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Interpretation aid in the use of the BNN orientation value for pesticides

1) Detection of metabolites

Metabolites (decomposition or breakdown products) of pesticides are also occasionally detected in organic products. The residue definition under the EU Regulation 396/2005 is ruling for an assessment according to the BNN orientation value. This means that the detection of a pesticide and its metabolite(s) is generally considered as evidence of the presence of the active ingredient and the sum of the metabolites is used to assess the level of the finding.

In individual cases, it may be useful to deviate from this rule because the BNN orientation value has a different objective from the legal MRLs and / or individual residue definitions are technically questionable. This may mean disregarding the BNN orientation value if the assessment of the is most likely due not to the parent compound but to environmental or process contamination (see for example 2) phthalidimide detection). In other cases, it may be useful to assess the metabolite individually if, as in the case of phosphonic acid (see fact sheet phosphonic acid), which although a pesticide active ingredient, is in the great majority of cases not due to the potential parent material (in this case fosetyl).

A case-by-case assessment of whether the metabolite should not be taken into account because it may have other parent substances / sources not associated with pesticide use is particularly recommended if the parent substance itself cannot be detected.

Version: April 2019

2) Phthalimid detection in organic products

From August 26th 2016 a new residue definition of the fungicide Folpet shall apply, including in addition to Folpet also the metabolite Phthalimid (“Folpet: Sum of Folpet and Phthalimid, expressed as Folpet, Regulation (EU) 2016/156). Moreover, Phthalimid is also a metabolite of the insecticide Phosmet (see EFSA reasoned opinion), but nevertheless not included in its residue definition.

As the laboratory circle relana® has shown on the basis of several hundred analysis results via correlations and practical experience of the laboratories and based on a hypothesis developed by Labor Friedle, Phthalimid is produced in many cases without the presence of Folpet or Phosmet. Phthalimid is formed by the ubiquitous chemicals „phthalic acid“ and „phthalic anhydride“ in reaction with primary amino-groups, which are usually part of the food matrix. This happens especially under heating conditions, so that dried products are particularly affected (relana® 2016). Phthalic anhydride is used f.ex. in resins, paintings and newspaper printings and is detected in nearly every (house) dust sample.

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Bundesverband
Naturkost Naturwaren

Thus Phthalimid is predominantly not a metabolite of Folpet – contrary to the new residue definition – and therefore does not indicate its application. BNN guideline value for Folpet/Phosmet/Phthalimid is only applicable, when in addition to Phthalimid also Folpet or Phosmet are detected.

Furthermore, above mentioned information shall be taken into consideration on a case-by-case basis if Folpet or Phosmet are detected as well, because it is not plausible that the entire amount of Phthalimid is derived by the metabolism of Folpet or Phosmet only.

Literature

relana (2016): POSITION PAPER No. 16 -03 "Phthalimid: Metabolite of Folpet or unavoidable Artefact ?" Version 2016/07/22
http://www.relana-online.de/wp-content/uploads/2016/07/PP_16-03_Folpet-PI_vers20160722.pdf

Commission Regulation (EU) 2016/156 of 18 January 2016 amending Annexes II and III to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for boscalid, clothianidin, thiamethoxam, folpet and tolclofos-methyl in or on certain products (Text with EEA relevance)
http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32016R0156&qid=1469718309915&from=EN

Reasoned opinion on the modification of the existing MRLs for phosmet in citrus fruits, pome fruits and rape seed (EFSA Journal: EFSA Journal 2013;11(12):3510 [33 pp.])
http://onlinelibrary.wiley.com/doi/10.2903/j.efsa.2013.3510/epdf

Version: July 2016

3) Dithiocarbamate detection in organic products

Dithiocarbamate is the generic term of a group of pesticides, which contain a carbon-sulphur (CS2) bond in their molecular structure. The fungicides Mancozeb, Maneb, Metiram, Propineb, Thiram and Ziram belong to this group. Dithiocarbamates are not permitted in organic agriculture.

Dithiocarbamates are determined indirectly as a total of the CS2 bonds found in the sample. This means that as a rule the individual substances cannot be determined.

In addition the analysis is affected when the plant contains natural sulphur or carbon-sulphur bonds, which may lead to false positive results. This is known to be the case for example with Brassicaceae-family (e.g. cabbage species, rape) and the Allium genus (onions and garlic). There are further specific anomalies that can occur in individual crops, which may also lead to false positive results. It is known that ripe papaya fruit which can produce carbon-sulphur as a result of strong enzyme activity (BUT it is also known that dithiocarbamates are applied in papaya production).

The information above is to be taken into consideration in a case by case assessment of analytical results showing the presence of dithiocarbamates in organic products.

Version: August 2012

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Naturkost Naturwaren

4) How to deal with findings of bromide in organic products

Bromide, chloride, and fluoride are the anionic (negative) parts of mineral salts and occur naturally in soil, water, and plants at varying concentration levels. Bromide is also present in salt aerosols, which can drift inland from the sea. The levels detected depend on how far agricultural fields are located from seacoasts [Short et.al.]. Sea salt aerosols show a typical chloride/bromide ratio and can therefore significantly increase the levels of both substances in soils. If sea salt aerosols are transported to agricultural soils and the crops growing there, this can significantly increase the bromide concentration in plants.

So why to analyse bromide in food products and especially in those from organic farming?

In the Pesticide Regulation (EC) No 396/2005, bromide is regulated as "bromide ion". The analysis of bromide can provide an indication of unauthorised fumigation with bromine-containing agents. These are gaseous substances such as methyl bromide or 1,2-dibromoethane, which form bromide ions very quickly after application. Therefore, the detection of a treatment is usually not done by analysing the fumigants themselves, but indirectly via the bromide ion. Consequently, the maximum residue level (MRL) is related to the bromide ion (see Regulation (EC) No 396/2005). However, when setting the maximum residue level, the specific background concentration of the individual plants and fruits in inorganic bromide was not taken into account, but a flat level for different groups (e.g., nuts, salads, vegetables) was taken as a basis. By applying the established analytical methods, it is not possible to distinguish whether the bromide ion detected is of natural or of anthropogenic origin.

The maximum residue levels listed in Regulation (EC) No 396/2005 are in principle applicable to all foodstuffs, irrespective of whether the plants or fruits are grown conventionally or organically. The respective background level of bromide will be reflected in the plant, no matter which cultivation method has been used.

The use of methyl bromide has been banned for a long time in conventionally produced products [Montreal Protocol], too. Consequently, the focus on setting the MRLs was on proving the use of a banned fumigant containing bromine when setting the MRL (incidence evidence approach). In this respect, there is no conclusive reason to set a separate or particularly low bromide level for organic products as an indication of possible illegal fumigation.

Since the agreed "phase-out" for methyl bromide according to the Montreal Protocol was reached in 2015, the use and thus also the detection of illegal use of methyl bromide is becoming increasingly unlikely. Within the framework of BNN-monitoring, not a single case is known from the last fifteen years in which there is an analytical finding on bromide that could be used as an indication of the illegal use of a fumigant containing bromine. Taking into account the natural bromide content discussed above and the possible influence of sea salt aerosols, it seems worth considering ordering the analysis of bromide only in cases of well-founded suspicion.

Bundesverband
Naturkost Naturwaren

Compliance with the requirements of Regulation (EC) No. 396/2005 (in the currently valid version) and thus compliance with the currently valid maximum residue levels for bromide are the prerequisite for marketing the corresponding organic food products. The requirements of the BNN e.V. guideline for the assessment of pesticides in organic products (BNN orientation value) are thus also met with regard to bromide.

Literature:

Short, M.A., P. de Caritat, D.C. McPhail (2017): Continental-scale variation in chloride/bromide ratios of wet deposition, Science of the Total Environment 574, S. 1533-1543.

Montreal protocol:

https://.admin.ch/opc/de/classified-compilation/19870179/201901010000/0.814.021.pdf (accessed on 28.02.2022).

Version: April 2022