

Phosphate Foliar Fertilisation as a Source of Phosphite Residues

L. Tosi
AGREA s.r.l.
S. Giovanni Lupatoto, Verona, Italy

M. Malusà
Experimental Institute for Plant Nutrition
Torino, Italy

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Abstract

In particular environments foliar fertilisation with phosphate is a common practice to overcome transient deficiency status. Phosphate liquid fertilisers are also used as acidifiers when hard water is available for pesticide treatments. Phosphites, a common by-product present in phosphate fertilisers, are among the metabolites of pesticides whose residues in foods are regulated by the law. Therefore, experiments were designed to evaluate the chances of finding phosphite residues in fruits and buds of apple trees treated with phosphate fertilisers. The study was carried out on two year-old apple (cultivar 'Golden Delicious'/M9) trees grown in pots and in an open field trial on 8 year-old apples trees (cultivar 'Mongerduft'/M26). Trees were treated either with a single phosphate fertilisation (SP) provided to soil at the beginning of the trials or with a foliar phosphate fertiliser (FP) (five treatments, from May 11 every 7 days). Control plants were not treated with any phosphate fertiliser. Phosphorous acid concentration in foliar fertilisers was 172 ppm. Bark and bud samples were collected only from the field trial in March and in December. Fruits were collected starting from May 18 till harvest, on a monthly base. Phosphite concentration was determined by GC. At the end of the season we found a two-fold increase in phosphorous acid content in FP treated trees as compared to untreated and SP treated trees. Phosphorous acid was detectable only in fruits treated with FP. It is concluded that phosphorous acid traces present in foliar phosphate fertilisers can enter the plant and be found in different organs (fruit and bark). The amount found in fruits at harvest was in both trials over the legal limit for this compound suggesting a possible interference of normal foliar fertilisation practices with pesticide treatments.

INTRODUCTION

Phosphorus (P) is involved in several plant metabolic pathways and is an important component of several macromolecules. However, P is among the least available nutrients in soils because of its low solubility. Normally is the H_2PO_4 form that is taken up by roots, transported into cells and then enters the cell metabolism to be sequestered or incorporated into organic forms (Plaxton, 1998). Thus, P fertilisers are intensively applied to fruit orchards in the phosphate form.

Phosphites (Phi), are salts of phosphorous acid and have been extensively used in the past thirty years to control soil-born plant disease as *Phytophthora* sp (Guest and Grant, 1991). The compound ethyl-phosphonate, better known as Fosetyl-Al and commercialised under the trade name Aliette[®], was the first developed for this purpose, but currently inorganic salts of Phi are also marketed for the same scope. The use of these compounds is common in fruit orchards managed by integrated practices, but it is forbidden in case of organic management or in some productions whose output is processed to obtain particular products, e.g. baby food. Since Phi cannot be oxidised in plant, the control of such produces is based on the analytical search of Phi residues, which level is regulated by EU laws.

Phosphate liquid fertilisers are seldom used as foliar fertilisers because P deficiency is rarely observed in fruit trees. However, they are commonly used as acidifiers of the water utilised to prepare pesticide solutions when waters rich in calcium carbonates are used. From a preliminary survey of some commercial phosphate fertilisers emerged that they contain some amount of Phi. This paper reports about the results of

trials conducted to test the possibility that foliar phosphate fertilisers cause plant Phi pollution.

MATERIAL AND METHODS

A first trial was set in apple commercial orchards of 8 year-old trees cultivar 'Morgenduft'/M26 in Verona area (North-Eastern Italy) using a randomised complete block design with 4 plots of 10 plants. A second experiment was conducted on 2 year-old trees maintained in 25 L pots filled with a sandy soil in a glasshouse. Twenty five plants for each treatment were set in a completely randomised design. Trees were treated with a foliar (54% of P_2O_5 ; FP) or a soil (46% P_2O_5 ; SP) phosphate fertilisers. Control was not treated with any phosphate fertiliser. Soil phosphate was distributed once, before bud burst (75 g plant⁻¹ equivalent to 108 Kg ha⁻¹ P_2O_5 for both field and pot trials), while foliar treatments were performed five times, on a weekly base from May 11 to June 8, with a solution containing 150 ml hl⁻¹ of P_2O_5 . Plants were treated till full and uniform wetting of foliage.

From the orchard trial, bud samples, including a portion of bark near the bud, were collected before bud burst (before treatments) and after leaf fall from one year-old shoots. Leaves were sampled five times on shoots following the standard methods for leaf diagnostic. Fruits were collected from both experiments three times during the season: after fruit set (May), in the period of fruit drop (mid June) and just before harvest. Ten fruits per plot were collected. Samples were stored at -25 °C before analysis.

Samples were extracted with sulphuric acid, diluted with isopropanol and metilated with diazomethane. Determination of phosphorous acid concentration was performed by GC using a capillary column (DB-WAX) and a flame photometric detector phosphorous specific. Analysis parameters were as follow: T_{in} 80 °C for 2 min, ΔT 15 °C min⁻¹, T_{fin} 140 °C for 6 min; T_{inj} 240 °C, T_{det} 250 °C; volume injected 3 μ l.

Data were analysed by ANOVA and means separated by Newman-Keuls test.

RESULTS

The concentration of phosphorous acid (PA) in the foliar fertiliser was 172 ppm.

PA was undetectable in buds from control and FP trees before bud burst, while some amount was found in buds of trees from the soil fertilised treatment (Fig. 1). In the second sampling period, only buds from trees treated with FP showed an increase in PA content.

Leaves of control and soil treated trees did not shown any detectable amount of PA (Tab. 1). Leaves treated with FP showed a steady increase of PA concentration along with the spraying period, followed by a decrease after the last application of the treatment. PA was not detectable three weeks after the last spray (Tab.1).

Phosphorous acid in fruits from control and soil treated trees was undetectable in all sampling dates of both experiments (Figs. 2 and 3). Fruits from FP treatment showed a PA content ranging from 0.02 mg·kg⁻¹ f.w. to 0.04 mg·kg⁻¹ f.w. in the samples from the period corresponding to the treatments. At harvest, PA concentration decreased to about 10% in fruits of the field trial (Fig. 2) and to about 50% in those of the pot experiment (Fig. 3).

DISCUSSION AND CONCLUSIONS

Foliar spray of phosphate fertilisers can provide an amount of phosphorous acid to trees that is found as a residue in fruits. Even though the concentration found was at a part per billion level, it was still over the legal limits set for residues of metabolites of Fosetyl-Al, a compound used for disease control and forbidden in some kind of fruit productions (e.g. organic or baby food). However, the concentration of PA in fruits of trees treated with the pesticide is about 100-fold higher than that of FP treated fruits (Malusà and Tosi, 2002), thus allowing a possible distinction between the source of the residue. Besides, the increase in fruit mass in the last period of fruit growth reduces the concentration of PA in fruits (Figs. 2 and 3). The potential yield of the tree is also another factor influencing the

concentration of the residue. The PA content of the fruits from the field experiment was almost 3 times lower as compared with the younger and lower producing trees of the pot experiment (Fig. 3).

PA can enter the plant from leaves and is rapidly transported into different organs (Tab. 1). This is in agreement with results showing PA content increase in plants after treatments with phosphites (Carswell et al., 1997; Foster et al., 1998). The increase of PA concentration in buds of FP-treated trees at the end of the season supports the findings of a phloem transport of this molecule and accumulation in storage organs (Carswell et al., 1996; Guest and Grant, 1991). The lack of detection of PA in samples from the soil treatment can be justified considering the low PA concentration in the fertiliser used and the possibility of oxidation of the molecule by soil bacteria (Ohtake et al., 1996; Metcalf and Wolfe, 1998).

We speculate that the presence of some PA in bud samples before the application of the soil treatment (Fig. 1) is considered as a residue of past application through the use of foliar fertilisers. This practice is normally utilised by the farmer to acidify spraying solutions. Even though we cannot reasonably explain the finding of residues only in these trees, we found the same level of PA also at the end of the season. In case of the FP treatment we found a marked increase of PA in comparison to the sample collected before the treatments, that was over passing also the concentration found in SP samples. This is supporting the hypothesis that PA can be stored and re-translocated in the plant in the years after foliar phosphite distribution has been carried out.

Phosphite interferes with the plant phosphate metabolism exacerbating the effect of P starvation in herbaceous plants (Carswell et al., 1996; 1997). Even tough trees are seldom showing P deficiency, in young trees, especially if treated with high amounts of phosphite or Phi-containing molecules for disease control, the possibility of reduction of growth and yield due to P deficiency should be taken into account. This risk is increased in acidic soils or with a low P content.

Literature Cited

- Carswell, M.C., Grant, B.R., Theodorou, M.E., Harris, J., Niere, J.O. and Plaxton, W.C. 1996. The fungicide phosphonate disrupts the phosphate-starvation response in *Brassica nigra* seedlings. *Plant Physiol.* 110:105-110.
- Carswell, M.C., Grant, B.R. and Plaxton, W.C. 1997. Disruption of the phosphate-starvation response of oilseed rape suspension cells by the fungicide phosphonate. *Planta* 203:67-74.
- Forster, H., Adaskaveg, J.E., Kim, D.H. and Stanghellini, M.E. 1998. Effect of phosphite on tomato and pepper plants and on susceptibility of pepper to *Phytophthora* root and crown rot in hydroponic culture. *Plant Path.* 82:1165-1170.
- Guest, D. and Grant, B.R. 1991. The complex action of phosphonates as antifungal agents. *Biol. Rev.* 66:159-187.
- Malusà, E. and Tosi, L. 2002. Phosphite residues in apples derived from phosphate foliar fertilisation. *Proc. 4th European Pesticide Residues Workshop*. Roma, Italy 28-31 May. p. 206.
- Metcalf, W.W. and Wolfe, R.S. 1998. Molecular genetic analysis of phosphite and hypophosphite oxidation by *Pseudomonas stutzeri* WM88. *J. Bacteriol.* 180:5547-5558.
- Ohtake, H., Wu, H., Imazu, K., Anbe, Y., Kato, J. and Kuroda, A. 1996. Bacterial phosphonate degradation, phosphite oxidation and polyphosphate accumulation. *Res. Cons. Recy.* 18:25-134.
- Plaxton, W.C. 1998. Metabolic aspects of phosphate starvation in plants. In: J.P. Lynch and J. Deikman (eds.), *Phosphorous in plant biology: regulatory roles in molecular, cellular, organismic and ecosystem processes*. Am. Soc. Plant Physiologists, Rockville (MD), USA.

Tables

Table 1. Phosphorous acid content of leaves from 8 year-old apple trees cv. 'Mongerduft' treated with soil or foliar phosphate fertilisers. ($\text{mg}\cdot\text{kg}^{-1}$).

Sampling dates	Control	Soil P	Foliar P
May			
11	< 0.001	< 0.001	< 0.001
18	< 0.001	< 0.001	0.30*
25	< 0.001	< 0.001	0.70*
June			
1	< 0.001	< 0.001	1.80*
8	< 0.001	< 0.001	1.70*
14	< 0.001	< 0.001	0.50*
21	< 0.001	< 0.001	0.40*
28	< 0.001	< 0.001	< 0.001

* Difference significant at $p < 0.01$.

Figures

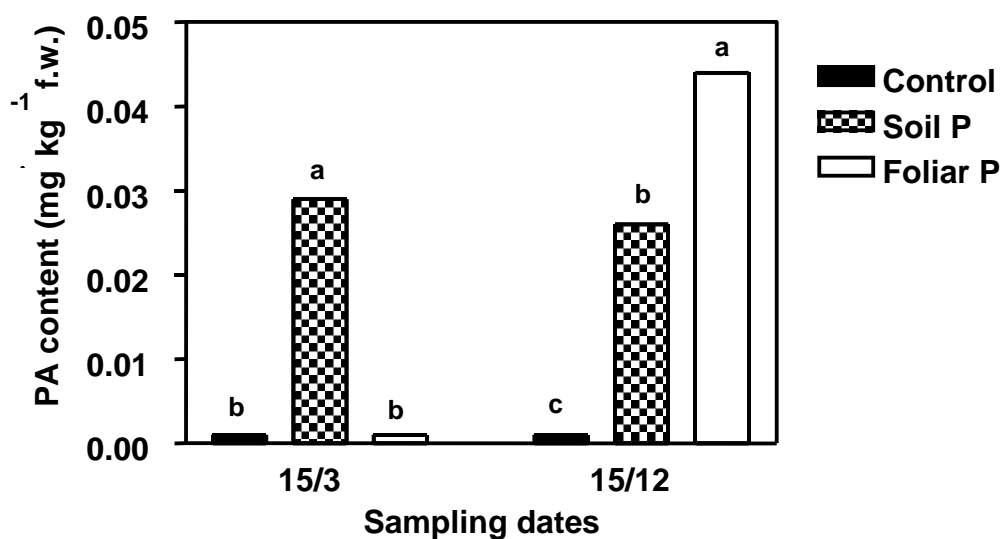


Fig. 1. Phosphorous acid (PA) content of buds and bark from 8 year-old apple trees cv. 'Mongerduft' treated with soil or foliar phosphate fertilisers. For each sampling date, bars with same letter are not significantly different at $p = 0.05\%$.

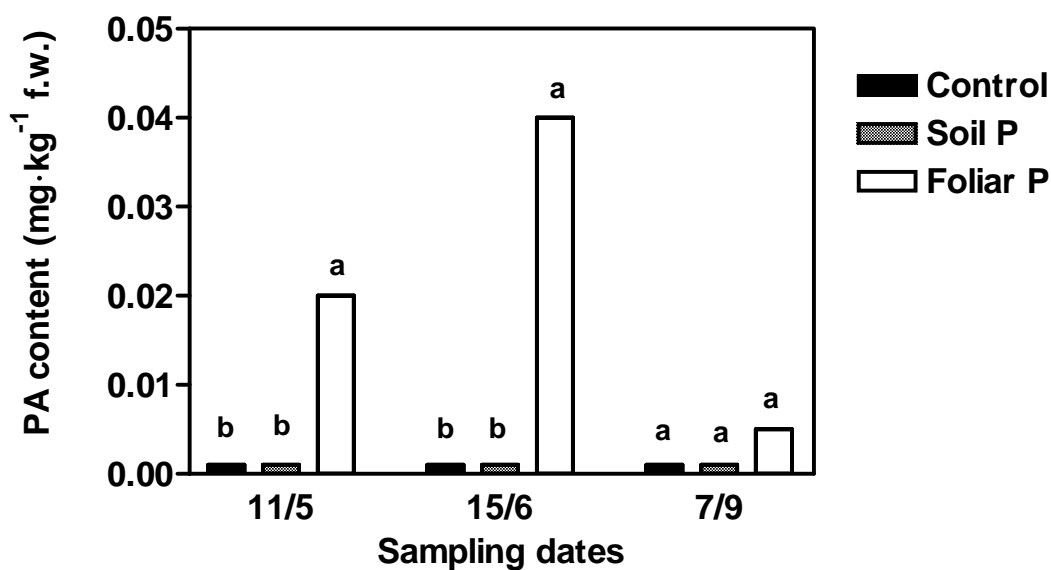


Fig. 2. Phosphorous acid (PA) content of fruits from 2 year-old apple trees cv. 'Golden Delicious' treated with soil or foliar phosphate fertilisers. For each sampling date, bars with same letter are not significantly different at $p = 0.05\%$.

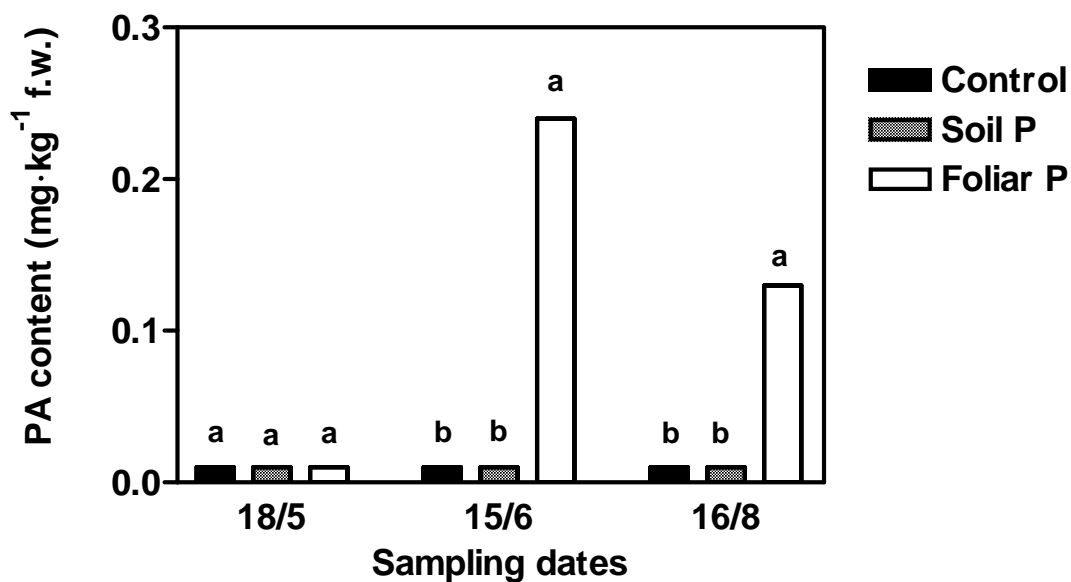


Fig. 3. Phosphorous acid (PA) content of fruits from 8 year-old apple trees cv. 'Mongerduft' treated with soil or foliar phosphate fertilisers. For each sampling date, bars with same letter are not significantly different at $p = 0.05\%$.