
Department of Crop and Soil Sciences - Cooperative Extension

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Contents

- Introduction
- What's in a name?
- Phosphonates as fungicides
- A unique mode of action
- Resistance risk
- Phosphonates as fertilizers

Introduction

If you've had difficulty sorting through the different products and claims surrounding a group of turfgrass products known as phosphonates (potassium phosphite, phosphorus acid, fosetyl-Al, etc.), you're probably not alone. Numerous phosphonate fungicide and fertilizer products are currently sold in the golf turf market. Although these products have similar active ingredients, they differ in trade name, formulation, label terminology, uses, and price. Some of these products are registered as fungicides and have explicit recommendations for disease control. Others, with ingredients that are virtually identical to the fungicides, are sold as fertilizers. Understanding the different phosphonate products and how they perform in the field should help you navigate through the marketing maze and make an appropriate choice for your needs.

What's in a name?

In the broadest sense, the term phosphonate describes any compound containing a carbon to phosphorus bond. Some examples of phosphonate compounds include organophosphate insecticides, antiviral medicines, flame retardants, and some herbicides. Phosphonate compounds also occur naturally in some lower life forms, including protozoa, mollusks, coelenterates, and oomycete fungi (6).

For this article, we use the term phosphonate to describe only those products made up of the salts and esters of phosphorous acid ($\text{HPO}(\text{OH})_2$). Phosphorous acid is a solid substance that can be purchased through chemical supply companies. When mixed with water, it forms a strong acid called phosphonic acid. This acid is too strong to be used on plants and must be combined with other chemicals to raise the pH of the solution and decrease the potential for plant injury.

One means of reducing the acidity of phosphonic acid is to neutralize it with an alkali salt; typically potassium hydroxide (KOH). The resulting solution contains mono- and di-potassium salts of phosphorus acid (often referred to as potassium phosphite), and is

the active ingredient in Alude, Magellan, Vital, Vital Sign, Resyst, and other phosphonate fungicides. Potassium phosphite is also the main ingredient in several phosphite fertilizer products, including K-Phite (0-29-26), Ele-Max Foliar Phosphite (0-28-26), and Nutri Phite P + K (0-28-26).

Alternatively, phosphonic acid can be reacted with ethanol to form ethyl phosphonate. Aluminum ions are added during the manufacturing process to neutralize the ethyl-phosphonate ions and the resulting product is referred to as fosetyl-Al or Aluminum tris O-ethyl phosphonate (10). This is the active ingredient in Aliette WDG and Chipco Signature fungicides, marketed by Bayer Environmental Science.

Phosphonate fungicides and fertilizers should not be confused with phosphate-derived fertilizers such as ammonium phosphate and triple super phosphate. Even though phosphonate and phosphate compounds are very similar chemically, they differ significantly in how they act in plants and fungi.

Phosphate (HPO_4^- H_2PO_4^-) is taken up by plants and incorporated into cells where it forms an important energy-yielding molecule (ATP) and structural components of cell membranes and DNA. It is essential for root growth, photosynthesis, and respiration in plants. Thus, it is found as the source of phosphorus in most turfgrass fertilizers. Phosphate does not have a strong direct effect on turfgrass diseases, although phosphorus-deficient plants will probably be more susceptible to certain diseases than phosphorus-sufficient plants. Phosphonate fungicides and fertilizers are absorbed by plants and incorporated into cells as phosphite ions (H_2PO_3^-). The fact that this ion has one less oxygen atom than phosphate means that it does not act in the same manner as phosphate in plants. Although the phosphite ion can be transported into plant cells, it does not appear to be involved in any phase of phosphorus metabolism (ATP production, photosynthesis, or respiration). Over time, phosphonate fertilizer can be converted by bacteria to phosphate in soil, where it can be taken up and metabolized by plants. This conversion can take several weeks and is not thought to be a very efficient means of phosphorus delivery to plants when compared with phosphate fertilizers. Phosphite ions have direct fungitoxic effects on certain plant pathogens, a benefit that is not found with phosphate (Fig. 1).

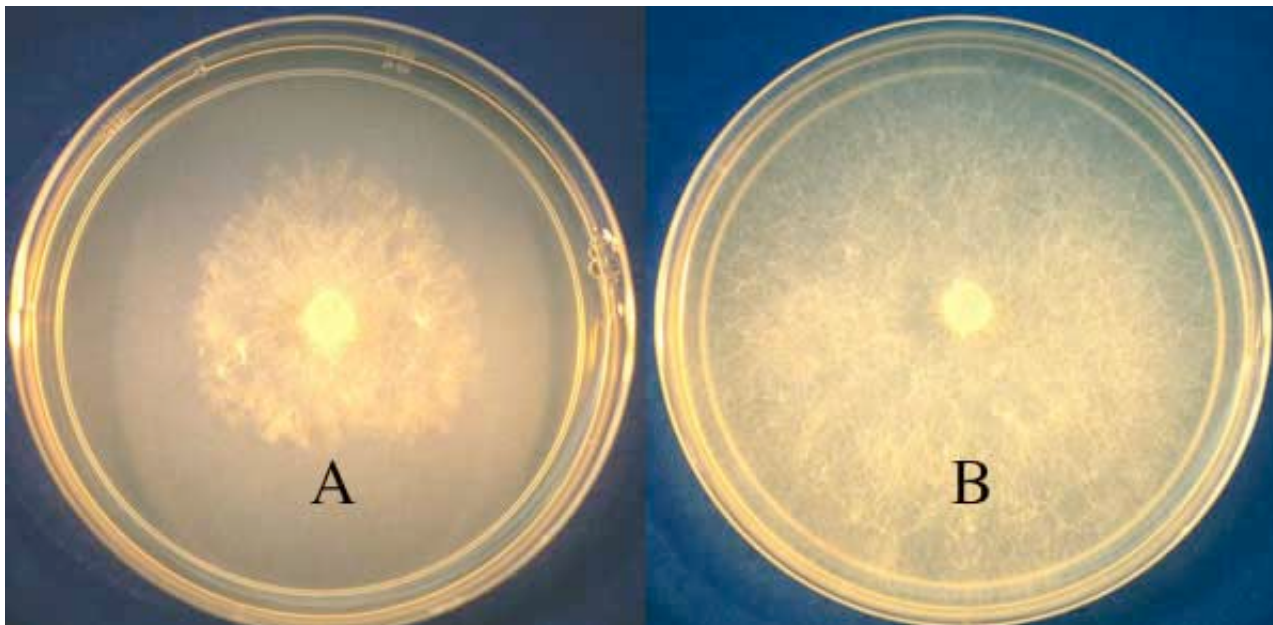


Fig. 1. *Pythium aphanidermatum* growing in cornmeal medium amended with (a) potassium phosphite and (b) potassium phosphate. The potassium phosphite is inhibiting growth of *Pythium* mycelia, whereas the potassium phosphate has no effect on growth.

Table 1. Understanding phosphonate terminology. This table summarizes some of the important terms used to describe the phosphonate products.

Phosphonate	Broadly, any compound containing a carbon to phosphorus bond. More commonly, used to describe products made of the salts or esters of phosphorous acid.
Phosphorous acid	Anhydrous solid substance, often cited by its chemical formula, $\text{HPO}(\text{OH})_2$ or H_3PO_3 . The basic ingredient in phosphonate products.
Phosphonic acid	Broadly, any compound containing a carbon to phosphorus bond. More commonly, used to describe products made of the salts or esters of phosphorous acid. Strong acid produced by dissolving phosphorous acid in water. The term phosphonic acid is often used synonymously with phosphorous acid.
Phosphite	Alkali metal salts of phosphorous acid. The most common phosphite is potassium phosphite, and is made by mixing a solution of potassium hydroxide with phosphonic acid. Potassium phosphite is also referred to as mono- and di-potassium salts of phosphorous acid on some phosphonate product labels. Plants take up phosphite ions (H_2PO_3^-) but they are not used in phosphorus metabolism. Phosphite products have fungicidal properties.
Ethyl phosphonate	Organic (carbon-based) compound bonded to an aluminum ion forming aluminum tris (O-ethyl phosphonate) or fosetyl Al; the active ingredient in Aliette and Chipco Signature fungicides.
Phosphoric acid	Strong acid used in the manufacture of phosphate fertilizer.
Phosphate	Principle component of phosphate fertilizer; usually in the form of ammonium phosphate, potassium phosphate, or calcium phosphate. Plants take up and use phosphate ions (H_2PO_4^- or HPO_4^-) for ATP, DNA, photosynthesis, respiration, and other metabolic functions. Phosphate does not have fungicidal properties.

Phosphonates as fungicides

Fungicidal properties of phosphonates were discovered by scientists at Rhone-Poulenc Agrochemical Laboratories in France during the 1970s. These scientists were screening various chemicals for fungicidal properties when they discovered that phosphonate salts were effective in controlling diseases caused by a group of fungi known as the oomycetes (*Phytophthora*, *Plasmopara*, *Pythium*, and others). Soon after this discovery, fosetyl-Al was formulated under the trade name Aliette, and released for commercial use (6). Aliette was initially labeled for the control of *Pythium* diseases on golf courses and used primarily on greens and fairways as a preventative treatment. In the early 1990s, Dr. L.T. Lucas at North Carolina State University found that Aliette combined with another fungicide, Fore (mancozeb), improved turf quality and controlled what has been referred to as “summer decline of bentgrass” or “summer stress complex” (8). Based on this discovery, scientists at Rhone Poulenc, Inc. developed and patented a formulation containing fosetyl-Al and a blue pigment which produced results similar to the Aliette/Fore combination (11). Based this finding, Chipco Signature was developed and released and has become widely used on golf courses throughout the U.S. Chipco Signature and Aliette are now labeled for control of *Pythium* diseases and yellow tuft in turf; as well as summer stress complex when combined with one of several other fungicides (Turf and Ornamental Reference, 2005). Chipco Signature is also labeled for the control of anthracnose and bentgrass dead spot diseases when combined with one of several fungicides listed on the label (2).



Fig. 2. Effects of reagent-grade potassium phosphite (H_3PO_3) and potassium phosphate (H_3PO_4) on symptom development of *Pythium* blight of creeping bentgrass. Potassium phosphite has good efficacy against this disease when applied preventatively.

During the mid 1990s, potassium phosphite products entered the turfgrass market and gained popularity as fungicides and fertilizers. Several of these products have been registered through the EPA as fungicides (Alude, Magellan, Vital, Vital Sign, and Resyst) and have specific information on labels for the control of *Pythium* diseases and in some cases, summer stress complex when combined with a mancozeb fungicide (2).

Whereas most turfgrass fungicides are either

contacts or translocated in plant xylem, phosphonate fungicides possess significant symplastic ambimobility, or movement in both xylem and phloem. Translocation in phloem allows the fungicide to move from leaf tissues to the crowns and roots. Because

of this unique property, phosphonates are viewed as excellent fungicides for controlling root rot diseases such as *Pythium* root rot and dysfunction caused by various *Pythium* species (5, 7).

Phosphonate fungicides have very good efficacy for *Pythium* diseases and other diseases caused by oomycete fungi when applied preventatively; but are thought to have poor efficacy when applied post-infection (after disease symptoms and signs are apparent) (Fig. 2).

A unique mode of action

The mode of action of phosphonate fungicides has long been a source of controversy and mystery. Some scientists believe that most of the fungicidal effects of these products are directly on the fungal pathogen; whereas others suspect that both a direct effect on the fungus and a stimulation of natural host defenses combine to prevent disease.

Early studies with phosphonate fungicides incorporated into artificial growth media showed no direct effect on *Pythium aphanidermatum*; thus it was assumed that the mode of action did not involve killing the fungus directly, rather it involved a stimulation of the plant's natural chemical and physical defenses against disease (13). However, subsequent studies showed the reason for the lack of fungal inhibition in phosphonate fungicide-amended media was that the phosphate concentration in the media was too high. Lowering the amount of phosphate in the media allowed direct inhibition of fungi by the phosphite ion. Apparently, both phosphite and phosphate compete for the same transporters across cell membranes and phosphate tends to out-compete phosphite for access to these sites, thereby blocking uptake of phosphite by fungi (10). This finding led scientist to explore how phosphonate fungicides disrupt phosphate metabolism in fungi.

In a study using three *Phytophthora* spp., Australian scientists found that phosphonate fungicides interfere with phosphate metabolism by causing an accumulation of two compounds, polyphosphate and pyrophosphate, in fungal cells. Accumulation of these compounds is thought to divert ATP from other metabolic pathways, resulting in a decrease in fungal growth (12).

More recently, phosphonate fungicides were found to inhibit several key enzymes needed for growth and development in *Phytophthora palmivora* (15). These studies suggest that the mode of action is at least partially, if not mostly, direct inhibition of the fungus. Also, the mode of action of phosphonate fungicides appears broad enough so that the potential for rapid resistance development is not as strong as with some other systemic fungicides.

Considering that the phosphite ion has little or no affect on phosphorus metabolism in plants, it seems unlikely that it could prevent disease by stimulating host defenses. Nevertheless, research has revealed that when certain species of *Phytophthora* infect certain plant species treated with phosphonate fungicides, fungus-inhibiting chemicals called phytoalexins are produced. A recent study involving *Eucalyptus* showed that the concentration of phosphite ions in plants may determine the extent of host defense

activation. When concentrations of phosphite ions in the roots were low, host defense enzymes were stimulated; but when concentrations of phosphite ions were high, host defense enzymes remained unchanged and the phosphite ions inhibited growth of the pathogen before it caused disease (7).

Studies on stimulation of host defense mechanisms are difficult to conduct and require the ability to detect minute quantities of complex compounds in the plant; thus much less is known about this mode of action than the direct fungitoxic effects of phosphonate fungicides. To our knowledge, very little is known about activation of host defenses in phosphonate-treated turfgrass, but many plant pathologists assume that this is possible, if not likely.

Resistance risk

The widespread use of phosphonate products as disease control agents and fertilizers, and for the improvement of turf quality during periods of environmental stress, has led to concerns about the development of pathogen resistance (16). To date, we are not aware of any confirmed reports of pathogen resistance to phosphonate fungicides in turfgrass (although phosphonate-resistant mutants of *Pythium aphanidermatum* have been induced in a laboratory) (14). Two factors are probably responsible for the reduced resistance risk with phosphonate products; (a) the mode of action in target fungi may involve several sites, and (b) the involvement of host defenses in disease suppression. Both of these factors create a broad front against disease development, and a difficult hurdle for pathogens to overcome through resistance. Nevertheless, a recent report from California suggests that sensitivity to phosphonate fungicides was compromised in populations of *Bremia lactucae* (causal agent of lettuce downy mildew) treated repeatedly with phosphonate fungicides and fertilizers (3). The California experience may be an isolated case, but it should serve as a reminder to turf managers that resistance development is a *possibility* with phosphonates, and that indiscriminant use of these products *may* lead to problems down the road.

Phosphonates as fertilizers

Phosphonates were first investigated as fertilizers in Germany and the U.S. during the 1930s and 40s. At that time, agricultural officials were concerned that war activities would disrupt vital shipments of rock phosphate for fertilizer production, so alternative sources of fertilizer phosphorus were explored (6). Results of studies conducted in both countries demonstrated that phosphonates were not effective substitutes for phosphate fertilizer. USDA scientists found that yields of legumes and grasses treated with calcium phosphite were lower than phosphate-treated plants, and in most cases, lower than controls plants receiving no phosphorus. However, a second crop seeded into the same soils that were treated with calcium phosphite showed improved yields. The authors attributed the delayed phosphorus response to the conversion of phosphite to phosphate in the soil (9). Subsequent research revealed that phosphite could be converted to phosphate primarily by soil-borne bacteria, but that these bacteria would not use phosphite until most phosphate was depleted (1). Based on the results of these studies, phosphonate fertilizer was viewed as an inefficient and costly means of supplying phosphorus to plants and scientists eventually lost interest in this compound as a phosphorus fertilizer.

Despite previous research findings, phosphonate compounds are marketed by some companies as a source of phosphorus and potassium fertilizer. Preliminary results with turfgrasses growing in sand culture and treated with equal amounts of potassium phosphite and potassium phosphate have supported claims that potassium phosphite does not supply usable phosphorus to turfgrasses (Fig. 3). Although potassium phosphite can be converted to phosphate in soil, turf managers should realize that this is an inefficient means of supplying phosphorus to plants when compared with phosphate fertilizer.



Fig. 3. Annual bluegrass treated with a nutrient solution containing potassium phosphate as the source of phosphorus (left); and the same nutrient solution with potassium phosphite as the source of phosphorus (right). Annual bluegrass treated with potassium phosphite shows phosphorus deficiency symptoms (stunted growth and a red tint to foliage) indicating that this compound is not supplying usable phosphorus to the plants.

Claims that phosphonates consistently enhance rooting are debatable and more evidence is needed to support these claims. A two-year study performed at North Carolina State University showed that bentgrass root mass was unaffected by phosphonate products (4). Certainly, more research using precise root measurement techniques is needed to determine if enhanced rooting due to phosphonates occurs under different environmental and management conditions. If enhanced rooting does occur, it could be due to product formulation, or from the suppression of minor root pathogens (*Pythium* spp.) due to fungitoxic action of the

phosphonate product, leading to healthier and more extensive roots.

Findings that phosphonates do not affect phosphorus metabolism or yield in grasses appears convincing, but should be tempered by the fact that many of these products have demonstrated improved turf quality. Quality enhancement with potassium phosphite products is probably not due to nutritional effects, as our studies have shown no such improvement with equal amounts of potassium phosphate fertilizer. Certainly, formulation enhancements, as in the case of Chipco Signature fungicide, have led to turf quality improvement, but when we apply reagent grade potassium phosphite (with no formulation enhancements) to turf we also see slight quality improvements (Fig. 4). It remains to be seen what causes turf quality improvement, but one proposed cause may be the suppression of minor, plant debilitating pathogens — such as *Pythium*

species. More research is needed to determine the cause of enhanced turf quality.

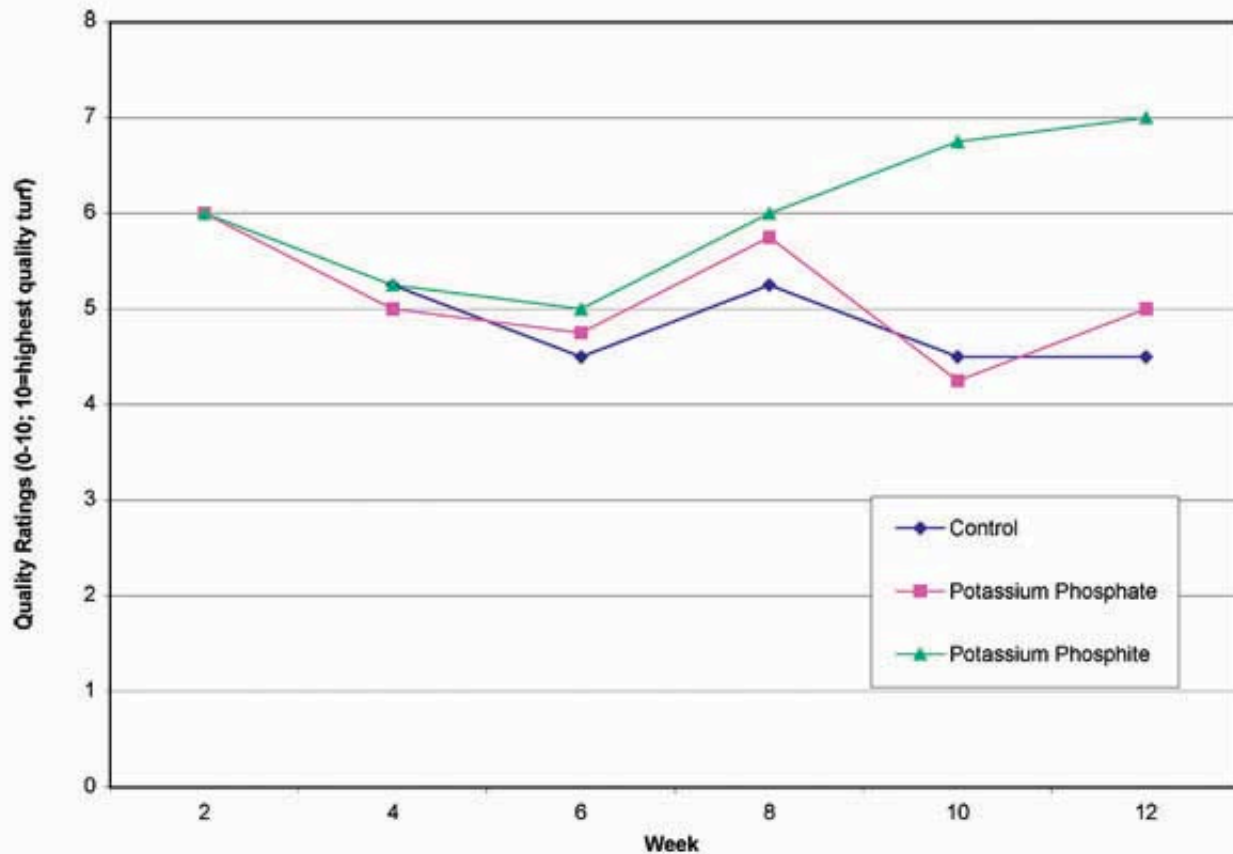


Fig. 4. Quality ratings of a creeping bentgrass/annual bluegrass putting green treated with potassium phosphate, potassium phosphite, and an untreated control. Differences in turf quality became apparent in week 10 of the study, when high temperatures and humidity caused a decline in the untreated and potassium phosphate plots, while potassium phosphite plots showed improved quality.

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