INFORMATION NOTE

BIOSUISSE

Spectrum of analyses for detecting pesticide residues in organic products

In collaboration with Research Institute of Organic Agriculture (FiBL)
August 2023

1 Introduction

Residue analyses are an inherent means of quality assurance for organic products today. They serve to identify weak points in the supply chain. These could involve the prohibited usage of plant protection products or dressed seed, contamination with undesirable substances, or the mix-up or commingling of organic and non-organic items. Such problems may occur during cultivation, harvesting, transport, storage or processing. The Swiss Ordinance on Organic Farming (SR 910.18) prescribes that appropriate measures must be taken to reduce the risk of contamination. This means that potential sources of contamination must be identified and, where possible, appropriate precautions implemented.

According to the Swiss Ordinance on Foodstuffs and Utility Articles (SR 817.02), every business is obliged to carry out internal monitoring, which also includes sampling and analysis in accordance with Article 75 of this Ordinance. In order to determine what should be sampled and tested, each operation must make a risk analysis to identify potential points of contamination (Bio Suisse Standards Part III, Chapter 1.5). A testing strategy can then be developed to determine which products at what processing steps or from which suppliers should be sampled, and how often. It would also determine which substances should be sought in the samples.

This spectrum of analyses is meant to give guidance on determining which substances to seek. It indicates the products in which, based on experience, residues of certain substances may occur. The following is divided according to substances which commonly occur (section 2) and substances which occur less often, but sporadically (section 3).[1] For the purpose of pesticide monitoring, it makes sense to primarily test for commonly occurring substances. Depending on the situation, it may also be necessary to test for more rarely occurring substances.

In addition, the applicable requirements in the Bio Suisse Standards Part V, Annex to Chapter 3.8 must be observed.

Recommendations:
Bio Suisse recommends monitoring pesticide residues by testing primarily (e.g., 90%) for commonly occurring substances, as per section 2, and testing occasionally (e.g., 10%) for more rarely occurring substances, as per section 3.
It would also be prudent to check ahead of time whether the selected laboratory is accredited for the analytical methods.

This information note only deals with pesticide analyses. Further analyses may also be important (depending on the food and its provenance), for instance to test for GMO content, heavy metals and other environmental contaminants, mycotoxins, microbiological parameters, etc.

The following recommendations are based on data from EFSA's European Union reports on pesticide residues in food, unless otherwise stated.

[1] Source: EFSA Pestizidmonitoring (2015)

Bio Suisse
Peter Merian-Strasse 34 · CH-4052 Basel
Tel. +41 61 204 66 66
www.bio-suisse.ch · bio@bio-suisse.ch

2 Regularly occurring substances and analytical methods for their detection

In this section, substances which commonly occur as pesticide residues are briefly described. Laboratories standardly offer testing for these substances. With the exception of "Pesticide screening", the methods below are designated by the specific substances which they detect.

2.1 Pesticide screening

Virtually all laboratories offer pesticide screening (there are many terms for this). In pesticide screening, technical methods are used to screen for hundreds of substances simultaneously. A selection of the most common pesticides, pesticide degradation products (so-called "metabolites") and other substances such as biocides are measured. The selection varies from laboratory to laboratory. If a specific substance is of particular interest, it must be clarified in advance with the laboratory whether this substance is included in the scope of the screening. Pesticide screening can detect the vast majority of fungicides, insecticides, herbicides and other pesticides and is therefore especially recommended for routine monitoring (i.e., when there is no concrete suspicion) to check for potential weak points, mix-ups or sources of contamination. Laboratories continually revise the range of substances they screen for based on new findings and substances.

2.1.1 Pesticide screening with special sample preparation for acidic herbicides

Some substances can only be partially detected by standard pesticide screening. This applies to the acidic herbicides ("phenoxy alkane carboxylic acids"). In such cases, pesticide screening only indicates whether the substances are present or not. To determine the amount, the analysis must be repeated on specially prepared samples (hydrolysis step). This is, for example, necessary for the following substances: 2,4-D, 2,4,5-T, 2-phenylphenol, acibenzolar acid, amitraz, bentazone, bifenazate, bromoxynil, captan, carbendazim, carbofuran, clethodim, clodinafop, cycloxidim, dalapon, daminozide, dazomet, dicamba, dichlorprop, diclofop, dinocap, dinoseb, dinoterb, dithiocarbamate, DNOC, ethofumesate, fenoprop, fenoxaprop-P, flufenacet, fluazifop, fluopyram, fluroxypyr, folpet, haloxyfop, isoxaflutole, ioxynil, MCPA, MCPB, mecoprop, meptyldinocap, phosphane, prochloraz, propachlor, pyridate, quizalofop and tepraloxydim.

2.2 Standard selective methods

In addition to pesticide screening, most laboratories standardly offer some further tests for detecting specific substances. These are referred to as selective methods. The most important selective methods are described in the rest of this section.
Recently, some laboratories have started to offer some of the individual analyses mentioned here in packages, where this is technically possible. In particular, the analyses for glyphosate, glufosinate and AMPA (Chapter 2.2.1), fosetyl and phosphonic acid (Chapter 2.2.2) and ethephon (Chapter 2.2.3) are sometimes offered in a so-called "multi-method for highly polar substances", although this package solution may also include other substances. As with pesticide screening, substance selection varies from laboratory to laboratory. Since these multi-methods are currently not very widespread, these substances are listed individually here.

2.2.1 Glyphosate, glufosinate and AMPA

The herbicides glyphosate and glufosinate are both detected by a selective method or a multi-method for highly polar substances. The method usually also detects AMPA (aminomethylphosphonic acid), the most important degradation product of glyphosate. Glyphosate is now the most widely applied herbicide in the world. It is used for various purposes:

- to keep clear the root area of permanent crops, for instance in fruit orchards, vineyards and berry plantations
- as a preemergence herbicide for annual crops (arable crops, vegetables)
- as a postemergence herbicide for herbicide-tolerant GMO crops (soybeans, rapeseed, maize/corn, sugar beets, etc.)
- for individual treatments to control perennial weeds in meadows and pastures
- to control weeds on nonagricultural land such as hobby gardens, road verges, railroad tracks, industrial parks, etc., as well as to control invasive plants
- for the "preharvest treatment" of grains, legumes and oilseeds.

The preharvest treatment of grains, legumes and oilseeds reduces moisture in the grain/seed (desiccation), which is particularly important in humid regions and years. It also facilitates harvesting because the leaves of the crop and any weeds die off. Preharvest treatments with glyphosate produce much higher levels of residues than any other kind of application. It is therefore especially important to test for glyphosate in grains, all grain products, legumes and oilseeds.

2.2.2 Fosetyl and phosphonic acid

The fungicides fosetyl (fosetyl-al, fosetyl-aluminium) and phosphonate (formerly called phosphite or phosphorous acid) are detected by a selective method or a multi-method for highly polar substances. They are mainly applied to grapevines, fruit, vegetables and hops. Particularly in Mediterranean countries, plant protection products and fertilisers containing phosphonates are sold with no declaration of the phosphonate content. Residues can then occur unbeknownst to the producers. Phosphonic acid is stored in the wood of perennial plants, and residues still occur for a few years after it is applied. Non-organic seedlings sometimes contain high levels of phosphonic acid. Residues significantly higher than 10 mg/kg are frequently found in crops to which phosphonic acid has been applied. Initial evidence has shown residues of 2 –8 mg/kg in the year following application.[2] When plants are treated with fosetyl, it slowly degrades to phosphonic acid in the plant. If both fosetyl and phosphonic acid are detected in a sample, the use of fosetyl is probable. If only phosphonic acid is found, then use of phosphonic acid or another source is likely. Selective methods separately detect fosetyl and phosphonic acid. Some laboratories only give the sum of both substances on their analytical reports, however. In such cases, the laboratory must be asked to provide the individual values. The legal maximum levels always apply to the sum of fosetyl and phosphonic acid[3]. Phosphonic acid has a higher intervention value than most other pesticides[4]. Further information is available in the basic paper "Information and statement on phosphonate/phosphonic acid residues".

2.2.3 Ethephon

Ethephon is the most widely sold plant growth regulator. It is used for the following purposes:
- as a straw-shortening agent in the cultivation of grain
- as a blossom- and fruit-thinning agent in the cultivation of apples and plums
- to induce flowering in pineapple crops
- to accelerate the ripening of tomatoes, apples, citrus fruit and figs
- to loosen the fruit in preparation for harvesting cherries, plums and various berries
- to accelerate the postharvest ripening of peppers, bananas and mangoes
- to regulate the maturity of cotton.

Ethephon is detected by selective method or a multi-method for highly polar substances. Residues of ethephon are most commonly found on citrus fruit and exotic fruit, table grapes, tomatoes and peppers. It is more rarely detected on domestic fruit and on grain.

2.2.4 Chlormequat and mepiquat

Chlormequat (also chlorocholine chloride, or CCC for short) and mepiquat are detected by a selective method. Both substances regulate plant growth and are used for the following purposes:
- as a straw-shortening agent in the cultivation of grain
- to stimulate fruit development on apple, almond and olive trees, grapevines and tomato plants
- to prevent the premature dropping of ripe fruit from pear, apricot and plum trees
- to stimulate the growth of fruit-bearing wood on pear trees.

Residues of chlormequat and mepiquat are most commonly found on pears, grain and cultivated mushrooms (contamination occurs via residues in straw), and are also found to a lesser degree on vegetables (esp. carrots) and table grapes. There is some indication that chlormequat and mepiquat may occur during the roasting of coffee beans and grain (esp. barley). Positive test results for these foods must therefore be interpreted with caution.

2.2.5 Hydrogen phosphide

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[2] In-house, unpublished FiBL study
www.fedlex.admin.ch/eli/cc/2017/151/de
[4] Directive on the procedure for residues in the organic sector:
https://www.blw.admin.ch/dam/blw/de/dokumente/Instrumente/Kennzeichnung/Biolandbau/weisung-zum-vorgehen-bei-rueckstaenden-im-bio-bereich.pdf.download.pdf/Weisung%20zum%20Vorgehen%20bei%20R%C3%BCckst%C3%A4nden%20im%20Bio-Bereich.pdf

Hydrogen phosphide (also known as phostoxin, phosphine or PH_3) is a gas. It is used as a storage pesticide in bins, warehouses, containers, railway cars, etc. and is effective against both insects and rodents. Often aluminium phosphide or calcium phosphide are applied. These are solid products which release hydrogen phosphide when exposed to air. However, this also produces phosphide dust which becomes distributed throughout the facilities and can be introduced into the supply chain along with grain. Usage of hydrogen phosphide has greatly increased in recent years.
There is a risk of contamination in all foods that are stored (grain, legumes and oilseeds). Experience has shown that residues most commonly occur in grain. In Switzerland the intervention level is lower for hydrogen phosphide than for other pesticides.[5] Testing strategies for the grain sector must therefore particularly target hydrogen phosphide.

2.2.6 Dithiocarbamates

Dithiocarbamates are a chemical class that includes various pesticides (dazomet, ferbam, mancozeb, maneb, metam, metiram, nabam, propineb, thiram, zineb, ziram and others). Many dithiocarbamates act as fungicides, while some also act as herbicides, insecticides, nematicides, algicides or repellents. Dithiocarbamates are mainly (but not exclusively) applied in the production of fruit and vegetables. The fungicide mancozeb in particular is widely applied. Certain dithiocarbamates (disulfiram, thiram and ziram) are also used as vulcanization accelerators in processing latex and may therefore occur in latex gloves. The use of such gloves may leave residues.[6]

Standard tests detect dithiocarbamates indirectly through the detection of carbon disulphide (CS_2). This method can detect the presence of dithiocarbamates as a chemical class, but not the exact chemical. Brassicas and alliums naturally contain sulphur compounds which may thwart this kind of testing by falsely indicating the presence of dithiocarbamates. It therefore makes little sense to analyse such cultures for dithiocarbamates. There is no certainty as to whether sulphur (a plant protection product approved for organic agriculture) also has this effect. False-positive results are therefore possible, and positive test results must be interpreted with caution.

3 Sporadically occurring substances and analytical methods for their detection

In addition to the above-named substances, many other substances are applied as plant protection products but according to current knowledge pose little risk of residue contamination. Laboratories do not standardly test for such substances. However, many such substances can be tested for upon request.
Some substances that have sometimes occurred as residues in food are listed below (they are much less common than the substances listed under section 2).

3.1 Ametoctradin

Ametoctradin is a fungicide. It is mainly added as a mixing partner to fungicide mixtures applied to grapevines and vegetable and potato crops. Residues have occasionally been detected on grapes. There is also a possible risk of residue contamination on leafy vegetables and hops.

3.2 Cyflufenamid

Cyflufenamid is a fungicide. It is mainly applied to grain crops, but also to pome fruit, berries, grapevines and vegetable crops (especially cucurbit crops). Residues have occasionally been found on table grapes, blueberries, blackberries, chili peppers and mushrooms.

3.3 Dithianon

[5] "Weisung zum Vorgehen bei Rückständen im Bio-Bereich" ("Directive on procedures in case of residue contamination in the organic sector"): https://www.blv.admin.ch/dam/blv/de/dokumente/lebensmittel-und-ernaehrung/rechts-und-vollzugsgrundlagen/hilfsmittel-vollzugsgrundlagen/weisungen-archiv/22-2015-weisung-rueckstaende-bio.pdf.download.pdf/Weisung_zum_Vorgehen_bei_Rueckstaenden_im_Bio-Bereich.pdf
[6] For further information, please see "Informationen und Stellungnahme zu Rückständen von Dithiocarbamaten" and "Declaration of compliance 'Free from dithiocarbamate'" (German only).

Dithianon is a fungicide. It is mainly applied to fruit, grapevines and hops. Residues are sometimes found on fruit (apples, pears, apricots, cherries, plums and various berries) and table grapes.

3.4 Dodine

Dodine is a fungicide. It is mainly applied to pome fruit, stone fruit and nuts. Residues have occasionally been found on apples and more rarely on stone fruit, berries and table grapes. There is also a possible risk of residue contamination on olives.

3.5 Maleic hydrazide

Maleic hydrazide is a growth regulator. It is mainly applied to potatoes and bulbous crops (to retard germination) as well as to citrus fruit and tobacco. In addition, some herbicides contain small amounts of maleic hydrazide. Residues have occasionally been found on potatoes and bulbous crops.

4 Overview of the significance of various substances for different foods

Tabelle 1 below is a summary of the information on the most important substances given in the previous sections. The substances are categorized according to the analytical methods.

Legend:
xx = Testing for this/these substance(s) on this food is important.
x = Testing for this/these substance(s) on this food is of some importance.
(blank space) = There is almost no reason to test for this/these substance(s) on this food.

Table 1: Overview of analytical methods

Substances	Fruit (incl. berries)	Table grapes, wine	Vegetables (incl. herbs and teas)	Potatoes	Grain	Legumes	Oilseeds	Cultivated mushrooms
Commonly occurring substances / analysis methods								
Pesticide screening	xx	xx	xx	xx	xx	xx	xx	x
Acidic herbicides					xx[7]	xx[8]	xx[9]	
Glyphosate, glufosinate					xx	xx	xx	
Fosetyl, phosphonic acid	xx	xx	x	x				
Ethephon	xx[10]	x	xx[11]					
Chlormequat, mepiquat	x[12]				xx			xx
Hydrogen phosphide[13]			xx[14]		xx	xx	x	
Dithiocarbamates	xx		xx[15]					
Sporadically occurring substances								
Ametoctradin		x						
Cyflufenamid	x[16]	x	x					x

[7] Of most importance for wheat.
[8] Of most importance for lentils and soy.
[9] Of most importance for sesame, linseed and rapeseed.
[10] Of most importance for citrus and exotic fruit.
[11] Of most importance for tomatoes and peppers.
[12] Of some importance for pears.
[13] Bio Suisse considers a detection limit of 0.01 mg/kg to suffice as evidence of prohibited use, thereby constituting a proven violation of the Bio Suisse standards for 'Bud' products.
[14] Of importance for imported spices.
[15] Not suitable for brassicas and bulbous crops.
[16] Of some importance for berries.

Dithianon	x	x						
Dodine	x	x						
Maleic hydrazide			x[17]	x				

[17] Of some importance for bulbous crops.