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REVIEW

Copper and Phosphonate fungicides in disease management: An insight

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Fungicide application is the most convenient way for plant disease control. Since the initial use of Bordeaux mixture in 1885 for plant disease control, various copper containing compounds have been developed and applied for crop protection. Copper based fungicides and bactericides are widely used in crop management globally. However, copper fungicides had its limitations because of its non-systemic interaction with the plants. In mid 1970's a systematic group of fungicides called phosphonates emerged in the area of disease management, which were unique in their ability to reduce some diseases by direct action as well as indirect action as a systemic acquired resistance initiator.They were very effective against oomycete diseases including *Phytophthora* blight and downy mildew. These two group of fungicides that is phosphonates and copper became predominant in the global fungicide market for control of plant diseases. The review highlights the importance, use, efficacy, toxicity, compatibility with biocontrol agents and mode of action of these two fungicides, for a better comprehensive understanding.

Key words: Copper, phosphonates, toxicity, compatibility, fungicides

INTRODUCTION

Plant disease is the prime menace to global food availability. As reported by the United Nations, the world population is anticipated to increase to approximately 10 billion by 2050 and in order to satisfy the hunger of increasing population dramatic rise in global crop harvest is mandate. This canbe done by expansion of cropland and intensifying cropyields (Folberth *et al.* 2020). However, high yielding crops are associated with increased vulnerability to diseases and pests (Lamichhane *et al*. 2018). For example the potential loss of wheat production due to fungal diseases increases from less than 10%, with an attainable yield of 2 tons/ha, to more than 20% when the intensity of production increased to 12 tons/ha (Oerke, 2005).

Use of chemical fungicides in agriculture have a successful history for more than a century which started as early as 1807 when B. Prévost discovered the effectiveness of copper for the control of seed borne bunt disease in wheat (Leadbeater 2016). Economic benefit studies showed that,without using fungicides for control of plant pathogens,production of some crops would be impossible in parts of the world (Gianessi and Reigner, 2005; Cuthbertson and Murchie, 2003). Fungicides have been responsible for ensuring the production of various crops over many years; such as protection of potato against late blight, downy mildew of grapes that almost caused economic ruin for the wine industry in Mediterranean orsecurity of banana production in Central America. Cooke in 1990's wrote that 'without the use of fungicides, large scale commercial potato production in Ireland would be impossible (Leadbeater 2016).

Out of more than 40 MoAs of fungicidal and bactericidal compounds,groups of FRAC

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(Fungicide Resistance Action Committee) copper (group M01), and in phosphonate group, ethyl phosphonate are extensively used for safe guarding the crops. Usage of copper as fungicide in agriculture started in 1880s with Pierre-Marie-Alexis Millardet's break through of lime-copper mixture better known as "Bordeaux mixture" (Borkow and Gabbay, 2005). Since then, copper has played a pivotal role in agriculture as both fungicide and bactericide. Wide range of activity of different compounds of copper include its toxicity against phytopathogenic microorganisms which makes this element one of the vital constituents of pesticide formulations worldwide. However, Bordeaux mixture was unable to inhibit most of the root diseases caused by oomycetes, neither cure the plants which were already infected, because the active principle, copper, does not cross the cuticle of leaf (Klittich, 2008). A systemically translocated fungicide was needed to control prior or current root infections. The phenylamides (acylalanines) and the phosphonates were the two new families of systemic fungicides introduced for control of diseases caused by oomycetes in mid-1970s. Phosphonates are unique in their ability to reduce some diseases by direct action as well as indirect action as a systemic acquired resistance initiator. Recently Fungicide Resistance Action Committee (FRAC) acknowledged mode of action of phosphonates and reclassified phosphonic acid U33 "Unknown mode of action" to P07 "Host plant defence induction".The fungicidal properties of phosphonates have been reported for soilborne pathogens belonging to the oomycetes including *Pythium* spp. and *Phytophthora* spp. (Cook *et al*. 2009). They also work very well at times on powdery mildew as well as some bacterial leaf spots (Dann and McLeod, 2020). Phosphonates are used against these pathogens on a very wide range of crops including tree crops (Crane and Shearer, 2014).

I. Copper Fungicides

a) Development

Revolution in crop protection was ushered in twentieth century, with rapid development of different copper compounds as fungicides followed by Bordeaux mixture. The prime benefits of copper as fungicide such as low cost, comparatively high toxicity to plant pathogenic species, very low mammalian toxicity of the fixed copper compounds, stability of chemicals and high residual capacity which restrain them from being easily washed from plant surfaces has led to the extensive use of copper in control of foliar plant pathogens with adequate degree of disease management.Since last two decades several organizations have been manufacturing copper based fungicides in soluble forms of sulphates, oxychlorides, acetates, carbonates, oleates, silicates, hydroxides etc (Rusjan, 2012).Hence, copper compounds have become an essential constituent of integrated pest management system which seeks to provide prolonged solutions for management of various diseases. In the structure of integrated pest management, copper compounds are combined with tolerant or resistant varieties, physical, cultural and biological methods of control. In organic farming, copper compounds are the most effective active ingredients against varied number of pathogens such as downy mildew of grapevine, late blight of potato, anthracnose and powdery mildew diseases. (Bruggen *et al.* 2016).

Different formulations of copper fungicides:

a) Copper sulphate : Cupric sulphate is the most frequently used form of Copper in fungicides against many diseases. The chemical form copper sulphate pentahydrate ($CuSO_4$ x $5H_2O$), a fungicide, mixed with hydrate lime ($Ca(OH)_2$), is called Bordeaux mixture or with sodium carbonate ($Na_2(CO)_3$) as Burgundy mixture. Cheshunt compound is usually prepared by mixing 2 parts of copper sulphate and 11 parts of ammonium carbonate (Rusjan, 2012).

b) Copper carbonate: Chaubattia paste is another wound dressing fungicide developed by Singh in 1942 at Government Fruit Research Station, Chaubattia in the Almora district of Uttar Pradesh. The paste is applied to pruned parts of apple, pear and peaches to control several diseases (Verma and Meshram, 2018).

c) Cuprous oxide: Cuprous oxide is a protective fungicide, used mainly for seed treatment and for foilage application against blight, downy mildew and rusts(Husak, 2015).

d) Copper oxychloride: It is a protective fungicide which controls *Phytophthora infestans* on potatoes and several leaf spot and leaf blight pathogens in field (Husak, 2015).

e) Copper hydroxide: During the preparation of the Bordeaux mixture, the reaction of calcium hydroxide with copper sulfate resulted in the formation of a colloidal blue suspension of copper hydroxide. It is used to control a wide range of diseases in citrus, tree fruit and many other crops (Lamichhane *et al*. 2018).

Effective application of emerging technologies like micro emulsions, liposomes and nano emulsions in agrochemical formulations reduced the use of petrochemicals in delivery of pesticides (Castro *et al*. 2013). Therefore, in the recent years, the use of nano technology for plant protection has emerged with a great impact. At nanoscale, the active ingredients of the products are able to provide increased efficiency or better penetration of essential components to the plants (Parisi *et al*. 2014). Moreover, soda lime glass powder of low melting point containing copper nanoparticles demonstrated effective antimicrobial activity against bacteria and fungi (Tejeda *et al.* 2009). The comparative antifungal effect of copper based nano particles (11–55 nm) and other commercial agrochemicals on *Phytophthora infestans* infected tomato (*Solanum lycopersicum*) led to the conclusion that synthesized copper-based nanoparticles possess more activity than the commercial agrochemicals at a lower concentration (Giannousi *et al*. 2013). The nano-based products such as nano-fungicides, nano insecticides, etc., are already in the market, while many others are under the developing stage (Chinnamuthu and Bhoopathi, 2009). Hence, in commercial agriculture, copper nano particles might be the most demanding nano formulations, in near future.

b) Toxicity

High intensity of copper in cultivated soil might cause stress in plants and reduce fertility in soil which have unfavorable effects on yield and quality of crop (Lamichhane *et al*. 2018). Copper ions are released by copper compounds when they are dissolved in water and therefore an excessive uptake of copper ions by plants may lead to damage, which is known as phytotoxicity. Numerous factors might lead to phytotoxicity of copper in plants, which includes application of highly soluble copper formulations for example copper sulfate and copper nitrate, or in excessive amounts (can be high rate of application or frequent applications), use of acidic spray solution (pH below 5.5) which results in excess soluble copper, tank mixing of copper with various products, application of copper at high temperature, dry weather and presence of impurities in the product (Behlau *et al.* 2017). Typical symptoms of phytotoxicity of copper on leaves consist of chlorosis, darkening of axial and abaxial surfaces, necrotic spots, and leaf margin burn. On fruit, copper might cause utility depreciating discoloration such as corky, dark, and star-shaped lesions. Altogether, plants may show loss of vigor or stunted growth (Dagostin *et al*. 2011). Continuous release of copper ions followed by phytotoxic effects is favoured by wet plant canopies, due to high humidity of the environment. Eventually, the application of copper compoundsat some plant stages might cause phytotoxic effects as mostplants are sensitive to copper compounds even at lower concentration (for example, during flushing or blooming; Renick *et al*. 2008). In general, multiple perennial fruit tree crops indicate frequent symptoms of copper phytotoxicity, especially attheir blooming phase, compared to annual crops. For instance, phytotoxic effects of copper have been noticed on tomato, apple (Lesnik *et al*. 2011), pear (Orboviæ *et al*. 2007), cherry (Holb and Schnabel, 2005), and citrus. Since the quantity and dynamics of copper content in the soil and leaves vary from organic to integrated production system (Holb and Nagy, 2009), phytotoxic effects on a given crop may differ between these systems.

In addition to the aerial parts, copper in high concentration is toxic to roots of plants as it hinders with the uptake of iron and other nutrients, specially in acidic soils where pH is not well-controlled. This is specifically the case for crops that are copper sensitive, grown in rotation with copper-treated crops. High levels of application of copper to soil and leaves critically impaired normal growth of tomato plants, which exhibited crucial reduction in yield, number of fruit, dry root biomass, and height of plant, with increasing levels of copper application to soil (Sonmez *et al*. 2006). Copper has also been reported to reduce seed germination and emergence of seedling (Lamichhane *et al*. 2018). For example, copper is toxic to seedling of sunflower due to the induction of oxidative stress (Pena *et al*. 2011). The rate of germination of various crops such as sunflower (Pena *et al*. 2011), bean (Sfaxi Bousbih *et al*. 2010), wheat (Singh *et al.* 2007), and maize (Boros and Micle, 2015), was

Table 1: Plant pathogens controlled by copper-based fungicides

Disease	Pathogen	Crop	References
Blight	*Rhizoctonia solani*	Soyabean	Kumar *et al.* 2017
Alternaria blight	*Alternaria solani*	Tomato	Garg *et al.* 2020
Anthracnose	*Colletotrichum gloeosporioides*	Grapes	Omonighoand Osazee, 2012
Anthracnose	*Colletotrichum gloeosporioides*	Mango	Omonighoand Osazee, 2012
Blast	*Magnaporthe oryzae*	Rice	Gopi *et al.* 2016
Brown spot	*Bipolaris oryzae*	Rice	Sunder *et al.* 2014
Canker	*Nectria galligena*	Apple	Un Nabi *et al.*2018
Die-back fruit rot	*Colletotrichum capsici*	Chilli	Khodke *et al*. 2009
Downy mildew	*Plasmopara viticola*	Grapes	La Torre *et al*. 2011
Late Blight	*Phytophthora infestans*	Potato	Pasca *et al.* 2019
Leaf Rust	*Puccinia recondita*	Wheat	Chaudhary *et al.* 2019
Leaf spot	*Cercospora capsici*	Chilli	Muthukumar *et al.* 2016
Powdery mildew	*Leveillula taurica*	Chilli	Khodke *et al*. 2009
Root rot	*Fusarium oxysporum*	Wheat	Bramhanwade *et al.* 2015
Scab	*Venturia inaequalis*	Apple	Marin *et al.* 2012
Bacterial leaf spot	*Xanthomonas campestris* pv. *viticola*	Grapes	Kamble*et al.* 2017
Bacterial spot	*Xanthomonas vesicatoria*	Tomato	Carvalho *et al.* 2019
Bacterial spot	*Xanthomonas campestris* pv. *mangiferae-indicae*	Mango	Gagnevinand Pruvost, 2001
Bacterial Wilt	*Ralstonia solanacearum*	Tomato	Han *et al*. 2011
Black rot	*Xanthomonas campestris* pv. *campestris*	Cabbage	Massomo *et al.* 2006
Citrus canker	*Xanthomonas citri* subsp. *citri*	Orange	Behlau *et al*. 2010

reduced by copper stress. Lastly, seed germination and seedling emergence of barley was straightly affected by water type that is used for irrigation when copper was present in high concentration in soil (Stephenson *et al*. 2001).

c) Mode of Action

Fungicides of copper can be grouped into three broad types: basic salts, normal salts and organic complexes. Till date huge part of most research on copper based fungicides has been focused on Bordeaux mixture, which also includes various attempts in explanation of the nature of fungicidal action. Most fungicides of copper are applied as foliar sprays followed by absorption into the pathogenic fungus or bacterium, the copper ions link itself to various chemical groups (imidazoles, phosphates, sulfhydryls, hydroxyls) present in numerous proteins and disrupt the function of the proteins and enzymes, which results in cell damage and leakage of membrane (Mirkovic *et al*. 2015). Thus, it can be said that the mode of action of copper hydroxide or any other fungicide of copper is the non specific denaturation (disruption) of cellular proteins after which toxic copper ions are taken up by the germinating fungal spores. However for best results copper should be reapplied as plants grow to maintain coverage and prevent establishment of disease (Martins *et al*. 2014a,b). Chemical control by using copper and relying on antibiotic sprays has been screened to control bacterial diseases (Obradovic *et al*. 2008). For example *Erwinia* soft rot (Gracia-Garza *et al*. 2002;Bhat *et al*. 2012;Rienzie *et al*. 2021), *Pseudomonas* leaf spots (Giraldi *et al*. 2010) and *Xanthomonas* leaf spots (Itako *et al*. 2014; Lamichhane *et al*. 2018; Carvalho *et al*. 2019). Copper products can also react with other mode of action group, in the conditions of bacterial diseases or resistance development to copper (Husak *et al*. 2015).

d) Compatibility

Awareness of compatibility of biocontrol agents with chemical components of the production system is importantfor development of suitable IDM strategies (Ons *et al*. 2020). Copper is a non-specific bactericide and fungicide which can possibly eliminate all the microorganisms including those that have been applied as biocontrol agents (Husak *et al*. 2015). However, various studies have showed compatibility of copper compounds with various biocontrol agents. Thomas in 2010 found Copper oxychloride highly compatible with *T. harzanium*. Bio control agents such as *Pseudomonas fluorescens, Bacillus subtilis* and *Trichoderma viride* also showed good compatibility with copper hydroxide (Valarmathi *et al*. 2013). Investigations indicated the compatibility of *Trichoderma* sp. in seed treatment or soil application with blue copper fungicide (Tapwal *et al*. 2012). When *Trichoderma harzianum* as bio-control agent was included with fungicide Blue Copper-50, for the treatment of pigeon pea wilt, the disease was more effectively controlled than when the fungicide was used alone (Soesanto *et al*.2018). Studies conducted by Sowndhararajan *et al*. (2013) also indicated that application of the liquid culture of *Ochrobactrum anthropi* was found to be effective in combined sprays with copper oxychloride for control of blister blight disease in tea.The combination of biological control agents with fungicides provided similar disease suppression as achieved with higher fungicide use. Apart from effective management of bacterial and fungal diseases by copper fungicides, the compatibility with bacterial and fungal bio control agents enhanced wider opportunity in the agro ecosystem with minimal residual effect (Ons *et al*. 2020).

II. Phosphonate Fungicides

a) Development

Ethyl phosphonate better known as aluminium tris is the aluminium salt of ethyl hydrogen phosphonate which is widely known as fosetyl aluminium or Fosetyl Al. Fosetyl Al was the first phosphonic acid or phosphonate based fungicide that came to the market, in the year 1977 as Aliette® WP. Phosphonates (H_2P0_3; Phi) are the reduced form of phosphate (H_2PO_4; Pi), and is formulated as fungicides as various alkali salts as well as esters of phosphoric acid (Dann and McLeod, 2021). The addition of potassium hydroxide to phosphoric acid results in the formation of phosphorous acid with mono or di-potassium, referred to as potassium phosphonate. Potassium phosphonate is the most commonly used formulation for phosphonate based fungicides (McDonald *et al*. 2001). Ethyl phosphonate is formed when phosphoric acid is combined with ethanol. Aluminium ions may be included within this solution to neutralize ethyl phosphonate ions, resulting in the formation of fosetyl Al, an aluminium tris-O- ethyl phosphonate (Mac Donald *et al*. 2001). Use of salts of phosphonic acid surpasses Fosetyl Al in agriculture world wide because of its high cost. Formulations of phosphonate fungicides commonly used in agriculture are phosphorous acid, ethyl phosphonate, potassium phosphonate including mono as well as dipotassium phosphate and potassium dihydrogen phosphate (Nyankanga *et al*. 2012; Arslan 2015, Sawant *et al*. 2017). Use of low risk chemicals like potassium dihydrogen phosphate has been reported to control several diseases (Dann and McLeod, 2021). Horticulture industries have chiefly employed phosphonate fungicides for the management of diseases by oomycetes, soilborne (e.g. *Phytophthora* and *Pythium* spp.) and foliar pathogens (e.g. *Plasmopara* and *Phytophthora* spp.). In grapes potassium salts of phosphorous have been reported to give excellent control of downy mildew (Sawant *et al*. 2017). Since phosphonates have several desired qualities of a good fungicide therefore it was considered to be an ideal fungicide in early1990s. Some of the ideal qualities of phosphonates are: “systemically translocated in both the xylem and phloem, have protective and therapeutic activity, a complex mode of action involving several biochemical mechanisms, are persistent in the plant but ephemeral in the environment, leave no toxic residues and is cheap enough to provide economic returns to the grower” (Dann and McLeod, 2021).

After three decades, the utility of phosphonates as crop protectants has widened to incorporate roles in plant disease management of agricultural crops caused by fungal and bacterial plant pathogens, and also prevention of agriculture ecosystems from dieback caused by *Phytophthora* pathogens. However, further validation is required for roles in plant nutrition, biostimulation, and as herbicides. Recently, there has been an enhancement in regulations around environmental and food safety, and in studies of translocation and responses triggered by phosphonates in both plants and pathogens which contributes to effective disease control. The systemic nature of phosphite permits the use of various application methods targeting different plant organs. These include soil drenching for root uptake, trunk injection, trunk paints or foliar sprays (Hardy *et al*. 2001; Garbelotto *et al*. 2007; Mcleod *et al*. 2018).

b) Toxicity

Phosphite in general is considered to have low toxicity in plants. However phytotoxicity symptoms have developed in a wide range of plant species after its application. Phytotoxic symptoms of phosphonates include leaf burn, foliar necrosis, defoliation, chlorosis, diminished root growth and plant death (Barrett *et al*. 2004; Hardy, 2001). Areas of South Africa experienced phytotoxic damage on mandarin fruit when phosphonate fungicide was applied at late fruit developmental stage, when color development is advanced it was first reported by Walker in late 1990’s (Niekerk *et al*. 2018). Phytotoxicity symptoms was also seen due to phosphonate application in horticultural crops such as almond, cherry and carrots (Hardy *et al*. 2001). The lowest concentration of phosphite at which leaf burn was reported was 0.4%(Pilbeam *et al*. 2000). Fosetyl-Al application had marked reduced growth, especially of roots and also inhibited mycorrhizal colonization in onion (Lambers *et al*. 2006). Treatment with 2% phosphite led to the development of severe phytotoxicity symptoms such as necrosis and leaf burn which occurred primarily at the margins or tips of leaves/ phyllodes in *Eucalyptus marginata* (Pilbeam *et al*. 2000). Le Roux (2000) reported that foliar sprays of phosphonic acid caused phytotoxic damage to citrus leaves and developing fruit. In an investigation 1% foliar spray of ammonium phosphonate caused phytotoxic effects on avocado fruits (Niekerk *et al*. 2018). Investigation carried out also showed leaf burn in avocado trees at foliar sprays of 1% phosphonate (Whiley *et al*. 2001). Nartvaranant *et al*. (2004) reported phytotoxicity of phosphonic acid in avocado pollen, reducing both the percentage germination and the number of tubes growing through the pistil to the ovary. Evaluation for phytotoxicity in greenhouse showed that radish and bok choy germination were reduced by phosphonate treatment (Abbasi and Lazarovits 2006). However, for the most part phosphonate fungicides can be considered as safe to use on crops with mild or no phytotoxicity when applied in recommended quantity.

c) Mode of Action

The mode of action of phosphonates is yet to be entirely elucidated. However, it is likely to involve a direct and indirect mode of action. The indirect mode of action involves the plant’s defence system, whereas direct mode of action involves a direct toxic effect against the pathogen (Dann and McLeod, 2021). The difficulty in elucidating the specific mode of action involved in each oomycete host pathogen system is likely due to the fact that it is influenced by (i) the time interval between phosphite treatment and inoculation; (ii) the concentration of phosphite applied and its translocation to the target plant organ, (iii) the tolerance of the pathogen to phosphite and (iv) the ability of the host to launch an effective host defence response following phosphite application (Jackson *et al*. 2000; Massoud *et al*. 2012).

The mode of action of phosphonates is more complicated by the fact that it is possibly dependent on phosphite concentration in plant tissues. Two studies using *Arabidopsis* and *Eucalyptus* have provided evidence that an indirect host defence

Table 2: Plant pathogens controlled by phosphonate fungicides

Disease	Pathogen	Crop	References
Blast	*Magnaporthe Oryzae*	Rice	Khanzada and Shah, 2012
Blue mould	*Penicillium expansum*	Apple	Amiri and Bompeix, 2011
Bunch Rot	*Cladosporium cladosporioides*	Grapes	Mengal *et al*. 2020
Foot rot	*Phytophthora nicotianae var. parasitica*	Citrus fruits	Thind, 2020
Downy Mildew	*Plasmopara viticola*	Grapes	Sawant *et al*. 2017
Dry root rot	*Rhizoctonia bataticola*	Chickpea	Khaliq*et al*. 2020
Early Blight	*Alternaria solani*	Tomato	Zafar and Shaukat 2018
Leaf Blight	*Rhizoctonia solani*	Turmeric	Sriraj *et al*. 2014
Panama Wilt	*Fusarium oxysporum f. sp. cubense*	Banana	Singh 2021
Powdery Mildew	*Uncinulane cator*	Grapes	Reuveni and Reuveni, 2008
Root rot	*Phytophthora cinnamomi*	Avocado	Whiley*et al.* 2001
Root Rot	*Macrophominaphaseolina*	Brinjal	Soomro*et al*. 2015
Root Rot	*Alternaria alternata*	Fenugreek	Khandare, 2014
White Rust	*Albugo candida*	Indian Mustard	Gairolaand Tewari, 2019
Wilt	*Fusarium oxysporum*	Brinjal	Soomro*et al*. 2015
Bacterial Blast	*Pseudomonas syringae*pv. *syringae*	Pear	Montesinos and Vilardell, 2004
Bacterial Blight	*Xanthomonas axonopodis*pv. *punicae*	Pomegranate	Bhise*et al.* 2017
Citrus Canker	*Xanthomonas axonopodis* pv. *citri*	Grapes	Naseera *et al*. 2019

response is involved at low phosphite plant tissue concentrations or application rates. This was evidenced by the upregulation of defence genes or compounds. In contrast, when high phosphite tissue concentrations or application dosages were involved, a lack of these host defence responses was seen in the host plant. However, *Arabidopsis* plants mutated in defence genes had less disease only when high phosphite application dosages were applied; at low phosphite dosages the mutant plant could not defend itself against the pathogen (Jackson *et al*. 2000; Massoud *et al*. 2012).

Direct mode of action on Oomycetes

In vitro studies have contributed convincing evidence of direct mode of action of phosphite. High concentration of phosphite reduced the growth and sporulation of oomycete pathogens (Wilkinson *et al*. 2001; Garbelotto *et al.* 2009). One of the highly prominent direct modes of action appeared to be the interference in biochemical processes (Dann and McLeod, 2021). Phosphite had also been demonstrated to interfere with gene expression at the transcription level (Varadarajan *et al.* 2002). In *P. cinnamomi* mycelia, genes coding for annexin and cellulose synthase were down-regulated, whereas genes for adenosine ribosylation factors were upregulated (King *et al.* 2010). Most of these genes initiated cell wall activity as well as membrane functionality, important for the survival of the pathogen (Konopka-Postupolska, 2007). The biochemical and gene expression alternations caused by phosphite ultimately also affected the morphology of oomycete pathogens. In *Phytophthora* spp. phosphite resulted in hyphal distortion (King, 2010; Wong, 2010). Even though considerable *in vitro* studies have been conducted for *Phytophthora* spp., limited information is available for *Pythium* spp. The *in vitro* studies on *Pythium* spp. also showed that species differ in their sensitivity.Mycelial growth inhibition was reported by of four *Pythium* spp. (*P. myriotylum, P. polymorphon, P. aphanidermatum* and *P. ultimum*) when grown on corn meal agar that was amended with 60 to 552 μg/ml phosphorous acid (Cook *et al*. 2009).

Indirect mode of action

The significant role of host plant defence induction in control of oomycetes pathogens by phosphonic acid has been acknowledged since 1980s (Hillebrand *et al*. 2019). These included increase in activity of phenylalanine ammonia lyase, lignification of cell wall, accumulation of phytoalexins as well as phenolic compounds, nuclear migration, papilla formation and hyper-sensitive response (Dann and McLeod, 2021). The application of Fosetyl-Al has been shown to induce the production of the phytoalexin capsidiol. Capsidiol provided good control against *P. nicotianae* in capsicum fruit. The capsidiol activity against *P. nicotianae*was shown to be produced within 18-24 hours following application. Fosetyl-Al was also shown to elicit the hypersensitive response on tobacco foliage (Mac Donald *et al*. 2001). Phosphonates can also improve the structural defence response of plants against pathogens including lignification, increased cell wall thickness and plant secondary metabolite production. Many of the secondary metabolites synthesized by the plant during defence induction possessed antimicrobial properties. Phosphonate application in *Banksia brownii*, inhibited *P. cinnamomi* attack through tissue compartmentalization and walling off (Pilbeam *et al*. 2011).The hypersensitive response was shown to be involved in the *Arabidopsis thaliana* interactions with *P. cinnamomi* and *P. palmivora* (Robinson and Cahill, 2003; Daniel and Guest, 2005). A primed host defence was shown to be involved in the *Arabidopsis Hyaloperonospora* spp. interactions, i.e. defence gene induction only occurs when the host plant is challenged with the pathogen (Massoud *et al*. 2012).

d) Compatibility with biocontrol agents

Combining biocontrol agents with fungicides have improved the extent of disease control and reduced the quantity of fungicides required for effective management (Buck, 2004). Therefore, the combined use of biocontrol agents and chemical pesticides has enticed much attention as a way to obtain synergistic effects in the control of pathogens. Phosphonate fungicides were found to be compatible with *Trichoderma* species which are the most commonly used biocontrol agents against plant pathogens. *In vitro* studies indicated that potassium phosphonate did not affect the radial growth and sporulation of *T. harzianum* (Veena *et al*. 2006; Shahida *et al*.2010). Similar results were observed where potassium phosphonate at 240 pg/ml to 3600 ug/ml, had no effect on the population of *T. harzianum* (Veena *et al*. 2006).In an investigation carried out both potassium phosphonate and fosetyl aluminium were found to be highly compatible with *T. viride* (Dhanya *et al*. 2017). Fosetyl-Al was also found compatible with *Trichoderma harzianum* used in Coorg mandarin-pepper-coffee plantations (Sonavane and Ravanappa, 2017). Biocontrol agent *Gliocladium virens* effectively inhibited *Phytophthora* foot rot of pepper when applied along with potassium phosphonate. Compatibility of bacterial bio control agent such as *Pseudomonas fluorescens* with different phosphonate fungicides was also observed (Kumar *et al*. 2017). Shahida *et al*. (2010) and Dhanya *et al*. (2017) reported that potassium phosphonate and fosetyl-Al was not inhibitory and highly compatible to *P. fluorescens.*

CONCLUSION

The dual role of copper in the paradigm of disease management is noteworthy. It is an irreplaceable metal regarding disease control in agriculture, with an increasing trend in consumption. Simultaneously it poses serious threats to sustainable agricultural concerning its accumulation and pollution of soils as well as its high residues in fruits and vegetables. Judicious use of copper is the need of the hour. Phosphonates have made a unique place in fungicides as systemic acquired resistance initiator. In fact, their use may continue to broaden as they are shown to be effective in reducing severity of oomycete and non-oomycete diseases in a broader range of crops including vegetables such as potato, forestry and natural ecosystems. The adoption of phosphonates as fertilizers, herbicides or other beneficial applications will likely to develop further, driven by demonstrated efficacy and safety, and a better understanding of specific interactions within the plant, pathogen and environment.

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