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Phosphorous Acid and Phosphoric Acid: When all P Sources are not Equal[1]

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While growers are familiar with phosphorus-containing fertilizer, the abundance of terms, apparently similar (such as phosphoric acid and phosphorous acid), may create some confusion on the actual content and efficacy of these products. Some common phosphorus-containing compounds are listed in Table 1. 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 the fungicidal activity and nutritional value of phosphorous acid.

Phosphorus (abbreviated P) is one of the essential elements for normal growth and development of plants. In fertilizers, it is normally found in the form of phosphoric acid (H_3PO_4) (Table 1), which readily disassociates to release hydrogen phosphate (HPO_4^{2-}) and dihydrogen phosphate ($H_2PO_4^-$). Both of these ions may be taken up by the plant but $H_2PO_4^-$ more readily (Street and Kidder, 1989). Once inside the plant, both ions are mobile.

The amount of phosphorus a fertilizer contains is represented as the middle number on the bag expressed as P_2O_5, i.e. 5-10-15, (the first number represents the nitrogen percentage and the third number 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).

Phosphor<u>ic</u> acid should not be confused with phosphor<u>ous</u> acid (H_3PO_3). A single letter difference in the name of a chemical compound can make a difference in its properties. Phosphorous acid releases the phosphonate ion (HPO_3^{2-}), also called phosphite, upon disassociation. Like phosphate, phosphonate is easily taken up and translocated inside the plant. Phosphorous acid and its related compounds are often referred to as phosphonate, phosphate, and phosphonic acid. One of the breakdown products of fosetyl-Al is mono-ethyl phosphonite, which may be taken up by the plant. Inside the plant, fosetyl-Al may ionize into phosphonate, and therefore fosetyl-Al belongs to the same group of phosphorous acid compounds (Cohen and Coffey, 1986; McGrath, 2004; Wilcox, n.y.).

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Phosphorous Acid as Fertilizer?

Phosphorous acid does not get converted into phosphate, which is the primary source of P for plants (Ouimette and Coffey, 1989b). In contrast, some soil bacteria are capable of transforming phosphonate into phosphate. However, this process is so slow that it is of no practical relevance (McDonald *et al.*, 2001). To date, no plant enzymes have been described that could oxidize phosphonate into phosphate. This explains why phosphonate is stable in plants and does not get converted into phosphate (Smillie *et al.*, 1989). Since phosphorous acid and its derivatives do not get metabolized in plants, claims that phosphonate can contribute to phosphorus nutritional needs of the plants should be taken with caution.

Phophorous acid has properties useful in agriculture. Like in many other publications investigating efficacy of phosphorous acid against oomycetes, Förster *et al.* (1998) found that phosphite is capable of controlling *Phytophthora* root and crown rot on tomato and pepper. These authors also investigated 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 making the general health of the crop better, thereby improving its natural defense system. Therefore, no valid evidence exists for the claim that phosphorous acid improves plant growth.

Control of Oomycetes

It is well documented that phosphorous acid is able to control diseases caused by organisms that belong to the Oomycota (or oomycetes) that are on agronomical crops. Oomycetes (a group of pathogens that include water molds and downy mildew) (Fig. 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 a mixture of cellulosic compounds and glycan. Another difference is the nuclei in the cells that form the filaments; each have two sets of genetic information in oomycetes (diploid) instead of just one set as in fungi (haploid) (Waggoner and Speer, 1995).

Figure 1. Downy mildew on lettuce. Credits: Tyler Harp and Syngenta Crop Protection

For most practical purposes, the oomycetes are grouped with fungi. Compounds that control plant pathogens belonging to the oomycetes are often called fungicides. It is important to dinstinguish between fungi and oomycetes; chemicals that are used to control one will often not be effective against the other, depending on their different biology. Several important plant pathogens belong to the oomycetes (Table 3); the one with the most economic impact is *Phytophthora infestans*, which causes late blight of potato (Fig. 2).

Phosphorous acid has both a direct and an indirect effect on oomycetes. It inhibits a particular process (oxidative phosphorylation) in the metabolism of oomycetes (McGrath, 2004). For instance, phosphonate compounds are ineffective against phosphonate-resistant oomycetes (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 *et al.*, 1989).

Figure 2. Potato late blight, caused by *Phytophthora infestans*. Credits: Tyler Harp and Syngenta Crop Protection

Efficacy

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

Some of the phosphorous acid-related compounds and research on their efficacy against potato late blight are summarized in Table 4. In most cases, research has been done with foliar applications of phosphorous acid. The compound gets translocated in the plant to the roots and is therefore effective against 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 *et al.*, 1989). The efficacy of different phosphonate compounds against nine *Phytophthora* spp., which 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). Even though sensitivity of each of the *Phytophthora* spp. used in their experiments in the laboratory was variable (Table 4), there was little difference in the ability of different phosphonate compounds to control the stem rot of pepper, as a curative or a preventive agent in pots. The level of control was better for *Persea indica* L. than for pepper (Ouimette and Coffey, 1989a).

Fosetyl-Al is a systemic fungicide that is often used against root pathogens because it is mobile in the plant and gets transferred to the roots (Cohen and Coffey, 1986). Cooke and Little (2001) found that foliar application of fosetyl-Al did not reduce tuber blight on potato caused by *P. infestans*, while foliar sprays with partially neutralized phosphonate reduced the number of tubers that developed symptoms after inoculation with the pathogen. Different host plants may take up, transport, and metabolize fosetyl-Al differently. This seems contradictory, since fosetyl-Al releases phosphonate as a breakdown product, but there may be other factors involved, such as environmental ones.

In general, Potassium phosphonate negatively affected mycelial growth more than phosphonates that had alkyl groups, but some exceptions were noted (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 of the compounds were equally effective when used as a protective agent (by root dip). Potassium phosphite was shown to be effective for control of strawberry leather rot caused by *P. cactorum* (Rebollar-Alviter *et al.*, 2005). 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 *et al.*, 2004; Fenn and Coffey, 1984). Phosphorous acid also appears very effective against downy mildew on grapes (Wilcox, n.y.), and against *Phytophthora* root and crown rot on tomato and green pepper in hydroponic culture (Förster *et al.*, 1998).

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 2001-2002 season (Datnoff *et al.*, 2005).

The existence of *Phytophthora* spp. resistant against phosphonate has been reported (Brown *et al.*, 2005; Dolan and Coffey, 1988; Fenn and Coffey, 1985, 1989; Griffith *et al.*, 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

A clear distinction exists between phosphoric acid and phosphorous acid: the former is a nutritional source of P for plants, and the latter helps control agricultural epidemics of oomycetes. Claims suggesting that either compound may fulfill the functions of the other are not supported by current literature and are therefore misleading. Since phosphonates are systemic and very stable in plants, they should not be applied frequently. To help control the phosphonate-resistant oomycetes described in this publication, care should be taken to alternate or mix phosphonate 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 that is important for numerous processes in all organisms. It does not occur as a free element in nature.
Phosphoric acid	H_3PO_4	Compound normally found in P-fertilizers.
Dihydrogen phosphate	H_2PO_4	Partially disassociated form of H_3PO_4, in which P is most readily taken up by the plant.
Hydrogen phosphate	HPO_4^{2-}	Partially disassociated for of H_3PO_4, in which P can also be taken up by the plant.
Phosphate	PO_4^{3-}	Completely disassociated form of H_3PO_4
Phosphor oxide	P_2O_5	Formula used to express P-content of fertilizers.
Phosphorous acid	H_3PO_3	Compound normally marketed as a fungicide.
Dihydrogen phosphonate	H_2PO_3	Partially disasssociated form of H_3PO_3
Hydrogen phosphonate	HPO_3^{2-}	Partially disassociated form of H_3PO_3
Phosphonate, phosphite	PO_3	Completely disassociated form of H_3PO_3

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

Product	Company	Active Ingredient	Marketed as	Reference
Terronate wdg	Agriliance, llc	Fosetyl-Al	Fungicide	Pesticide Action Network, 2004
Aliette®	Bayer Cropscience, lp	Fosetyl-Al	Fungicide	Bayer, 2004
Nutri-Phite®	Biago 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, 2001
ProPhyt®	Helena Chemical	Potassium phosphite	Systemic fungicide	Helena, 2001, 2002; Wilcox, n.y.; Nufarm, n.y.
Phostrol®	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

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

[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 phosphoric or phosphorous 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 phosphoric acid.

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

Genus	Disease
Aphanomyces	Root rot
Bremia, Peronospora, Plasmopara, Pseudoperonospora, Sclerospora	Downy mildew (Fig. 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	Cook and Little, 2001
Phosphonate	Good in field, variable against oomycetes in the lab	Foliar spray	Cook and Little, 2001
Phosphonate compounds	Good in pots	Root dip	Ouimette and Coffey, 1989a
Phosphonate	Variable against *P. infestans* isolates in the lab	To detached leaves	Bashan, 1990
Phosphorous acid	Good against *P. infestans* in the field	Foliar spray	Johnson *et al.*, 2004