

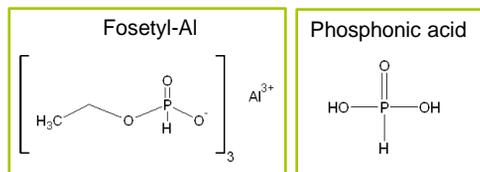
Phosphonic Acid: Pesticide or "Foliar Fertilizier"? Residues in Organic and Conventional Samples from the German Market

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Introduction

Residues of phosphonic acid in crops can occur as a result of applying plant protection products (PPPs) containing phosphonic acid itself or of applying fosetyl aluminium, which degrades to phosphonic acid. To reflect this situation, the current residue definition of fosetyl-Al is defined as follows: "sum fosetyl and phosphonic acid and their salts, expressed as fosetyl" (Reg. 459/2010/EC, effective since 29/05/2010).



Legal Aspects

Fosetyl is approved within the EU and fosetyl-containing PPPs are authorized in practically all EU member states. In Germany PPPs containing fosetyl as active substance are registered against certain fungi such as phytophthora and pythium-type plant pathogens on salads, cucumbers, tomatoes, herbs, hops, strawberries and vines. PPPs containing phosphonic acid used to be authorized and marketed as "plant strengtheners" or "foliar fertilizers". These PPPs were immensely popular among organic farmers for their positive effects on their cultures and as an alternative to the application of copper. The allegedly natural "plant strengtheners" or "fertilizers", however, essentially acted as fungicides. As phosphonic acid or derivatives thereof also appear naturally in small concentrations the situation regarding its status was initially unclear and much debated. However, new regulations in 2013 (369/2013/EU and 832/2013/EU) approving the use of potassium phosphonate and disodium phosphonate as active substances in plant protection products clarified the issue. As a result, Germany withdrew its authorizations for phosphonic acid containing PPPs which were marketed as "plant strengtheners" or "foliar fertilizers".

Analytical Method

Following the introduction of the QuPPE (Quick Polar Pesticides) method by the EURL-SRM, CVUA Stuttgart has been routinely testing for fosetyl residues in crops since 2008. The routine analysis of phosphonic acid however only started in 2012 (initially on targeted samples and from 2013 onwards on all samples) using the QuPPE M1.3, which allowed simultaneous analysis of the two compounds. The samples are extracted with acidified methanol, centrifuged, then passed through a syringe filter and finally subjected to LC-MS/MS analysis using a Hypercarb column.

Reference <http://www.cvuas.de>; www.eurl-pesticides.eu



Results

2,340 samples, including both conventional (1,929 samples) and organic (411 samples), have been analyzed since the beginning of 2012. Approximately 40% of all the analyzed samples and 43% of the conventional samples contained residues of fosetyl or phosphonic acid above the reporting levels with phosphonic acid being by far more frequently detected (in all, 46 samples contained fosetyl and 928 samples phosphonic acid). Residues of phosphonic acid were detected in a wide range of conventionally grown fruit and vegetables (see table), with concentrations ranging from 0.01 mg/kg to 173 mg/kg in a rocket lettuce sample. 25 of the 1929 conventional samples (1.3%) exceeded the maximum residue level (MRL) for the sum of fosetyl and phosphonic acid. These were mainly in stone fruits and exotic fruits.

Commodity	Number of samples	Samples containing phosphonic acid	Samples exceeding the MRL	Maximum and minimum contents [mg/kg]
Berry fruits	246	185 (75%)	2 (0.8%)	0.03–33.9
Pome fruits	121	71 (59%)	0	0.01–24.3
Stone fruits	46	24 (52%)	5 (11%)	0.02–21.2
Citrus fruits	169	109 (64.5%)	2 (1.2%)	0.03–35.0
Exotic fruits	196	93 (47%)	11 (5.6%)	0.03–23.5
Fruiting vegetables	353	101 (29%)	1 (0.3%)	0.03–32.0
Leaf vegetables	307	104 (34%)	2 (0.7%)	0.08–173
Stem vegetables	96	24 (25%)	1 (1.0%)	0.07–24.0
Potatoes	61	11 (18%)	0	0.04–16.3
Fungi	61	12 (20%)	0	0.06–0.85
Wine	28	23 (82%)	0	0.41–36.8
Dry pulses	17	9 (53%)	0	0.04–1.0

Almost 23% of organically grown samples (94 of 411) also contained residues of phosphonic acid (mainly table grapes, wine, cucumbers, tomatoes, lettuce, citrus fruits and pome fruits), in some cases at levels > 20 mg/kg. One sample exceeded the MRL. This situation was surely a result of the deceptive advertisement of phosphonic acid containing PPPs in the organic sector. Since phosphonic acid is not listed in Annex II of Reg. 889/2008/EC as a product authorized for organic farming, its application in organic farming is not allowed and residues in organic products should disappear in the near future. In the meantime, however, organic farming organizations are working towards including phosphonic acid in the EU's organic product regulation, their main argument being the reduction of copper-usage. Monitoring will continue.



Summary

43% of the analyzed conventionally grown samples contained detectable residues of phosphonic acid with a maximum content of 173 mg/kg in a conventionally grown rocket sample. 25 of these samples exceeded the MRL. Furthermore more than 20% of the organic samples also contained residues of phosphonic acid, which is an active substance not authorized for use in organic farming. Monitoring will be continued.

