. Jackson, W.L. Lindsay, N.J. Barrow, S.R. Olsen, S.A. Barber, F.J. Hingston, E.J. Kamprath, D.L. Curtin, J.K. Syers, and others, the solubility dynamics of this complex nutrient can be reduced into a somewhat crude but comprehensive diagram such as Figure 1, redrawn from Price [1]. This figure, redrawn by Barrow [2], was focused on by the author in rejection of the notion that P availability to plants is generally maximized at near-neutral pH. The author contended that this view was “based on an outdated view of soil phosphate chemistry”, and that P uptake by plants and desorption by soil occur “with a much lower pH optimum”.

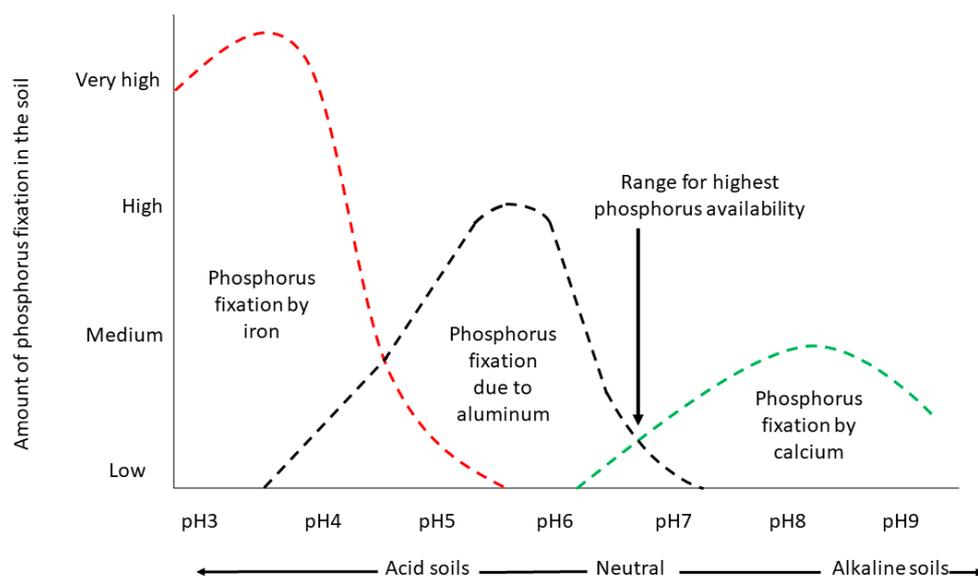


Figure 1. General qualitative representation of soil phosphorus availability as impacted by pH. Redrawn from Price [1].

In the classic view, there are two main “valleys” of maximum P solubility occurring at around pH 4.5 and 6.5, coinciding with the lowest degree of P fixation by Ca, Al, and Fe minerals. We contend that although the exact pH value of maximum P solubility (and therefore plant availability) will vary somewhat between soils, the recommendation of near-neutral pH to maximize plant P availability is generally sound. While it is true that there are some valid reports in the literature that contradict this classic view, this is sometimes confounded by methodology, especially equilibration time and method of pH adjustment. The objective of this paper is to provide further evidence for the classical view and provide an explanation for how differences in soil properties and P retention mechanisms can influence the observed effects of pH on P solubility, which may at times, contradict the classical view.

Much of the research on basic soil P chemistry was conducted from the 1950s to the 1970s; even at that time there were some contradictory reports. Amarasiri and Olsen [3] commented that “the experimental evidence on the effect of lime on P availability to plants is inconclusive”, citing studies that showed that lime increased [4,5], decreased [6,7], or did not change [8,9] plant P concentration. Similarly, in a review that included P by lime interactions, Sumner and Farina [10] showed that there were many inconsistencies in the literature regarding the impact of pH on P uptake. In assessing changes in soil P availability with pH adjustment, it is necessary to examine both P release from, and P sorption to, soil constituents as determinants of solution P concentration. In this case, “sorption” is defined as any mechanism whereby P is taken out of solution by soil. For the literature review conducted in this paper, several studies indicated increasing pH caused a decrease in soluble P or an increase in P sorption [11–16], as well as an increase in soluble P and plant uptake or a decrease in P sorption [17–29].

The purpose of this paper is to (1) examine the classic view of the impact of pH on plant P availability with a maximum value occurring around 6.5–7, (2) illustrate how pH can impact soil P solubility among different P forms in isolation and also when combined together in soils; and (3) explain how real exceptions to the classic view can occasionally occur due to the dynamics between different solubility mechanisms, use of certain experimental procedures, or a temporary transitional/equilibration period after pH adjustment. Although our review is focused on soil pH effects on inorganic P, sorption processes of organic and inorganic P in soil are similar [30], and pH may also affect organic P in an analogous manner. Also note that this discussion is focused on how pH impacts soil chemical processes that control P solubility, not biological processes.

2. Review and Discussion

2.1. The Need to Consider Context of Observations and Soil-Solution Dynamics

Examination of the impact of pH on plant P uptake must consider the context of the soil rather than the solution and plant biology alone. In other words, while hydroponics provides a great tool with regards to studying plant nutrient needs, environmental factors, and physiology, it excludes any dynamics between the soil and the plant, which is what makes it so advantageous for certain types of plant studies. Since plants grow in and derive nutrients from soil, the soil cannot be ignored when examining plant nutrient availability. Although raw plant biology can partly dictate nutrient uptake from solution, the soil is the medium by which such nutrients are provided to solution. Changing the pH of a hydroponics solution does not produce the same impacts on P availability as changing the pH of a soil. For example, in studies by Vange et al. [31] and Sentenac and Grignon [32], both cited by Barrow [2] as evidence of minimum P uptake at near-neutral pH, it was observed that P uptake by barley (*Hordeum vulgare* L.) and corn (*Zea mays* L.) grown in a soil-less solution was minimal at near-neutral pH with maximum P uptake at acid pH. This was attributed to the distribution of H_2PO_4^- vs HPO_4^{2-} and plant preference for the former. While it is true that plants prefer the solution species of H_2PO_4^- over HPO_4^{2-} and that the former species is more abundant at acid pH, this oversimplification ignores the source of P to the solution, i.e., soil P solubility. It does not follow that maximum P uptake in a soil system occurs at acid pH due to preference for this species in soil-less media. One must consider both the quantity of P in solution and the form, not just the form alone.

For another example illustrating the need for considering the dynamic between soil and solution, consider that hydroponics solutions are not usually created to include Al, which is an important element from the perspective of both phytotoxicity and P solubility. In soils, even when plants prefer the more prevalent P species at low pH, H_2PO_4^- , there also exists increased concentration of solution Al^{3+} , which is not only toxic to most plant species but can also precipitate with solution P, rendering it plant-unavailable. Either of these phenomena would reduce P uptake at acid pH levels in most plants. In the studies conducted by Vange et al. [31] and Sentenac and Grignon [32], both used solutions that only contained some form of Ca (CaCl_2 or CaSO_4), pH adjustment chemicals, and P. The experiments were also conducted exclusively on the excised root portion (i.e., no shoots) of young plants (5 days and 6–8 days old) for a duration of only 5 and 20 min.

2.2. How Are Different Individual P Sorption Mechanisms Impacted by pH?

Phosphorus in the soil-solution-plant system is typically described in terms of three generic pools: non-labile P, labile P, and solution P. “Labile” P is a general term that is meant to indicate a generic and operationally-defined soil P pool that is available for plant uptake over a relatively short time period, and consists of P held by the soil through several possible mechanisms. However, this labile P must first be released to solution before a plant root can uptake it. As the labile P pool supplies the P in solution through equilibrium, the non-labile P pool is in equilibrium with the labile-P pool and supplies it. The dynamic is often illustrated as:



Thus, when P does not sorb to the soil, it remains in the solution. This logic is in contrast to Barrow [2], who claims that the effect of pH on desorption is not the opposite of adsorption (i.e., ligand exchange mechanism): “As the pH is decreased from say 6 to 4, the rate of uptake of phosphate by roots increases, the amount desorbed from soil increases, and the amount sorbed by soil often also increases”. Such a claim contradicts the notion of thermodynamic equilibrium and Le Chatlier’s principle. While the rate and magnitude of sorption and their reverse reactions will not be equal under the same conditions for a single P retention mechanism, the chemical conditions that favor the reverse of any single reaction are indeed opposite. As evidence of this, chemists are conveniently

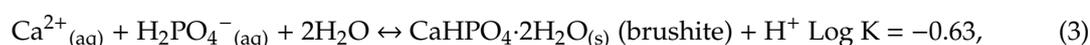
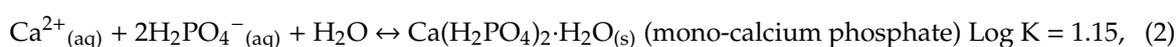
able to simply write any given equilibrium reaction in reverse and calculate the K value as the inverse of the K value for the forward reaction. In general, the rate at which the labile soil P pool equilibrates with solution P is faster than the equilibrium between the non-labile and labile soil P pools [19,22–24,33–35]. Equilibrium is maintained by a number of different P sorption reactions described below. The degree, and rate of such reactions will vary greatly as a function of soil properties and pH. The dynamic between these three pools is what ultimately controls the impact of pH on solution P concentrations and the ability to replenish it, and therefore plant P availability. In contrast to Barrow [2], adsorption (a.k.a. ligand exchange) followed by diffusion into an Fe mineral is not the only P sorption/release mechanism occurring in soils. We agree with the assessment of McDowell et al. [36] and McDowell and Sharpley [33], who found that P release to solution was from a combination of Al, Fe, and Ca related P, including several precipitates, as determined by solubility diagrams (i.e., thermodynamics), P fractionations, and nuclear magnetic resonance. In addition, modern solid-state spectroscopic techniques have confirmed the presence of various P forms previously predicted to exist based on thermodynamics and sequential chemical P fractionations [37–43]. The effects of pH on these P removal/release mechanisms are discussed below. It is important to keep in mind that any of the P retention mechanisms described below can be important components in both the non-labile and labile soil P pools described in Reaction (1); one exception is P held by weak outer-sphere mechanisms via anion exchange, which is exclusive to the labile P pool.

2.2.1. Anion Exchange

Anion exchange is a simple mechanism of attraction of an anion to a positively charged surface whereby the surface charge is partly neutralized through sorption of the anion in the outer-sphere layer. Because the bonding consists of a water molecule located between the anion and surface, it is considered a weak and reversible electrostatic bond. This occurs on variable charged minerals, especially Fe and Al oxides and hydroxides and 1:1 minerals such as kaolinite. Thus, anything that influences surface charge on these minerals will also have an effect on P sorption by anion exchange. First, as pH increases above the mineral's point of zero charge (PZC), the surface becomes less positive and can retain less P. If pH is greater than the PZC, then an increase in ionic strength will make the surface less positive; the opposite effect occurs if pH is less than PZC. However, increasing ionic strength will additionally influence the surface electrical potential at the plane of sorption, producing the opposite effect on P sorption. At high pH values when $\text{pH} > \text{PZC}$ (i.e., negatively charged surface), increases in ionic strength will make the electrical potential in the plane of sorption less negative, and increase P sorption. The opposite effect occurs when $\text{pH} < \text{PZC}$. Thus, the balance between changes in surface charge and electrical potential with changes in ionic strength will dictate how ionic strength impacts P sorption [27–29,44]. Regardless of ionic strength effects, several authors investigating P sorption onto variable charged minerals have shown a decrease in P sorption (therefore an increase in solution P) or an increase in solution P concentration as pH increased from 4 to 7 [27–29,45,46] due to a decrease in surface positive charge.

2.2.2. Precipitation of Ca Phosphates

Precipitation of Ca phosphate minerals occurs when the ion activity product in solution exceeds the equilibrium constant, K, for a particular mineral. In other words, when the solution becomes “saturated” with the reactants, which in this case are dissolved P and Ca^{2+} , precipitation of Ca phosphate minerals (i.e., products) can occur. Solution hydronium (H^+) is often a reactant or product in several Ca phosphate precipitation equilibrium reactions, which therefore can also be written in terms of hydroxide (OH^-).





From these reaction equilibria and many observations spanning several decades, it is evident that formation of Ca phosphates is favored by increasing solution P and Ca concentrations (i.e., Le Chatelier's principle), as well as an increase in pH (i.e., decrease in solution H^+ concentration). This concept is illustrated in Figure 2. Often, the source of soluble Ca for precipitation of Ca phosphates exists in the soil as Ca bound to the cation exchange sites, various Ca minerals, or residual limestone. In addition, many chemical P fertilizers, such as triple superphosphate and single superphosphate, are composed of Ca phosphates such as mono-calcium phosphate (Reaction (2)). These highly soluble Ca phosphate minerals dissolve quickly and saturate the solution with Ca and P relative to less soluble Ca phosphate minerals such as brushite, monetite, and amorphous forms, allowing them to precipitate [47]. However, these Ca phosphate minerals are considered meta-stable (i.e., Gay-Lussac-Oswald (GLO) theory), and slowly transform into more stable (i.e., less soluble) minerals, such as hydroxyapatite [48]. Early work conducted on chemical reactions around fertilizer granules demonstrated that the residual P compounds closest to the fertilizer granule are Ca phosphates [47,49–51], with P associated with Fe and Al further away from the granule [52]. In addition to chemical fertilizer, dairy, swine, and poultry manure contain appreciable amounts of Ca phosphates of varying solubility derived from Ca-P minerals added to their feed.

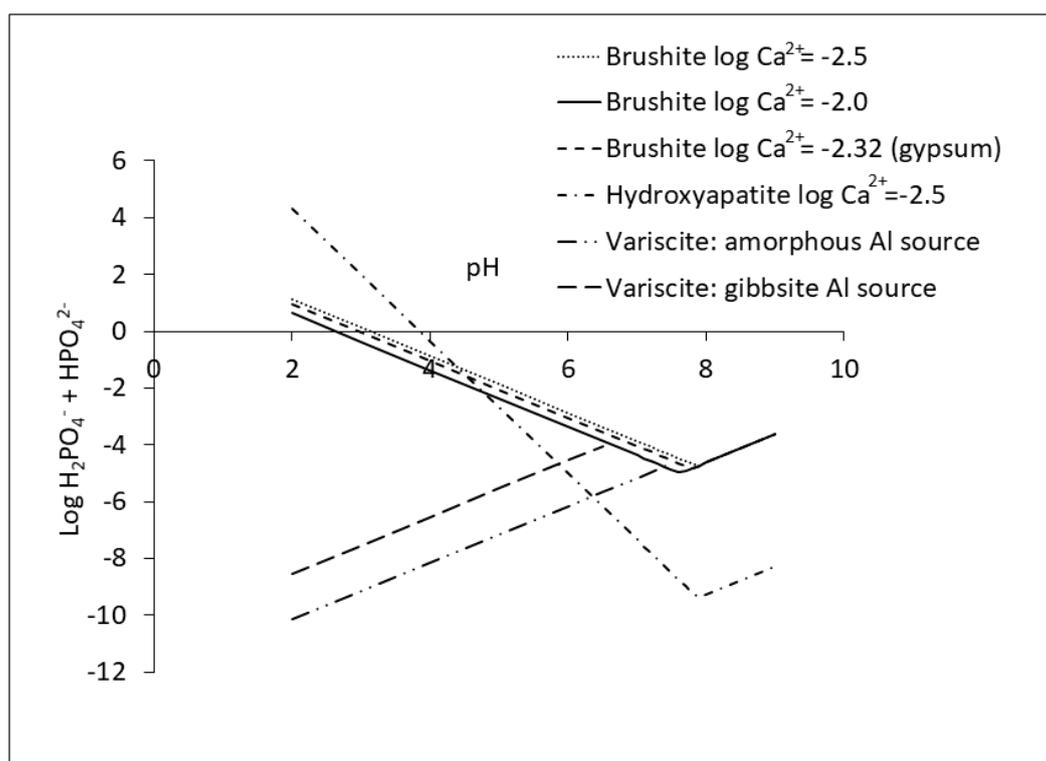


Figure 2. Solubility diagram for Al (variscite) and Ca (brushite and hydroxyapatite) phosphate minerals calculated with thermodynamic constants from Lindsay [47] and using different sources or concentrations of Ca^{2+} and Al^{3+} .

While it is often assumed that Ca phosphates only exist in high pH soils, numerous studies have identified Ca phosphates in acid soils by a variety of methods [3,11,12,17,22,33,36,39,53,54]. Calcium phosphate can occur in acid soils for several reasons. First, thermodynamic equilibria do not consider reaction kinetics, therefore certain existing Ca phosphate minerals could continue to persist for many years, even their dissolution is favored thermodynamically. Second, Ca phosphate minerals may

become occluded within other minerals, such as Fe or Al hydroxides, shielding them from solution. Last, increased concentrations of solution Ca can decrease the pH required for precipitation of Ca phosphate minerals, allowing appreciable amounts to be precipitated at pH values less than 7. Often, calcite (CaCO_3) from residual limestone applications provides soluble Ca to solution for precipitation with P, and therefore anything that impacts the solubility of calcite, such as CO_2 concentration, will also affect precipitation of Ca phosphate minerals. The solubility diagram in Figure 2 illustrates how the Ca phosphate mineral, brushite, is formed more readily at higher pH values, yet an increase in the supply of Ca^{2+} to solution will depress the pH required to precipitate it, allowing for its greater presence in acid soils. From Figure 2 and Reactions (2)–(5), it is evident that increasing pH can decrease solution P concentrations by precipitating Ca phosphate, but to a degree that is a function of the amount of Ca^{2+} supplied to solution by the cation exchange capacity (CEC) or Ca minerals. Likewise, decreasing pH will dissolve Ca phosphate minerals. Therefore, soil properties such as mineralogy and exchangeable Ca should be considered when ascertaining the degree of impact of pH on solution P concentrations. The importance of soluble and exchangeable Ca^{2+} for P removal among acid soils was demonstrated by Curtin et al. [17], who concluded that Ca controlled the solubility of P in 11 acidic soils (pH 5 to 6.3) of New Zealand. The authors used a combination of sequential NaCl extractions and mixtures of anion and cation exchange resin (AER and CER, respectively) to desorb P from soils, some of which were limestone-treated. Both pre-treatment with a NaCl wash and use of CER increased the solubility of P due to removal of soil Ca that would have precipitated Ca phosphates.

In calcareous soils, notice that at some pH level the solubility of the mineral changes direction with increasing pH; i.e., Ca phosphate solubility begins to increase with further pH increase (Figure 2). This is due to the consumption of Ca by carbonate, as carbonate becomes an effective competitor with phosphate for Ca. With formation of calcium carbonate (calcite), the carbonate can remove solution Ca^{2+} that would have precipitated Ca phosphate at lower pH.

For pure Ca-based systems, although the impact of pH on Ca phosphate solubility is the same regardless of supporting Ca concentrations (i.e., increased solubility with decreasing pH), the degree of mineral solubility will vary with supporting Ca concentrations. Thus, it is not uncommon to observe Ca-phosphate minerals in acid soils which contribute to shifting the pH of maximum solubility.

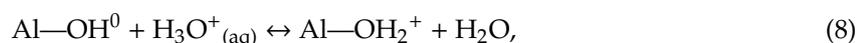
2.2.3. Ligand Exchange (Adsorption) to Al and Fe Oxides/Hydroxides and Edges of Alumino-Silicate Minerals

Similar to anion exchange reactions, phosphate adsorption occurs onto variable charged minerals such as Al and Fe oxides/hydroxides and 1:1 minerals. However, unlike anion exchange, the reaction is not dependent on surface charge of the mineral, and it does utilize a strong covalent bond between the phosphate and a valence un-satisfied surface with no water molecule occurring between the sorbent and sorbate. Thus, the surface adsorption, also referred to as ligand exchange and surface complexation, is a much stronger sorption mechanism compared to anion exchange. An example mono-dentate surface reaction is shown below for a terminal hydroxide bound to Al:



The K values for ligand exchange reactions vary as a function of the nature of the mineral and the functional group that P is adsorbing to. Variations of this reaction can occur on positive and negatively charged surfaces as well as with formation of multiple bonds [48]. In this way, phosphate becomes part of the surface of the mineral, as it is within the inner sphere of the charged surface. These reactions are favored by low pH (as evidenced by the typical release of an OH^- to solution), not necessarily because of the positive charge that often accompanies these variable-charged surface functional groups at low

pH, but because these surface functional groups tend to possess H₂O groups at low pH that are easier to displace than OH groups [55]. An example protonation of the surface OH group is as follows:



where H₃O⁺ is hydronium, expressed as H⁺ in shorthand. In addition, solution hydroxide is considered a superior type of ligand, classified as a “potential determining ion”, compared to phosphate, which is a “charge determining ion” [56]. As a result, solution hydroxide is more competitive for surfaces than phosphate, with this preference magnified as pH increases (i.e., solution hydroxide concentration increases). Thus, ligand exchange of phosphate onto variable charged minerals tends to decrease with increasing pH. On the other hand, extreme acid pH levels can potentially limit surface adsorption, as described by the “adsorption envelope” phenomenon [57]. Briefly, anion solution species protonate with decreasing pH, decreasing their negative charge and attraction to a positively charged surface. Although this tends to be less important for phosphate compared to anions such as fluoride and silicate [58], some studies have identified dramatic decreases in P surface adsorption onto kaolinite and alumina surfaces after pH decreased below about 4.5 [59]. Part of the reason for this observation may be due to the dissolution of the mineral sorbent itself.

In addition, ligand exchange of P onto variable charged Al and Fe minerals can be a “seed” by which P begins to precipitate as Al and Fe phosphate on the surface of the mineral, or similarly becomes “occluded” into the interior of the mineral through a slow diffusion process. In such a scenario, ligand exchange occurs rapidly, followed by the slower surface precipitation reaction and diffusion into the interior i.e., “absorption” [35,57,60–62]. Thus, ligand exchange and surface precipitation are considered to exist on a continuum sometimes occurring simultaneously as precipitation can occur rapidly if solution P concentrations are highly elevated, as is found near fertilizer granules [41–43,60,63–67]. In addition to kinetics, another practical difference between ligand exchange of P onto variable charged Al and Fe minerals and precipitation is the resulting metal:P ratio, which is 1:1 for Al and Fe phosphates and around 6:1 for surface adsorbed P. The lower efficiency of P removal by surface adsorption compared to precipitation can have a major impact on how pH adjustments can affect P solubility. Even in a pure Al or Fe mineral-based system, the interaction between P removal by ligand exchange and Fe/Al phosphate precipitation can shift the pH of maximum P solubility. Examples of this are discussed in a later section.

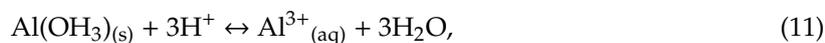
2.2.4. Precipitation of Al and Fe Phosphates

The precipitation theory based on thermodynamics previously described for Ca phosphate formation also applies to Al and Fe phosphates. Example precipitation reactions are shown below for variscite and strengite, but non-crystalline Al and Fe phosphates mostly occur in soils [50], providing a range in K values in this same form:

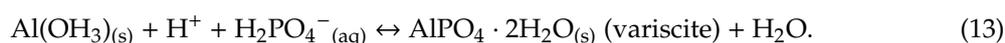


While low solution P concentrations tend to interact with soils via ligand and anion exchange reactions, the high solution P concentrations that occur with addition of P fertilizer will precipitate as Ca, Al, and Fe phosphates [63]. In fact, several studies have demonstrated that high P solutions will partly dissolve/decompose soil minerals beyond releasing exchangeable cations, and precipitate Al and Fe phosphate minerals at the surface. This has been observed for minerals such as kaolinite, montmorillonite, illite, goethite, and gibbsite [41,42,60,65,67–70].

Although Fe and Al phosphates are considered insoluble at low pH, examination of the equilibrium reactions suggests the opposite; thus it is important to consider all components of the reaction, other minerals that support it, and how changing pH could affect those components. While increased acidity directly promotes dissolution of Al and Fe phosphates, increased acidity can also indirectly affect solubility based on how pH controls the solution supply of Al^{3+} and Fe^{3+} :



Essentially, decreased pH (i.e., increased H^+) will promote dissolution of Al and Fe oxides and hydroxides through hydrolysis of Al and Fe. The resulting solution Al^{3+} and Fe^{3+} can then directly precipitate with solution P; i.e., increased acidity promotes Reactions (4) and (5), which provide the chemical potential for Reactions (9) and (10) to proceed, thereby removing P from solution by precipitation. From the combination of Reactions (9)–(12), it should be apparent how the solubility of Al and Fe oxides and hydroxides can impact the formation and dissolution of Al and Fe phosphates; soils containing more soluble Al and Fe oxides and hydroxides (i.e., higher K values for Reactions (11) and (12)) will result in less soluble Al and Fe phosphates. Consider two different Al hydroxide sources (Reaction (11)) for supplying Al^{3+} for formation of variscite; amorphous Al hydroxide with a log K value of 9.66 and gibbsite at 8.04. The resulting equilibrium produces a log K value of 7.16 and 5.54 when Al^{3+} is supplied by amorphous Al hydroxide and gibbsite, respectively.



Reaction (13) and Figure 2 illustrate the widely held notion that Al and Fe phosphates are less soluble at low pH, as increased acid promotes the reaction to proceed as written. Also evident from both empirical observation [19] and examination of the chemical equilibria, the consumption of solution Al and Fe through metal phosphate precipitation (Reactions (9) and (10)) will further promote dissolution of metal hydroxides (Reactions (11) and (12)).

Therefore, when considering the impact of pH on Al and Fe phosphate solubility, there exists a balance between the innate solubility of the metal phosphate (more soluble with decreasing pH), and the supply of solution Al^{3+} and Fe^{3+} that consumes solution P, with the Al and Fe source being more potent at lower pH levels. Again, thermodynamic equilibrium does not consider kinetics, which can have a significant impact on observed effects of pH on precipitation and dissolution. For example, with decreasing pH, if the rate of Al phosphate precipitation is slower than the dissolution of other P pools, then an increase in solution P concentration could occur at some point, even though raw thermodynamic equilibrium suggests otherwise. These interactions between Al/Fe phosphate and Fe/Al hydroxide solubility, along with differences in kinetics, can have an impact on Al/Fe phosphate maximum solubility. Some examples of this are discussed later.

2.3. Dynamics among P Reactions in Soil

The dynamic between surface adsorption, anion exchange, and precipitation of Ca, Al, and Fe phosphates also helps to explain why P solubility often increases with increasing pH among acid soils, and why there may be exceptions to this. Ideally, as pH increases, variable charged surfaces eject phosphate due to decreased positive charge, and Al and Fe phosphates dissolve as it becomes more thermodynamically favorable for Al and Fe to form hydroxide minerals (Reactions (9)–(12)). This newly soluble P adsorbs to the surfaces of the Al and Fe hydroxide minerals, but at a lower efficiency than the previously precipitated P due to the higher Al:P ratio [71–73]. For example, Hsu and Rennie [72] added P to Al saturated cation resin and found that the Al:P ratio on the resin increased with increasing pH from an initial value of 1:1 indicating Al phosphate formation and then surface adsorption to Al hydroxide at higher pH. Next, with further pH increase, solution P continues to increase due to

increased solution hydroxide concentrations that can out-compete P for surface adsorption sites [55,59]. This classic system is illustrated in Woodruff and Kamprath [73], in which five acidic soils were tested for P sorption maximum before and after limestone addition. Limestone neutralized exchangeable Al^{3+} and reduced P sorption maximum for three of five soils; two soils were non-responsive since they possessed little to no initial exchangeable Al^{3+} for potential Al phosphate precipitation at low pH.

If there is sufficient soluble Ca in the system, then another complicating factor is that with increasing pH the Ca will begin to remove P from solution via precipitation, depending on the rate of formation. The larger the amount of soluble Ca, the greater impact Ca precipitation can have at sub-7 pH (Figure 2). While most studies generally show that increasing pH tends to increase P solubility in non-calcareous soils, there can be some exceptions to this due to the balance between all P retention mechanisms, which varies among soils.

Hsu and Rennie [19] adjusted the pH of an Al hydroxide mineral from 3.8 to 7 with NaOH and added P at several different concentrations. The resulting equilibrium solution P concentrations are shown in Figure 3 as a function of both pH and solution P concentration. Notice that for all the initial P concentrations added to the Al hydroxide, the solution P concentration decreased as pH decreased, until the pH reached 3.8, where it increased again. The authors identified both surface adsorption and Al phosphate precipitation reactions. A plausible explanation for the increase in P solubility at pH 3.8 could be the balance between P adsorption, Al hydroxide dissolution, and Al phosphate precipitation. Surface adsorption of P, which is fast, occurs more readily at low pH (Reactions (6) and (7)), increasing P removal even though Al hydroxide is dissolving (Reaction (11)). This dissolution removes the surface in which P is adsorbing to, yet provides Al^{3+} to solution for Al phosphate precipitation, which is more efficient for P removal based on the ratio of Al:P. However, if the precipitation rate of Al phosphate is slow, then a change of mechanism from surface adsorption to precipitation would at least temporarily produce a spike in solution P concentrations below that critical pH level. The authors conducted further experiments to confirm that Al phosphate precipitation was indeed occurring at pH 3.8, and that this slow precipitation proceeded after a fast surface adsorption of P.

Similarly, although acid pH helps provide Al^{3+} and Fe^{3+} to solution (Reactions (11) and (12)) for Al and Fe-P precipitation, excessive protons in solution can inhibit the precipitation reaction (Reactions (9) and (10)). For example, Coleman et al. [34] treated Al-saturated montmorillonite with various concentrations of K, Ca, and Na salt solution for the purpose of displacing exchangeable Al^{3+} into solution to promote Al phosphate precipitation. As an alternative comparison, the same solutions were titrated with NaOH to maintain pH 4. First, addition of the salts displaced Al^{3+} and allowed for Al phosphate precipitation as expected, but the precipitation reaction caused pH to further decrease because protons are a product of this reaction (Reaction (9)). This inhibited further Al phosphate precipitation. Next, when the reaction product (protons) were removed via neutralization to maintain pH 4, much greater Al phosphate precipitation occurred. In fact, the amount of P removed was positively correlated to the amount of NaOH required to neutralize the protons produced from Al phosphate precipitation. This illustrates how excessive acidity could reduce Al phosphate precipitation and cause a spike in soluble P at low pH levels, depending on soil Al solubility and pH buffer capacity.

In addition to the importance of the mechanism rates and efficiency, consider that at low pH, exchangeable Al^{3+} and Fe^{3+} must be able to enter the solution phase in order to precipitate with P. This has been demonstrated in several studies [11,34,73] and can impact how pH affects P solubility. For example, Coleman et al. [34] determined two different pH levels for peak P sorption onto Al-saturated montmorillonite depending on the balance between surface adsorption and precipitation and the ability of exchangeable Al^{3+} to enter into solution. Peak P sorption occurred at pH 4 if salts were present to displace Al^{3+} from the montmorillonite surface, allowing Al phosphate precipitation. However, if the exchangeable Al was not displaced by the presence of salts, then Al phosphate precipitation was not possible, and Al hydrolyzed in place with increasing pH, which created Al hydroxide mineral for surface P adsorption resulting in peak sorption at pH 7. The authors similarly demonstrated how certain soil properties can prevent shifting in P removal mechanisms with increasing

pH. Among 60 acidic Piedmont soils, P sorption was measured after lime addition; P sorption was highly correlated to initial exchangeable Al concentrations as this Al hydrolyzed with lime addition and provided a surface for P adsorption. The experiment was repeated a second time, except the exchangeable Al was first displaced with a salt solution before adding lime. For soils with high levels of exchangeable Al, the pre-wash resulted in a significant decrease in P removal, but for acid soils that did not have much exchangeable Al, the pre-wash had no effect. The former group of soils lost their ability to remove P by Al phosphate precipitation due to the loss of the source of Al^{3+} that would become a surface for adsorption after hydrolysis. However, the latter group was unaffected because there was no exchangeable Al to be leached.

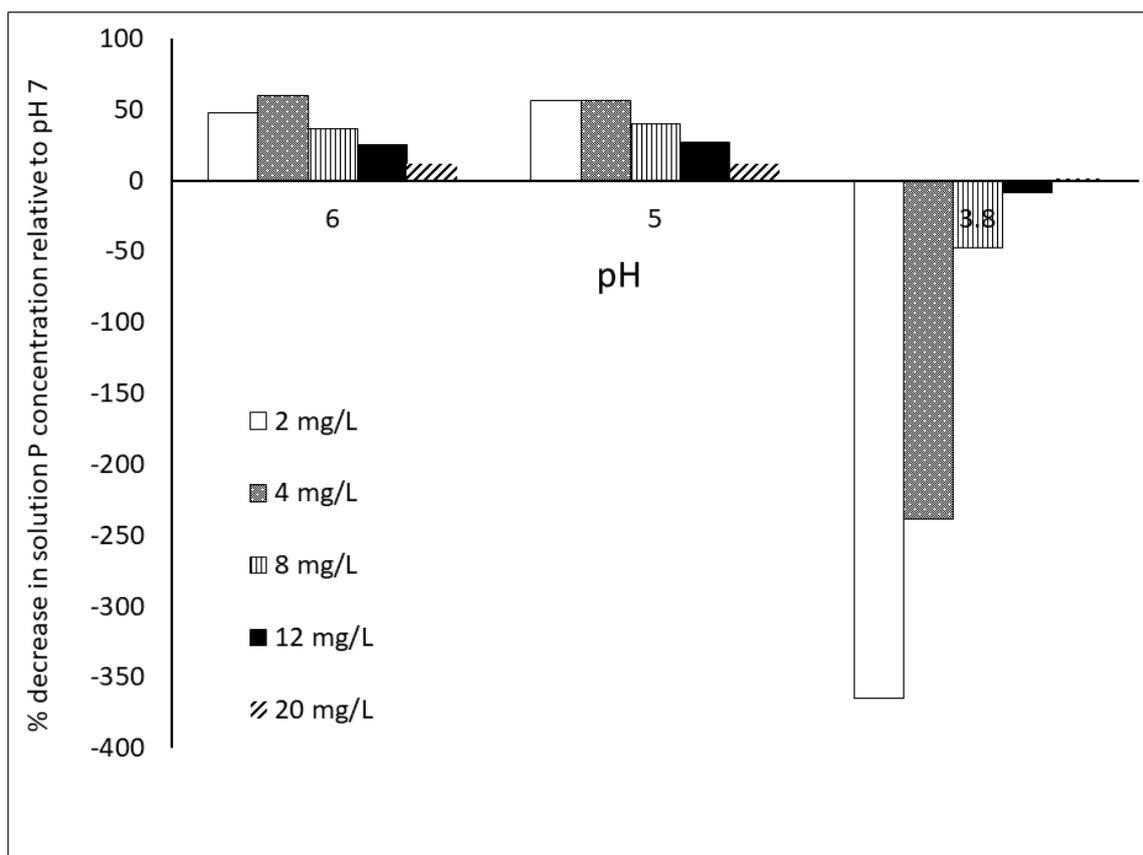


Figure 3. Percent decrease in equilibrium solution phosphorus (P) concentrations relative to pH 7 for an amorphous aluminum hydroxide mineral, shown as a function of pH (adjusted with NaOH) and P addition (2, 4, 8, 12, and 20 mg P/L). Drawn with data from Hsu and Rennie [19]. Positive values indicate a decrease in equilibrium solution P concentration compared to pH 7, within a given P addition level.

As previously mentioned, formation of Ca phosphates remains an important factor even in acid soils. Thus, the amount of Ca^{2+} available to solution for precipitation with P can be a significant mechanism when considering the balance among P sorption mechanisms with changing pH. Not only does the amount of native soil-soluble Ca^{2+} impact P removal, but the use of a Ca-rich mineral for increasing pH can provide a Ca source. In some cases, addition of Ca with the method of pH increase (which is common) can confound the intended objective of testing how pH affects P solubility. For acid soils, if the initial dominant P form is either Al-P or P adsorbed to Al hydroxides, then an increase in pH would increase soluble P. However, if appreciable Ca is added through pH adjustment via Ca carbonate or Ca hydroxide, then added Ca could precipitate the solution P released by P associated with Al and Fe. Recall that both increased pH and solution Ca^{2+} concentrations promote Ca phosphate precipitation (Figure 2). In other words, there exists a balance between the amount and solubility of P held with Al and Fe, increase in pH, and the amount of added Ca that remains soluble for potential Ca-P

precipitation. This concept is demonstrated in Curtin and Syers [11]; six acid soils were adjusted in pH from 4.8 to 6.7 using Ca carbonate and equilibrated 4 weeks, followed by P addition at several different rates and equilibration for another 4 weeks. Five of six soils decreased in water-extractable P with increasing pH. This suggested that the amount or solubility of P initially associated with Al and Fe in the acid soils was small compared to the amount of Ca added and the final soil Ca solubility, which was able to associate with the P (possibly through precipitation). The authors confirmed their hypothesis by demonstrating that removal of soil Ca by NaCl wash or addition of CER caused an increase in water extractable P. Although the results would be the same, it is possible that phosphate may have sorbed or co-precipitated to Ca that previously sorbed to the surface of the Fe and Al oxides rather than direct solution precipitation. Similarly, Amarasiri and Olsen [3] added Ca carbonate to an Oxisol to achieve soil pH 3.8 to 7 and added several levels of P after eight wet-dry cycles. Phosphorus sorption increased, likely due to the formation of Ca phosphate since the authors predicted the presence of hydroxyapatite based on plotting data on a double function solubility diagram. This phenomenon also explains the results of Riley and Barber [15], who adjusted soil pH from 5 to ~7.8 using Ca hydroxide and measured a decrease in P water solubility and P uptake with increasing pH.

2.4. Impact of Methodology: Time of Equilibration and P Extraction Solution

Time is a critical factor regarding the dynamics between different P sorption mechanisms that shift with pH. This is manifested in two ways, both of which can impact interpretation of experimental results: the amount of time allowed for equilibration after adjusting the pH, and the amount of time allowed after P is added. Each of the previously described P retention mechanisms require different amounts of time, including the reverse of the reactions. Experimentally, while pH may be changed immediately, the faster P removal and release mechanisms will dominate the overall impact of that pH change on P solubility. Sufficient equilibration time is required for understanding the true impact of pH on P solubility for individual soils. Faster reactions will dominate initially until a “pseudo-equilibrium” occurs. This is illustrated in the data from Penn and Bryant [74] shown in Figure 4. Two dairy-impacted soils (initial pH ~8) were gradually acidified with 0.5 M HCl to achieve a range in pH from 7.5 to 5.0, by adding one-eighth of the required acid to reach the target pH, per week. At the end of 8 weeks, the samples were tested for water extractable P, and then incubated for an additional 2 weeks with no further acid additions before measuring water extractable P a second time. Results in Figure 4 clearly show that the relationship between water extractable P and pH changed after allowing an additional 2 weeks for further equilibrium.

Prior to the additional 2-week equilibration period, the P solubility was determined to be a function of Ca phosphates, as partly evidenced by the similarity in shape to pure Ca phosphate minerals (Figure 2). Essentially, prior to equilibrium with other soil components P solubility was immediately controlled by Ca phosphate solubility, which increased in solubility with decreasing pH below 7.5; apparently this dissolution occurred relatively fast. Then with further time allowed for reaction of previously dissolved Ca phosphate with Al and Fe via ligand exchange, anion exchange, and precipitation, samples at pH <7.5 decreased in water extractable P. Regarding the balance between P sorption mechanisms at different pH, in this case the amount of potential sorption sites associated with Al and Fe was greater than the amount of Ca phosphate that dissolved. Without sufficient equilibration time, the results would have fallaciously indicated that acid pH levels impart maximum P solubility. For example, Murrmann and Peech [14] may not have allowed sufficient time for equilibration after pH adjustment. Consider that the authors found that minimum P water solubility coincided with the non-pH adjusted soils, which ranged from 4.48 to 6.30. Adjusting pH in either direction resulted in an increase in water extractable P, likely due to the fact that samples were only equilibrated for 48 h. A similar example is found in the studies of Gustafsson et al. [16] and Devau et al. [75], in which soils were only equilibrated for 144 and 84 h, respectively. Examples of soil pH changes in the rhizosphere that disrupt the equilibrium between non-labile and labile P fractions arising from the activities of microorganisms and plant roots were described by Hinsinger et al. [76].

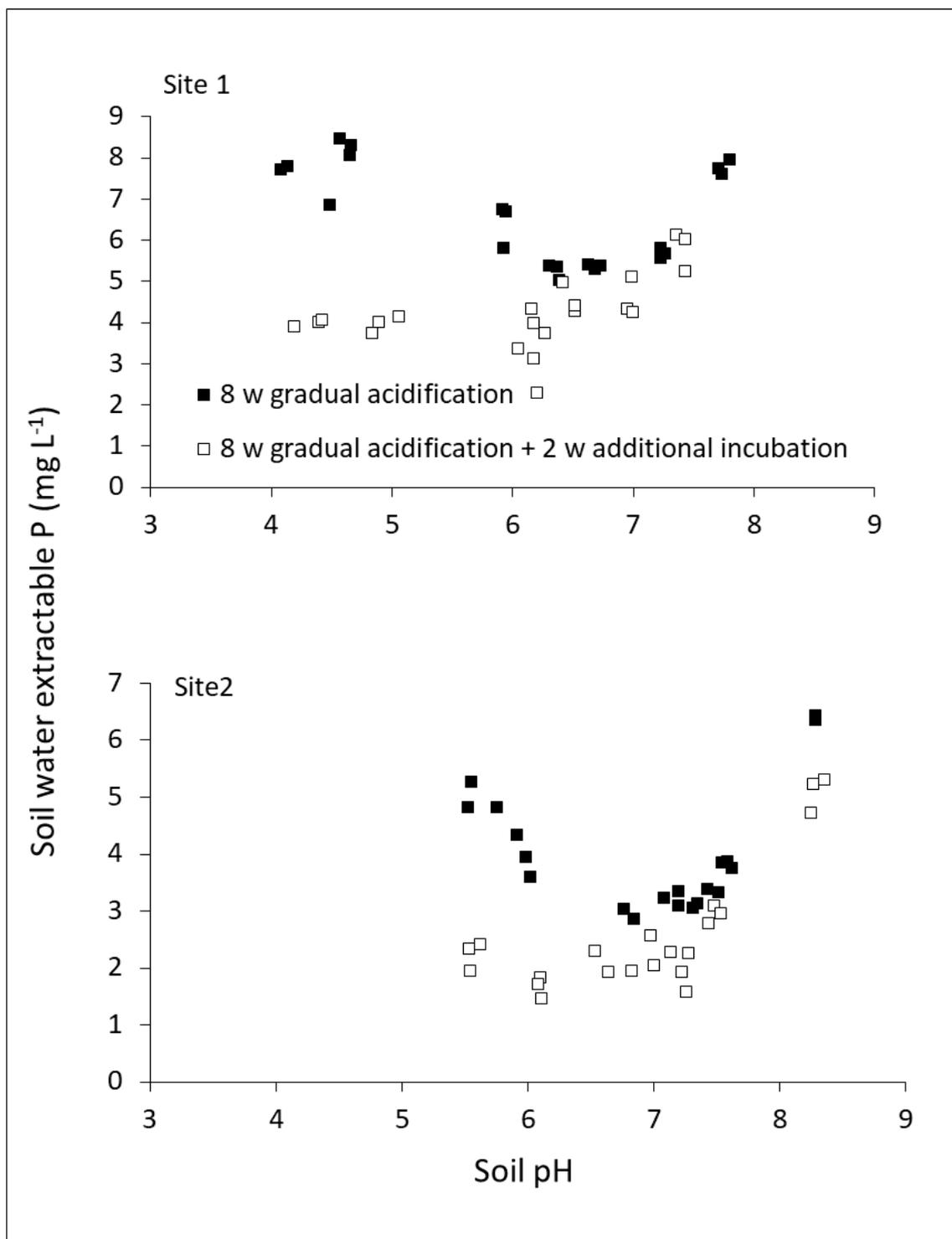


Figure 4. Relationship between soil pH and water extractable phosphorus (P) among soils gradually acidified for 8 weeks (8 w) compared to the same soils incubated for 2 further weeks (+2 w) without receiving any additional acidification. Soils at both sites were a Lindside silt loam. Adapted from Penn and Bryant [74].

Also regarding experimental technique, the method of extraction for water soluble P can have a significant impact on the observed impact of pH on P solubility. Specifically, 0.01 M CaCl₂ is often used as a soil nutrient extractant since the ionic strength of this solution is sometimes considered to be typical of the soil-solution environment. However, the addition of soluble Ca is likely to influence P

dynamics. For example, Riley and Barber [15] adjusted a Chalmers soil to pH 7 using Ca hydroxide, followed by acidification at several different levels to ~4.2 and subsequent extraction with 0.1 and 0.01 M CaCl₂ over 24 h. The authors found that use of the higher concentration of CaCl₂ decreased extraction of P, which could be a result of both ionic strength effects on surface charge/potential and Ca phosphate precipitation. Indeed, prediction of thermodynamic equilibrium for a simple system representing various P concentrations added to a 0.01 M CaCl₂ solution illustrates how favorable it is for Ca phosphate to precipitate (Figure 5).

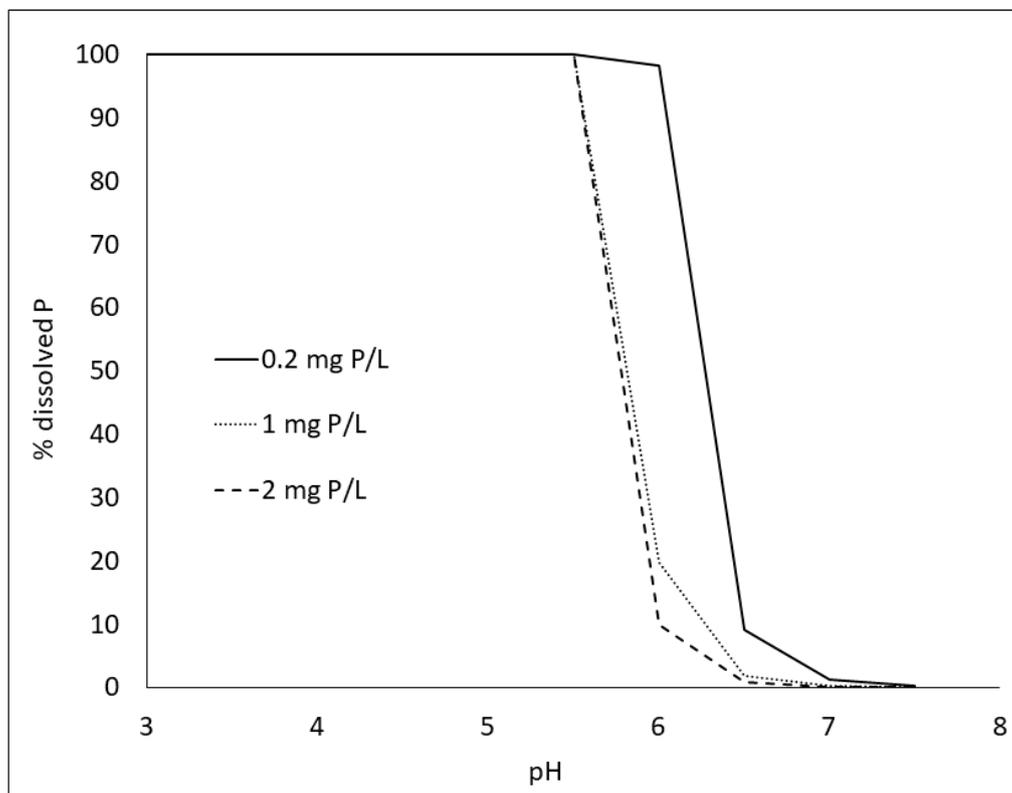


Figure 5. Percent dissolved phosphorus (P) as a function of pH, predicted with speciation modelling software (MINTEQA2; Allison et al. [77]) in a system containing 0.01 M CaCl₂ and varying concentrations of total P.

Racz and Soper [78] demonstrated formation of Ca phosphate through use of 0.01 M CaCl₂. Various studies have shown how use of CaCl₂ both increased P sorption and decreased P desorption from soils compared to de-ionized water [27,79–83].

2.5. Measuring P Uptake in Soil with Changing pH and the Interaction between Yield, Plant P Uptake, and Other Soil Properties Affected by pH

Even if the soil can supply sufficient P into solution for potential uptake by plant roots, one must be cautious in attributing changes in plant biomass and P uptake that occur with pH adjustments, to P availability. Since correlation does not necessarily equal causation, factors other than P solubility that are impacted by pH can strongly control the measured plant performance through either toxicity or deficiency. In addition, the mass of P uptake is confounded with biomass since biomass is used to calculate P uptake, and therefore anything that impacts biomass will also have an effect on calculated P uptake. Sumner and Farina [10] discuss this notion in detail, illustrating how crop response to P depends on interactions with other nutrients.

Similarly, consider that certain plants prefer acid conditions and their increased vigor at low pH will translate to greater P uptake, even if P solubility is lower compared to higher soil pH conditions.

Thus, the increased P uptake or vigor (i.e., apparent solubility) occurs in such plants despite reduced soil P solubility. An example is found in Barrow [84], for biomass of *Trifolium subterraneum* L. cultivars Yarloop and Mount Barker, which mostly decreased in biomass with increasing pH, but Wimmera ryegrass (*Lolium rigidum* Gaud.) increased. Certain plants such as Congo grass (*Brachiaria ruziziensis* Germ. & C.M. Evrard) have developed the ability to efficiently solubilize P that is normally “non-labile” under acid soil conditions where P is poorly soluble due to Al and Fe related P [85,86]. Osaki et al. [87] identified eight different plants that produced greater biomass in pH 4 solution cultures when Al was added, relative to when no Al was added. Several of these plants were also able to uptake a greater mass of P compared to the non-Al treatments. The authors attributed the ability of Al to stimulate P uptake to changes in metabolic energy. In a separate experiment where growth was evaluated at pH 3.5 to 5.5 with Al excluded, only three of the nine plants tested displayed an increase in biomass production with increasing pH.

Of course, plant P uptake is normally impacted by soil P solubility, but it is also important to consider the balance between biomass and P uptake. For example, Chen and Barber [88] reported maize maximum total dry weight, root length, and root surface area at pH 6.5, among soils adjusted from pH 3.8 to 8.3, even though maximum P uptake occurred at pH 4.7. None of these parameters (including P uptake) were statistically significantly different at pH 4.7 vs 6.5. Maximum P solubility occurred at pH 3.8, although P uptake and yield greatly suffered due to Al toxicity. Last, consider that not only was the soil allowed to equilibrate for only 10 days (d) after pH adjustment, maize was only grown for 18.5 d; therefore, soil P forms were still shifting and much of the P in the plant over that short time period could have arisen from the seed itself. Irrespective of whether conducted in soil or hydroponic solutions, studies intended to examine P availability to plants should involve growth for a time period long enough to begin to depend on P beyond that of the seed [89]. Seeds can contain relatively large amounts of P reserves that can mask the impact of treatments meant to affect soil P solubility and therefore P uptake. A case study by White and Veneklaas [90] examined the importance of seed P reserves among several different plants, including maize. The authors calculated that P reserves of high- and low-P maize seeds alone would produce maximum plant growth for 17.5 and 13.5 d, respectively.

3. Conclusions

Contrary to Barrow [2], the classic understanding of maximum P availability near pH 6.5 as described by Lindsay [47] and reported in many studies cited in this paper remains true today. At times, however, real exceptions to this rule of thumb may occur due to a shift in the balance between various P sorption mechanisms that are affected in different ways by pH, and partly dictated by soil properties. Due to existence of several different P retention mechanisms, it is incorrect to assume that only a single P retention mechanism is occurring, except perhaps for pure mineral systems. This dynamic interaction among mechanisms is further complicated through the use of Ca-rich minerals to increase soil pH. Other real exceptions can occur because certain plants simply thrive better under acid conditions, thereby exhibiting an increase in “apparent solubility” of P at low pH levels even though the soil P solubility in solution is depressed.

Occasionally, apparent exceptions occur simply due to methodology. Examples include allowing insufficient time for equilibration of soil components after pH adjustment before measuring response variables, use of CaCl₂ for measuring soluble P, and limiting the time in which plant growth and P uptake observations are taken, thereby preventing the soil P source from being influential. Regarding studies intended to examine impact of pH on plant P uptake and yield, caution should be exercised in interpretation of results since pH has a profound impact on many factors other than just soil P solubility.

Author Contributions: C.J.P.: conceptualization, formal analysis, investigation, writing—original draft preparation. J.J.C.: investigation, writing—review and editing.

Funding: This research was funded by the United States Department of Agriculture, Agriculture Research Service (USDA-ARS).

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

| | |
|-----|-----------------------------------|
| CEC | cation exchange capacity |
| K | thermodynamic solubility constant |
| PZC | point of zero charge |
| AER | anion exchange resin |
| CER | cation exchange resin |
| d | days |
| w | weeks |

References

- Price, G. *Australian Soil Fertility Manual*; Fertilizer Industry Federation of Australia, Inc. & CSIRO: Collingwood, Australia, 2006.
- Barrow, N.J. The effects of pH on phosphate uptake from the soil. *Plant Soil* **2017**, *410*, 401–410. [[CrossRef](#)]
- Amarasiri, S.L.; Olsen, S.R. Liming as Related to Solubility of P and Plant Growth in an Acid Tropical Soil. *Soil Sci. Soc. Am. J.* **1973**, *37*, 716–721. [[CrossRef](#)]
- MacLean, A.J.; Cook, R.L. The Effect of Soil Reaction on the Availability of Phosphorus for Alfalfa in Some Eastern Ontario Soils. *Soil Sci. Soc. Am. J.* **1955**, *19*, 311–314. [[CrossRef](#)]
- Paton, D.F.; Loneragan, J.F. An effect of lime of residual phosphorus in soil. *Aust. J. Agric. Res.* **1960**, *11*, 524–529. [[CrossRef](#)]
- Neller, J.R. Effect of Lime on Availability of Labeled Phosphorus of Phosphates in Rutlege Fine Sand and Marlboro and Carnegie Fine Sandy Loams. *Soil Sci.* **1953**, *75*, 103–108. [[CrossRef](#)]
- Ensminger, L.E.; Pearson, R.W. Residual Effects of Various Phosphates as Measured by Yields, P³² Uptake, and Extractable Phosphorus. *Soil Sci. Soc. Am. J.* **1957**, *21*, 80–84. [[CrossRef](#)]
- Shoop, G.J.; Brooks, C.R.; Blaser, R.E.; Thomas, G.W. Differential Responses of Grasses and Legumes to Liming and Phosphorus Fertilization. *Agron. J.* **1961**, *53*, 111–115. [[CrossRef](#)]
- Abruna, F.; Vicente-Chandler, J.; Pearson, R.W. Effects of Liming on Yields and Composition of Heavily Fertilized Grasses and on Soil Properties Under Humid Tropical Conditions. *Soil Sci. Soc. Am. J.* **1964**, *28*, 657–661. [[CrossRef](#)]
- Sumner, M.E.; Farina, M.P.W. Phosphorus interactions with other nutrients and lime in field cropping systems. In *Advances in Soil Science*; Springer: Heidelberg, Germany, 1986; pp. 201–236.
- Curtin, D.; Syers, J.K. Lime-induced changes in indices of soil phosphate availability. *Soil Sci. Soc. Am. J.* **2001**, *65*, 147–152. [[CrossRef](#)]
- MacKenzie, A.F. Inorganic soil phosphorus fractions of some Ontario soils as studied using isotopic exchange and solubility criteria. *Can. J. Soil Sci.* **1962**, *42*, 150–156. [[CrossRef](#)]
- Talibudeen, O. Isotopically exchangeable phosphorus in soils: Part II. Factors influencing the estimation of 'labile' phosphorus. *J. Soil Sci.* **1957**, *8*, 86–96. [[CrossRef](#)]
- Murmann, R.P.; Peech, M. Effect of pH on Labile and Soluble Phosphate in Soils. *Soil Sci. Soc. Am. J.* **1969**, *33*, 205–210. [[CrossRef](#)]
- Riley, D.; Barber, S.A. Effect of Ammonium and Nitrate Fertilization on Phosphorus Uptake as Related to Root-Induced pH Changes at the Root-Soil Interface. *Soil Sci. Soc. Am. J.* **1971**, *35*, 301–306. [[CrossRef](#)]
- Gustafsson, J.P.; Mwamila, L.B.; Kergoat, K. The pH dependence of phosphate sorption and desorption in Swedish agricultural soils. *Geoderma* **2012**, *189*, 304–311. [[CrossRef](#)]
- Curtin, D.; Syers, J.K.; Smillie, G.W. The importance of exchangeable cations and resin-sink characteristics in the release of soil phosphorus. *J. Soil Sci.* **1987**, *38*, 711–716. [[CrossRef](#)]
- Vaz, M.D.R.; Edwards, A.C.; Shand, C.A.; Cresser, M.S. Phosphorus fractions in soil solution: Influence of soil acidity and fertiliser additions. *Plant Soil* **1993**, *148*, 175–183.
- Hsu, P.H.; Rennie, D.A. Reactions of phosphate in aluminum systems.: I. adsorption of phosphate by "X-ray amorphous" aluminum hydroxide". *Can. J. Soil Sci.* **1962**, *42*, 197–209. [[CrossRef](#)]
- Scanlan, C.; Brennan, R.; Sarre, G.A. Effect of soil pH and crop sequence on the response of wheat (*Triticum aestivum*) to phosphorus fertiliser. *Crop Pasture Sci.* **2015**, *66*, 23–31. [[CrossRef](#)]

21. Von Tucher, S.; Hörndl, D.; Schmidhalter, U. Interaction of soil pH and phosphorus efficacy: Long-term effects of P fertilizer and lime applications on wheat, barley, and sugar beet. *Ambio* **2018**, *47*, 41–49. [[CrossRef](#)]
22. Murrmann, R.P.; Peech, M. Relative significance of labile and crystalline phosphates in soil. *Soil Sci.* **1969**, *107*, 249–255. [[CrossRef](#)]
23. Chen, C.R.; Sinaj, S.; Condron, L.M.; Frossard, E.; Sherlock, R.R.; Davis, M.R. Characterization of phosphorus availability in selected New Zealand grassland soils. *Nutr. Cycl. Agroecosyst.* **2003**, *65*, 89–100. [[CrossRef](#)]
24. De Smet, J.; Vanderdeelen, J.; Hofman, G. Effect of soil properties on the kinetics of phosphate release. *Commun. Soil Sci. Plant Anal.* **1998**, *29*, 2135–2147. [[CrossRef](#)]
25. Penn, C.J.; Rutter, E.B.; Arnall, D.B.; Camberato, J.; Williams, M.; Watkins, P. A discussion on mehlisch-3 phosphorus extraction from the perspective of governing chemical reactions and phases: Impact of soil pH. *Agriculture* **2018**, *8*, 106. [[CrossRef](#)]
26. Penn, C.; Bryant, R. Incubation of dried and sieved soils can induce calcium phosphate precipitation/adsorption. *Commun. Soil Sci. Plant Anal.* **2006**, *37*, 1437–1449. [[CrossRef](#)]
27. Pardo, M.T.; Guadalix, M.E.; Garcia-Gonzalez, M.T. Effect of pH and background electrolyte on P sorption by variable charge soils. *Geoderma* **1992**, *54*, 275–284. [[CrossRef](#)]
28. Xu, R.; Jiang, J.; Cheng, C. Effect of Ionic Strength on Specific Adsorption of Ions by Variable Charge Soils: Experimental Testification on the Adsorption Model of Bowden et al. In *Molecular Environmental Soil Science at the Interfaces in the Earth's Critical Zone*; Springer: Heidelberg, Germany, 2010; pp. 78–80.
29. Bolan, N.S.; Syers, J.K.; Tillman, R.W. Ionic strength effects on surface charge and adsorption of phosphate and sulphate by soils. *J. Soil Sci.* **1986**, *37*, 379–388. [[CrossRef](#)]
30. Darch, T.; Blackwell, M.S.A.; Hawkins, J.M.B.; Haygarth, P.M.; Chadwick, D. A meta-analysis of organic and inorganic phosphorus in organic fertilizers, soils, and water: Implications for water quality. *Crit. Rev. Environ. Sci. Technol.* **2014**, *44*, 2172–2202. [[CrossRef](#)]
31. Vange, M.S.; Holmern, K.; Nissen, P.E.R. Multiphasic uptake of sulfate by barley roots I. Effects of analogues, phosphate, and pH. *Physiol. Plant.* **1974**, *31*, 292–301. [[CrossRef](#)]
32. Sentenac, H.; Grignon, C. Effect of pH on orthophosphate uptake by corn roots. *Plant Physiol.* **1985**, *77*, 136–141. [[CrossRef](#)]
33. McDowell, R.W.; Sharpely, A.N. Phosphorus solubility and release kinetics as a function of soil test P concentration. *Geoderma* **2003**, *112*, 143–154. [[CrossRef](#)]
34. Coleman, N.T.; Thorup, J.T.; Jackson, W.A. Phosphate-sorption Reactions That Involve Exchangeable A1. *Soil Sci.* **1960**, *90*, 1–7. [[CrossRef](#)]
35. Guedes, R.S.; Melo, L.C.A.; Vergütz, L.; Rodríguez-Vila, A.; Covelo, E.F.; Fernandes, A.R. Adsorption and desorption kinetics and phosphorus hysteresis in highly weathered soil by stirred flow chamber experiments. *Soil Tillage Res.* **2016**, *162*, 46–54. [[CrossRef](#)]
36. McDowell, R.W.; Condron, L.M.; Mahieu, N.; Brookes, P.C.; Poulton, P.R.; Sharpely, A.N. Analysis of potentially mobile phosphorus in arable soils using solid state nuclear magnetic resonance. *J. Environ. Qual.* **2002**, *31*, 450–456. [[CrossRef](#)]
37. Hunger, S.; Sims, J.T.; Sparks, D.L. How accurate is the assessment of phosphorus pools in poultry litter by sequential extraction? *J. Environ. Qual.* **2005**, *34*, 382–389. [[CrossRef](#)]
38. Prietzel, J.; Dümig, A.; Wu, Y.; Zhou, J.; Klysubun, W. Synchrotron-based P K-edge XANES spectroscopy reveals rapid changes of phosphorus speciation in the topsoil of two glacier foreland chronosequences. *Geochim. Cosmochim. Acta* **2013**, *108*, 154–171. [[CrossRef](#)]
39. Beauchemin, S.; Hesterberg, D.; Chou, J.; Beauchemin, M.; Simard, R.R.; Sayers, D.E. Speciation of phosphorus in phosphorus-enriched agricultural soils using X-ray absorption near-edge structure spectroscopy and chemical fractionation. *J. Environ. Qual.* **2003**, *32*, 1809–1819. [[CrossRef](#)]
40. Sato, S.; Solomon, D.; Hyland, C.; Ketterings, Q.M.; Lehmann, J. Phosphorus speciation in manure and manure-amended soils using XANES spectroscopy. *Environ. Sci. Technol.* **2005**, *39*, 7485–7491. [[CrossRef](#)]
41. Ler, A.; Stanforth, R. Evidence for surface precipitation of phosphate on goethite. *Environ. Sci. Technol.* **2003**, *37*, 2694–2700. [[CrossRef](#)]
42. Kim, Y.; Kirkpatrick, R.J. An investigation of phosphate adsorbed on aluminium oxyhydroxide and oxide phases by nuclear magnetic resonance. *Eur. J. Soil Sci.* **2004**, *55*, 243–251. [[CrossRef](#)]
43. Kittrick, J.A.; Jackson, M.L. Rate of Phosphate Reaction with Soil Minerals and Electron Microscope Observations on the Reaction Mechanism. *Soil Sci. Soc. Am. J.* **1955**, *19*, 292–295. [[CrossRef](#)]

44. Barrow, N.J.; Ellis, A.S. Testing a mechanistic model. V. The points of zero salt effect for phosphate retention, for zinc retention and for acid/alkali titration of a soil. *J. Soil Sci.* **1986**, *37*, 303–310. [[CrossRef](#)]
45. Barrow, N.J.; Debnath, A. Effect of phosphate status on the sorption and desorption properties of some soils of northern India. *Plant Soil* **2014**, *378*, 383–395. [[CrossRef](#)]
46. Strauss, R.; Brümmer, G.W.; Barrow, N.J. Effects of crystallinity of goethite: II. Rates of sorption and desorption of phosphate. *Eur. J. Soil Sci.* **1997**, *48*, 101–114. [[CrossRef](#)]
47. Lindsay, W.L. *Chemical Equilibria in Soils*; John Wiley and Sons Ltd.: Hoboken, NJ, USA, 1979; ISBN 0471027049.
48. Essington, M.E. *Soil and Water Chemistry: An Integrative Approach*, 2nd ed.; Routledge: Abingdon, UK, 2015; ISBN 9781466573154.
49. Haseman, J.F.; Brown, E.H.; Whitt, C.D. Some reactions of phosphate with clays and hydrous oxides of iron and aluminum. *Soil Sci.* **1950**, *70*, 257–272. [[CrossRef](#)]
50. Huffman, E.O. *Reactions of Phosphate in Soils: Recent Research by TVA*; Fertiliser Society: Colchester, UK, 1962.
51. Lindsay, W.L.; Stephenson, H.F. Nature of the Reactions of Monocalcium Phosphate Monohydrate in Soils: II. Dissolution and Precipitation Reactions Involving Iron, Aluminum, Manganese, and Calcium. *Soil Sci. Soc. Am. J.* **1959**, *23*, 18–22. [[CrossRef](#)]
52. Lindsay, W.L.; Lehr, J.R.; Stephenson, H.F. Nature of the Reactions of Monocalcium Phosphate Monohydrate in Soils: III. Studies with Metastable Triple-Point Solution. *Soil Sci. Soc. Am. J.* **1959**, *23*, 342–345. [[CrossRef](#)]
53. Eriksson, A.K.; Gustafsson, J.P.; Hesterberg, D. Phosphorus speciation of clay fractions from long-term fertility experiments in Sweden. *Geoderma* **2015**, *241*, 68–74. [[CrossRef](#)]
54. Luo, L.; Ma, Y.; Sanders, R.L.; Xu, C.; Li, J.; Myneni, S.C.B. Phosphorus speciation and transformation in long-term fertilized soil: Evidence from chemical fractionation and P K-edge XANES spectroscopy. *Nutr. Cycl. Agroecosyst.* **2017**, *107*, 215–226. [[CrossRef](#)]
55. McBride, M.B. *Environmental Soil Chemistry*; Elsevier: Amsterdam, Netherlands, 1994.
56. Zelazny, L.W.; He, L.; Vanwormhoudt, A.N. Charge analysis of soils and anion exchange. In *Methods of Soil Analysis Part 3—Chemical Methods*; Sparks, D.L., et al., Eds.; SSSA, ASA: Madison, WI, USA, 1996; pp. 1231–1253.
57. Sparks, D.L. *Environmental Soil Chemistry*; Elsevier: Amsterdam, The Netherlands, 2003; ISBN 0080494803.
58. Hingston, F.J. A review of anion adsorption. In *Adsorption Inorganic Solid Liquids Interfaces*; Ann Arbor Science: Ann Arbor, MI, USA, 1981; pp. 51–90.
59. He, L.M.; Zelazny, L.W.; Martens, D.C.; Baligar, V.C.; Ritchey, K.D. Ionic strength effects on sulfate and phosphate adsorption on γ -alumina and kaolinite: Triple-layer model. *Soil Sci. Soc. Am. J.* **1997**, *61*, 784–793. [[CrossRef](#)]
60. Penn, C.J.; Warren, J.G. Investigating phosphorus sorption onto kaolinite using isothermal titration calorimetry. *Soil Sci. Soc. Am. J.* **2009**, *73*, 560–568. [[CrossRef](#)]
61. Penn, C.J.; Zhang, H. Isothermal titration calorimetry as an indicator of phosphorus sorption behavior. *Soil Sci. Soc. Am. J.* **2010**, *74*, 502–511. [[CrossRef](#)]
62. Barrow, N.J. A mechanistic model for describing the sorption and desorption of phosphate by soil. *J. Soil Sci.* **1983**, *34*, 733–750. [[CrossRef](#)]
63. Sample, E.C.; Soper, R.J.; Racz, G.J. Reactions of phosphate fertilizers in soils. In *Role of Phosphorus in Agriculture*; Khasawneh, F.E., et al., Eds.; SSSA: Madison, WI, USA, 1980; pp. 263–310.
64. Kittrick, J.A.; Jackson, M.L. Electron-microscope observations of the reaction of phosphate with minerals, leading to a unified theory of phosphate fixation in soils. *J. Soil Sci.* **1956**, *7*, 81–89. [[CrossRef](#)]
65. Van Riemsdijk, W.H.; Lyklema, J. Reaction of phosphate with gibbsite (Al (OH)₃) beyond the adsorption maximum. *J. Colloid Interface Sci.* **1980**, *76*, 55–66. [[CrossRef](#)]
66. Chen, Y.S.R.; Butler, J.N.; Stumm, W. Kinetic study of phosphate reaction with aluminum oxide and kaolinite. *Environ. Sci. Technol.* **1973**, *7*, 327–332. [[CrossRef](#)]
67. Lindsay, W.L.; Frazier, A.W.; Stephenson, H.F. Identification of reaction products from phosphate fertilizers in soils. *Soil Sci. Soc. Am. J.* **1962**, *26*, 446–452. [[CrossRef](#)]
68. Philen, O.D.; Lehr, J.R. Reactions of Ammonium Polyphosphates with Soil Minerals. *Soil Sci. Soc. Am. J.* **1967**, *31*, 196–199. [[CrossRef](#)]
69. Hashimoto, I.; Hughes, J.D.; Philen, O.D. Reactions of Triammonium Pyrophosphate with Soils and Soil Minerals. *Soil Sci. Soc. Am. J.* **1969**, *33*, 401–405. [[CrossRef](#)]

70. Low, P.F.; Black, C.A. Phosphate-Induced Decomposition of Kaolinite. *Soil Sci. Soc. Am. J.* **1948**, *12*, 180–184. [[CrossRef](#)]
71. Robarge, W.P.; Corey, R.B. Adsorption of phosphate by hydroxy-aluminum species on a cation exchange resin. *Soil Sci. Soc. Am. J.* **1979**, *43*, 481–487. [[CrossRef](#)]
72. Hsu, P.H.; Rennie, D.A. Reactions of phosphate in aluminum systems: II. Precipitation of phosphate by exchangeable aluminum on a cation exchange resin. *Can. J. Soil Sci.* **1962**, *42*, 210–221. [[CrossRef](#)]
73. Woodruff, J.R.; Kamprath, E.J. Phosphorus Adsorption Maximum as Measured by the Langmuir Isotherm and Its Relationship to Phosphorus Availability. *Soil Sci. Soc. Am. J.* **1965**, *29*, 148–150. [[CrossRef](#)]
74. Penn, C.J.; Bryant, R.B. Phosphorus solubility in response to acidification of dairy manure amended soils. *Soil Sci. Soc. Am. J.* **2008**, *72*, 238–243. [[CrossRef](#)]
75. Devau, N.; Hinsinger, P.; Le Cadre, E.; Colomb, B.; Gérard, F. Fertilization and pH effects on processes and mechanisms controlling dissolved inorganic phosphorus in soils. *Geochim. Cosmochim. Acta* **2011**, *75*, 2980–2996. [[CrossRef](#)]
76. Hinsinger, P.; Herrmann, L.; Lesueur, D.; Robin, A.; Trap, J.; Waithaisong, K.; Plassard, C. Impact of roots, microorganisms and microfauna on the fate of soil phosphorus in the rhizosphere. *Annu. Plant Rev. Online* **2018**, *48*, 377–407.
77. Allison, J.D.; Brown, D.S.; Novo-Gradac, K.J. *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual*; Environmental Research Laboratory, Office of Research and Development, US Environmental Protection Agency: Washington, DC, USA, 1991.
78. Racz, G.J.; Soper, R.J. Solubility of dimagnesium phosphate trihydrate and trimagnesium phosphate. *Can. J. Soil Sci.* **1968**, *48*, 265–269. [[CrossRef](#)]
79. Fuhrman, J.K.; Zhang, H.; Schroder, J.L.; Davis, R.L.; Payton, M.E. Water-Soluble Phosphorus as Affected by Soil to Extractant Ratios, Extraction Times, and Electrolyte. *Commun. Soil Sci. Plant Anal.* **2005**, *36*, 925–935. [[CrossRef](#)]
80. Eriksson, A.K.; Ulén, B.; Berzina, L.; Iital, A.; Janssons, V.; Sileika, A.S.; Toomsoo, A. Phosphorus in agricultural soils around the Baltic Sea—comparison of laboratory methods as indices for phosphorus leaching to waters. *Soil Use Manag.* **2013**, *29*, 5–14. [[CrossRef](#)]
81. Ryden, J.C.; Syers, J.K. Rationalization of ionic strength and cation effects on phosphate sorption by soils. *J. Soil Sci.* **1975**, *26*, 395–406. [[CrossRef](#)]
82. Ryden, J.C.; Syers, J.K. Calcium Retention in Response to Phosphate Sorption by Soils. *Soil Sci. Soc. Am. J.* **1976**, *40*, 845–846. [[CrossRef](#)]
83. Kuo, S. Phosphorus. In *Methods of Soil Analysis Part 3; Chemical Methods*; SSSA Book Series 5; Sparks, D.L., et al., Eds.; SSSA, ASA: Madison, WI, USA, 1996; pp. 869–919.
84. Barrow, N.J. Further investigations on the use of lime on established pastures. *Aust. J. Exp. Agric.* **1965**, *5*, 442–449. [[CrossRef](#)]
85. Merlin, A.; Rosolem, C.A.; He, Z. Non-labile phosphorus acquisition by *Brachiaria*. *J. Plant Nutr.* **2016**, *39*, 1319–1327. [[CrossRef](#)]
86. Almeida, D.S.; Penn, C.J.; Rosolem, C.A. Assessment of phosphorus availability in soil cultivated with ruzigrass. *Geoderma* **2018**, *312*, 64–73. [[CrossRef](#)]
87. Osaki, M.; Watanabe, T.; Tadano, T. Beneficial effect of aluminum on growth of plants adapted to low pH soils. *Soil Sci. Plant Nutr.* **1997**, *43*, 551–563. [[CrossRef](#)]
88. Chen, J.-H.; Barber, S.A. Soil pH and phosphorus and potassium uptake by maize evaluated with an uptake model. *Soil Sci. Soc. Am. J.* **1990**, *54*, 1032–1036. [[CrossRef](#)]
89. Nadeem, M.; Mollier, A.; Morel, C.; Vives, A.; Prud'homme, L.; Pellerin, S. Relative contribution of seed phosphorus reserves and exogenous phosphorus uptake to maize (*Zea mays* L.) nutrition during early growth stages. *Plant Soil* **2011**, *346*, 231–244. [[CrossRef](#)]
90. White, P.J.; Veneklaas, E.J. Nature and nurture: The importance of seed phosphorus content. *Plant Soil* **2012**, *357*, 1–8. [[CrossRef](#)]

