European Organic Certifiers Council

cooperating for reliability!

EOCC Factsheet on Phosphonic Acid

Version: 0.1 (07-04-2018)
Version 0.2 (10-04-2018: amendments by operator handling red fruits)
Version 0.3 (15-04-2018: including comments from TF Res members)
Version 0.4 (23-04-2018: including comments from CAAE)
Version 0.5 (13-05-2018: including comments from KIWA/BCS and SKAL)
Version 0.6 (ECOCERT feedback)
Version 0.61 integrate and rework ECOCERT Feedback
Version 0.62 (without tracked changes)
Version taking into account Position paper Federbio (November 2018)
Version 0.63 reworked for better understanding
Version 0.64: new approach + review CAAE
Version 0.7 final proposal (March 2019)

The main questions are:

How do EOCC members handle the presence of phosphonic acid in products?
How do EOCC members handle the presence of Fosetyl in organic products?

Summary:

Phosphonic acid (H_3PO_3) is considered as a pesticide residue because it is included in laboratory reporting for the fungicide fosetyl-aluminum (Fosetyl-Al). Fosetyl-Al is not a stable molecule and degrades easily into fosetyl. Fosetyl degrades easily into phosphonic acid and it's salts. From a laboratory perspective, when looking for Fosetyl-Al or metabolites of Fosetyl-Al, it's correct to state that detections of phosphonic acid have to be related to Fosetyl-Al.

However, in practice, the presence of phosphonic acid and its salts in plants and plant products can be explained by other reasons as well. Some of the reasons are in line with organic production where others are not. The use of Fosetyl-Al is not allowed in organic farming.

In practical situations, it is very difficult to identify the real origin(s).

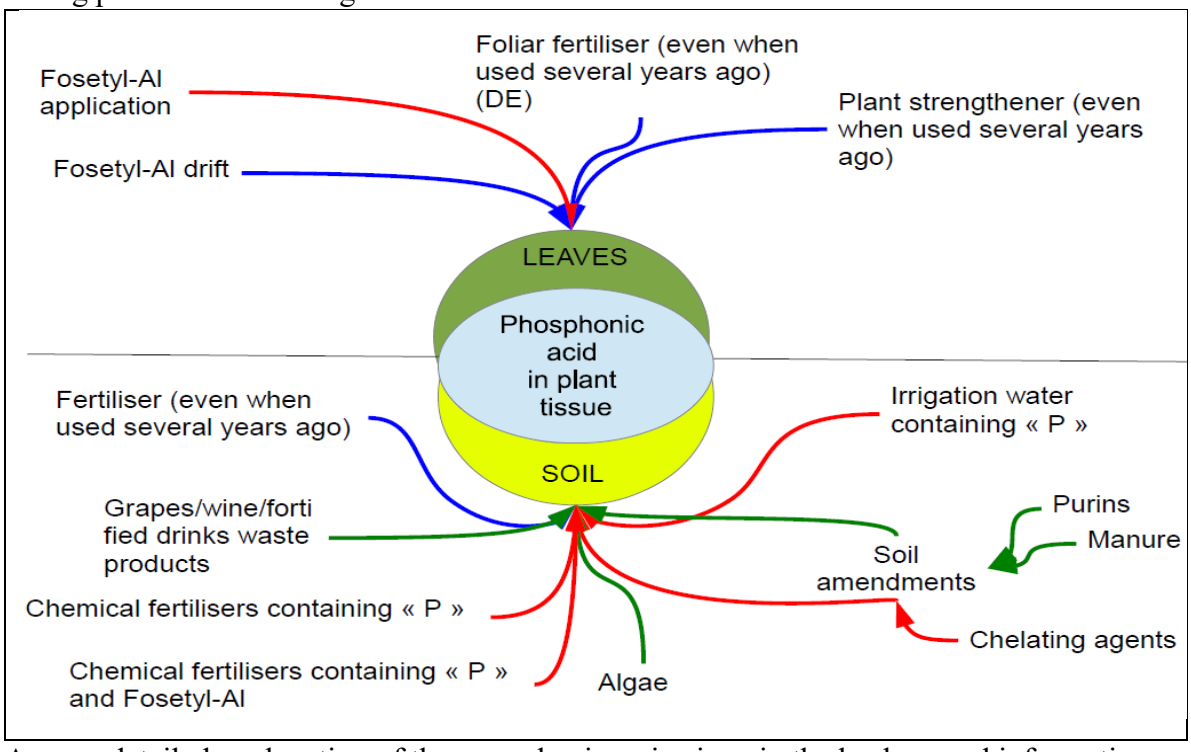
This situation is problematic for the organic sector because detections of phosphonic acid in organic products result in blocking concerned products and operators from using those products while operators and control bodies investigate the situation to identify the true origin of the phosphonic acid. Experience shows that the presence of phosphonic acid in an organic product does not necessarily result from use of the unauthorized substances like the fungicide Fosetyl-Al or chemical fertilizers.

Proposal for harmonization:

1. Actions to be taken by control bodies/authorities:
    a. Investigation: the decision how to investigate the case depends on the data available from the lab report and the sampling protocol:
        i. In those cases where Fosetyl is detected in a concentration equal to or exceeding 0.01 mg/kg, the control bodies/authorities start an official investigation. In those cases, where no Fosetyl is detected, only phosphonic acid is detected in a concentration equal to or exceeding 0.2 mg/kg, control bodies/authorities start an official investigation.
        ii. The official investigation results in the blocking of the concerned products for further use/sale as organic during the period of the investigation.
        iii. The official investigation aims at identifying the source of the phosphonic acid by following the methodology indicated in this document.
        iv. The official investigation results in a conclusion which is in line with the possible sources of phosphonic acid as highlighted in this document
        v. The official investigation is finalised as soon as possible.
    b. Certification decision after the investigating:
        i. If the phosphonic acid is due to the use of unauthorized substances during organic management of the crop, application of article 30 of Regulation 834/2007 and the applicable catalogue of measures.
        ii. If the phosphonic acid is due to use of authorized substances and the applicable MRL value is not exceeded, the batch can be used and sold as organic.
        iii. If the phosphonic acid is due to the use of substances not allowed for use under organic management, but the use has taken place prior to organic managent, the batch can be used and sold as organic.
        iv. In case the source of the phosphonic acid has not been identified, the product has to be released as organic. The operator is considered as higher risk operator. Additional audits (and sampling/analysis of other batches) will have to be performed.
2. Actions to be taken by operators receiving analytical results indicating
    a. The presence of fosetyl: inform their control body/authority and cooperate with the control body which shall investigate the case while the operator blocks the products of the concerned batches during the period of the investigation.
    b. The presence of phosphonic acid in a concentration
        i. Equal to or exceeding 0.2 mg/kg , inform the control body/authority and cooperate with the control body/authority.
        ii. not exceeding 0.2 mg/kg, keep records available for their control body/authority.

3. Looking at results of recent scientific research, it can be summarized that the presence of **<u>phosphonic acid (H_3PO_3) and its salts</u>** in plant products can be explained by three types of origins:
   (i) The **unavoidable presence** in the plant and/or the soil due to use of plant strengtheners, foliar fertilisers (possibly containg "P" when used before 2013 in DE), other kind of fertilizer/soil amendments or plant protection products based on Cu but also containing "P", even two or three years before sampling , due to spray drift and/or growth under stressful conditions e.g. drought.
   (ii) The **use of prohibited substances** on the plant or soil due to the use of Fosetyl-Al application, the use of chemical fertilisers containing phosphorous, the use of chemical fertilisers containing phosphorous mixed with Fosetyl-Al, the use of chelating agents in the preparation of soil amendments and/or irrigation water containing "P".
   (iii)The **use of authorized substances** on organic land due to use of purins or manure as soil amendments, algae or waste products from grapes/wine/fortified drinks preparation.

These studies also state that the presence of **<u>Fosetyl</u>** can be directly linked to the use of Fosetyl-Al, but French experience shows that fosetyl could also be formed as an artefact during production or storage of wine.



A more detailed explanation of these mechanisms is given in the background information (see further)

4. The methodology of the investigation: start by collecting evidence to support each of the hypothesis mentioned hereunder. If there is no evidence supporting the first hypothesis, start with the second. (Worst case scenario first)

Hypothesis 1: not authorized substances have been used

To confirm or deny this hypothesis, consider at least the follow elements:

Regarding Fosetyl-Al application:

- Is the use of Fosetyl-Al authorized on this crop in non organic farming in the country where the crop is grown?
- Is the use of Fosetyl-Al authorized on crop grown under non organic management in another production unit on the same holding?
- Is the use of Fosetyl-Al relevant in relation to the risk of fungi in the period of 1 month prior to sampling?

Regarding chemical fertilizer:

- Is the sampled crop sensitive to lack of "P" in the soil?

Regarding the use of soil amendments, "enriched" with Fosetyl-Al:

- Is there any documentation left of soil amendments used?
- Is there any product remaining for sampling?

Regarding the use of soil amendments containing "P" in the chelating agents?

- Is there any documentation left of soil amendments used?
- Is there any product remaining for sampling?

Regarding the use of irrigation water "enriched" with soluble forms of "P"

- Is there any record keeping in relation to irrigation water quality?
- Is the irrigation system a closed system?
- Is there an organic and non organic production unit which is irrigated by using the same source?

Hypothesis 2: Authorised substances containing phosphonic acid (natural presence) have been used

Regarding the possible sources of phosphonic acid, verify whether one or more of the following substances have been used

as soil amendment:

- Algae
- Purins

- Manure
- Waste products of the wine industry

plant strengtener or foliar fertilizer containing “P”.

micro-organisms

other inputs containing aminoacids

Hypothesis 3: Spray drift from neighbouring non organic productions:

Regarding Fosetyl-Al application by neighbouring farmers:

- Is the use of Fosetyl-Al authorized on those crops in non organic farming in the country where the crop is grown?
- Is the use of Fosetyl-Al relevant in relation to the risk of fungi in the period of 1 month prior to sampling?

Regarding plant strengtheners or foliar fertilizer containg “P”: check the plant records and needs of the crops of the neigbouring farmer.

Vocabulary

Phosphonic acid	Phosphorous acid		H_3PO_3
Phosphite salts, salts of phosphourous acid	phosphites	phosphonate	$H_2PO_3^-$, HPO_3^{2-} and PO_3^{3-}
Fosetyl	Ethyl phosphonic acid		$CH_3\text{-}CH_2\text{-}PO_3^-$
Fosetyl aluminum	Fosetyl-Al		$Al(CH_3\text{-}CH_2\text{-}PO_3)_3$
phosphate			$PO4^{3-}$

Fosetyl-Al

It is an organic phosphate compound used as a systemic fungicide with protective activity. It is rapidly absorbed through the plant leaves or roots, with translocation both up and down inside the plant. The active substance in the plant is potassium phosphonate which is active by inhibiting spore germination and penetration into the plant, and by blocking mycelial growth and spore production of mildew (*Peronospora*) in particular. In 2014 and in Germany, plant protection products containing fosetyl as active substance are registered against certain fungi such as phytophtora and Pythium-type plant pathogens (on salads, cucumbers, tomatoes, herbs, hops strawberries and vines. Also has a useful activity against several bacterial plant pathogens. Use of Fosetyl-Al is not allowed in organic farming.

Laboratory analysis

Laboratories are able to detect fosetyl, phosphonic acid and its salts, in a multi-residue method. Specific individual methods for the determination of fosetyl in fruit and vegetables also exist. The applied methodology is LC-MS/MS. Reporting limits (RL) may vary between laboratories. Examples of reporting limits are given in the table below:

Lab	RL Fosetyl (mg/kg)	RL phosphonic acid (mg/kg)	RL Fosetyl-Al (sum) (mg/kg)	
1	0.01	0.2	0.01	
2	0.01	0.1		ECOCERT SA labs
	0.05	0.2		ECOCERT France labs
3	0.01	0.01		

In cases where more than one analysis took place, it's important to know these RL. Currently, in different Member States, the RL for phosphonic acid of labs used by EOCC members vary widely (from 0.01 mg/kg to 0.2 mg/kg). It's obvious that a lab reporting "no phosphonic acid detected" while the RL is 0.1 mg/kg can not be compared to the result of a lab reporting 0.063 mg/kg phosphonic acid with a RL of 0.01 mg/kg.

Determining the level of fosetyl-Al in plant tissues is a difficult task.

Reporting after analysis

The laboratory has to respect requirements on reporting after analysis of pesticides. When the laboratory reports the analytical results of the analysis for the fungicide Fosetyl-Al, it has to add up the measured concentrations of fosetyl, phosphorous acid and salts of phosphorous acid expressed as fosetyl. "Expressed as fosetyl" means that the measured amount (in mg/kg) of phosphonic acid and salts of phosphorous acid needs to be calculated in terms of amounts of molecules (mol) and according to the reporting requirements, that amount of molecules originates from the same amount of molecules of fosetyl. The last step is to calculate the amount of mg/kg from that amount of molecules of fosetyl.
The molecular weight of fosetyl is 110 (g/mol) and the molecular weight of phosphonic acid is 82 (g/mol). That means that if the analysis shows that the product contains 0.1 mg/kg of phosphonic acid, in the reporting, the lab has to report 0.1*(110/82) = 0.13 mg/kg of fosetyl due to the presence of phosphonic acid.
This is only true in clean laboratory environments. This reporting does not take into account the possibility that the phosphorous acid is present in the plant due to another source.
Laboratories report the result of the sum but also the measured amounts of phosphonic acid and fosetyl separately.

Fosfonato (Sal del Ácido Fosfónico)	0,031	mg/kg	**LC/MS-MS**; SOP-LC-23 (LC/MS-MS) Límite de cuantificación: 0,01 mg/kg.
Fosetil	No detectado	mg/kg	**LC/MS-MS;** SOP LC 010 2009-10 Límite de Cuantificación: 0,01 mg/kg.
Fosetil-aluminio (1)	0,043	mg/kg	

(1) Suma de Fosetil y Ácido Fosforoso junto con sus sales, expresada como Fosetil.

Example of a (Spanish) lab report indicating 0.031 mg/kg phosphonic acid, no detectable amount of fosetyl and the official amount of Fosetyl-Al.

Fosetyl may degrade in part or fully into phosphorous acid (and salts of phosphorous acid), but phosphorous acid will not transform into fosetyl.

This means that the presence or absence of fosetyl makes a big difference: presence of fosetyl should be linked to presence of fosetyl-Al where absence of fosetyl could be linked to fosetyl-Al as much as it can be linked to one or more other sources (see above).
Stakeholders of the organic sector are invited to interpret the presence of fosetyl (with or without presence of phosphorous acid) as a substantiated doubt (cfr art 91 of Reg 889/2008) and act accordingly while the presence of phosphonic acid in the absence of fosetyl should not be a case of substantiated doubt and by consequence products can be released for sale/use as organic. Therefore, in case of detection of fosetyl, the AL is set at 0.01 mg/kg.

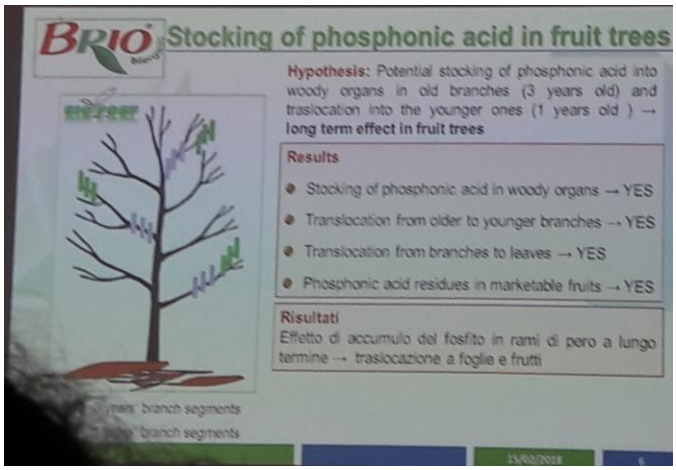
Summary of reasons which have been found to explain the presence of phosphonic acid in plants and plant products:

The result of absorption out of the plant's environment taking into account the following

a. Perennial crops

- e.g. fruit trees which accumulate the phosphonic acid which has been used on the plant as plant strengthener or on the soil in the past. Murcia CARM-imida study concluded that "phosphonates accumulate in woody tissues and are taken up from the soil, to be released in the plant even after many years after application. The BIOFOSF research project funded by Italian Ministry of Agriculture, referred to in the Federbio paper of November 2018, also came to the conclusion that phosphites, present in authorized for use by organic farmers were deposited in wood tissue for several years and were slowly released in the fruits up to five years after the take up.

The CREA project Italy reaches the same conclusion stating that "phosphonic acid is translocated to young tree branches, leaves and fruits. Even if there is no use on the tree, productions containing phosphonic acid or salts thereof can be seen up to more than two years after the last application". (historical pollution)



- vineyards (leaves) which have been treated with foliar fertilizer containing potassium phosphonate (authorized until 2013 in DE, thus also historical pollution) provided that use of such fertilizers was authorized in organic farming (which was not the case in FR)
- vineyard treated with copper solutions also containing phoshonic acid (not theoritically authorized but problematic for farmer if labelling does not comply with content)
- crops treated with foliar fertilizers made from conventional grapes must/marc or from sludge of conventional distillery and which contain phosphonic acid (example in France : 28ppm) provided that the use of such fertilizers is authorized.

b. Crops

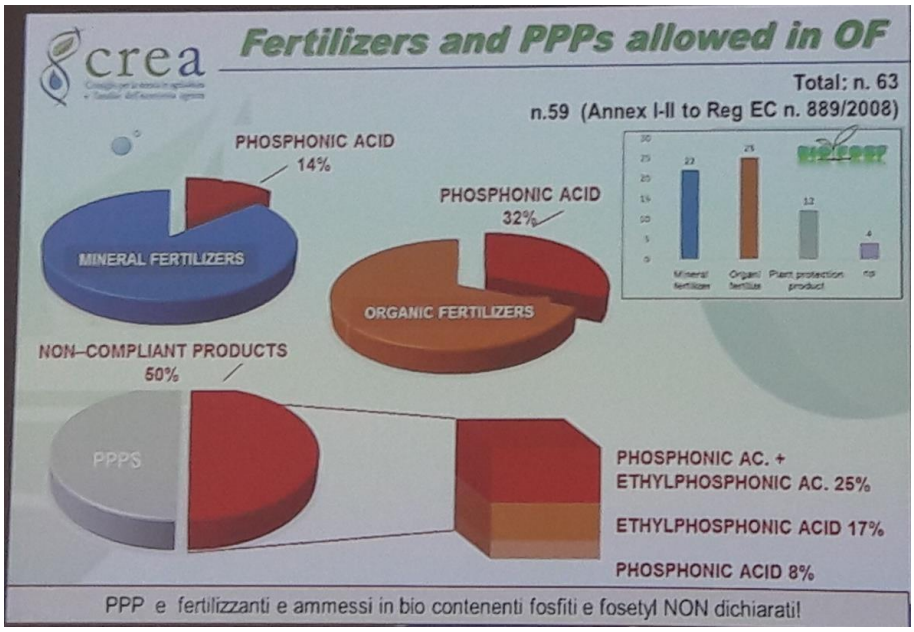
- Grown in soil that has received soil amendments containing purins and manure which contain phosphonic acid salts (authorized)
- Which received algae or seaweed as organic foliar fertilizers (authorized). Yet, according to BNN this 'natural source of phosphonates' is considered rather suspicious
- Or soils which received substances that have been treated with chelating agents which contain phosphorous (not authorized but very difficult to detect in raw materials of soil amendments/fertilizers)

- Grown in soils which received chemical fertilizer/pesticides containing phosphate/phosphite (not authorized) examples

Product	Company	Country	Active ingredient	Use
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 Uranla	Germany	Potassium Phosphite	EC Fertilizer
Foliaphos**	Plantin	France	Potassium Phosphite	EC Fertilizer

- Grown in soil which received allowed fertilizers and plant protection products containing phosphite/ fosetyl-al **above 2mg/kg.**

  example : some commercial copper formulations



- v. . Grown in soil which has been treated with irrigation water which has received (water)treatments (not authorized)

- Crops have been treated with the fungicide fosetyl-aluminum which metabolized into fosetyl which degrades further into phosphonic acid salts (not authorized)

c. Suspicion that fosetyl is formed as an artefact during production or storage of wine.

d. Crops grown organically but having a conventional environment with use of fosetyl-al : fungicide with high volatility, easily transported by air (contamination source)

e. The result of plant growth under stressful conditions e.g. drought (supported by one source only)

Organic products containing phosphonic acid (filtered by country)

Reporting by stakeholders of the organic sector shows that phosphonic acid is detected in different kinds of products and in different countries.

Product	**Number of samples analysed**	**% with phosphonic acid**
Asparagus	21	38
Grapefruit	21	28.6
Cucumber	47	27.7
Orange	36	25
Clementine	22	18.2
Table grapes	57	18
Potato	24	16.7
Pepper	30	13
Pear	26	11.5
Melon	24	8.3

Analysis of phosphonic acid in samples of organic fruits and vegetables. 05-09-2016, BNN. Thomas Kimmel & Kirsten Arp

Products	Number of cases
Berries	8
Cereals	2
Citrus	12
Vegetables	20
subtropical	4

Data provided by CAAE (Spain), representing the number of cases between 2013 and 2018

Country	Number of samples analysed	% with phosphonic acid
Greece	31	51.6
Spain	230	17.8
Italy	173	9.2
France	30	6.7
Germany	96	4.2
The Netherlands	20	

Analysis of phosphonic acid in samples of organic fruits and vegetables. 05-09-2016, BNN. Thomas Kimmel & Kirsten Arp

EOCC members have been confronted with the following individual cases which required international investigation:

Country of initial sampling	Product	Analytical results	Outcome of the investigation	Certification decision(s)
Ivory Coast	pineapple (young fruits, before and after harvest)	Varying from 9.0 till 3.0 mg/kg	Potassium Sulfate (solid) was used as fertilizer and contained phosphonic acid and fosetyl. The presence of fosetyl is supposed to be due to contamination while producing the fertilizer but can also be intentionally applied to the fertilizer (by the farmer or seller of the fertilizer)	

Costa Rica	unidentified	Not given	(conducted by Dole) investigation of rock phosphate by analysis showed presence of phosphonic acid	
Costa Rica			Analysis of liquid fertilizer show absence of phosphonic acid or fosetyl.	
South-Africa			Inspectors information about injection of fosetyl-Al in trunks.	

EOCC Task Force Residues, internal inquiry 2018.

Non organic products containing phosphonic acid

CVUA Stuttgart reports after the analysis of 4265 samples (from January 2014 to December 2015) that:

- 36% of all analysed samples contained residues of fosetyl and/or phosphonic acid above the LOQ
- Phosphonic acid is detected in concentrations approximately 40 times the concentration of fosetyl.
- Conventionally grown products contained phosphonic acid levels exceeding the LOQ more frequently than products labelled as organic (39% vs 17% respectively)

Food safety and MRL values

MRL values for Fosetyl-Al (sum of fosetyl, phosphonic acid and their salts, expressed as fosetyl) can be found in the MRL pesticide database (related to Reg 396/2005).

Product	**MRL**
Asparagus	2.0*
Grapefruit	75.0

Cucumber	75.0
Orange	75.0
Clementine	75.0 (for mandarine)
Table grapes	100.0
Potato	30.0
Pepper	130.0
Pear	75.0
Melon	75.0

http://ec.europa.eu/food/plant/pesticides/eu-pesticidesdatabase/public/?event=pesticide.residue.CurrentMRL&language=EN

* indicating the lowest analytical value for determination = the applicable MRL value.

MRL values for fosetyl-Al have been updated (increased) in 2015.
Before 2013, phosphonic acids were accepted as foliar fertilizer which could be authorized in organic farming (grape production). Since 2013, the double activity as foliar fertilizer and fungicide as no longer possible. Phosphonic acid has been included in the formulation of the fungicide fosetyl-Al and is no longer allowed as foliar fertilizer in organic farming.

Imported products

Red fruits (strawberries, raspberries, blueberry) imported from Chile, Argentina, Canada (countries listed in Ann III of Reg 1235/2008 having in place an organic legislation equivalent to the EU Regulation 834/2007 for organic production and labelling). Suppliers from Chile already informed EU buyers that the plants have received authorized foliar fertilizer based on natural algae. "These algae may give a positive phosphonic acid result on residue testing".
Red fruits from Serbia, Turkey, Ukraine (countries which do not have an organic legislation equivalent to the EU Regulation 834/2007) can be imported provided these products have been certified as compliant to it's own standard by a control body recognized for issuing certificates of import for product category A (because always deep frozen) in each specific country.
Some red fruits in particular blueberries and cranberries are the result of wild collection/wild harvest. The particularity with that is that the areas where such products are collected do not receive any treatment at all. In such a context, the presence of phosphonic acid need to be investigated to exclude commingling with products not resulting from wild collection/wild harvest.
Red fruits are also interesting products for groups of operators (wild harvest or small scale production areas or a combination thereof). Such products, collected by groups of operators often consist of many and small size batches. Groups of operators are invited to develop

their traceability system by installing batch numbers which allow to trace problematic batches back as far as possible. The smaller the problematic batch, the smaller the negative impact of blocking and downgrading.

Preventive measures for operators (How to facilitate the investigation?)

Farmers need to have complete and up-to-date records which allow to identify that preventive measures are in place to reduce the risk of raw material contamination with phosphonates, and that only authorized substances have been used.
Processors need to be aware of the risks of false positive readings of residue analysis related to fosetyl-Al and anticipate the request for comments by knowing the production process of the organic products they process. Small size batches of raw material reduce the risk of blocking/downgrading raw materials and finished products. Samples of raw materials could be helpful to trace back where the problem comes from.
Control bodies need to inform their authorities about particular procedures related to the pesticide residue testing for Fosetyl-Al.
Authorities need to upgrade verification of compliance of labelling of inputs suitable for organic farming

Phosphonic acid, organic food and babyfood.

Contrary to the organic EU Regulation 834/2007, there is a system with MRL thresholds for babyfood (see Commission Directive 2006/141/EC). Any food placed on the market with reference to infants, should be free of pesticide residues exceeding 0.01 mg/kg. This level also applies to phosphonic acid.

Member State specific policies

The Ministerial Note Prot. Uscita N.0041936 (IT) states that: "The presence of phosphorous acid in wine or other matrices, cannot and should not be directly attributed to the use of plant protection products based on Fosetyl-Al. From an analytical point of view, it is much more relevant to link the contamination with Fosetyl-Al to the simultaneous presence of phosphonic acid and fosetyl." The Italian accreditation body (Accredia) has reported several cases of false positive reporting.
The Flemish (BE) decree of 2015 contains tresholds for pesticides in organic products. The protocol of the Flemish umbrella organization Bioforum Vlaanderen, included phosphonic acid as a substances for which an exception applies.

Similar issues

In the past, the presence of chloormequat in pear has also been considered as problematic. Investigations showed that pear tree accumulates chloormequat and gradually releases it

which results in detectable amounts in pears while there has been no direct neither indirect application on the tree.
Phtalamide and Folpet. See other Fact Sheet EOCC TF Residues.

Sources of information:

- BNN
- Consiglio per la ricerca in agricoltura e l'analisi dell'economia agraria (CREA) (IT)
- CARM Imida study (ES)
- EOCC Task Force Residues (with special thanks to CAAE, TUV Nord Integra, SKAL, CCPB, CCPAE, Certisys, ECOCERT/IMO)
- Primoris (pesticide residue laboratory in BE)
- BIOFOSF research project funded by the Italian Ministry of Agriculture
- Federbio paper (November 2018)
- CREA project (Italy)