Phosphites and Phosphates: When Distributors and Growe

There has been some confusion lately in Europe and North America, now spreading to other parts of the world, over terms used for fertilizers and chemicals containing phosphorus. Distributors and growers have been using phosphate fertilizers for many long years. They are familiar with formulations like single super phosphate (SSP), triple super phosphate (TSP) diammonium phosphate (DAP) but also MAP and MKP (Monopotassium Phosphate). All of them provide phosphate derived from phosphoric acid (H_3PO_4). The phosphate that plants use is in the form HPO_4 and H_2PO_4, which is quickly converted in soil from fertilizers. Recently, new terms are being used including phosphorous acid (not phosphoric acid), phosphite (not phosphate), and phosphonite or phosphonate. Unlike the phosphoric acid that contains four oxygen atoms, phosphorous acid (H_3PO_3) and the related compounds contain only three oxygen atoms. Is that difference of one oxygen atom very important? In fact a clear distinction exists between Phosphoric acid and phosphorous acid: the former is a plant nutrient and the latter has primarily fungicide applications. It is thus very obvious that claims suggesting that either compound may exactly fulfill the functions of the other are misleading. Therefore, is the bottom line that on the one side phosphates are what is needed for fertilizer but will have no effect on plant diseases and on the other side that phosphites are useful in managing diseases but will not provide plants with the phosphate they need? Maybe not so simple! New Ag International went to investigate among suppliers and scientists to try sorting out what is really true, untrue and partly true? Our findings: What is true is that plants can absorb the phosphorous acid compounds through roots and leaves. What is also true is that plants are incapable of using DIRECTLY the phosphorus acid as a nutrient source. What is partly true is that the phosphorous acid compounds can break down in the soil to available forms of P, but this process is very slow and will not provide adequate P nutrition. What is untrue is that they can complement and even replace phosphate fertilizers in all instances. And what is very true above all is that a number of people from various bodies entertain confusion in the market!

For many years foliar applications of sulphur and some trace elements such as Zinc, Copper and Manganese have been used in combatting plant pathogens. More recently it was also proved that e.g. MKP (Mono Potassium Phosphate) has a fungicidal activity, not only MonoPotassium Phosphites! So where is the problem? Is it primarily that the plant protection industry, which is being subject to tough and expensive regulation to market its products including phosphite-based fungicides, is not happy with the plant nutrition industry declaring and registering phosphite based products as fertilizers-generally at no cost and without any delay- even if they may have more fungicidal properties than nutritional impact at the prescribed application rate? The plant protection industry may get even more nervous when the accompanying promotional literature for such products describes them more as "biostimulants and fortifying ingredients " or even "plant protectors" than as simple source of nutrients!

SOME BASICS ABOUT PHOSPHORUS

Phosphorus is the chemical element that has the symbol P and atomic number 15. A multivalent nonmetal of the nitrogen group, phosphorus is commonly found in inorganic phosphate rocks. Phosphorus is a component of DNA and RNA and an essential element for all living cells. Due to its high reactivity, phosphorus is never found as a free element in nature. It is very reactive and rapidly combines with other elements such as oxygen and hydrogen. When fully oxidized, it is bonded with four oxygen atoms to form the well known phosphate molecule. If not fully oxidized, then hydrogen occupies the place of one oxygen atom and the resulting molecule is called phosphite. The most important commercial use of phosphorus-based chemicals is the production of fertilizers, based on phosphates. In agriculture, an other important use of phosphorus-based chemicals is the production of fungicides based on phosphites.

This is all very simple but it becomes confusing and misleading when some web literature of a company having pioneered the use of phosphites (deriving from Phosphorous acid) as fertilizer, in its FAQ page, compares Phosphorous to Phosphorus (what for?) and describes the latter as "A poisonous nonmetallic element of the nitrogen group, obtained as a white, or yellowish, translucent waxy substance, having a character-

rs alike could get confused!

istic disagreeable smell". Which one would you use after reading this and knowing nothing about chemistry?

PHOSPHITES PRIMARILY USED AS FUNGICIDES

As early as 1930, a study was carried out to determine the efficiency of various phosphorus (P) containing compounds as fertilizers. It concluded that Phosphite was a poor source of nutritional Phosphorus since plants treated by phosphite grew weakly. Therefore at this time phosphite couldn't find a niche in the market as a potential source of plant nutrient. Fourty years later, phosphites returned to the market when it was found that they were very efficient against the Oomycota (i.e. species of phytophthora and pythium). Today it is well documented that the toxic effect of phosphite to Phytophthora comes from the activation of defense mechanisms in plants or by direct action on this fungal-like organism, and phosphorous acid compounds (phosphite and phosphonites) play an important role in agriculture as active ingredients in fungicide materials. This market was pioneered by Bayer Cropscience with world-famous brands Aliette and Fosetyl-Al. When the patent for the trademark Fosetyl-Al expired, several other fungicide manufacturers created phosphite-based fungicides by simple formulation of phosphite with potassium, ammonium, sodium, and aluminum. Trademarks now also include, among others ProPhyt (sold by Helena Chemicals), Phostrol (Nufarm America), Phosguard, , etc. Phosphite fungicides are first formulated as ethyl phosphonate by reacting phosphite with ethanol to form the ethyl phosphonate anion and an aluminum ion as the counter ion. The problem (see table 2) is that whereas some of the phosphite compounds are labeled as pesticides, which required the manufacturer/distributor to spend the time and money to register the compound, others, in North America but also in a number of European countries (Spain, Italy, Germany, etc…) are advertised and registered as fertilizers, which of course bypasses the expensive and time consuming registration process, and are even now tested in organic farming production (e.g. on grapes in France, Germany, Italy)! These phosphorous acid compounds, most of them based on potassium phosphites, although active against the Oomycota and some fungal diseases, are claimed to provide phosphorus nutrition to the plant. True, untrue, partly true? What is true is that plants can absorb these compounds through roots and leaves and once in the plant, the phosphorous acids compounds are very stable. What is also true is that plants are incapable of using DIRECTLY the phosphorus acid as a nutrient source. What is partly true is that the phosphorous acid compounds can break down in the soil to available forms of P, but this

process is quite slow and will not provide adequate and speedy P nutrition. What is untrue is that they can complement and even replace phosphate fertilizers in all instances.

A RENEWED INTEREST ON PHOSPHITES AS PLANT NUTRIENT SINCE THE EARLY NINETIES

What is also true is that the effectiveness of phosphites in controlling plant diseases has been hiding their potential as fertilizers. However, interest in the subject was renewed when Lovatt (1990), now Professor of Plant Physiology at the University of Davis in California and the recent co-author of an article on the topic (in Better Crops/Vol 90, 2006, N°4) with Mikkelsen (IPNI), discovered that P deficiency in citrus species caused changes in nitrogen metabolism. Through the application of potassium phosphite the biochemical response as well as a normal plant growth were restored. Furthermore, Lovatt showed that fruit set and yield of avocado were improved when potassium phosphite was applied with foliar sprays. This work led to the first commercialization of phosphite compounds as a fertilizer. A product was patented and sold under the trademark Nutri-Phite (Biagro Western Sales Inc), which is potassium phosphite, derived from phosphorous acid, potassium hydroxide, and the organic tripotassium citrate. This product is sold as a P nutrient fertilizer for foliar application and is used in a wide variety of field and horticultural crops. The list of phosphite products that are available in the American and European markets and are sold as fertilizers now includes tens of brand names. All of them are formulated as alkali salts of phosphorous acid and all are registered under the fertilizer laws. The possibility of registration of phosphite as a P fertilizer in most European countrries is surely due to the predefinition in the EU fertilizer laws that the composition of a P fertilizer should be expressed in terms of P2O5. This is based on long established practices, which report elements in oxides, hence, the reporting of P as "% P2O5". Therefore, although a fertilizer may contain phosphite instead of phosphate this would still be conform to the law if Phosphorus is declared as P2O5 in the fertilizer analysis!

The "funny" and somewhat confusing part of the phosphite story is that whereas some companies primarily in the fungicide business logically register their phosphite based products as fertilizer when they can do so, some other companies primarily involved in plant nutrition register some phosphite products as ….fungicides! Is this driven by the search for higher mark-ups? Most of them will find themselves disappointed as the market is very crowded and is increasingly price driven.

Table 1: Some products of the Phosphorus family used in agriculture

Name	Symbol	Comments
The Phosphate Family		
Phosphorus	P	The chemical element. Does not occur as a free element in nature
Phosphoric acid	H3PO4	Compound found in most phosphate fertilizers. Contains 32% P
Phosphate	PO4	Completely dissociated form of H3PO4
Phosphorus oxide	P2O5	Formula used to express the phosphorus content in fertilizers. It does not occur as a free element in nature
Finished Phosphate Fertilizers:		
Single Super Phosphate	SSP	Dry fertilizer containing about 19% P2O5
Di Ammonium Phosphate	DAP	18-46-0 dry fertilizer
Triple Super Phosphate	TSP	0-45-0 dry fertilizer
Monopotassium Phosphate	MKP	0-52-34 dry fertilizer
MonoAmmoniumphosphate	MAP	12-0-61 dry fertilizer
Ammonium Polyphosphate	APP	10-34-0 liquid fertilizer
The Phosphite family:		
Phosphorous acid	H3PO3	Compound normally marketed as a fungicide. Contains 39% P
Phosphonate, Phosphite, Phosphonite	PO3	Completely dissociated form of H3PO3
Some phosphite derived products		
Aluminium Phosphite		Only marketed as a fungicide
Potassium Phosphite		Marketed as a liquid fertilizer, e.g. 0-58-38, 0-30-20 or 0-24-16
Magnesium & Calcium Phosphite		Marketed as fertilizers
Ammonium Phosphite		Marketed as fertilizer, e.g. 11-35-0
Various micronutrients phosphites (Zn, Mn)		Marketed as fertilizers

Source: Various

Avocado is a crop where the application of phosphite as foliar sprays proved beneficial to fruit set and yield in the early nineties and helped relaunch the commercialization of phosphites as fertilizers.

CONFLICTING EXPERIMENTAL RESULTS

The number of products based on potassium phosphites, magnesium phosphites, calcium phosphites, etc. wouldn't have mushroomed in the market if there were no documented positive effects of phosphite application on crops and in particular if foliar application of such products had not proven more than just a fungicide effect. Research from Lovatt and more recently Abrigo clearly shows that foliar applications of phosphite can replace phosphate in citrus and avocado crops suffering from P deficiency. In these and other crops, such application has proved to be beneficial to floral intensity, yield, fruit size, total soluble solids and anthocyans concentration. At the same time however, Lowatt and Mikkelsen warn that "phosphite is most effective when the rate and the application are properly timed to match the needs of the crop" and they underline that since phosphite is chemically different from phosphate, these differences must be taken into consideration to avoid plant toxicity. Toxicity, the key word for the "anti-phosphites" people? To be honest, toxicity of phosphites is as well documented as their positive effects, if not more! The toxic effect and the additional expenses associated to the use of phosphites were indeed the reasons why research almost stopped for many years!

The effectiveness of ammonium phosphite application as a starter fertilizer for cotton needs further study.

Citrus is also a crop where some good results have been achieved with foliar sprays of phosphites but there is no definite certainty that such results can be replicated every time.

In 1975, problems were encountered again on over 750 ha of corn in southern Michigan that was traced back to a 9-18-9 liquid fertilizer containing phosphite. The fertilizer was either foliar applied or applied in a band in contact with the seed. About 40 litres/ha was used. "Plants showed white, variegated streaking of the leaves in mild cases and spindly, rolled, yellowish-white leaves in severe toxicity", said Lucas when he published the results of investigations in 1979. Interesting, no such symptoms were observed in 1976 when the same material was used.

More recently in 2003, ammonium phosphite (11-35-0) was compared with the well known liquid fertilizer ammonium polyphosphate (10-34-0) as a starter fertilizer on cotton on irrigated and non-irrigated sites in South Georgia by Dr. Glen Harris, UGA-Tifton. Both materials were applied at 12 gallons per acre (slightly less than 100 litres/ ha) in a 2x2 band at planting and applied on the surface. The

Table 2: From Fungicides to Fertilizers: The marketing of some products with phosphorous acid & phosphites as active ingredient

Product	Company	Country	Active ingredient	Marketed as
Aliette	Bayer Cropscience	Germany	Fosetyl-Al*	Fungicide
Nutri-Phite	Biagro Western Sales	USA	Phosphites & organic acids	Fertilizer
Ele-Max	Helena Chemical	USA	Phosphorous acid	Foliar Fertilizer
ProPhyt	Luxembourg-pamol	USA	MonoPotassium Phosphite	Systemic fungicide
Nutrol	Lidochem	USA	Potassium Phosphite	Fertilizer and fungicide
Phostrol	NuFarm America	USA	Phosphorous acid	Biochemical pesticide
Agrifos	Liquid Fert Pty (Agrichem)	USA	MonoPotassium Phosphite	Fungicide
Foli-r-fos 400	UiM Agrochemicals	Australia	MonoPotassium Phosphite	Fungicide
Fosphite	Jh Biotech	USA	MonoPotassium Phosphite	Fungicide
Lexx-a-phos	Foliar Nutrients Inc	USA	MonoPotassium Phosphite	Fungicide
Trafos line	Tradecorp	Spain	Potassium Phosphite	Fertilizer & defense stimulator
Phytos'K	Valagro	Italy	Potassium Phosphite	Biostimulant (registered as EC Fertilizer)
Phosfik line	Biolchim	Italy	Phosphorous acid	EC fertilizer
Fosfisan, Vigorsan, etc	Agrofill	Italy	Potassium Phosphite	Defense Stimulator (registered as fertilizer)
Geros-K	L-Gobbi	Italy	Potassium Phosphite	EC fertilizer
Kalium Plus	Lebosol	Germany	Potassium Phosphite	EC fertilizer
Frutoguard	Spiess Urania	Germany	Potassium Phosphite	EC Fertilizer
Foliaphos**	Plantin	France	Potassium Phosphite	EC Fertilizer

*: Fosetyl-Al is an aluminium phosphite. **: not sold in France. Source: New Ag International database & others.

AN INTERVIEW WITH

Prof Lawrence E. Datnoff, Plant Pathology Department and E.H Simonne, Assistant Professor, Horticultural Science Dpt, University of Florida

Both scientists are well placed to have a critical view on the claims attributed to phosphites. Prof Datnoff is the co-editor of the recently released reference book "Mineral Nutrition and Plant Diseases" and E.H. Simonne, an expert in water and nutrient management of vegetable crops, is the co-author with L. Datnoff of a reference article published in 2005, entitled "Phosphorous acid and Phosphoric acid: When all P sources are not equal".

Does phosphonate get converted into phosphate in plants and in soils?
From what is in the literature, some chemical conversion (slow) of phosphonate to phosphate may occur in soil by microorganisms and non-enzymatic oxidative processes since no enzymes such as phosphonite oxidase or phosphate reductase are known to occur. This leaves the conversion of phosphonates into phosphate once inside the plant with no documented answer. However, Orbovic and his colleagues recently demonstrated that citrus seedlings supplied with phosphonate or phosphate grew equally well and the P content of the leave tissue did not differ significantly between these two sources [Citrus seedling growth and susceptibility to Phytophthora root rot are affected by phosphate and phosphate sources of phosphorus 2007, J. Plant Nutr. (in press)].

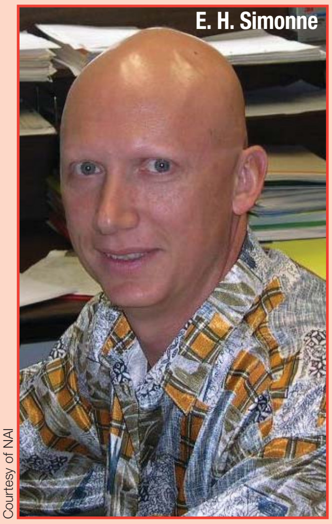
Is there any valid evidence that phosphorous acid and phosphites improve plant growth?
Phosphorous acid is known to have a direct effect against the Oomycota (i. e. species of Phytophthora and Pythium). This fungal-like group of plant pathogens causes a number of important plant diseases. The mechanism of action of phosphorus acid is believed to be due to its stimulating the plant's natural defense response against pathogen attack. As such, by controlling disease you would improve plant health and consequently plant growth. There is some literature also suggesting that phosphorus acid or its salts promotes plant growth even in the absence of plant pathogens (J. Plant Nutrition 23:161-180).

Can some phosphate containing fertilizers such as MonoPotassiumPhosphate help control some pathogens?
It is widely reported in the literature that balanced and adequate fertility for any crop reduces plant stress, improves physiological function, and decreases disease risk. However, information on P nutrition on plant diseases in the literature is inconsistent. Depending on the P source, form, crop and plant disease, P can increase, decrease or have no effect on plant disease. That being said, Reuveni and his collaborators demonstrated that foliar applications of mono-potassium phosphate induced systemic and local protection of cucumber to powdery mildew development (Crop Protection 19:355-361 2000).

Is there in the USA an official method of analysis that allows laboratories to list separately within the overall Phosphorus content of a commercial fertilizer, the proportion coming from the phosphate and phosphite forms respectively?
Not currently but if something is to be found, it will be in looking at colorimetric methods vs. spectrophotometric ones. Perhaps, ion chromatography could be used, too.


E. Datnoff

Courtesy of NAI


E. H. Simonne

Courtesy of NAI

ammonium phosphite resulted in shorter plants at the fourth true leaf stage but no differences in leaf P concentration and no significant differences in yield at harvest were observed. Therefore, conclusions from this one-year test were ". . .inconclusive and the effectiveness of 11-35-0 (ammonium phosphite) as a starter fertilizer for cotton needs further study."

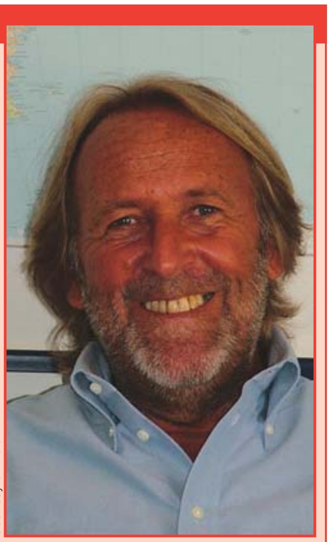
In 2004, farmers in southeastern Alabama, southern Georgia and northern Florida have experienced problems on maize (toxicity) that were described as being related to the use of a "non-conventional fertilizer material" as a starter fertilizer. The material, ammonium phosphite, was used in a manner similar to ammonium polyphosphates. The symptoms of phosphite toxicity were even described as very similar to glyphosate damage, which prompted Monsanto in 2005 to issue again reports and releases stipulating that glyphosate was degraded into inorganic phosphates/phosphoric acid in the soil and the environment, not phosphites or phosphorous acid as suggested by Whiley already 10 years before.

A NEED FOR A BETTER LEGISLATION AND TRANSPARENCY ON LABELS?

In Europe, the most recent findings published in 2006 by the Institute of Plant Nutrition and Soil Science and the Institute of Ecological Chemistry and Waste Analysis, both located in Braunschweig, Germany, seem to well summarize

WHAT THEY THINK ABOUT PHOSPHITES

Peter Marti, Export Director , Biolchim Spa, Italy



Courtesy of Biolchim

"We offer to the growers a complete range of twenty phosphites based products under the trademark PHOSFIK®, characterized by the addition to the phosphorus of one or more elements (K, Fe, Cu, Mg, Mn, Zn, etc.), each formula specifically tailored to the most important crops (industrial, horticultural and fruit trees), for foliar or fertigation application.

By means of their peculiar chemical formulation the whole PHOSFIK® line is processed at our factory by a reaction that starts from phosphorous acid reacting with various components generating stabilized phosphite salts. These phosphites quickly penetrate the crop tissues and provide a nutritional action as well as a boosting coadjuvant effect to fungicides applied to control the main fungal diseases.

By enlarging the vascular system of the plant, our products stimulate to the optimum the assimilation of phosphite ions and other nutrients carried in the formulation, allowing the plant to maximize phosphorus availability along with a better nutritional balance, growth and subsequent increased yield.

In the recent years, the efforts of our tech & sales teams helped us develop a substantial presence in the key Italian crop segments, namely grapes, citrus, stone fruits, olives and hydroponic crops. At international level, I just want to mention our massive success in Germany with PHOSFIK® 3-27-18 + T.E. on strawberries and Solavit Mn, specifically tailored for potatoes to increase yield and to promote homogeneous tuber calibration and quality parameters. For us at Biolchim, the PHOSFIK® line represents indeed the very best answer to the need of growers for a correct and innovative nutritional and disease-control coadjuvating strategy in agricultural crops".

and reconfirm earlier research done elsewhere on maize: *"The detection of different phosphite concentrations in phosphite fertilized maize plants indicates that this P compound is well absorbed by plant roots. After phosphite foliar application, this compound was also detectable in all parts of maize plants, which proves its phloem and xylem mobility. The phosphite accumulation was notably high in developing corncobs. Phosphite is obviously stable within the plant metabolism process as only small amounts appeared to be oxidized to phosphate. The reduced growth observed in phosphite treated plants was especially evident under conditions of P deficiency. This could result from a suppression of the natural mechanisms of plants to respond to P deficiency. These results should be considered as an aspect of the German fertilizer law: in the future, the P content of marketable mineral fertilizers is to disclose specifically in terms of soluble phosphate or phosphite instead of generalized "P2O5", as hitherto".*

The last sentence from the conclusions from German researchers is a key point indeed! Phosphite may go undetected by most agricultural testing laboratories that are set up to test for orthophosphate. So far, approved techniques for fertilizer testing only measures orthophosphates. However, some non-regulatory laboratories are switching to inductively coupled argon plasma technology for rapid analysis of several elements simultaneously. This technology has the capability of measuring total P whether orthohosphate, phosphite, or solubilized organic P. If this technique were used to measure total P, it could create the impression that plant-available P is higher than it really is if some of this P was phosphite. Testing for the phosphite anion alone is tedious and expensive but it may be the price to pay for a better transparency in the market. In Europe, most Potassium Phosphite based products (using the raw material 0-58-38 at a usual dilution rate of 50-60%) are registered as PK fertilizers (e.g. Italian law 217, EU 2003 regulation, etc.). Until recently there were no official analytical methods to individuate the content of PO3. For this reason, the inspection of such products was always finding a 0% content for PO4, which is of course not acceptable for a "phosphate fertilizer"! Today, an official analytical method exists for PO3 that is used by inspectors when the presence of Phosphites is indicated on the label, which is not compulsory because the only compulsory mention for fertilizers is the P2O5 content! Therefore a problem of transparency is still there!

The market for phosphites based plant nutrition products has grown during the past years and it would

Corn is one of the most tested crops for effect of phosphite application, with contrasted and sometimes controversial results.

COULD PHOSPHITE BE A NEW FUNGICIDE FOR ORGANIC FARMING?

Bernhard Speiser

Lucius Tamm

Courtesy of FiBL

Bernhard Speiser and Lucius Tamm, FiBL, Switzerland

"Potassium phosphite, also called «phosphonate», is a salt of phosphonic acid with the formula K2HPO3. It should not be confounded with phosphates, nor with the organophosphorous insecticides which are also called «phosphonates». Potassium phosphite can be used as a fungicide against oomycetes in various crops. In the early 1990ies, it was extensively tested on organically grown grapevines in Switzerland. It was effective against downy mildew (Plasmopara viticola), and blocked the disease up to 3 days after infection. Phosphite was mobile and very persistent in plants and could be detected in grapes harvested one year after the last application. Analyses of 53 wine samples reveiled that the treatment inevitably leads to phosphite residues in wine, usually ranging between 5000 – 10000 ppb phosphite. Phosphite residues were also found in other crops (e.g. potato, celery) treated with potassium phosphonate.
From a toxicological point of view, these residues are of no concern. However, consumers of organic wine expect to buy a «natural» product, and we assume that they would not approve the presence of such quantities of fungicide residues in organic wine.
Currently, potassium phosphonate is not authorized as a fungicide for organic farming in the EU, and we do not recommend its use in the future".

certainly necessitate a bit more transparency. Some suppliers firmly believe in the future of the market while others are not so enthusiastic: " it is a sort of commodity, we have one product but it is not a strategic line for us", says one Italian supplier while others, e.g. Biolchim (see interview) or Tradecorp (Spain) are expanding their range. The mood seems to be as contrasted in North America, with one big supplier of specialty plant nutrition products saying " we are presently not involved in phosphites- we have been presented with a number of opportunities but have thus far chosen to stay with other foliar products and biological disease control agents. The market is pretty crowded and the margins are pretty thin for a number of these products".
The future will tell who was right, especially after the lion's share of the supply to most processors has been taken over by Chinese manufacturers (currently already supplying a number of Italian processors and a good part of the spanish ones) although it seems that the performance of the cristalline raw material coming from China (then dissolved by European importers to make a liquid finished product) is not as good as that of liquid product directly obtained through some different manufacturing processes. In the meantime, distributors and growers should be aware that phosphite fertilizers, if not formulated and used correctly in consultation with professionals, have a significant potential to be phytotoxic whereas if formulated and used correctly they may well fit in an optimized crop cultivation package, especially for selected cash crops. ■