Abstract. Phosphorous acid \((H_3PO_3)\) is neutralized with either potassium carbonate or potassium hydroxide to form potassium phosphonate. This compound is used worldwide as an anti-oomycete fungicide. Potassium phosphonate can be applied either as a root drench, a stem paint, stem injection or foliar application. In the plant, it breaks down rapidly into phosphonate anions, which reduce the mycelial growth of several species of \textit{Phytophthora}, thereby inhibiting fungal growth. In citrus, this inhibition allows time for the plant’s natural defence mechanisms to further inhibit fungal growth through accelerated production of the phytoalexin scoparone. Scoparone levels in citrus bark inoculated with \textit{Phytophthora citrophthora} can be increased two to four fold by treatments of \(H_3PO_3\) at \(125\ g/m^2\). Many questions still exist about the relationship between the direct and the indirect action of the phosphonates. It is known that there is a phosphonate/phosphate antagonism within the fungal cell and that phosphate can in certain instances reverse the antifungal action of phosphonate. Potassium phosphonate applied as a foliar spray is broken down to phosphonate ions which peak in the roots after 28 days. Phosphorous acid results in higher phosphonate levels in citrus than fosetyl-Al, which is also broken down into phosphonate ions. Foliar applications of potassium phosphonate control brown rot on the fruit in addition to
controlling *Phytophthora* root and foot rot, whereas stem applications and drenches control the latter only. Although most of the phosphonate usage to date is against the oomycetes there is evidence that the spectrum is considerably wider and its effectiveness has also been shown against other root pathogens, e.g. *Rhizoctonia, Fusarium* and *Armillaria*.

Until the 1970’s there were no fungicides available for the treatment of soil-borne diseases caused by oomycetes. At that stage, two new groups of systemic fungicides active against these fungi were introduced, viz. the acylalanines and the phosphonates (Schwinn & Staub, 1987). The acylalanines are used widely for agricultural purposes but are exposed to the development of resistance (Davidse, 1981; Le Roux, *et al.*, 1993).

Unlike the acylalanines the phosphonates have a remarkable ability of translocation via both the phloem and the xylem. There has thus far also been no confirmed report of resistance to phosphonates in the field, despite the relative ease with which mutants with reduced sensitivity can be induced in the laboratory (Bower & Coffey, 1985; Dolan & Coffey, 1988; Duvenhage, 1994; Neema, *et al.*, 1998, Sanders & Coffey, 1990).

The term phosphonate is used to describe the salts or esters of phosphonic acid, HPO(OH)$_2$. The term phosphorous acid has been widely applied to phosphonic acid and phosphates to its alkali metal salts (Boenig, *et al.*, 1982). Phosphonic acid and its metal salts are commodity chemicals which are used widely in manufacturing and in chemical industries. The best known novel phosphonate compound used in agriculture is the herbicide, glyphosate [N-(phosphonomethyl) glycine] (Toy & Walsh, 1987).
In 1977, Aliette WP (fosetyl-Al), the aluminium salt of phosphonic acid was released. Nina, the sodium salt of ethyl phosphonate and the calcium salts were tested but never commercially released (Anding et al., 1987; Muchovej, et al., 1980). Darvas (1984) injected avocado trees with both phosphorous acid and fosetyl-Al in the early 1980’s and found that phosphorous acid was more effective against *Phytophthora cinnamomi* than fosetyl-Al. It also became clear that the alkyl phosphonates were degraded in the plant to phosphonate anions (Bompeix et al., 1980; Bompeix & Saindrenan, 1984; Bower & Coffey, 1985; Coffey & Joseph, 1985; Dolan & Coffey, 1988; Fenn & Coffey, 1984; 1985).

A successful challenge of the patent protection obtained by Rhône-Poulenc in Australia led to the registration of potassium phosphonate and stimulated research into its efficacy as a treatment for a number of plant diseases (De Boer, et al., 1990; Pegg et al., 1985; Piccony et al., 1987). Schutte et al., (1991), determined the phosphite concentrations and distribution in mature citrus trees after trunk injections and foliar sprays either with phosphorous acid or fosetyl-Al and a trunk paint with fosetyl-Al. It was found that phosphorous acid (H₃PO₃) used as a trunk injection resulted in the highest phosphite levels over the longest period of time. Application intervals therefore depend upon the application method and formulation used and should not exceed 42 days. Fosetyl-Al, potassium phosphonate and phosphorous acid cannot be treated as identical in terms of efficacy. These differences are as a result of differing rates of assimilation and transport within the plant, and in the case of the alkyl phosphonates, different rates of breakdown to phosphonate in different plant species. The cation associated with alkyl phosphonate could in certain cases have a supplementary protective antifungal effect (Guest et al., 1996).
Physiological interactions of phosphorous acid

Phosphorous (phosphonic) acid shows very low mammalian toxicity. The toxicity is largely dependant on the cation. Sodium phosphonate has comparable toxicity to table salt whereas that of potassium phosphonate is even lower. Neither mammals nor plants have the capacity to oxidize phosphonate to phosphate. Non-enzymic oxidation is dependant on pH but is very slow at biological temperatures (Smillie et al., 1988).

Results by Bower & Coffey (1985) and Dolan & Coffey (1988), suggest that the phosphonates first act within the fungus and then within the plant’s defence system. The concentrations required to inhibit mycelial growth of strains with reduced sensitivity in the laboratory were never more than 20-fold that of the parental strains. This falls within the range of natural occurring isolate sensitivities and are not the same as, e.g. insensitivity to the benzimidazoles where a 1000-fold concentration increase could not give satisfactory control of the diseases.

The direct effect of phosphonate ions on the fungus is but part of the mode of action of this compound. Ouimette & Coffey (1989b) discovered that crops were protected after the residues could no longer be detected. It was also found that phosphonates could control Phytophthora in vitro at concentrations (<28 M) which were ineffective against the mycelial growth on medium (Farih et al., 1981). De Boer et al. (1990) showed that phosphonates could provide effective control of P. clandestine which causes root rot of subterranean clover with as little as 0.3kg potassium phosphonate/ha. Black shank of tobacco caused by P. nicotianae was also controlled by application of 0.1mM of phosphonates whereas the ED$_{50}$ for the pathogen was 1mM (Smillie et al., 1989).
Bompeix et al., 1980) observed enhanced activities of the plant’s defence system after phosphonate applications. This was confirmed by Afek & Sztejnberg (1989) and Guest (1984b; 1986). The response stimulated by phosphonates were rapid cytological changes, nuclear migration, papilla deposition and hypersensitive cell death (Durand & Sallé, 1981; Guest, 1982) ethylene biosynthesis, phenylalanine ammonia lyase activation (Nemestothy & Guest, 1990, Saindrenan, et al., 1988) lignification (Nemestothy & Guest, 1990), respiration and pentose phosphate metabolism and phytoalexin accumulation in infected plants (Afek & Sztejnberg, 1989; Guest, 1984b).

**Effect of phosphonates on scoparone in citrus**

The phytoalexin scoparone (6,7-dimethoxycoumarin) is involved in defence mechanisms of citrus against several pathogens such as Phytophthora citrophthora (Smith & Smith), Leonian (Afek & Sztejnberg, 1988; 1993; Afek et al., 1986; Sulistyowati et al., 1990). Scoparone exists in low concentrations in healthy citrus bark and fruit peels (Tatum & Berry, 1977) but increases rapidly following the inoculation with pathogens (Afek & Sztejnberg, 1988; De Lange et al., 1976). Treatments with chemicals such as fosetyl-Al and phosphorous acid increased scoparone in citrus bark inoculated with *P. citrophthora* much more than untreated citrus (Afek & Sztejnberg, 1989). In doing so, the phosphonates induce resistance in citrus. Afek and Sztejnberg (1989) also showed that to obtain the same scoparone accumulation, the concentration of H$_3$PO$_3$ required for the same effect as fosetyl-Al was 41%.
The work done by Afek & Sztejnberg was conducted on four citrus spp., viz. macrophylla and sour orange (*Phytophthora* resistant) and rough lemon and niva (*Phytophthora* susceptible). The first three had the potential to produce scoparone and therefore the potential for resistance. As a result of this, only 300 g of fosetyl-Al or 125 g of H$_3$PO$_3$ per millilitre was required to stimulate scoparone in the first three species. In niva, 500 g of fosetyl-Al and 200 g of H$_3$PO$_3$ per millilitre decreased lesion size. This was without influencing the scoparone, indicating a more direct mode of action against the pathogen. Their research also led to the suggestion that the phosphonates affect *Phytophthora* in citrus in two ways, (i) it increases the host defence mechanisms at low level treatments; and (ii) it acts directly as a fungistat at higher levels.

*Phosphonates used on citrus in South Africa:* Fosetyl-Al, formulated as Aliette WP was the first phosphonate used on citrus in South Africa. It was used as a foliar application at 250g/100ℓ of water. It was later registered as a stem paint, initially at 500g/ℓ which was reduced to 300g/ℓ. During the 1980’s Aliette Ca was formulated for stem injections not only on avocado trees but also for citrus. Le Roux, *et al.* (1991) reported a 66% increase in income 44 months after citrus trees were injected with Aliette CA at 0.4g a.i./m$^2$ canopy volume.

When the patent protection held by Rhône-Poulenc expired during the early 1990’s, research was conducted to compare stem applications of potassium phosphonate with those of Aliette. The results showed that a 20% formulation of potassium phosphonate was superior to Aliette stem applications. This formulation was registered as Phytex by Horticura CC. It provided excellent control of *Phytophthora* foot and root rot when applied as a stem application, by painting 30-40cm of the trunk from just above the soil surface. However, the stem applications did not give any brown rot control. Le Roux, *et al.* (1999) tested it as a
foliar spray and obtained control of brown rot for more than 8 weeks. Growers could now apply Phytex one month prior to harvesting in order to ensure protection against the development of brown rot as a post-harvest disease. The Phytex is applied at 1ℓ/100ℓ of water as a light cover spray (2000ℓ/ha). It is important not to spray trees which are under drought stress or when the day temperatures exceed 30°C. The foliar applications control feeder root rot, foot rot and brown rot. Orchards infected with *Phytophthora* receive three Phytex applications commencing with the rainy season. This would mean during October in the summer rainfall areas and during April in the winter rainfall areas. The applications are two months apart and co-incide with the increase of inoculum/disease severity rather than with the root growth flushes as is the case with avocado root rot (Whiley, *et al*., 1995). If necessary, due to excessive rains, a fourth foliar application is applied one month prior to harvesting to prevent the development of brown rot. When stem applications are used, a dye is added to the Phytex by the manufacturer. This does not only show which trees have been painted but also increases the sticking capabilities of the product.

De Lange *et al.* (1976) showed that scoparone was induced in citrus peel by black spot, *Guignardia citricarpa* Kiely. Rhône-Poulenc combined fosetyl-Al with mancozeb to produce a formulation known as Mikal-M to control black spot and *Phytophthora* with the same spray. It was decided to test potassium phosphonate with mancozeb as well. The results, however, indicated that the potassium phosphonate was less effective against *Phytophthora* when used in a mixture with mancozeb than when used on its own. Mason (Pers. comm., 1998) experienced the same when applying Phytex with and without mancozeb against powdery mildew (*Plasmopara viticola*) on grapes.
Phytex was also tested as an aerial spray. The same amount of product (15ℓ Phytex/ha) was applied using a crop sprayer which could apply 90ℓ mixture/ha instead of the 1800-2000ℓ which is applied by normal tractor driven spray machines. The aerial applications failed to deliver brown rot control and the effect on feeder root rot control was also not convincing. This concept was therefore abandoned.

It is known that the phosphonates are stable in plants but that they are oxidised in the soil by soil microbes (Adams & Conrad, 1953; Malacinski & Konetzka, 1967). The use of phosphonates were therefore never recommended in orchards. Aliette was, however, registered as a drench in nurseries. With the change to open hydroponic irrigation systems, where the water and nutrients applied through the system are absorbed by the roots within minutes after application, it was decided to put Phytex through these systems. The results to date are promising and sufficient data will be available during the coming season for registration.

**Other root diseases**

Phosphonate is effective against *Rhizoctonia solani* Kühn when applied as soil treatments to wheat (Wehner et al., 1987) and Medicago pastures (Pankhurst et al., 1998) and against *Fusarium oxysporum* on a number of different plants (Pankhurst, et al., 1998; Yamada et al., 1986). However, the current registrations held by the phosphonates are mainly for the systemic control of diseases caused by foliar and soilborne members of the Peronosporales and even within that group the efficacy differ from specie to specie. Voegele et al. (1997) showed that in the case of *Rhizobium (Sinorhizobium) meliloti* phosphate uptake by the plants were severely inhibited by phosphonates under phosphate limiting conditions.
Conclusion

Low concentrations of the citrus phytoalexin scoparone exist naturally in healthy citrus bark and fruit peel. This phytoalexin, which is associated with resistance against *Phytophthora*, increases rapidly following inoculation with the pathogen. In trees treated with phosphonates, the scoparone concentration in citrus bark inoculated with *Phytophthora* increased more than in untreated citrus. Potassium phosphonate proved to be the most inhibitory of the phosphonate formulations tested against most *Phytophthora* isolates.

Phytex (potassium phosphonate) controls feeder root rot and foot rot effectively for 8 weeks after a stem paint application. A foliar application will also control brown rot in the fruit effectively. Farmers have an inexpensive and long-lasting control of most of the *Phytophthora* root rots in the form of phosphonates.

Improvements in the effectiveness of phosphonates in disease control may be expected once there is an improved understanding of the factors that control phosphonate distribution in plants and by timing applications to co-incide with particular growth stages or disease pressure.

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