Review of Phosphite as a Plant Nutrient and Fungicide

John L. Havlin 1,* and Alan J. Schlegel 2

1 Department of Crop & Soil Science, North Carolina State University, Raleigh, NC 27695, USA
2 Southwest Research-Extension Center, Kansas State University, Tribune, KS 67879, USA; schlegel@ksu.edu

* Correspondence: jlhavlin@ncsu.edu

Abstract: Phosphite (Phi)-containing products are marketed for their antifungal and nutritional value. Substantial evidence of the anti-fungal properties of Phi on a wide variety of plants has been documented. Although Phi is readily absorbed by plant leaves and/or roots, the plant response to Phi used as a phosphorus (P) source is variable. Negative effects of Phi on plant growth are commonly observed under P deficiency compared to near adequate plant P levels. Positive responses to Phi may be attributed to some level of fungal disease control. While only a few studies have provided evidence of Phi oxidation through cellular enzymes genetically controlled in plant cells, increasing evidence exists for the potential to manipulate plant genes to enhance oxidation of Phi to phosphate (Pi) in plants. Advances in genetic engineering to sustain growth and yield with Phi + Pi potentially provides a dual fertilization and weed control system. Further advances in genetic manipulation of plants to utilize Phi are warranted. Since Phi oxidation occurs slowly in soils, additional information is needed to characterize Phi oxidation kinetics under variable soil and environmental conditions.

Keywords: phosphorus; phosphite; plant disease; plant nutrition; genetics; soil chemistry

1. Introduction

Although phosphate (Pi) fertilizers are initially soluble in soils, \( H_2PO_4^- / HPO_4^{2-} \)-adsorption and precipitation reactions can substantially reduce their availability to and recovery by crops. Reduced phosphorus (P) compounds containing phosphate (Phi) have been investigated since the 1930s as potential sources to meet P requirements of crops [1,2]. Because these early results demonstrated that \( H_2PO_3^- / HPO_3^{2-} \) oxidation to plant available \( Pi \) was a slow process, few reduced P products were developed. Interest in the use of reduced P compounds in agriculture increased in the 1970s when it was shown that Phi compounds exhibited antifungal properties particularly with Oomycetes fungi [3]. Over the last several decades, Phi-based fungicide products were widely integrated into agricultural plant disease management programs. Because of significantly less complex and costly approval processes required for fertilizers compared to fungicides, many Phi-based products are often labeled as biostimulants or fertilizers, while they still maintain activity in suppressing fungal diseases [4]. A number of recent studies have indicated phytotoxicity related yield losses with Phi-based products. The purpose of this review is to summarize the pertinent scientific literature related to the use of Phi as a nutrient and/or fungicide source in plant production. As fertilizer industry marketing materials increasingly support Phi as a potential P source, this review provides a comprehensive summary of the Phi/Pi chemistry and reaction in soil, metabolism in plants, and use as a nutrient and fungicide source. Several research needs are suggested to enhance the future potential of Phi as a plant nutrient source.

2. Reduced Phosphorus Chemistry in Soil

Phosphorus occurs in seven oxidation states including phosphate (+5), phosphite (+3), hypophosphite (+1), elemental phosphorus (0), tetraphosphide (−0.5), diphosphide (−2), and phosphide (−3). Reduced P species represent any of the above with <+5 oxidation...
state. Phosphate \((H_2PO_4^-, HPO_4^{2-})\) is widely distributed in the biosphere, hydrosphere, and lithosphere and is an essential nutrient in diverse organisms. Only a few reduced P forms exist in nature (Table 1).

Phosphate \((H_2PO_3^-; HPO_4^{2-})\) represents the inorganic salt of phosphorous acid \((H_3PO_3)\). In phosphite, the P atom is in the +3 oxidation state, compared to +5 in phosphate, where an oxygen \((O)\) atom has been replaced by a non-ionizable hydrogen \((H)\) atom (Figure 1). When an “H” in phosphate, phosphite, or hypophosphite is replaced with carbon \((C)\), the species are termed phosphate ester, phosphonate, or phosphinate, respectively. All three species occur in organic matter and living organisms. Although relatively rare, phosphides are naturally occurring in the earth under highly reduced conditions [5,6]. Phosphine \((H_3P)\) can be emitted as an atmospheric trace gas under anaerobic conditions common in waste sludge and manure, reduced sediments and soils, and landfills [7]. Thus, \(H_3P\) is formed naturally during the anaerobic decomposition of organic matter, and subsequent adsorption to mineral surfaces can reduce its release to the atmosphere. It is likely that organisms with the ability to utilize reduced P may be at an ecological advantage in “O” limiting conditions. Excellent reviews of reduced phosphorus compounds and reactions in soils and sediments include Pasek [8], Morton and Edwards [9], Hanrahan [5], and Lindsay [10].

![Figure 1. Structural differences between phosphate ester and phosphonate/phosphinate species. The ester contains P-O-C and the reduced phosphorus species contain P-C, where “R” represents a carbon chain of variable structures.](image)

### Table 1. Common phosphorus compounds and ions in the environment.

| Phosphorus Form \(^1\) | Chemical Formula | Redox State \(^2\) | Dissociation Reaction (in \(H_2O\)) | \(K_a\) \(^3\) |
|------------------------|-----------------|-----------------|-----------------------------------|--------|
| phosphoric acid        | \(H_3PO_4\)     |                 | \(H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+\) | \(10^{-2.15}\) |
| phosphate              | \(H_2PO_4^-, HPO_4^{2-}\) | +5              | \(H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+\) | \(10^{-7.2}\) |
|                        |                 |                 | \(HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+\) | \(10^{-12.35}\) |
| phosphorous acid       | \(H_3PO_3\)     | +3              | \(H_3PO_3 \rightleftharpoons H_2PO_3^- + H^+\) | \(10^{-1.5}\) |
| phosphite (phosphonate)| \(H_3PO_3^-\), \(HPO_4^{2-}\) |                 | \(H_2PO_3^- \rightleftharpoons HPO_4^{2-} + H^+\) | \(10^{-6.79}\) |
| hypophosphorous acid   | \(H_3PO_2\)     | +1              | \(H_3PO_2 \rightleftharpoons H_2PO_2^- + H^+\) | \(10^{-1.1}\) |
| hypophosphite (phosphinate) | \(H_2PO_2^-\) |                 |                                   |        |
| phosphine              | \(H_3P\)        | −3              |                                   |        |
| phosphonium            | \(H_4P^+\)      |                 |                                   |        |

\(^1\) P-C species in parentheses; \(^2\) P oxidation state; \(^3\) dissociation constant [10].
Although similarities between the two molecules (\textit{Phi} and \textit{Pi}) cause confusion in understanding how each reacts in the plant, differences in oxidation state, size, and charge suggest that \textit{Phi} does not substitute for \textit{Pi} in the majority of biochemical reactions. McDonald [11] provides an excellent description of how the structural differences between \textit{Phi} and \textit{Pi} strongly influence their binding to the surface of enzymes specific to \textit{Pi} metabolism. While both \textit{Pi} and \textit{Phi} have a tetrahedral coordinated structure (Figure 1), \textit{Pi} is symmetrical, resulting in a uniform charge distribution in the ion. In contrast, the asymmetry related to the P-H bond in \textit{Phi} results in a non-uniform or slightly polar charge distribution. With \textit{Pi}, each side of the tetrahedron has an equal chance of binding to an enzyme surface, where the remaining “O” atom protrudes from the enzyme surface. In \textit{Phi}, only one side of the tetrahedron can bind with the enzyme surface, with the remaining “H” exposed. Apparently, this difference between \textit{Pi} and \textit{Phi} interaction with the enzyme surface prevents \textit{Phi} from participating in the same enzyme activated reactions associated with \textit{Pi} metabolism.

The effect of solution pH on the relative concentrations of \textit{Pi} and \textit{Phi} ions in solution is determined by their aqueous dissociation constant (Ka) (Table 1). With \textit{Pi}, for example, the common species in soil solution over the normal pH range of 3 to 10 are $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$ (Figure 2). With a Ka of $10^{-7.2}$, concentration of $\text{H}_2\text{PO}_4^-$ = $\text{HPO}_4^{2-}$ at pH 7.2 [10]. Below pH 7.2, $\text{H}_2\text{PO}_4^-$ is the dominant anion in solution, whereas above pH 7.2, $\text{HPO}_4^{2-}$ is the dominant species. This is not a particularly important distinction, since plants readily absorb either \textit{Pi} form. In the soil pH range of 3 to 10, $\text{H}_2\text{PO}_4$ and $\text{PO}_4^{3-}$ would not exist. Similar relationships can be developed for \textit{Phi} (Figure 3). In this case, $\text{H}_2\text{PO}_3^-$ = $\text{HPO}_3^{2-}$ at pH 6.8, and $\text{H}_3\text{PO}_3$ would not exist under the normal soil pH range of 3 to 10.

![Figure 2](image_url)

**Figure 2.** Distribution of phosphate species in water as influenced by pH. Shaded area represents normal range in soil pH.
Figure 3. Distribution of phosphite species in water as influenced by pH. Shaded area represents normal range in soil pH.

Under typical pH (3–10) and redox (≥−600 mV) conditions on the Earth surface, the most stable P species should be Pi (Figure 4). The redox potential of Phi oxidation to Pi is approximately −690 mV [12]. Therefore, reduced P should not exist in soil. However, reduced P species have been measured, where Phi and hypophosphite maintain some stability under aerobic conditions [8,13–15]. Figure 4 illustrates that under extreme anaerobic and acidic aquatic environments (e.g., acid mine spoil drainage) H₃PO₃ is potentially stable. Although chemical thermodynamic considerations predict that reduced P species would not be stable, redox kinetics is not considered. Likely, oxidation of reduced P species is slow, allowing them to exist and be measured.

Figure 4. Influence of pH and oxidation (Eh) on Phi and Pi species in solution. Area in white represents current atmospheric conditions, red represents reduced conditions, and blue is highly oxidized (not common under normal atmospheric conditions).

Although Phi is more soluble than Pi, Phi is thermodynamically unstable or reactive, but kinetically stable. The rate-limiting step in Phi oxidation is the P–H bond (Figure 1),
which requires ~370 kJ to break. Thus, Phi is stable under mildly reducing conditions that remove oxidants from solution (Figure 4). As stated earlier, oxidation of Phi to Pi is a relatively slow process [1,2]. Unfortunately, few studies document the influence of soil properties or conditions on Phi oxidation kinetics. Research on Phi fate and transport and the influence of variable electron acceptors that facilitate Phi oxidation in soils is needed.

Since P is an integral component of soil organic matter, transformations of mineral P in parent materials to inorganic and organic soil P dominantly involves Pi; however, Phi is also involved depending on soil environmental conditions. In a review of organic P compounds in soils, organic P is dominantly comprised of Pi-based compounds (phosphate esters), although Phi-based compounds generally comprised ~ 2% of total P [16]. Cade-Menun [17] reported Phi-based compounds (phosphonates) commonly accumulated in wet, cold, or acidic soils with few phosphonate enzymes.

Although Phi compounds have been used as agricultural fungicides for several decades, and Phi residues are more soluble in soils than Pi, concerns regarding water quality have not surfaced. However, since Phi was traditionally regarded as metabolically inert in animal and plant systems [3], Phi residues in soil can affect metabolism of soil microflora, and these effects are very detrimental to their growth under low-Pi conditions [11].

Chemical extraction methods are commonly used to quantify inorganic and organic P concentrations in soil [18]. As described above, the dominant P fractions contributing to plant available P in agricultural soils are Pi-based. Inorganic and organic Phi represents a relatively small fraction of total P [16]. While P fractionation methods are widely used to segregate P reserves into estimates of relative P availability [19], the contribution of individual fractions to plant P uptake is difficult to quantify. Common soil test methods used to extract soluble and readily available P fractions are well established and are correlated with crop response to applied P, crop P removal, and provide the basis for fertilizer and waste P recommendations [20]. Therefore, the primary driver to replenish solution P from labile and non-labile P is the soil’s P status as measured by accepted soil test extraction, which represents P lability (availability) and bioavailability.

3. Microbial Oxidation of Phi to Pi

Oxidation of Phi to Pi is mediated by soil microorganisms, especially when Pi is limiting. Adams and Conrad [21] were one of the first to study microbial oxidation of Phi, concluding that Phi oxidation only occurred when bacteria were present; Phi was preferentially incorporated by the bacteria (Phi absorbed after Pi was depleted); and the oxidation process was intracellular. In addition, Phi was metabolized by a variety of microorganisms (e.g., bacteria, fungi, and actinomycetes). Again, when Phi and Pi are included in the substrate, microbes preferentially used Pi until depleted, then utilized Phi. Similarly, Casida [22] showed that Pseudomonas fluorescens 195 oxidized Phi with subsequent Pi transport out of the cell. The rate (half-life) of microbial oxidation of Phi was reported to be ~15 weeks [23]. In contrast, Loera-Quezada [24] reported several species of microalgae (C. reinhardtii, B. braunii, E. oleabundans) were unable to oxidize Phi to Pi and utilize Phi as a sole P source. Although growth of C. reinhardtii was inhibited by Phi, transfer to Pi restored normal growth, demonstrating Phi is not toxic to microalgae.

Bezuidenhout [25] and Ohtake [26] reported that Phi may be microbially oxidized within plant tissues. They isolated entophytic bacteria (e.g., alcaligenes, pseudomonas, and serratia) capable of in vitro oxidation of Phi in avocado root and leaves. Although most suggest Phi is fairly persistent within the plant due to limited capacity to oxidize Phi to Pi, few studies provide careful analysis of the Phi → Pi transformation kinetics following application and absorption in the plant. Other researchers have also studied bacterial oxidation of Phi in soil [9,27,28].

Since the Phi to Pi oxidation rate will be influenced by soil chemical conditions (e.g., pH, redox potential, soil water content, soil organic matter content, etc.), observations of plant responses to soil applied Phi are likely related to conditions favorable to increased
reaction kinetics of Phi to Pi oxidation [29]. Since Phi is more soluble and less reactive with charged surfaces in soils, increased Phi transport in gravitational water could increase Phi access by deeper roots, which may increase total P uptake. If Phi adsorption potential is less than Pi, then reduced P fixation may explain improved growth on Phi-treated soils, following the normal delay associated with microbial oxidation.

In most cases, organisms were able to oxidize Phi or hypophosphate under aerobic and anaerobic conditions. Evidence from *Pseudomonas stutzeri* WM88 suggests that hypophosphate is oxidized to Phi, then to Pi [28]. In addition, anaerobic bacteria *Bacillus* and *Pseudomonas stutzeri* can oxidize Phi under denitrifying conditions [30,31]. Costas [32] were the first to identify a specific enzyme phosphite dehydrogenase that catalyzes Phi oxidation by *Pseudomonas stutzeri* WM88. Phosphite dehydrogenase enables microbial growth using Phi as the sole P source, where the enzyme catalyzes oxidation of Phi to Pi with the concurrent reduction of NAD\(^+\) to NADH [33].

In addition, *Desulfotignum phosphitoxidans* was isolated from marine environments that coupled anaerobic oxidation of Phi with reduction of sulfate (SO\(^4\)) to hydrogen sulfide (H\(_2\)S) [34]. Other bacteria including *agrobacterium tumafaciens*, *bacillus caldolyticus*, *escherichia coli*, *erratia marcescens*, and numerous *pseudomonas* species (aeruginosa, fluorescens, and stutzeri) are capable of oxidizing Phi or hypophosphate [5]. Recently, Simeonova [35] identified specific genes involved in Phi uptake and oxidation by these and other bacteria. Clearly, diverse microorganisms are capable of metabolizing reduced P species such that these compounds may be important to P cycling in terrestrial ecosystems [12,36].

Specific pathways for metabolic oxidation of Phi have been recently described. In *Escherichia coli* and *Pseudomonas stutzeri*, P-C lyase and alkaline phosphatase enzymes hydrolyze Phi and phosphate esters [37–39]. In *Pseudomonas stutzeri*, Phi is also oxidized through Phi:NAD\(^+\) oxidoreductase [32,40]. Potential mechanisms for enzyme mediated oxidation of Phi in soils have been suggested by Figueroa and Coates [41] and White and Metcalf [40]. Similarly, Yang and Metcalf [39] documented that bacterial alkaline phosphatase enzyme in *Escherichia coli* can oxidize Phi in vivo and in vitro using only water as the electron acceptor.

Phosphate solubilizing microorganisms (PSMs) represent microflora important to organic P mineralization, solubilizing inorganic P minerals, and storing large amounts of P in microbial biomass. Rawat et al. [42] documented the diversity in PSMs in soil including over 40 bacteria, cyanobacteria, and actinomycetes and 15 fungi including several vesicular arbuscular mycorrhizae. PSMs exude phosphatase enzymes, chelates, and organic acids, with a concomitant decrease in soil pH to solubilize (oxidize) soil P into plant available Pi. One class of enzymes exuded are phosphonatas/ Carbon–Phosphorus (C–P) lyases, which catalyze cleavage of the C–P bond of Phi and conversion to Pi [43,44], although the activity of C–P lyases is generally lower than PSMs for Pi. While the mechanisms behind P solubilization by PSM are relatively well documented in vitro [44,45], less is known about potential PSM mediated oxidation of Phi to Pi. Raymond [46] provided an alternative perspective that although PSMs dominantly have the capacity to solubilize P to meet their own needs, it is the turnover of the microbial biomass that subsequently provides Pi to plants over a longer time. Thus, it likely will require substantial research to identify and quantify soil amendments that may facilitate microbial oxidation of Phi to Pi.

Since abiotic Phi oxidation is very slow, microbial oxidation dominates Phi oxidation [11,47]. After Phi addition, soil microorganisms must adapt to the elevated soil Phi where oxidation to Pi would likely occur from two weeks to four months depending on soil environmental conditions [48,49]. Therefore, additional studies designed to quantify Phi oxidation kinetics in soil may guide management decision for Phi use as a soil applied P source.

4. Phi Uptake, Translocation, and Utilization in Plants

It is suggested that plants absorb Phi and Pi by the same active transport system, competing for entry into the cell, although some suggest that plant cells may absorb Phi
more rapidly than Pi [50]. Elevated Phi concentrations throughout the plant following foliar or root application demonstrates that Phi is readily transported in the xylem and phloem [51–54]. Absorption and accumulation of Phi applied to either roots or leaves have been quantified in in vivo experiments [55,56].

Although plants readily absorb and translocate Phi, it does not appear to be readily oxidized or metabolized in plants and, thus, does not contribute to Pi nutrition [57–59]. Using in vivo 31P-NMR techniques, Danova-Alt [55] demonstrated that plant cells did not oxidize Phi to Pi, while metabolite concentrations increased following Pi supplied to cells previously treated with Phi. Phi was found to have negative effects on the growth and metabolism of Pi deficient plants by suppressing the molecular and developmental responses of plants to Pi deficiency [60]. McDonald [11] suggested that Phi may intensify the effects of Pi deficiency by tricking Pi deficient cells into sensing they are Pi sufficient. Thus, Phi accumulation and toxicity in plants is likely related to reduced Pi assimilation and/or the inability to metabolize Phi or its oxidation to Pi in the cell [61]. Phi may also be recognized or sensed in plants as Pi, preventing expression of Pi starvation responses critical to sustaining plant growth and function under low soil P [11].

Once in the plant, Phi interferes with Pi metabolism likely by disrupting the induction of enzymes characteristic for the Pi starvation response [62]. For example, Phi interferes by down-regulating the induction of Pi enzymes including acid phosphatase, phosphoenol pyruvate phosphatase, inorganic pyrophosphate-dependent phosphofructokinase, and high-affinity Pi transporters [57,58]. Ticconi and Abel [63] and Varadarajan [60] quantified Phi repression of nucleolytic enzyme activities and Pi starvation-induced genes in Brassica and Arabidopsis. Moreover, Singh [64] demonstrated that Phi increases the onset of programmed cell death in response to Pi starvation. These data suggest that despite its mobility and transport through the plant, Phi is not recognized as a substrate by metabolic Pi enzymes. Another distinct difference is that Pi can be assimilated into organic P compounds within minutes of uptake, whereas plants lack the ability to assimilate Phi [1,3]. Furthermore, enzymes that catalyze the transfer of Pi discriminate between Pi and Phi [3].

If biotechnology can be utilized to enhance Pi acquisition in plants grown on Pi deficient soils, then it may be possible to alter plant genes to enhance Phi metabolism or oxidation to Pi [65,66]. Manipulation of selected genes in the bacteria Klebsiella aerogenes resulted in increased oxidation and utilization of Phi [27]. More recently, Herrera-Estrella [67] proposed methods to develop transgenic plants and fungi with modified genes carrying a nucleic acid construct encoding an enzyme specific for Phi oxidation. Using transgenic Arabidopsis and tobacco plants grown under greenhouse conditions, similar growth with 30–50% less Phi compared to Pi was reported, in addition to reduced weed pressure related to Phi toxicity to weeds [68]. Using genetically engineered rice (codon-optimized ptxD gene) Manna [69] reported enhanced root growth in the presence of Phi, while providing significant control of weed species not able to metabolize Phi. These authors suggested the potential for Phi as a pre- and post-emergent herbicide applied to Phi-metabolizing transgenic crops. Ram [70] also demonstrated Phi-metabolizing properties in genetically (phoA) altered rice. Using the phosphite dehydrogenase gene (ptxD) in cotton plants, Pandey [71] also demonstrated Phi to Pi metabolism, while providing significant control of numerous weed species. Achary [72] summarized the potential for genetic engineering of commercial plants to metabolize Phi, while maintaining biomass yield and quality and providing valuable weed and disease control. Therefore, the technology and opportunity exists for development of transgenic plants capable of metabolizing Phi or oxidizing Phi to Pi.

5. Phi Use as a Plant Nutrient Source

Although Phi is used extensively as a fungicide, it is increasingly used as a P nutrient source. While significant increases in plant growth to Phi application have been documented, most studies report either no response or decreased plant growth (Table 2).
Table 2. Summary of reported Phi use as a P source.

| Plant                          | Application Method | Plant Response * | Reference       |
|--------------------------------|--------------------|------------------|-----------------|
| Arabidopsis                    | Hydroponic         | Negative         | [62]            |
| Bentgrass                      | Foliar             | Yes              | [73,74]         |
| Celery, spinach                | Hydroponic         | Negative         | [75]            |
| Citrus, avacado                | Foliar             | Yes              | [76–78]         |
| Citrus                         | Foliar             | Negative         | [79]            |
| Common bean                    | Soil, foliar       | Negative         | [80,81]         |
| Corn                           | Foliar             | Negative         | [54]            |
| Corn                           | Hydroponic         | Negative         | [82]            |
| Corn                           | Foliar             | No               | [83]            |
| Cotton                         | Foliar             | Yes              | [71]            |
| Cucumber                       | Foliar             | Negative         | [84]            |
| Komatsuna                      | Hydroponic         | Negative         | [85]            |
| Oat, mustard, pea, (lupin)     | Soil               | No (Negative)    | [48]            |
| Onion                          | Hydroponic         | Negative         | [58]            |
| Red clover, ryegrass           | Soil               | No               | [1]             |
| Strawberry, lettuce, chard     | Hydroponic         | No               | [86,87]         |
| Strawberry                     | Hydroponic         | No               | [88]            |
| Sweet potato                   | Tissue culture     | No               | [89]            |
| Tomato                         | Hydroponic         | Negative         | [60]            |
| Tomato, pepper                 | Hydroponic         | Negative         | [59]            |
| Tomato                         | Foliar             | No               | [90]            |
| Winter wheat                   | Foliar             | No               | [91]            |
| Zucchini                       | Soil, foliar       | Negative         | [51]            |

* negative = reduced growth; no = no response; yes = increased growth. ¹ negative growth response under low P, no response under adequate P supply. ² response only with pxsD gene.

Reduced P fertilizers (H₃PO₃, Ca-Phi) were first used on red clover (Trifolium pretense L.) and ryegrass (Lolium spp.), where forage yield decreased with Phi compared to Pi, and was similar to untreated soil [1]. Fortunately, the residual Phi/Pi response was evaluated where subsequent soybean (Glycine max L.) yield was greater in Phi and Pi treated soil compared to untreated soil; likely residual applied Phi oxidized to Pi. More recently, Fontana [48] conducted greenhouse studies to compare Ca-Phi (industrial waste) with Ca-Pi (triple superphosphate) applied to several agronomic crops and found no differences in biomass yield, microbial biomass P, and NaHCO₃ extractable P. The lack of response to Pi or Phi was due to sufficient soil test P levels. An increase in NaHCO₃-P with applied Phi suggests microbial oxidation of Phi to Pi occurred resulting in a residual value to soil applied Phi reported by MacIntire [1]. Unfortunately, few studies quantify residual availability of soil applied Phi. With soil applied Phi, soil microorganisms must adapt to increased soil Phi requiring two weeks to four months for oxidation of Phi to Pi depending on soil environmental conditions [48,49]. Thus, it is important to evaluate plant response to soil applied Phi following sufficient time for Phi oxidation.

Interest in Phi as a potential P source greatly increased when Lovatt [76] documented foliar Phi replaced Pi in some crops (e.g., citrus, avocados, summer squash, watermelon). For example, foliar application of Phi to P deficient citrus seedlings increased growth compared to Pi. She concluded that Phi was absorbed by citrus leaves and replaced Pi in normal cell metabolism. Other studies with citrus showed increased flowering, fruit set,
and fruit size with \( \text{Phi} \) application [77,78,92]. Unfortunately, the reported yield increases were only compared to “untreated” trees; there were no significant differences in fruit size between \( \text{Phi} \) and urea (no \( \text{Phi} \)), and neither study compared foliar \( \text{Phi} \) to \( \text{Pi} \). In contrast, Zambrosi [79] reported \( \text{Phi} \) applied to citrus root stocks grown in hydroponic or sand culture decreased total dry matter, root growth, chlorophyll content, and net CO\(_2\) assimilation.

Rickard [93] concluded \( \text{Phi} \) improved both yield and quality in numerous crops (e.g., broccoli, celery, onion, potato, pepper, tomato, orange, cherry, peach, raspberry, cotton, alfalfa, and rice). Unfortunately, the field data presented were incomplete or misinterpreted. In most of the studies reviewed, \( \text{Phi} \) treatments were compared to an “untreated control” and not with \( \text{Pi} \). Where \( \text{Pi} \) was applied, foliar \( \text{Phi} \) treatments were compared to soil applied \( \text{Pi} \). Finally, where mean separations were provided, \( \text{Phi} \) treatment effects were generally not significant. In only two studies (alfalfa and oranges) were equivalent rates of foliar \( \text{Phi} \) and \( \text{Pi} \) compared. There were no significant differences between P sources in orange leaf P or root weight. Alfalfa dry matter was 11% greater with \( \text{Pi} \) than \( \text{Phi} \). Rickard [93] concludes that in each study \( \text{Phi} \) increased yield or P content over the untreated control, which demonstrates that plants can utilize \( \text{Phi} \) as a nutrient source, assuming that the response to \( \text{Phi} \) was not related to a reduction in disease pressure. McDonald [11] suggested that claims of higher yields with \( \text{Phi} \) treated crops could be related to \( \text{Phi} \) oxidation to \( \text{Pi} \) or from the fungicidal effects on selected plant pathogens.

Subsequent reviews on \( \text{Phi} \) use in agriculture argue that there is no published evidence documenting \( \text{Phi} \) as a direct source of plant available P [61]. Ratjen and Gerendás [51] showed increasing \( \text{Phi} \) decreased zucchini (\( \text{Cucurbita pepo} \)) dry matter yield, regardless of \( \text{Phi} \) applied to roots or leaves. Increasing foliar \( \text{Phi} \) rate linearly decreased plant growth with leaves exhibiting \( \text{Phi} \) toxicity symptoms at the highest \( \text{Phi} \) rate (4.5 g L\(^{-1}\)). Leaf P concentration increased with increasing \( \text{Phi} \), likely due to decreased growth. These authors confirm that P deficient plants are very sensitive to \( \text{Phi} \), are nutritionally ineffective, and are not a suitable P fertilizer. Using in vitro cultures of sweet potato nodes, Hirosse [89] reported that increasing the proportion of \( \text{Phi} \) (0 → 100%) in solution decreased shoot and root growth. As tissues matured, the negatives effects of \( \text{Phi} \) were less pronounced, which was attributed to \( \text{Pi} \) translocation to new growth reducing the negative effects of \( \text{Phi} \). These results indicated that \( \text{Phi} \) cannot replace \( \text{Pi} \) in sweet potato tissue cultures. Similarly, Sutradhar [83] showed foliar \( \text{Phi} \) did not increase corn yield and tissue P concentration compared to soil applied \( \text{Pi} \). They concluded that while significant \( \text{Phi} \) absorption occurred, \( \text{Phi} \) contributed little or nothing to P nutritional needs of the plants.

Many studies reported \( \text{Pi} \) deficient plants are more sensitive to \( \text{Phi} \) application compared to plants supplied with some \( \text{Pi} \), where negative effects of \( \text{Phi} \) could be overcome by \( \text{Pi} \) addition [11,56,58,64]. In field studies with corn grown in P deficient soil, foliar \( \text{Pi} \) and \( \text{Phi} \) resulted in a 29% increase and 18% decrease in biomass yield, respectively [54]. Similar results were shown in greenhouse studies, although further yield loss was reported with foliar \( \text{Phi} \) applied to plants grown under soil applied \( \text{Phi} \), compared to foliar \( \text{Phi} \) with soil applied \( \text{Pi} \). They documented that \( \text{Phi} \) was readily absorbed by roots and leaves, translocated throughout the plant, and was relatively stable in the plant (little \( \text{Phi} \) oxidation to \( \text{Pi} \)), thus \( \text{Phi} \) was not available to the plant.

Substantial research demonstrates a significant difference in plant response to \( \text{Phi} \) between deficient and sufficient plant or soil P status. In low (0.1 mM) or high (0.5 mM) \( \text{Pi} \) nutrient solutions with \( \text{Phi} \) supplied at 0.1 and 2.0 mM, celery (\( \text{Apium graveolens} \)), root and shoot growth were significantly reduced with high \( \text{Phi} \) and low \( \text{Pi} \) [75]. Normal growth was observed with high \( \text{Phi} \) and \( \text{Pi} \), whereas no reduction in growth of low \( \text{Phi} \) treated plants at either \( \text{Pi} \) rate was observed. Increased shoot P in \( \text{Phi} \) treated plants did not result in improved growth at low \( \text{Pi} \), suggesting that absorbed \( \text{Phi} \) was not oxidized or metabolized in the plant. Thao [52] also reported partial oxidation of \( \text{Phi} \) in plant tissue is unlikely to be involved in increasing \( \text{Pi} \) in the plant. Similar studies with komatsuna plants (\( \text{Brassica} \))
rapa) showed Phi had no effect on shoot or root growth under high Pi, whereas growth significantly decreased under low Pi and concluded that Phi inhibited Pi uptake [85].

Avila [80] grew common bean (Phaseolus vulgaris) in low and adequate soil Pi fertilized with increasing Phi (0 → 100 mg P dm⁻³ soil). In low Pi soil, Phi reduced plant growth and grain yield only when Phi was ≥25 mg P dm⁻³ soil; Phi toxicity symptoms were also observed. Moreover, foliar Phi (1 or 2 applications of 40 µM Phi or Pi) significantly reduced bean growth and grain yield in low Pi soil, with no yield loss in adequate Pi soil. Similarly, Avila [81] grew common bean in nutrient solutions at low and high Pi with increasing Phi rates (0 → 512 µM). At low Pi, plant growth and grain yield were reduced, such that when Phi was ≥64 µM plants were severely P deficient and bean pods failed to develop. Concentration of P in Pi deficient plants was increased with increasing Phi; however, there was no response in grain yield.

A number of studies documented significant effects of Phi on P starvation response in plants. Plant response to Pi deficiency (Pi starvation response) includes changes in root/shoot growth and morphology normally associated with increased root/shoot ratio; anthocyanin accumulation; enhanced biochemical capacity for Pi acquisition; increased root exudates that enhance mycorrhizal infection; and reduced cellular Pi demand for metabolism [94–96]. Pi starvation responses are dominantly related to complex changes in gene expression regulating cellular access to Pi, which some suggest also functions with Phi [3,63,97,98].

With increasing Phi (0 → 3 mM) in hydroponic solutions, tomato (Lycopersicon esculentum) growth was substantially reduced without Pi compared to adequate Pi [60]. In addition, typical plant responses to Pi deficiency (increased root growth and root/shoot ratio) were suppressed with added Phi (no Pi), compared to adequate Pi. Evaluating treatment effects on gene expression, these authors provided molecular evidence that Pi starvation induced genes (high-affinity Pi transporters, phosphatases, and glycerol-3-Pi permease) are suppressed with Phi. Similarly, Carswell [58] reported decreased root/shoot ratio with Phi treated onion (Allium cepa) and Brassica nigra plants compared to control plants, which was attributed to Phi interference of Pi starvation response.

Using nutrient solutions containing 52 and 644 µM Pi, where each contained either 100% Pi or 75/25% Pi/Phi, Avila [82] reported Phi reduced corn root/shoot growth and total leaf area. Plants were subsequently removed from these solutions and immersed in 100% ³¹ Pi and 50/50% ³¹ Pi/³¹ Pi solutions. These data showed that Phi inhibits Pi uptake regardless of plant Pi status. In addition, Phi replacement stimulated guaiacol peroxidase activity and lignin biosynthesis, which are both responses to P starvation.

Ticconi [62] grew Arabidopsis seedlings in low and high Pi (±RNA) nutrient solutions with increasing Phi (1 → 12 mM). Phi (≥2.5 mM) significantly reduced plant growth in high Pi and severely reduced growth in low Pi solution. The Phi inhibited growth was correlated with lower plant Pi, which suggests competition between Phi and Pi absorption and assimilation. At ≤2.5 mM, Phi influenced Pi starvation responses including greater root/shoot ratio; enhanced root hair formation; anthocyanin accumulation; and repression of nucleolytic enzymes (ribonuclease, phosphodiesterase, and acid phosphatase).

Foliar application of Phi on tomato had no effect on biomass yield, partitioning of photosynthesis-related parameters, or nutrient concentration in plant tissues [90]. They further concluded that Phi applications can be used to activate plant-defense responses, but is not a relevant P source since Phi-containing products might suppress Pi-starvation response in plants growing under low Pi conditions.

In nutrient solution studies with strawberry grown under increasing Phi supply (0 → 50% total P), leaf P concentration increased with increasing Phi in the fruit development phase [86]. Although fruit size or yield were not significantly increased compared to the control (no P), supplying 30% Phi improved fruit quality and increased anthocyanins, which are important plant defense mechanisms.

Over the last several decades, many experiments have been conducted to evaluate the nutritional value of Phi compared to Pi. Although positive yield responses have been
reported, the majority documented negative or no response to Phi compared to Pi. Results from most studies must be carefully evaluated, because:

1. With any study conducted in hydroponic nutrient solutions, oxidation of Phi to Pi will be limited, although maintaining Phi throughout the study is critical to evaluating plant response to Phi compared to Pi.
2. Most studies do not include an assessment of fungal infections or their control with Phi treatment.
3. In studies conducted in soil or other potting media, Phi oxidation to Pi is not generally assessed. More importantly, the residual availability of soil applied Phi is not commonly quantified.
4. Although few have documented the potential for Phi oxidation in plant cells, most studies do not assess Phi to Pi transformation in the plant, critical to assessing Phi oxidation potential in the plant.
5. Results suggesting increased P nutrition by measuring total P (%) need to be moderated with the nutrient concentrating effects of reductions in biomass yield.

6. Phi Use as a Plant Fungicide

Although some consider Phi effects on plant diseases an “indirect” effect, Phi can enhance plant health directly through control of selected fungi on cultivated or native plants. In general, Phi acts as a priming agent of several plant defense responses. Excellent reviews on the use of Phi to control or reduce the severity of selected plant diseases have been published [11,65,99,100]. Phi-based fungicides often are labeled as fertilizers because of significantly less complex and costly regulatory approval processes required for fertilizers compared to fungicides.

Use of Phi as a fungicide is primarily targeted to control of oomycete pathogens Phytophthora cinnamoni, P. citrophthora, P. infestans, Plasmopara viticola, and others (Table 3). Phytophthora strains vary in their sensitivity to Phi [50,101]. In these studies, growth of a Phi-sensitive strain was inhibited regardless of Pi supply, whereas resistant strains were inhibited by Phi only under low Pi supply. These strains excluded Phi more effectively than the sensitive isolate at higher Pi levels. Phi is effective in controlling root and crown rot caused by Phytophthora capsici [59]. Silva [102] reported a linear reduction in the severity of downy mildew and a significant improvement in leaf area index in soybean with an increase Phi. Shearer and Fairman [103] used foliar Phi on native Australian wildflowers (Banksia brownii, B. baxteri or B. coccinea) infected with Phytophthora cinnamoni. Plant mortality rate was significantly reduced following Phi application. Phi also controls Fusarium oxysporum and Rhizoctonia solani [3], while Oka [104] reported control of nematodes with soil applied Phi. In contrast, Graham [105] described significant Phi control of phytophthora disease in citrus through both soil and foliar applications. Soil applied Phi was more effective in controlling citrus root rot.
Table 3. Summary of reported Phi control of fungal diseases in crops. Adapted from [99].

| Plant  | Disease       | Causal Agent             | Reference |
|--------|---------------|--------------------------|-----------|
| Apple  | Mouldy core   | Alternaria alternate     | [106]     |
| Avocado| Dieback       | Phytophthora cinnamomi   | [107]     |
| Banksia| Dieback       | Phytophthora cinnamomi   | [108]     |
| Bentgrass| Summer decline| Pythium                  | [73]      |
| Cabbage| Clubroot      | Plasmophthora brassicae   | [109]     |
| Chestnut| Ink disease   | Phytophthora cambivora   | [110]     |
| Cucumber| Damping-off   | Pythium ultimum         | [111]     |
| Grape  | Downy mildew  | Plasmopara viticola      | [112]     |
| Lupin  | Dieback       | Phytophthora cinnamomi   | [113]     |
| Maize  | Downy mildew  | Peronosclerospora sorgii | [114]     |
| Orange | Brown rot     | Phytophthora citrophthora | [53]      |
| Papaya | Fruit rot     | Phytophthora palmivora   | [113]     |
| Pecan  | Scab          | Fuscidium effusum        | [115]     |
| Pepper | Crown and root rot | Phytophthora capsici | [59]      |
| Potato | Late blight   | Phytophthora infestans   | [116]     |
| Potato | Late blight   | Phytophthora infestans   | [117]     |
| Potato | Pink rot      | Phytophthora erythroseptica | [118] |
| Potato | Bacterial soft rot | Erwinia carotovora     | [119]     |
| Soybean| Downey mildew | Peronospora manshurica   | [102]     |
| Strawberry| Leather rot  | Phytophthora cactorum    | [120]     |
| Tangelo| Brown spot    | Alternaria alternata     | [121]     |
| Tobacco| Black shank   | Phytophthora nicotianae  | [113]     |

The antifungal properties of Phi were initially thought to occur in either the pathogen (reducing spore germination and growth rate) or the host plant (stimulation of the plants’ own defense mechanisms). Fenn and Coffey [122] observed that Phi inhibited Phytophthora mycelia in sterile culture. Guest and Grant [3] concluded that Phi inhibits phosphorylation and disrupts P metabolism in Phytophthora by accumulation of polyphosphate and pyrophosphate. Griffith [50] concluded that reduced adenylate synthesis in the fungi, which causes a reduction ATP and NAD, is a primary site of action. As described earlier, Phi also competes for Pi binding sites of phosphorylating enzymes. Thus, the antifungal effect of Phi on oomycetes is likely related to interference of Phi with Pi metabolism. Since there is evidence that plants do not metabolize Phi, its stability or persistence in plants provides the deterrent to fungal attack [123].

Although most researchers agree with the direct antifungal effect of Phi on Phytophthora metabolism, plants exhibit highly developed response mechanisms to reduce the effects of an infectious organism [124]. Smillie [113] documented that Phi enables the plant to maintain an antimicrobial environment. The fungal defense system has been documented in studies measuring selected chemical inhibitors (e.g., aminoxyacetic acid; aminohydrazinophenylpropionic acid) produced by the plant [3]. In addition, the Phi concentration at the site of infection appears to be correlated with the expression of selected genes involved in the antimicrobial response; at low Phi levels the antifungal metabolism is triggered, whereas at higher concentrations, Phi directly inhibits fungal growth before infection [124].

Ink disease (chestnut blight) in chestnut and walnut trees was significantly reduced through stem injection of Phi before artificial inoculation with Phytophthora cinnamomi [110].
In these trees, Phi confines the fungus by localized deposition of protective compounds that subsequently dehydrate. Foliar Phi is also effective and recommended for use in chestnut and walnut nurseries to prevent fungal infections. In addition, foliar applied Phi has been shown effective in controlling pecan scab (*Fusicladium effusum*), although elevated levels of Phi residues in pecan products is a concern [115]. With increasing use of Phi products in organic production systems, management protocols to minimize Phi residues in fruit and vegetable products are needed [125].

Several varieties of hot and sweet pepper, both resistant and susceptible to *Phytophthora capsici*, were grown in Phi treated media [126]. Phi application reduced fungal infection on the susceptible lines and several of the resistant varieties. In greenhouse hydroponic culture studies on *Phytophthora capsici* inoculated pepper plants, *Phytophthora* crown rot was significantly reduced with Phi compared with untreated or Pi treated plants.

Fungicides containing Phi can suppress foliar and soil-borne diseases [113]. With foliar diseases, repeated applications are frequently needed as Phi should be present at the time infection occurs. In contrast to non-systemic fungicides (e.g., mancozeb) labeled for oomycetes, Phi is readily translocated throughout the plant, which is especially advantageous for disease control in potato tubers and other underground plant tissue [127]. In potatoes, Phi has been foliar applied during the growing season or sprayed on potatoes after harvest both with excellent fungal disease control [118,128]. Field studies were conducted to evaluate the effect of foliar application of Phi during potato tuberization [119]. After harvest, potato slices were incubated following inoculation with *Phytophthora infestans*, *Fusarium solani* and *Erwinia carotovora*. Tuber yield and dry weight were not affected by Phi treatment; however, a significant reduction in disease infection was observed. Increased phytoalexin content, as well as peroxidase and polyphenol oxidase activities in Phi treated plants, suggests a Phi induced systemic defense response [129]. Similarly, Mohammad [117,130] demonstrated potato plants treated with potassium Phi produced tubers with enhanced *phytophthora* resistance compared to untreated plants. They determined the increased disease resistance was related to increased specific phenol and phytoalexins production in Phi treated plants. In field studies, Liljeroth [116] reported effective control of potato late blight with Phi applied in combination with a non-systemic fungicide.

Evaluating effective management of summer decline in creeping bentgrass caused by *pythium*, Lucas [73] documented improved turf quality and shoot growth after foliar application of Phi. Similarly, Vincelli and Dixon [131] documented excellent control of dollar spot and some improvement in turf quality with foliar applications of Phi. Similar results were reported for *pythium* control in bluegrass [132]. Pythium blight suppression due to Phi treatments on perennial ryegrass (*Lolium perenne* L.) and creeping bentgrass (*Agrostis stolonifera* L.), and anthracnose basal rot on an annual bluegrass (*Poa annua* L.) were reported [133,134]. Oka [104] reported significant control of nematodes (*Heterodera avenae, Meloidogyne marylandi*) in wheat with soil applied Phi. Further studies are needed to evaluate Phi as a cost effective alternative to traditional nematicides.

Over the last several decades, considerable evidence has been provided to establish the value of Phi in suppressing a number of plant diseases. Several potential precautions related to Phi use as a foliar or soil applied fungicide include:

1. The concern over increasing Phi persistence in soil that may impart selective pressure on fungal resistance mechanisms, which may negatively influence symbiotic relationships between plants and mycorrhizal fungi [11,135,136].

2. Use of Phi products may result in accumulation of presence of Phi residues in horticultural products. For example, the European Union established a 2 ppm maximum residue level (MRL) for Phi in horticultural products [125]. It takes relatively small foliar or soil Phi application rates to result in Phi residues in marketable products [115].

7. Conclusions

Phosphite products are increasingly used for their antifungal and nutritional value. Although there is substantial literature describing several mechanisms of plant disease
control by \( \Phi_i \), less is known about \( \Phi_i \) oxidation in plants to provide nutritional \( \Pi_i \). Applied to soil, chemical oxidation of \( \Phi_i \) is too slow to provide \( \Pi_i \); however, microbial oxidation in soils has been documented and likely provides some level of plant available \( \Pi_i \), increasing with reaction time. Additional research is needed to quantify the kinetics of residual availability of soil applied \( \Phi_i \). Although \( \Phi_i \) can be absorbed by most plants through the leaves and/or roots, its direct use as a nutrient source has been questioned. Generally, the effects of \( \Phi_i \) on crops are strongly dependent on the P nutrient status of the plant. Any negative effect of \( \Phi_i \) on plant growth is usually observed in severely \( \Pi_i \) deficient plants compared to plants with elevated \( \Pi_i \) supply. Literature supporting positive plant responses to \( \Phi_i + \Pi_i \) applied to plants with less than optimum \( \Pi_i \) supply is variable; where positive responses to \( \Phi_i \) have been attributed to some level of fungal disease control. While considerable evidence exists for cellular oxidation of \( \Phi_i \) in soil microorganisms, only a few studies have provided evidence of \( \Phi_i \) oxidation through specific enzymes genetically controlled in plant cells. There is increasing evidence of the potential to manipulate plant genes to enhance plant metabolism of \( \Phi_i \) in plants. Since \( \Phi_i \) oxidation occurs slowly in soils, additional information is needed to characterize \( \Phi_i \) oxidation kinetics under variable soil and environmental conditions. It may also be important to evaluate the impact of electron acceptors applied in combination with \( \Phi_i \) to control the kinetics of \( \Phi_i \) oxidation to benefit plant recovery of applied \( \Phi_i \). Genetic engineering of crop plants to sustain growth and yield with \( \Phi_i + \Pi_i \) provides a dual fertilization–weed control system. Further advances in genetic manipulation of plants to utilize \( \Phi_i \) are warranted.

**Author Contributions:** Conceptualization, methodology, and writing—original draft preparation, J.L.H.; writing—review and editing, J.L.H. and A.J.S.; supervision and project administration, J.L.H. and A.J.S. Both authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

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

**References**

1. MacIntire, W.; Winterberg, S.; Hardin, L.; Sterges, A.; Clements, L. Fertilizer evaluation of certain phosphorus, phosphorous, and phosphoric materials by means of pot cultures. *Agron. J.* 1950, 42, 543–549. [CrossRef]

2. Jackman, R.; Lambert, J.; Rothbaum, H. Red phosphorus as a fertiliser for grass-clover pasture. *New Zealand J. Agric. Res.* 1970, 13, 232–241. [CrossRef]

3. Guest, D.; Grant, B. The complex action of phosphonates as antifungal agents. *Biol. Rev.* 1991, 66, 159–187. [CrossRef]

4. Lovatt, C.; Mikkelsen, R. Phosphite fertilizers: What are they? Can you use them? What can they do? *Better Crops* 2006, 90, 11–13.

5. Hanrahan, G.; Salmassi, T.; Khachikian, C.; Foster, K. Reduced inorganic phosphorus in the natural environment: Significance, speciation and determination. *Talanta* 2005, 66, 435–444. [CrossRef]

6. Pasek, M.; Harmmeijer, J.; Buick, R.; Malseen, G.; Atlas, Z. Evidence for reactive reduced phosphorus species in the early Archean ocean. *Proc. Natl. Acad. Sci. USA* 2013, 110, 10089–10094. [CrossRef]

7. Glindemann, D.; Bergmann, A.; Stotmeister, U.; Gassmann, G. Phosphine in the lower terrestrial troposphere. *Naturwissenschaften* 1996, 83, 131–133. [CrossRef]

8. Pasek, M. Rethinking early Earth phosphorus geochemistry. *Proc. Natl. Acad. Sci. USA* 2008, 105, 853–858. [CrossRef]

9. Morton, S.; Edwards, M. Reduced Phosphorus Compounds in the Environment. *Crit. Rev. Environ. Sci. Technol.* 2005, 35, 333–364. [CrossRef]

10. Lindsay, W.L. *Chemical Equilibria in Soils;* John Wiley & Sons: New York, NY, USA, 1979.

11. McDonald, A.; Grant, B.; Plaxton, W. Phosphite (phosphorous acid): Its relevance in the environment and agriculture and influence on plant phosphate starvation response. *J. Plant. Nutr.* 2001, 24, 1505–1519. [CrossRef]

12. Schink, B.; Friedrich, M. Bacterial metabolism: Phosphite oxidation by sulphate reduction. *Nature* 2000, 406, 37. [CrossRef] [PubMed]

13. Morton, S.; Glindemann, D.; Edwards, M. Phosphates, Phosphites, and Phosphides in Environmental Samples. *Environ. Sci. Technol.* 2003, 37, 1169–1174. [CrossRef] [PubMed]

14. Pasek, M.; Sampson, J.; Atlas, Z. Redox chemistry in the phosphorus biogeochemical cycle. *Proc. Natl. Acad. Sci. USA* 2014, 111, 15468–15473. [CrossRef]
15. Benitez-Nelson, C. The biogeochemical cycling of phosphorus in marine systems. *Earth Sci. Rev.* **2000**, *51*, 109–135. [CrossRef]

16. Huang, L.; Jia, X.; Zhang, G.; Shao, M. Soil organic phosphorus transformation during ecosystem development: A review. *Plant. Soil*. **2017**, *417*, 17–42. [CrossRef]

17. Cade-Menun, B.; Berch, S.; Preston, C.; Lavkulich, L. Phosphorus forms and related soil chemistry of Podzolic soils on northern Vancouver Island A comparison of two forest types. *Can. J. For. Res.* **2000**, *30*, 1714–1725. [CrossRef]

18. Condron, L.M.; Newman, S. Revisiting the fundamentals of phosphorous fractionation of sediments and soil. *J. Soils Sediments* **2011**, *11*, 830–840. [CrossRef]

19. Havlin, J.L.; Tisdale, S.L.; Nelson, W.L.; Beaton, J.D. *Soil Fertility and Nutrient Management: An Introduction to Nutrient Management*, 8th ed.; Pearson: Upper Saddle River, NJ, USA, 2014; p. 516.

20. Adams, F.; Conrad, J. Transition of Phosphite to Phosphate in Soils. *Soil Sci.* **1953**, *75*, 361–371. [CrossRef]

21. Malacinski, G.; Konetzka, W. Bacterial oxidation of orthophosphite during growth. *J. Bacteriol.* **1987**, *169*, 237–241. [CrossRef]

22. Metcalf, W.; Wolfe, R. Molecular Genetic Analysis of Phosphite and Hypophosphite Oxidation by *Pseudomonas stutzeri* WM88. *Appl. Microbiol. Biotechnol.* **1998**, *46*, 575–582. [CrossRef]

23. Morton, S.; Glindemann, D.; Wang, X.; Niu, X.; Edwards, M. Analysis of Reduced Phosphorus in Samples of Environmental Interest. *Environ. Sci. Technol.* **2005**, *39*, 4369–4376. [CrossRef]

24. Howard, K.; Dell, B.; Hardy, G. Phosphate and mycorrhizal formation in seedlings of three Australian Myrtaceae. *Aust. J. Botany*. **2001**, *48*, 725–729. [CrossRef]

25. Ohtake, H.; Wu, H.; Imazu, K.; Anbe, Y.; Kato, J.; Kuroda, A. Bacterial phosphonate degradation, phosphate oxidation and polyphosphate accumulation. *Resour. Conserv. Recycl.* **1996**, *18*, 125–134. [CrossRef]

26. Imazu, K.; Tanaka, S.; Kuroda, A.; Anbe, Y.; Kato, J.; Ohtake, H. Enhanced Utilization of Phosphonate and Phosphite by *Klebsiella aerogenes*. *Appl. Environ. Microbiol.* **1998**, *64*, 3754–3758. [CrossRef]

27. Schink, B.; Thiemann, V.; Laue, H.; Friedrich, M. Desulfitognum *phosphitoxidans* sp. nov., a new marine sulfate reducer that oxidizes phosphite to phosphate. *Arch. Microbiol.* **2002**, *177*, 381–391. [CrossRef] [PubMed]

28. Simeonova, D.; Wilson, M.; Metcalf, W.; Schink, B. Identification and Heterologous Expression of Genes Involved in Anaerobic Dissimilatory Phosphate Oxidation by Desulfitobacter phosphatis. *J. Bacteriol.* **2010**, *192*, 5237–5244. [CrossRef]

29. Howard, K.; Dell, B.; Hardy, G. Phosphate and mycorrhizal formation in seedlings of three Australian Myrtaceae. *Aust. J. Botany*. **2001**, *48*, 725–729. [CrossRef]

30. Costas, A.; White, A.; Metcalf, W. Purification and Characterization of a Novel Phosphorus-oxidizing Enzyme from *Pseudomonas stutzeri* WM88. *J. Biol. Chem.* **2001**, *276*, 17429–17436. [CrossRef] [PubMed]

31. Hung, J.; Fogle, E.; Christman, H.; Johannes, T.; Zhao, H.; Metcalf, W.; van der Donk, W. Investigation of the Role of Arg301 Identified in the X-ray Structure of Phosphate Dehydrogenase. *Biochemistry* **2012**, *51*, 4254–4262. [CrossRef] [PubMed]

32. Shink, B.; Thiemann, V.; Laue, H.; Friedrich, M. Desulfitognum *phosphitoxidans* sp. nov., a new marine sulfate reducer that oxidizes phosphite to phosphate. *Arch. Microbiol.* **2002**, *177*, 381–391. [CrossRef] [PubMed]

33. White, A.; Metcalf, W. Two C-P lyase operons in *Pseudomonas stutzeri* and their roles in the oxidation of phosphonates, phosphate, and hypophosphite. *J. Bacteriol.* **2004**, *186*, 4730–4739. [CrossRef]

34. Figueroa, I.; Coates, J. Microbial Phosphate Oxidation and Its Potential Role in the Global Phosphorus and Carbon Cycles. *Adv. Appl. Microbiol.* **2017**, *98*, 93–117. [CrossRef] [PubMed]

35. Rawat, P.; Das, S.; Shankhdhar, D.; Shankhdhar, S. Phosphate-Solubilizing Microorganisms: Mechanism and Their Role in Phosphate Solubilization and Uptake. *J. Soil Sci. Plant. Nutr.* **2020**, *21*, 49–68. [CrossRef]

36. Tian, J.; Ge, F.; Zhang, D.; Deng, S.; Liu, X. Roles of Phosphate Solubilizing Microorganisms from Managing Soil Phosphorus Deficiency to Mediating Biogeochemical P Cycle. *Biology* **2021**, *10*, 158. [CrossRef] [PubMed]

37. Rodriguez, H.; Fraga, R. Phosphate solubilizing bacteria and their role in plant growth promotion. *Biotech. Adv.* **1999**, *17*, 319–339. [CrossRef] [PubMed]

38. Rafi, M.; Krishnaveni, M.; Charyulu, P. Phosphate-Solubilizing Microorganisms and their Emerging Role in Sustainable Agriculture. In *Recent Developments in Applied Microbiology and Biochemistry*; Buddolla, S., Ed.; Elsevier: London, UK, 2019; pp. 223–233. [CrossRef] [PubMed]
Soil Syst. 2021, 5, 52

75. Thao, H.; Yamakawa, T. Growth of celery (Apium graveolens var. dulce) as influenced by phosphite. J. Fac. Agric. Kyushu Univ. 2008, 53, 375–378. [CrossRef]

76. Lovatt, C. A definitive test to determine whether phosphite fertilization can replace phosphate fertilization to supply P in the metabolism of “Hass” on Duke 7. Calif. Avoc. Soc. Yearb. 1990, 74, 61–64.

77. Lovatt, C. Timing citrus and avocado foliar nutrient applications to increase fruit set and size. HortTechnology 1999, 9, 607–612. [CrossRef]

78. Lovatt, C. Properly timing foliar applied fertilizers increases efficacy: A review and update on timing foliar nutrient applications to citrus and avocado. Hort. Technol. 2013, 23, 536–541. [CrossRef]

79. Zambrosi, F.; Mattos, D.; Syvertsen, J. Plant growth, leaf photosynthesis, and nutrient-use efficiency of citrus rootstocks decrease with phosphite supply. J. Plant. Nutr. Soil Sci. 2011, 174, 487–495. [CrossRef]

80. Avila, F.; Faquin, V.; Silva, D.; Bastos, C.; Oliveira, N.; Soares, D. Phosphite as Phosphorus Source to Grain Yield of Common Bean Plants Grown in Soils Under Low or Adequate Phosphate Availability. Ciênc. Agrotec. 2012, 36, 639–648. [CrossRef]

81. Estrada-Ortiz, E.; Trejo-Tellez, L.; Gómez-Merino, F.; Núñez-Escobar, R.; Sandoval-Villa, M. The effects of phosphite on strawberry yield and fruit quality. J. Soil Sci. Plant. Nutr. 2013, 13, 612–620. [CrossRef]

82. Albrigo, L. Effects of foliar applications of urea or Nutriphite on flowering and yields of Valencia orange trees. Sci. Hortic. 2002, 95, 2501–2514. [CrossRef]

83. Sutradhar, A.; Arnall, D.; Dunn, B.; Raun, W. Does phosphite, a reduced form of phosphate contribute to phosphorus nutrition in cotton (Gossypium L.)? J. Plant. Nutr. 2019, 42, 982–989. [CrossRef]

84. Estrada-Ortiz, E.; Trejo-Tellez, L.; Gómez-Merino, F.; Silva-Rojas, H.; Castillo-González, A.; Avitia-García, E. Physiological Responses of Chard and Lettuce to Phosphate Supply in Nutrient Solution. J. Agr. Sci. Tech. 2016, 18, 1079–1090. [CrossRef]

85. Shearer, B.; Fairman, R. Application of phosphite in a high-volume foliar spray delays and reduces the rate of mortality of four Banksia species infected with Phytophthora cinnamomi. Austalas. Plant. Pathol. 2001, 30, 133–139. [CrossRef]

86. Oka, Y.; Tkachi, N.; Mor, M. Phosphate Inhibits Development of the Nematodes Heterodera avenae and Meloidogyne marylandi in Cereals. Phytopathology 2007, 97, 396–404. [CrossRef] [PubMed]

87. Graham, J.H. Phosphate for control of phytophthora diseases in citrus: Model for management of phytophthora species on forest tress? New Zealand J. For. Sci. 2011, 41, S49–S56.
106. Reuveni, M.; Sheglov, D.; Cohen, Y. Control of moldy-core decay in apple fruits by β-aminobutyric acids and potassium phosphites. *Plant Dis.* 2003, 87, 933–936. [CrossRef] [PubMed]

107. Cervera, M.; Cautil, R.; Jeria, G. Evaluation of calcium phosphate; magnesium phosphite and potassium phosphate in the control of phytophthora cinnamomi in Hass avocado trees (Persea americana Mill) grown in container. In Proceedings of the VI World Avocado Congress (Actas VI Congreso Mundial del Aguacate), Viña Del Mar, Chile, 12–16 November 2007; ISBN 978-956-17-0413-8.

108. Barrett, S.; Shearer, B.; Hardy, G. The efficacy of phosphite applied after inoculation on the colonisation of Banksia brownii stems by *Phytophthora cinnamomi*. *Australas. Plant Pathol.* 2003, 32, 1–7. [CrossRef]

109. Abbasi, P.; Lazarovits, G. Effect of soil application of AG3 phosphonate on the severity of clubroot of bok choy and cabbage caused by *Plasmodiophora brassicae*. *Plant Dis.* 2006, 90, 1517–1522. [CrossRef]

110. Gentile, S.; Valentino, D.; Tamietti, G. Control of Ink Disease by truck Injection of Potassium Phosphite.

111. Bock, C.; Brenneman, T.; Hotchkiss, M.; Wood, B. Evaluation of phosphite fungicide to control pecan scab in the southeastern USA. *Crop. Prot.* 2012, 36, 58–64. [CrossRef]

112. Fenn, M.; Coffey, M. Quantification of phosphonate and ethyl phosphonate in tobacco and tomato tissues and its significance for the mode of action of phosphite fungicides. *Crop. Prot.* 1999, 18, 115–118. [CrossRef]

113. Smillie, R.; Grant, B.; Guest, D. The Mode of Action of Phosphite: Evidence for Both Direct and Indirect Modes of Action on *Three Phytophthora* sp. in Plants. *Phytopathol.* 1979, 89, 921–926. [CrossRef]

114. Panicker, S.; Gangadharan, K. Controlling downy mildew of maize caused by *Peronosclerospora sorghi* by foliar sprays of phosphonic acid compounds. *Crop Prot.* 1999, 99, 207–213. [CrossRef]

115. Johnson, D.; Inglis, D.; Miller, J. Control of potato tuber rots caused by oomycetes with foliar applications of phosphorous acid. *Crop Prot.* 2000, 19, 559–564. [CrossRef]

116. Abbasi, P.; Lazarovits, G. Seed treatment with phosphonate (AG3) suppresses Pythium damping-off of cucumber seedlings. *Plant Dis.* 2006, 90, 459–464. [CrossRef]

117. Nilesh, M.; Han, X.; Zhang, Z.; Xi, Y.; Boorboori, M.; Wang-Pruski, G. Phosphite Application Alleviates Strobilurine Resistance in Oomycete Pathogens. *Appl. Environ. Microbiol.* 2011, 77, 7599–7606. [CrossRef] [PubMed]

118. Mohammadi, M.; Han, X.; Zhang, Z.; Xi, Y.; Boorboori, M.; Wang-Pruski, G. Effects of potassium phosphite on biochemical acid compounds. *Crop Prot.* 1999, 17, 305–312. [CrossRef]

119. Lobato, M.; Machinandiarena, M.; Tambascio, C.; Dosio, G.; Caldiz, D.; Daleo, G.; Andreuss, A.; Olivieri, F. Effect of foliar applications of phosphite on post-harvest potato tubers. *Eur. J. Plant. Path.* 2011, 139, 155–163. [CrossRef]

120. Rebollar-Alviter, A.; Madden, L.; Ellis, M. Pre- and post-infection activity of azoxystrobin, pyraclostrobin, mefenoxam, and phosphite against leather rot of strawberry, caused by *Phytophthora cinnamomii*. *Plant Dis.* 2000, 84, 17–25. [CrossRef]

121. Yogev, E.; Sadowsky, A.; Solel, Z.; Oren, Y.; Orbach, Y. The performance of potassium phosphite for controlling Alternaria brown spot of citrus fruit. *J. Plant Dis. Prot.* 2006, 113, 207–213. [CrossRef]

122. Speiser, B.; Berner, A.; Haseli, A.; Tamm, L. Control of downy mildew of grapevine with potassium phosphonate: Effectivity and phosphonate residues in wine. *Biol. Agric. Hortic.* 2000, 17, 305–312. [CrossRef]

123. Smillie, R.; Grant, B.; Guest, D. The Mode of Action of Phosphite: Evidence for Both Direct and Indirect Modes of Action on Three *Phytophthora* sp. in Plants. *Phytopathol.* 1979, 89, 921–926. [CrossRef]

124. Jackson, T.; Burgess, T.; Colquhoun, I.; Hardy, G. Action of the Fungicide Phosphite on Eucalyptus marginata Inoculated with Phytophthora capsici. *Appl. Ecol. Environ. Res.* 2011, 17, 111873. [CrossRef]

125. Trinchera, A.; Parisi, B.; Baratella, V.; Roccuzzo, G.; Soave, I.; Bazzocchi, C.; Fichera, D.; Finotti, M.; Riva, F.; Mocciaro, G.; et al. Assessing the origin of phosphonic acid residues in organic vegetable and fruit crops: The Biofosf project multi-factor approach. *Agronomy* 2020, 10, 421. [CrossRef]

126. Sala, F.; Costa, C.; Echer, M.; Martins, M.; Blat, S. Phosphate effect on hot and sweet pepper reaction to *Phytophthora capsici*. *Sci. Agric.* 2004, 61, 492–495. [CrossRef]

127. Mayton, H.; Myers, K.; Fry, W. Potato late blight-The role of foliar Phosphonates applications in suppressing pre-harvest tuber infections. *Crop. Protect.* 2008, 27, 943–950. [CrossRef]

128. Cooke, L.; Little, G. The effect of foliar application of phosphonate formulations on the susceptibility of potato tubers to late blight. *Pest. Manag. Sci.* 2002, 58, 17–25. [CrossRef]

129. Han, X.; Xi, Y.; Zhang, Z.; Mohammadi, M.; Joshi, J.; Borza, T.; Wang-Pruski, G. Effects of phosphate as a plant biostimulant on metabolism and stress response for better plant performance in *Solanum tuberosum*. *Ecotox. Environ. Safety* 2021, 210, 111873. [CrossRef] [PubMed]

130. Mohammadi, M.; Zhang, Z.; Xi, Y.; Han, H.; Lan, F.; Zhang, B.; Wang-Pruski, G. Effects of potassium phosphite on biochemical contents and enzymatic activities of Chinese potatoes inoculated by *Phytophthora infestans*. *Appl. Ecol. Environ. Res.* 2019, 17, 4499–4514. [CrossRef]

131. Vincelli, P.; Dixon, E. Performance of selected phosphate fungicides on greens. *Golf. Course Manag.* 2005, 73, 77–81.

132. Landschoot, P.; Cook, J. Sorting out the Phosphonate Products. *Golf. Course Manag.* 2005, 73, 73–77.
133. Cook, P. Inhibition of *Pythium* ssp. and Suppression of Pythium Blight and Anthracnose with Phosphonate Fungicides. Master’s Thesis, Pennsylvania State University, State College, PA, USA, 2009.

134. Ervin, E.; McCall, D.; Horvath, B. Efficacy of phosphite fungicides and fertilizers for control of pythium blight on a perennial ryegrass fairway in Virginia. *Appl. Turfgrass Sci.* 2009. [CrossRef]

135. McComb, J.; O’Brien, P.; Calver, M.; Staskowski, P.; Jardine, N.; Eshraghi, L.; Ellery, J.; Gilovitz, J.; Scott, P.; O’Brien, J.; et al. Research into Natural and Induced Resistance in Australian Native Vegetation of *Phytophthora cinnamomi* and Innovative Methods to Contain and/or Eradicate within Localised Incursions in Areas of High Biodiversity in Australia; No. 19/2005DEH Sub Project 19.2.2; Centre for Phytophthora Science and Management for the Australian Government Department of the Environment, Water, Heritage and the Arts: Perth, Australia, 2008.

136. Lambers, H.; Ahmedi, I.; Berkowitz, O.; Dunne, C.; Finnegan, P.; Hardy, G.; Jost, R.; Laliberté, E.; Pearse, S.; Teste, F. Phosphorus nutrition of phosphorus-sensitive Australian native plants: Threats to plant communities in a global biodiversity hotspot. *Cons. Physiol.* 2013, 1, 1–21. [CrossRef]