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Review

Review of Phosphite as a Plant Nutrient and Fungicide

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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

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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 phosphite (*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).

Phosphite ($H_2PO_3^-$; HPO_3^{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].

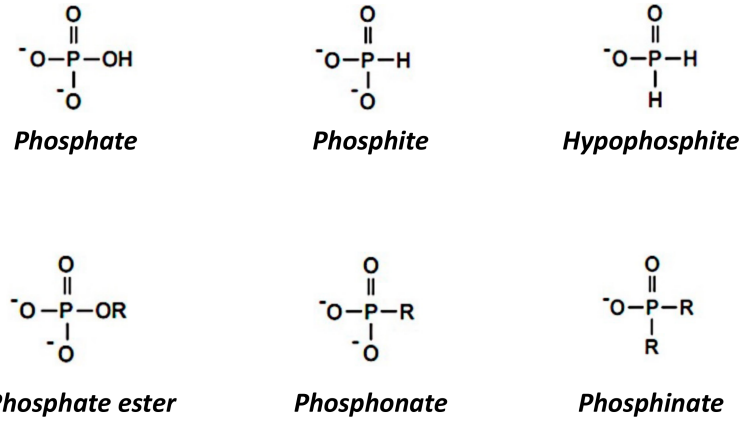

Figure 1. Structural differences between *phosphate ester* and *phosphonate/phosphinate* species. The ester contains P-O-C and the reduced phosphorus species contain P-C, where "R" represents a carbon chain of variable structures.

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

Phosphorus Form [1]	Chemical Formula	Redox State [2]	Dissociation Reaction (in H_2O)	Ka [3]
phosphoric acid	H_3PO_4	+5	$H_3PO_4 \rightleftarrows H_2PO_4^- + H^+$	$10^{-2.15}$
phosphate	$H_2PO_4^-$, HPO_4^{2-}		$H_2PO_4^- \rightleftarrows HPO_4^{2-} + H^+$	$10^{-7.2}$
			$HPO_4^{2-} \rightleftarrows PO_4^{3-} + H^+$	$10^{-12.35}$
phosphorous acid (phosphonic acid)	H_3PO_3	+3	$H_3PO_3 \rightleftarrows H_2PO_3^- + H^+$	$10^{-1.5}$
phosphite (phosphonate)	$H_2PO_3^-$, HPO_3^{2-}		$H_2PO_3^- \rightleftarrows HPO_3^{2-} + H^+$	$10^{-6.79}$
hypophosphorus acid	H_3PO_2	+1	$H_3PO_2 \rightleftarrows H_2PO_2^- + H^+$	$10^{-1.1}$
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 (*Phi* and *Pi*) cause confusion in understanding how each reacts in the plant, differences in oxidation state, size, and charge suggest that *Phi* does not substitute for *Pi* in the majority of biochemical reactions. McDonald [11] provides an excellent description of how the structural differences between *Phi* and *Pi* strongly influence their binding to the surface of enzymes specific to *Pi* metabolism. While both *Pi* and *Phi* have a tetrahedral coordinated structure (Figure 1), *Pi* is symmetrical, resulting in a uniform charge distribution in the ion. In contrast, the asymmetry related to the P-H bond in *Phi* results in a non-uniform or slightly polar charge distribution. With *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 *Phi*, only one side of the tetrahedron can bind with the enzyme surface, with the remaining "H" exposed. Apparently, this difference between *Pi* and *Phi* interaction with the enzyme surface prevents *Phi* from participating in the same enzyme activated reactions associated with *Pi* metabolism.

The effect of solution pH on the relative concentrations of *Pi* and *Phi* ions in solution is determined by their aqueous dissociation constant (Ka) (Table 1). With *Pi*, for example, the common species in soil solution over the normal pH range of 3 to10 are $H_2PO_4^-$ and HPO_4^{2-} (Figure 2). With a Ka of $10^{-7.2}$, concentration of $H_2PO_4^-$ = HPO_4^{2-} at pH 7.2 [10]. Below pH 7.2, $H_2PO_4^-$ is the dominant anion in solution, whereas above pH 7.2, HPO_4^{2-} is the dominant species. This is not a particularly important distinction, since plants readily absorb either *Pi* form. In the soil pH range of 3 to 10, H_3PO_4 and PO_4^{3-} would not exist. Similar relationships can be developed for *Phi* (Figure 3). In this case, $H_2PO_3^-$ = HPO_3^{2-} at pH 6.8, and H_3PO_3 would not exist under the normal soil pH range of 3 to10.

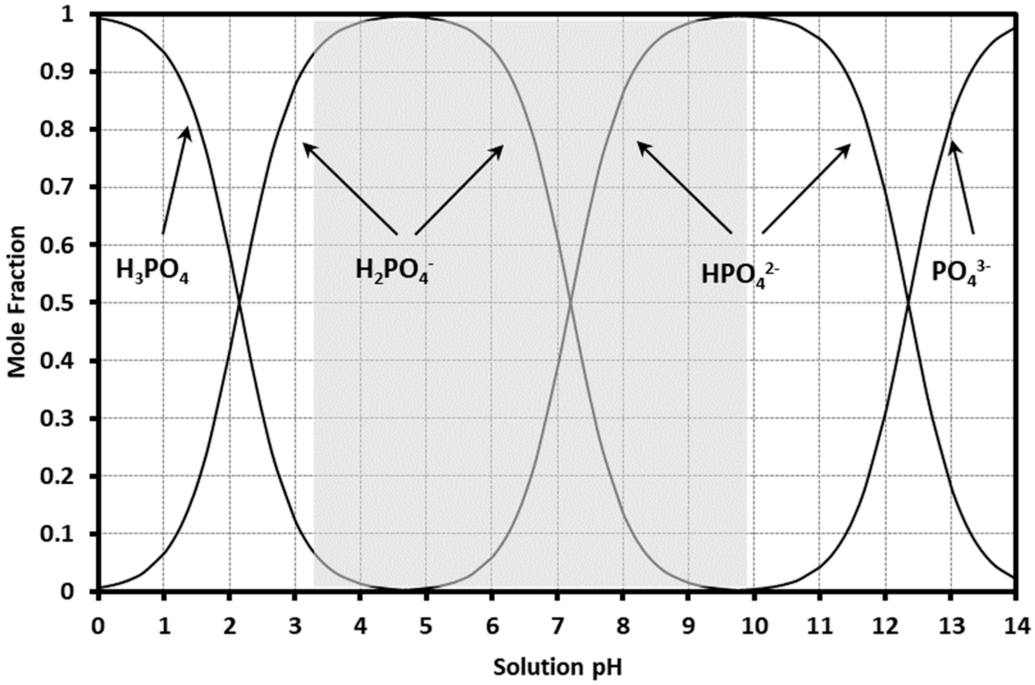

Figure 2. Distribution of *phosphate* species in water as influenced by pH. Shaded area represents normal range in soil pH.

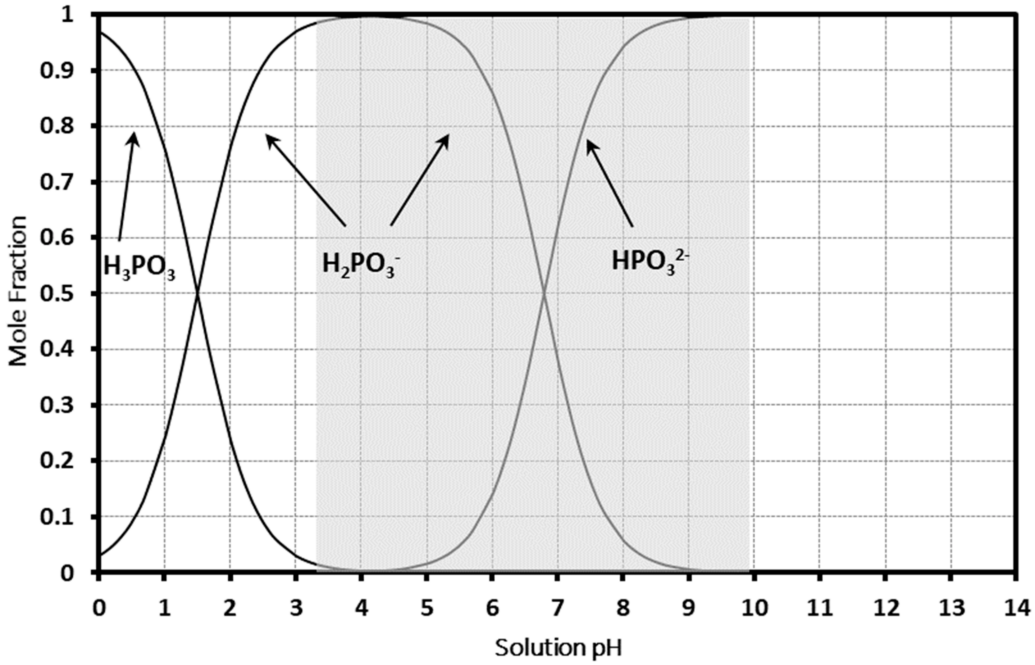

Figure 3. Distribution of *phosphite* species in water as influenced by pH. Shaded area represents normal range in soil pH.

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) H_3PO_3 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.

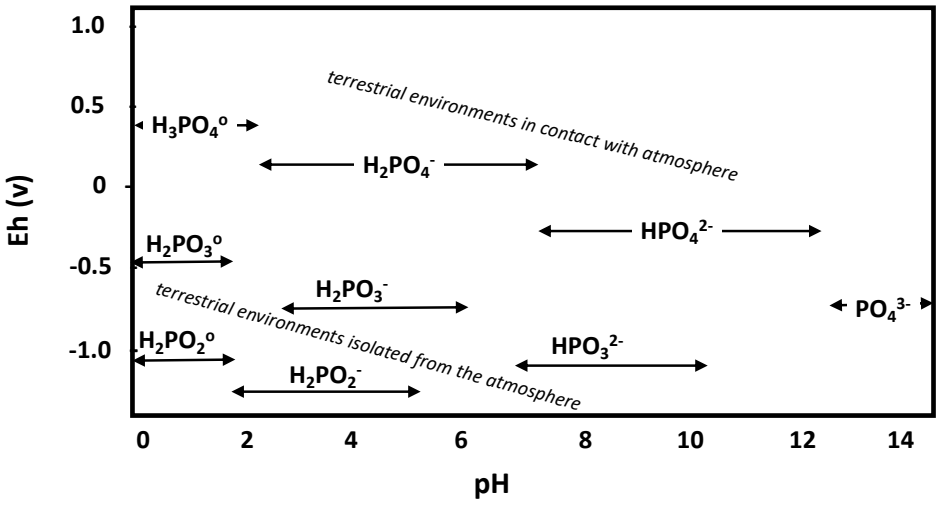

Figure 4. Influence of pH and oxidation (Eh) on *Phi* and *Pi* species in solution. Area in white represents current atmospheric conditions, red represents reduced conditions, and blue is highly oxidized (not common under normal atmospheric conditions).

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; *Pi* 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. oleoabundans*) 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 *hypophosphite* under aerobic and anaerobic conditions. Evidence from *Pseudomonas stutzeri* WM88 suggests that *hypophosphite* 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^{2-}) to hydrogen sulfide (H_2S) [34]. Other bacteria including a*grobacterium tumafaciens*, *bacillus caldolyticus*, *escherichia coli*, *serratia marcescens*, and numerous *pseudomonas* species (*aeruginosa*, *fluorescens*, and *stutzeri*) are capable of oxidizing *Phi* or *hypophosphite* [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 phosphonatases/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 ^{31}P-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, Pandeya [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 [1]	[75]
Citrus, avacado	Foliar	Yes	[76–78]
Citrus	Foliar	Negative	[79]
Common bean	Soil, foliar	Negative [1]	[80,81]
Corn	Foliar	Negative [1]	[54]
Corn	Hydroponic	Negative	[82]
Corn	Foliar	No	[83]
Cotton	Foliar	Yes [2]	[71]
Cucumber	Foliar	Negative [1]	[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 [1]	[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 ptxD gene.

Reduced P fertilizers (H_3PO_3, 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 $NaHCO_3$ extractable P. The lack of response to *Pi* or *Phi* was due to sufficient soil test P levels. An increase in $NaHCO_3$-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 *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 *Phi* and urea (no *Phi*), and neither study compared foliar *Phi* to *Pi*. In contrast, Zambrosi [79] reported *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 *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, *Phi* treatments were compared to an "untreated control" and not with *Pi*. Where *Pi* was applied, foliar *Phi* treatments were compared to soil applied *Pi*. Finally, where mean separations were provided, *Phi* treatment effects were generally not significant. In only two studies (alfalfa and oranges) were equivalent rates of foliar *Phi* and *Pi* compared. There were no significant differences between P sources in orange leaf P or root weight. Alfalfa dry matter was 11% greater with *Pi* than *Phi*. Rickard [93] concludes that in each study *Phi* increased yield or P content over the untreated control, which demonstrates that plants can utilize *Phi* as a nutrient source, assuming that the response to *Phi* was not related to a reduction in disease pressure. McDonald [11] suggested that claims of higher yields with *Phi* treated crops could be related to *Phi* oxidation to *Pi* or from the fungicidal effects on selected plant pathogens.

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

Many studies reported *Pi* deficient plants are more sensitive to *Phi* application compared to plants supplied with some *Pi*, where negative effects of *Phi* could be overcome by *Pi* addition [11,56,58,64]. In field studies with corn grown in P deficient soil, foliar *Pi* and *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 *Phi* applied to plants grown under soil applied *Phi*, compared to foliar *Phi* with soil applied *Pi*. They documented that *Phi* was readily absorbed by roots and leaves, translocated throughout the plant, and was relatively stable in the plant (little *Phi* oxidation to *Pi*), thus *Phi* was not available to the plant.

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

Ávila [80] grew common bean (*Phaseolus vulgaris*) in low and adequate soil *Pi* fertilized with increasing *Phi* ($0 \rightarrow 100$ mg P dm^{-3} soil). In low *Pi* soil, *Phi* reduced plant growth and grain yield only when *Phi* was $\geq$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 ($0 \rightarrow 512$ µM). At low *Pi*, plant growth and grain yield were reduced, such that when *Phi* was $\geq$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* ($0 \rightarrow 3$ 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*, Ávila [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% $^{31}Pi/^{31}Phi$ 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* ($1 \rightarrow 12$ mM). *Phi* ($\geq$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 $\leq$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 ($0 \rightarrow 50\%$ 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 cinnamomi*, *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 cinnamomi*. 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]
Avacado	Dieback	Phytophthora cinnamomi	[107]
Banksia	Dieback	Phytophthora cinnamomi	[108]
Bentgrass	Summer decline	Pythium	[73]
Cabbage	Clubroot	Plasmodiophora 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 sorghi	[114]
Orange	Brown rot	Phytophthora citrophthora	[53]
Papaya	Fruit rot	Phytophthora palmivora	[113]
Pecan	Scab	Fusicladium 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., aminooxyacetic 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*, less is known about *Phi* oxidation in plants to provide nutritional *Pi*. Applied to soil, chemical oxidation of *Phi* is too slow to provide *Pi*; however, microbial oxidation in soils has been documented and likely provides some level of plant available *Pi*, increasing with reaction time. Additional research is needed to quantify the kinetics of residual availability of soil applied *Phi*. Although *Phi* 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* on crops are strongly dependent on the P nutrient status of the plant. Any negative effect of *Phi* on plant growth is usually observed in severely *Pi* deficient plants compared to plants with elevated *Pi* supply. Literature supporting positive plant responses to *Phi* + *Pi* applied to plants with less than optimum *Pi* supply is variable; where positive responses to *Phi* have been attributed to some level of fungal disease control. While considerable evidence exists for cellular oxidation of *Phi* in soil microorganisms, only a few studies have provided evidence of *Phi* 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* in plants. Since *Phi* oxidation occurs slowly in soils, additional information is needed to characterize *Phi* 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* to control the kinetics of *Phi* oxidation to benefit plant recovery of applied *Phi*. Genetic engineering of crop plants to sustain growth and yield with *Phi* + *Pi* provides a dual fertilization–weed control system. Further advances in genetic manipulation of plants to utilize *Phi* are warranted.

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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.; Harnmeijer, J.; Buick, R.; Maheen, 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.; Stottmeister, 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 I A comparison of two forest types. *Can. J. For. Res.* **2000**, *30*, 1714–1725. [CrossRef]
18. Hedley, M.; Stewart, J.; Chauhan, B. Changes in the inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubation. *Soil Sci. Soc. Am. J.* **1982**, *46*, 970–976. [CrossRef]
19. Condron, L.M.; Newman, S. Revisiting the fundamentals of phosphorous fractionation of sediments and soil. *J. Soils Sediments* **2011**, *11*, 830–840. [CrossRef]
20. 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.
21. Adams, F.; Conrad, J. Transition of Phosphite to Phosphate in Soils. *Soil Sci.* **1953**, *75*, 361–371. [CrossRef]
22. Casida, L. Microbial oxidation and utilization of orthophosphite during growth. *J. Bacteriol.* **1960**, *80*, 237–241. [CrossRef]
23. Malacinski, G.; Konetzka, W. Bacterial oxidation of orthophosphite. *J. Bacteriol.* **1966**, *91*, 578–582. [CrossRef]
24. Loera-Quezada, M.; Leyva-Gonzalez, M.; Lopez-Arredondo, D.; Herrara-Estrella, L. Phosphite cannot be used as a phosphorus source but is non-toxic for microalgae. *Plant. Sci.* **2015**, *231*, 124–130. [CrossRef] [PubMed]
25. Bezuidenhout, J.; Darvas, J.; Kotze, J. The dynamics and distribution of phosphite in avocado trees treated with phosetyl-Al. *S. Afr. Avocado Grow. Assoc. Yearb.* **1987**, *10*, 101–103.
26. Ohtake, H.; Wu, H.; Imazu, K.; Anbe, Y.; Kato, J.; Kuroda, A. Bacterial phosphonate degradation, phosphite oxidation and polyphosphate accumulation. *Resour. Conserv. Recycl.* **1996**, *18*, 125–134. [CrossRef]
27. 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]
28. Metcalf, W.; Wolfe, R. Molecular Genetic Analysis of Phosphite and Hypophosphite Oxidation by Pseudomonas stutzeri WM88. *J. Bacteriol.* **1998**, *180*, 5547–5558. [CrossRef] [PubMed]
29. 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] [PubMed]
30. Foster, T.; Winans, L.; Helms, S. Anaerobic utilization of phosphite and hypophosphite by *Bacillus* sp. *Appl. Environ. Microbiol.* **1978**, *35*, 937–944. [CrossRef] [PubMed]
31. Pao, S.; Paulsen, I.; Saier, M. Major facilitator superfamily. *Microbiol. Mol. Biol. Rev.* **1998**, *62*, 1–34. [CrossRef]
32. 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]
33. 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 Phosphite Dehydrogenase. *Biochemistry* **2012**, *51*, 4254–4262. [CrossRef] [PubMed]
34. Schink, B.; Thiemann, V.; Laue, H.; Friedrich, M. Desulfotignum *phosphitoxidans* sp. nov., a new marine sulfate reducer that oxidizes phosphite to phosphate. *Arch. Microbiol.* **2002**, *177*, 381–391. [CrossRef] [PubMed]
35. Simeonova, D.; Wilson, M.; Metcalf, W.; Schink, B. Identification and Heterologous Expression of Genes Involved in Anaerobic Dissimilatory Phosphite Oxidation by Desulfotignum phosphitoxidans. *J. Bacteriol.* **2010**, *192*, 5237–5244. [CrossRef]
36. Howard, K.; Dell, B.; Hardy, G. Phosphite and mycorrhizal formation in seedlings of three Australian Myrtaceae. *Aust. J. Botany.* **2001**, *48*, 725–729. [CrossRef]
37. Metcalf, W.; Wanner, B. Involvement of the Escherichia coli phn (psiD) gene cluster in assimilation of phosphorus in the form of phosphonates, phosphite, *Pi* esters, and *Pi*. *J. Bacteriol.* **1991**, *173*, 587–600. [CrossRef] [PubMed]
38. Woodyer, R.; van der Donk, W.; Zhao, H. Relaxing the nicotinamide cofactor specificity of phosphite dehydrogenase by rational design. *Biochemistry* **2003**, *42*, 11604–11614. [CrossRef] [PubMed]
39. Yang, K.; Metcalf, W. A new activity for an old enzyme: Escherichia coli bacterial alkaline phosphatase is a phosphite-dependent hydrogenase. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 7919–7924. [CrossRef] [PubMed]
40. White, A.; Metcalf, W. Two C-P lyase operons in Pseudomonas stutzeri and their roles in the oxidation of phosphonates, phosphite, and hypophosphite. *J. Bacteriol.* **2004**, *186*, 4730–4739. [CrossRef]
41. Figueroa, I.; Coates, J. Microbial Phosphite Oxidation and Its Potential Role in the Global Phosphorus and Carbon Cycles. *Adv. Appl. Microbiol.* **2017**, *98*, 93–117. [CrossRef] [PubMed]
42. 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]
43. 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]
44. Rodríguez, H.; Fraga, R. Phosphate solubilizing bacteria and their role in plant growth promotion. *Biotech. Adv.* **1999**, *17*, 319–339. [CrossRef]
45. 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.

46. Raymond, N.; Gomez-Munoz, B.; van der Bom, F.; Nybroe, O.; Jensen, L.; Muller-Stover, D.; Oberson, A.; Richardson, A. Phosphate-solubilising microorganisms for improved crop productivity: A critical assessment. *New Phytol.* **2021**, *229*, 1268–1277. [CrossRef] [PubMed]
47. White, A.; Metcalf, W. Microbial Metabolism of Reduced Phosphorus Compounds. *Ann. Rev. Microbiol.* **2007**, *61*, 379–400. [CrossRef] [PubMed]
48. Fontana, M.; Bragazza, L.; Guillaime, T.; Santonja, M.; Buttler, A.; Elfouki, S.; Sinaj, S. Valorization of calcium phosphite waste as phosphorus fertilizer: Effects on green manure productivity and soil properties. *J. Environ. Manag.* **2021**, *285*, 112061. [CrossRef] [PubMed]
49. Kehler, A.; Haygarth, P.; Tamburini, F.; Blackwell, M. Cycling of reduced phosphorus compounds in soil and potential impacts of climate change. *Eur. J. Soil Sci.* **2021**, *2021*, 1–21.
50. Griffith, J.; Coffey, M.; Grant, B. Phosphonate inhibition as a function of phosphate concentration in isolates of Phytophthora palmivova. *J. Gen. Microbiol.* **1993**, *139*, 2109–2116. [CrossRef]
51. Ratjen, A.; Gerendás, J. A critical assessment of the suitability of phosphite as a source of phosphorus. *J. Plant. Nutr. Soil Sci.* **2009**, *172*, 821–828. [CrossRef]
52. Thao, H.; Yamakawa, T.; Myint, A.; Sarr, P. Effects of phosphite, a reduced form of phosphate, on the growth and phosphorus nutrition of spinach (*Spinacia oleracea* L.). *Soil Sci. Plant. Nutr.* **2008**, *54*, 761–768. [CrossRef]
53. Orbovic, V.; Syvertsen, J.; Bright, D.; van Clief, D.; Graham, J. Citrus seedling growth and susceptibility to root rot as affected by phosphite and phosphate. *J. Plant. Nutr.* **2008**, *31*, 774–787. [CrossRef]
54. Schroetter, S.; Angeles-Wedler, D.; Kreuzig, R.; Schnug, E. Effects of phosphite on phosphorus supply and growth of corn (*Zea mays*). *Landbauforsch. Völkenrode* **2006**, *56*, 87–99. [CrossRef]
55. Danova-Alt, R.; Dijema, C.; Dewaard, P.; Kock, M. Transport and compartmentation of phosphite in higher plant cells–kinetic and ^{31}P nuclear magnetic resonance studies. *Plant. Cell Environ.* **2008**, *31*, 1510–1521. [CrossRef] [PubMed]
56. Lee, T.; Tsai, P.; Shya, Y.; Sheu, F. The effects of phosphite on phosphate starvation responses of Ulva lactuca (Ulvales, Chlorophyta). *J. Phycol.* **2005**, *41*, 975–982. [CrossRef]
57. Carswell, M.; Grant, B.; Plaxton, W. Disruption of the phosphate-starvation response of oilseed rape suspension cells by the fungicide phosphonate. *Planta* **1997**, *203*, 67–74. [CrossRef] [PubMed]
58. Carswell, M.; Grant, B.; Theodorou, M.; Harris, J.; Niere, J.; Plaxton, W. The fungicide phosphonate disrupts the phosphate-starvation response in *Brassica nigra* seedlings. *Plant Physiol.* **1996**, *110*, 105–110. [CrossRef] [PubMed]
59. Förster, H.; Adaskaveg, J.; Kim, D.; Stanghellini, M. Effect of Phosphite on Tomato and Pepper Plants and on Susceptibility of Pepper to Phytophthora Root and Crown Rot in Hydroponic Culture. *Plant. Dis.* **1998**, *82*, 1165–1170. [CrossRef]
60. Varadarajan, D.; Karthikeyan, A.; Matilda, P.; Raghothama, K. Phosphite, an Analog of Phosphate, Suppresses the Coordinated Expression of Genes under Phosphate Starvation. *Plant. Physiol.* **2002**, *129*, 1232–1240. [CrossRef]
61. Thao, H.; Yamakawa, T. Phosphite (phosphorous acid): Fungicide, fertilizer or bio-stimulator? *Soil Sci. Plant. Nutr.* **2009**, *55*, 228–234. [CrossRef]
62. Ticconi, C.; Delatorre, C.; Abel, S. Attenuation of Phosphate Starvation Responses by Phosphite in Arabidopsis. *Plant. Physiol.* **2001**, *127*, 963–974. [CrossRef]
63. Ticconi, C.; Abel, S. Short on phosphate: Plant surveillance and countermeasures. *Trends Plant. Sci.* **2004**, *9*, 548–555. [CrossRef]
64. Singh, V.; Wood, S.; Knowles, V.; Plaxton, W. Phosphite accelerates programmed cell death in phosphate starved oilseed rape (Brassica napus) suspension cell cultures. *Planta* **2003**, *218*, 233–239. [CrossRef] [PubMed]
65. Gomez-Merino, F.; Trejo-Tellez, L. Conventional and novel uses of phosphite in horticulture: Potentialities and challenges. *Italus Hortes* **2016**, *23*, 1–13.
66. Rouphael, Y.; Colla, G. Editorial: Biostimulants in Agriculture. *Front. Plant. Sci.* **2020**, *11*, 40. [CrossRef] [PubMed]
67. Herrera-Estrella, L.; Lopez-Arredondo, D.; Heriberto, A. 2012. Fungi Adapted to Metabolize Phosphite as a Source of Phosphorus. U.S. Patent Application 2012/0285210 A1, 15 November 2012.
68. Lopez-Arredondo, D.; Herrera-Estrella, L. Engineering phosphorus metabolism in plants to produce a dual fertilization and weed control system. *Nat. Biotech.* **2012**, *30*, 889–893. [CrossRef]
69. Manna, M.; Archary, V.; Islam, T.; Agrawal, P.; Reddy, M. The development of a phosphite mediated fertilization and weed control system for rice. *Sci. Rep.* **2016**, *6*, 24941. [CrossRef]
70. Ram, B.; Fartyal, D.; Sheri, V.; Varakumar, P.; Borphukan, B.; James, D.; Yadav, R.; Bhatt, A.; Achary, P.A.V.; Reddy, M. Characterization of phoA, a bacterial alkaline phosphatase for *Phi* use efficiency in rice plant. *Front. Plant. Sci.* **2019**, *10*, 37–47. [CrossRef]
71. Pandeya, D.; Lopez-Arrendondo, D.; Janga, M.; Campbell, L.; Estrella-Hernandez, P.; Bagavathiannan, M.; Herrera-Estrella, L.; Rathore, K. Selective fertilization with phosphite allows unhindered growth of cotton plants expressing the ptxD gene while suppressing weeds. *Proc. Natl. Acad. Sci. USA* **2018**, *115*, E6946–E6955. [CrossRef]
72. Achary, V.; Ram, B.; Manna, M.; Datta, D.; Bhatt, A.; Reddy, M.; Agrawal, P. Phosphite: A novel P fertilizer for weed management and pathogen control. *Plant Biotech. J.* **2017**, *15*, 1493–1508. [CrossRef]
73. Lucas, L. Development and management of summer decline of bentgrass. *PACE Insights* **1995**, *1*, 2–3.
74. Dorer, S. Nutritional Effects of a Fungicide Combination on Summer Bentgrass Decline. Master's Thesis, North Carolina State University, Raleigh, NC, USA, 1996.

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. Ávila, 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. Ávila, F.; Faquin, V.; Lobato, A.; Ávila, P.; Marques, D.; Guedes, E.; Tan, D. Effect of phosphite supply in nutrient solution on yield, phosphorus nutrition and enzymatic behavior in common bean (*Phaseolus vulgaris* L.) plants. *Aust. J. Crop. Sci.* **2013**, *7*, 713–722.
82. Ávila, F.; Faquin, V.; Araújo, J.; Marques, D.; Ribeiro, P.; Lobato, A.; Ramos, S.; Baliza, D. Phosphite supply affects phosphorus nutrition and biochemical responses in maize plants Austr. *J. Crop. Sci.* **2011**, *5*, 646–653.
83. Sutradhar, A.; Arnall, D.; Dunn, B.; Raun, W. Does phosphite, a reduced form of phosphate contribute to phosphorus nutrition in corn (*Zea mays* L.)? *J. Plant. Nutr.* **2019**, *42*, 982–989. [CrossRef]
84. Constán-Aguilar, C.; Sánchez-Rodríguez, E.; Rubio-Wilhelmi, M.; Camacho, M.; Romero, L.; Ruiz, J.M.; Blasco, B. Physiological and Nutritional Evaluation of the Application of Phosphite as a Phosphorus Source in Cucumber Plants. *Commun. Soil Sci. Plant. Anal.* **2014**, *45*, 204–222. [CrossRef]
85. Thao, H.; Yamakawa, T. Phosphate absorption of intact komatsuna plants as influenced by phosphite. *Soil Sci. Plant. Nutr.* **2010**, *56*, 133–139. [CrossRef]
86. Estrada-Ortiz, E.; Trejo-Téllez, 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]
87. Estrada-Ortiz, E.; Trejo-Téllez, L.; Gómez-Merino, F.; Silva-Rojas, H.; Castillo-González, A.; Avitia-García, E. Physiological Responses of Chard and Lettuce to Phosphite Supply in Nutrient Solution. *J. Agr. Sci. Tech.* **2016**, *18*, 1079–1090.
88. Glinicki, R.; Sas-Paszt, L.; Jadczuk-Tobjasz, E. The Effect of Plant Stimulant/Fertilizer "Resistim" on growth and Development of Strawberry Plants. *J. Fruit Ornament. Plant. Res.* **2010**, *18*, 111–124.
89. Hirosse, E.; Creste, J.; Custódio, C.; Barbosa, N.; Machado-Neto, N. In vitro growth of sweet potato fed with potassium phosphite. *Acta Sci. Agron.* **2012**, *34*, 85–91. [CrossRef]
90. Vinas, M.; Mendez, J.; Jiménez, V. Effect of foliar applications of phosphites on growth, nutritional status and defense responses in tomato plants. *Sci. Hortic.* **2020**, *265*, 109200. [CrossRef]
91. Ali, M.; Sutradhar, A.; Edano, M.; Edwards, J.; Girma, K. Response of Winter Wheat Grain Yield and Phosphorus Uptake to Foliar Phosphite Fertilization. *Int. J. Agron.* **2014**, *2014*, 1–8. [CrossRef]
92. Albrigo, L. Effects of foliar applications of urea or Nutriphite on flowering and yields of Valencia orange trees. *Proc. Florida State Hortic. Soc.* **1999**, *112*, 1–4.
93. Rickard, D. Review of Phosphorus Acid and Its Salts as Fertilizer Materials. *J. Plant. Nutr.* **2000**, *23*, 161–180. [CrossRef]
94. Jost, R.; Pharmawati, M.; Lapis-Gaza, H.; Rossig, C.; Berkowitz, O.; Lambers, H.; Finnegan, P. Differentiating phosphate-dependent and phosphate-independent systemic phosphate-starvation response networks in Arabidopsis thaliana through the application of phosphite. *J. Exp. Bot.* **2016**, *66*, 2501–2514. [CrossRef]
95. Panigrahy, M.; Rao, D.; Sarla, N. Molecular mechanisms in response to phosphate starvation in rice. *Biotech. Adv.* **2009**, *27*, 389–397. [CrossRef]
96. Abel, S.; Ticconi, C.; Delatorre, C. Phosphate sensing in higher plants. *Physiol. Plant.* **2002**, *115*, 1–8. [CrossRef]
97. Raghothama, K. Phosphate transport and signaling. *Curr. Opin. Plant. Biol.* **2000**, *3*, 182–187. [CrossRef]
98. Marschner, H. *Mineral. Nutrition in Plants*, 2nd ed.; Academic Press: San Diego, CA, USA, 1995.
99. Deliopoulus, T.; Kettlewell, P.; Hare, M. Fungal disease suppression by inorganic salts: A review. *Crop. Prot.* **2010**, *29*, 1059–1075. [CrossRef]
100. Gomez-Merino, F.; Trejo-Tellez, L. Biostimulant activity of phosphite in horticulture. *Sci. Hort.* **2015**, *196*, 82–90. [CrossRef]
101. Hardy, G.; Barrett, S.; Shearer, B. The future of phosphite as a fungicide to control the soilborne plant pathogen *Phytophthora cinnamomi* in natural ecosystems. *Australas. Plant Pathol.* **2001**, *30*, 133–139. [CrossRef]
102. Silva, O.; Santos, H.; Pria, M.D.; Mio, L.M. Potassium phosphite for control of downy mildew of soybean. *Crop. Prot.* **2011**, *30*, 598–604. [CrossRef]
103. 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. *Australas. Plant. Path.* **2007**, *36*, 358–368. [CrossRef]
104. Oka, Y.; Tkachi, N.; Mor, M. Phosphite Inhibits Development of the Nematodes Heterodera avenae and Meloidogyne marylandi in Cereals. *Phytopath* **2007**, *97*, 396–404. [CrossRef] [PubMed]
105. Graham, J.H. Phosphite 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.; Cautin, R.; Jeria, G. Evaluation of calcium phosphite; magnesium phosphite and potassium phosphite in the control of phytophthora cinnamomic 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 cinnamomic*. *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. *J. Plant. Path.* **2009**, *91*, 565–571.
111. Abbasi, P.; Lazarovits, G. Seed treatment with phosphonate (AG3) suppresses Pythium damping-off of cucumber seedlings. *Plant Dis.* **2006**, *90*, 459–464. [CrossRef]
112. 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]
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. *Phytopath* **1989**, *79*, 921–926. [CrossRef]
114. Panicker, S.; Gangadharan, K. Controlling downy mildew of maize caused by *Peronosclerospora sorghi* by foliar sprays of phosphoric acid compounds. *Crop Prot.* **1999**, *18*, 115–118. [CrossRef]
115. 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]
116. Liljeroth, E.; Lankinen, A.; Wiik, L.; Burra, D.; Alexandersson, E.; Andreasson, E. Potassium phosphite combined with reduced doses of fungicides provides efficient protection against potato late blight in large-scale field trails. *Crop. Prot.* **2016**, *86*, 42–55. [CrossRef]
117. Mohammadi, M.; Han, X.; Zhang, Z.; Xi, Y.; Boorboori, M.; Wang-Pruski, G. Phosphite Application Alleviates *Pythophthora infestans* by Modulation of Photosynthetic and Physio-Biochemical Metabolites in Potato Leaves. *Pathogens* **2020**, *9*, 170. [CrossRef]
118. Johnson, D.; Inglis, D.; Miller, J. Control of potato tuber rots caused by oomycetes with foliar applications of phosphorous acid. *Plant. Dis.* **2004**, *88*, 1153–1159. [CrossRef]
119. Lobato, M.; Machinandiarena, M.; Tambascio, C.; Dosio, G.; Caldiz, D.; Daleo, G.; Andreu, A.; Olivieri, F. Effect of foliar applications of phosphite on post-harvest potato tubers. *Eur. J. Plant. Path.* **2011**, *130*, 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 cactorum*. *Plant Dis.* **2007**, *91*, 559–564. [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. Fenn, M.; Coffey, M. Quantification of Phosphonate and Ethyl Phosphonate in Tobacco and Tomato Tissues and its Significance for the Mode of Action of Two Phosphonate Fungicides. *Phytopathology* **1989**, *79*, 76–82. [CrossRef]
123. Ouimette, D.; Coffey, M. Phosphonate levels in avocado (*persea americana*) seedlings and soil following treatment with fosetyl-Al or potassium phosphonate. *Plant. Dis.* **1989**, *73*, 212–215. [CrossRef]
124. Jackson, T.; Burgess, T.; Colquhoun, I.; Hardy, G. Action of the Fungicide Phosphite on Eucalyptus marginata Inoculated with Phytophthora cinnamomi. *Plant. Path.* **2000**, *49*, 147–154. [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. Phosphite 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 phosphite 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 phosphite 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]