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Are Phosphorous and Phosphoric Acids Equal Phosphorous Sources for Plant Growth?[1]

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Phosphorus (P) is one of the 17 elements essential for plant growth and development (nickel is the 17th) (Association of American Plant Food Control Officials 2005; Bai, Reilly, and Wood 2006). Phosphorus is also a key component in some agrochemicals, such as phosphorous acid (H_3PO_3). Thus, there are two types of P closely associated with crop production. While growers are familiar with P-containing fertilizers, the abundance of terms, apparently similar (such as phosphoric acid and phosphorous acid), may create some confusion as to the actual content and efficacy of these products. Table 1 lists some P-containing compounds used for crop production. Some claims found in commercial literature and product descriptions refer to phosphorous acid as a "supplemental fertilizer," while others present it as a fungicide (Table 2). The purpose of this article is to explain what phosphorous acid is and to examine both its fungicidal activity and nutrient value.

The amount of phosphorus in a fertilizer is represented as the middle number on the bag expressed as phosphorus pentoxide (P_2O_5) (e.g., 5-10-15). The first number represents the nitrogen percentage, and the third number represents potassium percentage as K_2O. The P_2O_5 unit used to represent P content in fertilizer is a conventional unit (in reality, there is little or no P in the form of P_2O_5 in fertilizer).

As an essential element for normal plant growth and development, P is utilized in the fully oxidized and hydrated form, orthophosphate (H_3PO_4). Plants absorb and utilize either hydrogen phosphate (HPO_4^{2-}) and/or dihydrogen phosphate ($H_2PO_4^-$), depending on the pH of the growing medium. At pH7, both $H_2PO_4^-$ and HPO_4^{2-} are approximately equal in amount.In fertilizers, P is normally not found in the form of phosphoric acid (H_3PO_4) unless the growth medium is very acidic. At pH levels below 2.1, H_3PO_4 can become the dominant form, but at pH levels more favorable for plant growth (near neutral pH), the amount of H_3PO_4 is negligible. Compared with either $H_2PO_4^-$ or HPO_4^{2-}, it is only one out of 100,000 because it always dissociates to $H_2PO_4^-$ and further to HPO_4^{2-}. Both of these $H_2PO_4^-$ and HPO_4^{2-} ions are the basic forms taken up by the plant, but $H_2PO_4^-$ is taken up more readily (Street and Kidder 1989) because in most growth conditions, soil solution pH is below 7. Once inside the plant, both ions are mobile.

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Phosphoric acid (H_3PO_4) should not be confused with phosphorous acid (H_3PO_3). A little difference in the name or formula of a chemical compound can make a dramatic difference in its properties.The former is a fully oxidized and hydrated form of P, whereas the latter is a partially oxidized and hydrated form. Therefore, phosphorous acid is a powerful reducing agent, but phosphoric acid is not. The former is a diprotic acid (readily ionizes two protons), but the latter is a triprotic acid (readily ionizes three protons). Phosphorous acid dissociates to form the phosphonate ion (HPO_3^{2-}), also called phosphite. Phosphorous acid and its ionized compounds are often referred to as phosphonate or phosphonite. Like phosphate, phosphonate is easily taken up (Street and Kidder 1989) and translocated inside the plant.

Fosetyl-Al, which was registered by the EPA in 1983 (EPA 1991), is an aluminum salt of the diethyl ester of phosphorous acid and is sold under the trade name Aliette®. It is a systemic fungicide used to control damping-off and rot of plant roots, stems, and fruit, and it may be taken up by the plant. Inside the plant, fosetyl-Al may ionize into phosphonate, and therefore fosetyl-Al belongs to the group of phosphorous acid compounds (Cohen and Coffey 1986; McGrath 2004).

Phosphorous Acid as Fertilizer?

Phosphorous acid is not converted into phosphate, which is the primary nutrient source of P for plants (Ouimette and Coffey 1989b). There are bacteria capable of transforming phosphonate into phosphate, but this process is so slow that it is of no practical relevance (Huang, Su, and Xu 2005; McDonald, Grant, and Plaxton 2001). To date, no plant enzymes described oxidize phosphonate into phosphate. This is consistent with the fact that phosphonate is stable in plants and is not converted into phosphate (Smillie, Grant, and Guest 1989). Since phosphorous acid and its derivatives are not metabolized in plants, claims that phosphonate can contribute to P nutrient requirements for plants should be taken with caution.

Phophorous acid is used in agriculture but for a different purpose than phosphoric acid. Confirming other investigations into the efficacy of phosphorous acid against oomycetes (a group of pathogens that include water molds and downy mildew), Förster et al. (1998) found that phosphite is capable of controlling *Phytophthora* root and crown rot on tomato and pepper. The authors also tested the ability of phosphorous acid to act as a nutrient source for plant growth and found that P-deficiency symptoms developed when plants were grown hydroponically with phosphorous acid as the sole source of P (without phosphate). This means that although phosphorous acid can control oomycetes in a number of host-parasite systems, it is not a substitute for phosphorus fertilization. The inverse is also true: Phosphate is an excellent source of P for plant growth but is unable to control pathogen attack by oomycetes, other than by improving the general health of the crop and, therefore, its natural defense system. At this point in time, no evidence exists to substantiate the claim that phosphorous acid provides P for plant growth.

Control of Oomycetes

It is well documented that phosphorous acid can control diseases caused by pathogens that belong to the Oomycota phylum (or oomycetes) on agronomical and horticultural crops. Oomycetes (Figure 1) are actually not fungi but are frequently grouped with fungi because they form structures (filaments) similar to the ones that fungi make. In reality, oomycetes are fungal-like organisms that differ from fungi in that their cell walls do not contain chitin but rather a mixture of cellulosic compounds and glycan (polymeric carbohydrate). Another difference is that the nuclei in the cells that form the filaments have two sets of genetic information (diploid) in oomycetes instead of just one set (haploid) as in fungi (Waggoner and Speer 1995).

Figure 1. Downy mildew on lettuce

Credits: Tyler Harp and Syngenta Crop Protection

For most practical purposes, oomycetes are grouped with fungi. Compounds that control plant pathogens belonging to the oomycetes are often called fungicides. It is important to distinguish between fungi and oomycetes. Chemicals that are used to control one will often not be effective against the other because of biological differences. Several important plant pathogens belong to oomycetes (Table 3), such as *Phytophthora infestans,* the causal agent of late

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blight of potato (Figure 2) and the culprit of the Irish Potato Famine between 1845 and 1849; *P. ramorum*, the causal agent of sudden oak death (Parke and Lucas 2008); and *Pythium* and *Peronospora* species, among others (Fry and Grünwald 2010).

Figure 2. Potato late blight caused by *Phytophthora infestans*.

Credits: Tyler Harp and Syngenta Crop Protection

Phosphorous acid has both direct and indirect effects on oomycetes. It directly inhibits a particular process (oxidative phosphorylation) in the metabolism of oomycetes (McGrath 2004). An indirect effect is the stimulation of the plant's natural defense response against pathogen attack (Biagro Western Sales, Inc. 2003; Smillie, Grant, and Guest 1989). It should be noted, however, that phosphonate-resistant oomycetes have been reported (Ouimette and Coffey 1989a). In addition, some evidence suggests that phosphorous acid has an indirect effect by stimulating the plant's natural defense response against pathogen attack (Biagro Western Sales, Inc. 2003; Smillie, Grant, and Guest 1989).

Efficacy

A major factor in the ability of phosphorous acid to control oomycetes appears to be its chemical stability in the plant (Smillie, Grant, and Guest 1989). Phosphorous acid does not convert into phosphate and is not easily metabolized (Ouimette and Coffey 1989b). The stability of different phosphonate-related compounds may depend on environmental factors, such as climate or crop type. Because phosphonate is systemic and stable in plants, it should be applied infrequently in order to avoid accumulation problems. Plant species may differ in phosphonate uptake and translocation (Cooke and Little 2001), and individual *P. infestans* isolates show great variation in sensitivity (Bashan, Levy, and Cohen 1990; Coffey and Bower 1984) to phosphonate compounds, which may impact the effectiveness of phosphonate.

Table 4 summarizes some of the phosphorous acid-related compounds and research on their efficacy against potato late blight. In most cases, phosphorous acid is applied to the foliage. The compound is translocated from the shoots to the roots and can, therefore, also control oomycetes that affect roots. Phosphorous acid was shown to be effective when applied as a root drench against *P. cinnamomi*, *P. nicotianae*, and *P. palmivora* in lupin, tobacco, and papaya, respectively (Smillie, Grant, and Guest 1989). The efficacy of different phosphonate compounds against nine *Phytophthora* spp. that cause stem rot of *Persea indica* L. and pepper was tested both as a curative and preventive method of control by Ouimette and Coffey (1989a). Although there were notable differences in the sensitivity of the *Phytophthora* spp. in their experiments (Table 4), there was little variation in the ability of phosphonates to control stem rot of pepper, regardless of its use as a curative or a preventive agent in pots. A greater level of control was obtained for *Persea indica* L. than for pepper (Ouimette and Coffey 1989a).

Similar to other phosphonate-based systemic fungicides, fosetyl-Al is often used to treat plants infected with root pathogens because it is mobile in the plant and is transferred to the roots (Cohen and Coffey 1986). Cooke and Little (2001) found, however, that foliar application of fosetyl-Al did not reduce tuber blight on potato caused by *P. infestans*, while foliar sprays with phosphonate reduced the number of symptomatic tubers. This result implies that different host plants may take up, transport, and metabolize fosetyl-Al differently.

In general, potassium phosphonate negatively affected mycelial growth more than phosphonates that had alkyl groups, with some exceptions (Ouimette and Coffey 1989a). None of the compounds used by Ouimette and Coffey (1989a) were able to control infections by *Phytophthora* spp. completely when they were used as a curative or protective agent. All the compounds were equally effective when used as a protective agent (by root dip). Potassium phosphite controlled strawberry leather rot caused by *P. cactorum* (Rebollar-Alviter, Madden, and Ellis 2005). It also controlled downy mildew of basil in its early stages (Roberts et al. 2009). Phosphonate was shown to be effective when applied to potato foliage against *P. infestans* and *P. erytrhoseptica* (causal agent of pink rot) but not against *Pythium ultimum* (causal agent of *Pythium* leak) (Johnson, Inglis, and Miller

2004; Fenn and Coffey 1984). Phosphorous acid is also effective against downy mildew on grapes and against *Phytophthora* root and crown rot on tomato and green pepper in hydroponic culture (Förster et al. 1998). Studies have shown that phosphonate can control the sudden oak death pathogen *in vitro* and *in planta* (Garbelotto, Harnik, and Schmidt 2009; Garbelotto and Schmidt 2009).

For control of oomycetes on turfgrass, Riverdale Magellan (a mixture of phosphorous acid compounds) and Chipco® Signature™ (Aluminum tris [O-ethyl phosphonate]) were found to be equally effective against *Pythium* blight development on perennial ryegrass (*Lolium perenne*) (Datnoff et al. 2003). Similarly, different commercial formulations of phosphorous acid suppressed *Pythium* blight on rough bluegrass (*Poa trivialis*) during the 2004 season (Datnoff et al. 2005).

The existence of *Phytophthora* spp. that are resistant to phosphonate has been reported (Brown et al. 2004; Dolan and Coffey 1988; Fenn and Coffey 1985, 1989; Griffith, Coffey, and Grant 1993; Nelson et al. 2004; Ouimette and Coffey 1989a). Hence, care should be taken to alternate phosphonates with other effective compounds to prevent a buildup of resistant *Phytophtora* spp. in the field.

Conclusion

Both phosphoric acid and phosphorous acid are essential agrochemicals in crop production. Under normal plant growth conditions, both dissociate and exist as corresponding anions, phosphate and phosphite. A clear distinction exists between the two agrochemical compounds: The former is a nutrient source of P essential for plants, and the latter helps control agricultural epidemics of oomycetes. Phosphate and phosphite are not equivalent inside the plant. Phosphoric acid or phosphate cannot function as phosphorous acid or phosphite and *vice versa*. Since phosphites are systemic and very stable in plants, they should not be applied frequently. To help delay the development of phosphite-resistant oomycetes, care should be taken to alternate or mix phosphite with other effective compounds.

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Table 1. Agriculturally relevant P-containing compounds

Name	Symbol	What is it?
Phosphorus	P	The chemical element indicated with the symbol P is a structural component of many things, including biological membranes, DNA, RNA, and ATP, and it is essential for numerous biochemical processes in all organisms. It does not occur as a free element in nature.
Phosphoric acid	H_3PO_4	Also known as orthophosphoric acid or phosphoric (V) acid, it is a mineral (inorganic) acid. This chemical compound normally does not exist in P fertilizers unless the fertilizer is put in a strong acidic solution. The P form in the fertilizer includes either phosphate salts or esters. Potassium or diammonium phosphate exemplifies the former, whereas phytate is an example of the latter. For acidic soils, phosphate rock can be directly used as a P source.
Dihydrogen phosphate	$H_2PO_4^-$	It is a partially dissociated form of H_3PO_4 in which P is most readily taken up by the plant. It is the major form of phosphate when pH is greater than 2.
Hydrogen phosphate	HPO_4^{2-}	It is a partially dissociated for of H_3PO_4, in which P can also be taken up by the plant. This form dominates when pH is greater than 7. At pH7, both dihydrogen phosphate and hydrogen phosphate are approximately equal in amount.
Phosphate	PO_4^{3-}	It is a completely dissociated form of H_3PO_4. Under growth conditions, it is present in negligible amounts, less than 1:100,000 that of either dihydrogen phosphate or hydrogen phosphate.
Phosphorus pentoxide	P_2O_5	It is a formula used to express the P content of fertilizers. It is a white and anhydride form of phosphoric acid. It is a powerful desiccant.
Phosphorous acid	H_3PO_3	It is a powerful reducing agent used for preparing phosphite salts, such as potassium phosphite. These salts, as well as aqueous solutions of pure phosphorous acid, control a variety of microbial plant diseases caused by Oomycota.
Dihydrogen phosphonate	H_2PO_3	It is a partially dissociated form of H_3PO_3, the major form of phosphonate at pH > 1.
Hydrogen phosphonate	HPO_3^{2-}	A completely dissociated form of H_3PO_3, it dominates at pH > 7. The hydrogen has a covalent bond with phosphorus that cannot be readily dissociated.

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Table 2. Marketing of products with active ingredient phosphorous acid or related compounds[z]

Product	Company	Active ingredient	Marketed as	Reference
K-Phite® 7LP	Plant Food Systems Inc.	Mono- and di-potassium salts of phosphorous acid	Fungicide	Raid, McAvoy, and Sui 2010
Terronate WDG	Agriliance LLC	Fosetyl-Al	Fungicide	Pesticide Action Network 2004
Aliette®	Bayer Cropscience LP	Fosetyl-Al	Fungicide	Bayer Cropscience 2004
Nutri-Phite®	Biagro Western Sales	Phosphite and organic acids	Fertilizer	Biagro Western Sales, Inc. 2003
CP Home and Garden Fungicide	Contract Packaging, Inc.	Fosetyl-Al	Fungicide	Pesticide Action Network 2004
Tree Tech® brand Aliette Injectable	Florida Silvics Inc.	Fosetyl-Al	Fungicide	Pesticide Action Network 2004
Ele-Max® Soil Phosphate Foliar Phosphate	Helena Chemical	Phosphorus acid[y]	Foliar fertilizer	Helena 2002
ProPhyt®	Helena Chemical	Potassium phosphite	Systemic fungicide	Helena 2002; Nufarm USA, n.d.
Phostro®	Nufarm America	Phosphorus acid	Biochemical pesticide	Pesticide Action Network 2004
Riverdale Magellan	Nufarm America	Phosphorous acid	Fungicide	Pesticide Action Network 2004
Plant Synergists Phosphorous Acid Technical	Plant Synergists, Inc.	Phosphorous acid	Fungicide	Pesticide Action Network 2004

[z] Products and companies are mentioned for educational purposes and are not recommended over similar products in this document.
[y] It is unclear whether "phosphorus acid" means phosphor<u>ic</u> or phosphor<u>ous</u> acid. The word "phosphite" in the name implies that phosphorous acid is the active ingredient. However, the fact that the product is marketed as a fertilizer implies that the active ingredient is phosphate.

Table 3. Genera of oomycetes that cause disease on horticultural crops and that are likely to be controlled by phosphorous acid (Heffer, Powelson, and Johnson 2002)

Genus	Disease
Aphanomyces	Root rot
Bremia, Peronospora, Plasmopara, Pseudoperonospora, Sclerospora	Downy mildew (Figure 2)
Pythium	Root rot and damping-off
Phytophthora	Late blight of potato and tomato, foliar blights on peppers and cucurbits, root and stem rots
Albugo	White rust on cruciferous plants

Table 4. Control of potato late blight by phosphorous acid and related products

Compound	Efficacy	Application	Reference
Fosetyl-Al	Not good in field	Foliar spray	Cooke and Little 2001
Phosphonate	Good in field, variable against oomycetes in the lab	Foliar spray	Cooke and Little 2001
Phosphonate compounds	Good in pots	Root dip	Ouimette and Coffey 1989a
Phosphonate	Variable against *P. infestans* isolates in the lab	Foliar spray to detached leaves	Bashan, Levy, and Cohen 1990
Phosphorous acid	Good against *P. infestans* in the field	Foliar spray	Johnson, Inglis, and Miller 2004
Potassium phosphite	Effective against *Peronospora belbahrii* (basil downy mildew) early in the trial	Foliar spray	Raid 2008