Composite Food of Organic Production

Eurofins Dr. Specht Laboratorien GmbH

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Analytical Service Manager

- Food Chemist with more than 10 years of experience in residue analysis (also for organic products)
- Specialised in food safety for tea and tea products, herbal infusions
- Member of working groups for tea and herbal products
Overview

- Introduction: knowledge vs. risk
- Evaluation of pesticide residues in mono products
- Extended measurement uncertainty
- Focus: Human health-based guidance value (ADI/ARfD)
- Example for an multi-ingredient product

Today's target: Gain an understanding on how to evaluate pesticide residues in composite organic food.
Introduction

Customer question:
Is this an organic product?

Can you use residue analysis to prove that this product is of organic production?

X No, this is not possible!

What can residue analysis do for you?

✓ Analysis can reduce your risk when selling composite organic products!
Laboratory …

… usually has only limited insights regarding the history of the samples send for testing

X Profound evaluation not possible!

What information is necessary?
Factors

Knowledge

- Processing
- Origin
- Availability
- Trust in the supplier
- Composition of the product

Possible risks

- Kind of product(s)
- Weather conditions
- Storage/Transport conditions

Composite food of organic production
Black box

Big data (statistics)

Risk

Knowledge

Analysis (final product)

Product

max knowledge = no analysis necessary

max risk = statistic & analysis helpful

knowledge + statistics + analysis → risk reduction
Statistics for 2017 (Eurofins)

53,5% of all grapes analysed contained Ethephon / no findings in organic grapes (total n=533 / organic n=25)

16,8% of all oats analysed contained Chlormequat / 7,1% findings in organic oats (total n=169 / organic n=58)

11,4% of all apples analysed contained Captan (THPI) / 0,5% findings in organic apples (total n = 4101 / organic n=392)

23,5% of all pumpkin kernels analysed contained Hexachlorobenzen / 25,6% findings in organic pumpkin kernels (total n = 1561 / organic n=219)

contamination → persistent residue
A sample can be a mixture of e.g. …

… several lots/charges of the same product

… different supplier/gardens/fields

… different products and/or origins
So far we have spoken about risk reduction using all available tools.

But now, we want to go the other way around …

… starting with the analytical results and want to draw possible conclusions.
Mono product (grapes) – natural contents

- Water
- Amino acids (Glutamic acid, Aspartic acid)
- Vitamins (Vitamin C, Tocopherols, Nicotinamide, B6)
- Fatty acids (Linoleic acid, Palmitic acid)
- Dietary fibres
- Sugars (Glucose, Fructose)
- Minerals (Potassium, Phosphorus)
- Fruit acids (Tartaric acid, Malic acid)

Composite food of organic production

Q: Souci, fachmann, Kraut, 7th E
Mono product (grapes) – risks

- Sulfites
- Other environmental contaminants (PAHs, PCBs)
- Disinfectants
- Heavy metals (Copper, Lead, Cadmium)
- Mycotoxins (Aflatoxins, Ochratoxin A)
- Mineral oils
- Germs (TPC, Moulds, Yeasts, Coliforms)
- Pesticide residues

Composite food of organic production
Mono product (grapes) – possible pesticide residues

- Dimethomorph
- Fenhexamid
- Metrafenon
- Ethephon
- Spinosad
- Myclobutanil
- Boscalid
- Carbendazim (0.012 mg/kg)
The analysed sample contains a residue of Carbendazim with a concentration of 0.012 mg/kg.

Carbendazim is not listed in annex II of Council Regulation (EC) No. 889/2008 and therefore its use for organic food is not allowed. In respect to this, it is to clarify, whether samples of the same quality comply with the requirements of EU Regulation 889/2008/EC (and its amendments). We recommend informing the responsible Certification Body. Irregular practices or violations of the current valid regulations for organic farming can only be ascertained by the responsible certification body or control authorities.
The analysed sample contains a residue of Carbendazim with a concentration of 0.012 mg/kg. Considering an expanded measurement uncertainty of 50% (k=2, without sampling), the analysed sample is still in accordance with the requirements for Pesticide Residue Levels of the Bundesverband Naturkost Naturwaren (BNN) e.V. (max 0.01 mg/kg per single compound)

The substance mentioned above however, is not listed in annex II of Council Regulation (EC) No 889/2008 and therefore its use for organic food is not allowed. In respect to this....
The analysed sample can be classified as processed food, which is concentrated during processing. When calculating the amount of detected residue on the basis of undried original product, there can be considered a concentration factor of 5.

The analysed sample contains a residue of Carbendazim with a concentration of 0.012 mg/kg (respectively 0.002 mg/kg calculated on basis of fresh grapes) which do not exceed the requirements for Pesticide Residue Levels of the Bundesverband Naturkost Naturwaren (BNN) e.V. ....

The substances mentioned above are not listed in annex II of Council Regulation (EC) No. 889/2008 and therefore.....
„BNN Orientation Value for Pesticides

1. Orientation Value

The Orientation value for each substance (active ingredient) is 0.010 mg/kg, and applies to the original unprocessed product (Primary product as defined in EC 178/2002).

[…..]

For multi-ingredient products, each individual ingredient must comply with the requirements of this guideline.”
Measurement uncertainty (MU)

Basis for analytical results:

SANTE/11813/2017

E10 A default expanded MU of 50% (corresponding to a 95% confidence level and a coverage factor of 2) has been calculated from EU proficiency tests. In general, this 50% value covers the inter-laboratory variability between the European laboratories and is recommended to be used by regulatory authorities in cases of enforcement decisions (MRL-exceedances). A prerequisite for the use of the 50% default expanded MU is that the laboratory must demonstrate that its own expanded MU is less than 50%. In cases where an exceedance of an MRL is also an exceedance of the acute reference dose, an expanded MU with a lower confidence level can be applied as a precautionary measure.
Measurement uncertainty

Gaussian distribution of analytical results

- 50%
- 50%
+ 50%

95% confidence level

Measurement value

frequency

concentration

Composite food of organic production
Different analytical results?

Example:
Grapes Carbendazim 0.012 mg/kg +/- 0.006 mg/kg

<table>
<thead>
<tr>
<th></th>
<th>Analysis 1</th>
<th>MU 1</th>
<th>Analysis 2</th>
<th>MU 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbendazim</td>
<td>0.012</td>
<td>+/- 0.006</td>
<td>0.007</td>
<td>+/- 0.0035</td>
</tr>
<tr>
<td>Boscalid</td>
<td>0.017</td>
<td>+/- 0.0085</td>
<td>0.023</td>
<td>+/- 0.0115</td>
</tr>
<tr>
<td>Chlormequat</td>
<td>0.021</td>
<td>+/- 0.0105</td>
<td>0.040</td>
<td>+/- 0.020</td>
</tr>
</tbody>
</table>

Red marked values exceed the BNN/IFOAM orientation/action value. Measurement uncertainty (MU) is mentioned.

Both analytical results are comparable, considering MU.
Focus: Toxicity (1/4)

How toxic is this?

Can I still eat this?

ARfD?

How much can I safely eat?

ADI?

Is this still suited for babyfood?
Human Health-based guided value (HBGV)

Guidance on safe consumption of substances that takes into account current safety data, uncertainties in these data, and the likely duration of consumption.

- Acute toxicity (within 24h) / ARfD
- Chronic exposure (over a lifetime) / ADI

The Acute Reference Dose is defined as "an estimate of the amount a substance in food or drinking water, normally expressed on a body weight basis, that can be ingested in a period of 24 h or less without appreciable health risks to the consumer on the basis of all known facts at the time of the evaluation" (JMPR, 2002).

The Acceptable Daily Intake provides a human health-based guidance value (HBGV) for chronic or long-term exposures to residues in food. (Sometimes a Tolerable Weekly Intake is defined.)

http://www.who.int/foodsafety/chem/jecfa/Guidance_ARfD.pdf?ua=1
Example: Carbendazim ADI 0.02 mg/kg bw/day (bw = body weight)

for 60kg bw: $0.02 \times 60 = 1.2$ mg Carbendazim every day

$\Rightarrow$ 100kg of our grapes every day in your life

Example: Carbendazim ARfD 0.02 mg/kg bw (bw = body weight)

$\Rightarrow$ 100kg of our grapes without acute negative effects

(from Carbendazim)
ARfD-Exhaustion (4/4)

- Indicator for your product
- Often body weight (bw) of a child with 16.15kg is used

Example: Carbendazim ARfD 0.323 mg/16.15 kg bw

- Portion grapes defined 0.2115 kg plus variation factor (VF) of 5

Our grapes contain 0.012 mg/kg Carbendazim:

0.012 x 5 x 0.2115 = 0.01269 mg consumption Carbendazim/portion

0.01269 * 100 / 0.323 = 3.9 %
Finally composite products - examples

- Herbal infusions
- Spice mixtures
- Pizza
- (Fruit) salads
- Breakfast cereals
Composite sample

Blueberries: 15%

Pumpkin kernels: 10%

Raisins: 20%

Sunflower kernels: 10%

Apples: 15%

Oats: 30%

Composite food of organic production
Composite sample, possible residues

Cypermethrin: 0.015 mg/kg
Hexachlorobenzen: 0.007 mg/kg
Chlormequat: 0.009 mg/kg
Cypermethrin: 0.017 mg/kg
Hexachlorobenzen: 0.009 mg/kg
Chlormequat: 0.014 mg/kg
Cypermethrin: 0.018 mg/kg
Hexachlorobenzen: 0.014 mg/kg
Chlormequat: 0.017 mg/kg

Fictional sample!
The analysed sample contains residues of Cypermethrin, Hexachlorobenzen, Chlormequat, Boscalid, Ethephon, Glyphosate and Acetamiprid.

The substances mentioned above are not listed in annex II of Council Regulation (EC) No. 889/2008 and therefore their use for organic food is not allowed. In respect to this, it is to clarify, whether samples of the same quality comply with the requirements of EU Regulation 889/2008/EC (and its amendments). We recommend informing the responsible Certification Body. Irregular practices or violations of the current valid regulations for organic farming can only be ascertained by the responsible certification body or control authorities.
The analysed sample can be classified as composed (and processed) food. Therefore the result for each ingredient has to be in accordance with the requirements for Pesticide Residue Levels of the Bundesverband Naturkost Naturwaren (BNN) e.V..

The substances mentioned above are not listed in annex II of Council Regulation (EC) No. 889/2008 ....

Looking at this result there is definitely need for clarification...
Exact numbers

Exact concentrations in the final product are often not relevant.

- Concentrations of residues are often diluted in the composite product (expect to find nothing anyway!)
- Organic status is not defined because of residue situation
- Homogeneity of the multi-component sample is difficult
- Measurement uncertainty

Exception 1: contamination of the final product itself

Exception 2: really high concentrations lead to immediate action (checking for MRL compliance)
Risks for the final product…

- Fumigation during transport (Phosphan, Methylbromide…)?
- Disinfection (QAC, chlorate etc.)?
- Storage/Container treatment (e.g. chlorpyrifos)?

... now look at the primary ingredients!
Composite sample, residue example

Cypermethrin

Hexachlorobenzenes

Chlormequat

Glyphosate

Boscalid

Ethephon

Acetamiprid

Have a look at the raw material statistics.
## Organic products 2017 (incl Glyphosate)

<table>
<thead>
<tr>
<th></th>
<th>Cypermethrin</th>
<th>Hexachlorobenzen</th>
<th>Chlormequat</th>
<th>Ethephon</th>
<th>Boscalid</th>
<th>Acetamiprid</th>
<th>Glyphosate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blueberries</td>
<td>(0%)</td>
<td>(0%)</td>
<td>unknown</td>
<td>unknown</td>
<td>(0%)</td>
<td>(0%)</td>
<td>unknown</td>
</tr>
<tr>
<td>Pumpkin kernels</td>
<td>0%</td>
<td>25,6%</td>
<td>(0%)</td>
<td>unknown</td>
<td>0%</td>
<td>0%</td>
<td>25,0%</td>
</tr>
<tr>
<td>Raisins (Grapes)</td>
<td>1,3%</td>
<td>0%</td>
<td>8,3%</td>
<td>0%</td>
<td>9,8%</td>
<td>1,6%</td>
<td>10,7%</td>
</tr>
<tr>
<td>Oats</td>
<td>0%</td>
<td>0%</td>
<td>7,1%</td>
<td>(0%)</td>
<td>0%</td>
<td>0%</td>
<td>7,0%</td>
</tr>
<tr>
<td>Sunflower kernels</td>
<td>0%</td>
<td>0%</td>
<td>6,3%</td>
<td>unknown</td>
<td>1,4%</td>
<td>0%</td>
<td>10,7%</td>
</tr>
<tr>
<td>Apples</td>
<td>0,26%</td>
<td>0%</td>
<td>1,0%</td>
<td>unknown</td>
<td>0%</td>
<td>11,37%</td>
<td>(0%)</td>
</tr>
<tr>
<td>Multi method</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

Composite food of organic production
• Hexachlorobenzen very probably originate from pumpkin (persistent residue)
• Check grapes for Boscalid
• Check apples for Acetamiprid
• Any further information about residues for Glyphosate and Chlormequat?
• No (sufficient) data for Cypermethrin and Ethephon

Looking at additional statistical information
<table>
<thead>
<tr>
<th></th>
<th>Cypermethrin</th>
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<th>Glyphosate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blueberries</td>
<td>4,66%</td>
<td>0%</td>
<td>(0%)</td>
<td>(0%)</td>
<td>13,53%</td>
<td>0,88%</td>
<td>(0%)</td>
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<tr>
<td>Pumpkin kernels</td>
<td>0%</td>
<td>23,50%</td>
<td>0%</td>
<td>0%</td>
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<td>0%</td>
<td>45,14%</td>
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<td>Raisins (grapes)</td>
<td>0,71%</td>
<td>0%</td>
<td>37,18%</td>
<td>53,47%</td>
<td>5,71%</td>
<td>1,26%</td>
<td>16,33%</td>
</tr>
<tr>
<td>Oats</td>
<td>0,42%</td>
<td>0%</td>
<td>21,30%</td>
<td>(0%)</td>
<td>0%</td>
<td>0%</td>
<td>19,49%</td>
</tr>
<tr>
<td>Sunflower kernels</td>
<td>0,83%</td>
<td>0%</td>
<td>4,08%</td>
<td>unknown</td>
<td>0,72%</td>
<td>0%</td>
<td>13,90%</td>
</tr>
<tr>
<td>Apples</td>
<td>0,46%</td>
<td>0%</td>
<td>13,02%</td>
<td>11,10%</td>
<td>4,99%</td>
<td>6,78%</td>
<td>46,08%</td>
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<tr>
<td>Multi method</td>
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</table>

Total products 2017
• Hexachlorobenzen very probably orginate from pumpkin (persistent residue)
• Check grapes for Ethephon (maybe apples?)
• Check apples for Acetamiprid
• Check blueberries for Boscalid
• Any further information about residues for Chlormequat?
• Still no (sufficient) data for Cypermethrin (anything but pumpkin)
### Statistical evaluation

Only looking at statistics it looks like this:

<table>
<thead>
<tr>
<th></th>
<th>Cypermethrin</th>
<th>Hexachloro-benzen</th>
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</tbody>
</table>

... in order to achieve more clarification further information is needed. Something which is not possible just looking at the final product.
Further eliminating possibilities?

Knowledge or results of several raw materials...

... for example:

- Confidence in supplier of blueberries and apples
- Certificates for mult method results of oats and sunflower kernels
- Good connections to supplier of pumpkin kernels (who confirms Hexachlorobenzenes)
- Use of raw material raisins in other products leads to residue findings of Boscalid, Ethephon and Cypermethrin
This leads to such an overview:

<table>
<thead>
<tr>
<th></th>
<th>Cypermethrin</th>
<th>Hexachlorobenzene</th>
<th>Chlormequat</th>
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<tr>
<td>Oats</td>
<td>SA</td>
<td>SA</td>
<td>7,1%</td>
<td>(0%)</td>
<td>SA</td>
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<td>7,0%</td>
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<td>SA</td>
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</table>

... still more information is necessary
Further clarification

- Multi method and Ethephon analysis for grapes to confirm raw material suspicion
- Analysis of raisins, oats and sunflower kernels for Chlormequat to clarify situation
- Analysis of Glyphosate in pumpkin kernels, raisins, oats and sunflower kernels
## Evaluation

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**Picture pretty clear – only Acetamiprid missing**
What to do…

… even if taking everything into account we can’t find the source?

So far we have taken a risk based approach…

What can we do more?

• Talking to our trusted supplier (unexpected contamination?)

• Checking unlikely statistics

• Cross-checking results

or…

• Testing all raw materials for every parameter
Finally evaluation

Solution: unexpected contamination of apples with Acetamiprid!

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</tbody>
</table>

All residues can be traced back to a specific raw material.
Wrap up for the product

- Of course such a residue situation is rare indeed
- There a limits to statistical evaluation. Each sample has to be reviewed at is own.
- Very likely(!) found the source for each positive finding
- Residue findings does not automatically disregard organic status
- Raw material have to be evaluated regarding their organic labelling (and have to comply e.g. orientation value of BNN)

... exchange raw material of raisins, oats, pumpkin kernels?
... pre-check risk in the raw materials?
• For multi ingredient organic products an action level of 0.01 mg/kg is not applicable (but findings an indication for something amiss).

• Evaluating results in such products is easy if you habe all tools available
  • Big data – statistics
  • Analysis data
  • Knowledge about your raw materials

• Re-evaluate raw material according to well-known action levels/organic standards
If you have questions, please contact

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JohannesJaschik@eurofins.de