

BioFach 2017

lach : bruns

Taking a closer look.

Pesticides and contaminants in organic products

Dr. Günter Lach - Dr. Silke Bruns, 16. February 2017



AGENDA

Processing factors

Haloxyfop (acidic herbicides) – analytical challenges

Phthalimide (PI)

Contaminations by contact



PROCESSING FACTORS

Application of Processing Factors (“PF”) on organic products



- The **main area of deliberate** (and hence **illegal**) **use** of pesticides is **during cultivation** on the field. Only in that case a shift of the pesticide levels in the processed product compared to the raw product may happen.
- Other critical points where organic products may be contaminated **after harvesting** are **processing, storage** and **transport**. At these points, a PF is not applicable.

Homogeneous distribution?



PROCESSING FACTORS

lach : bruns

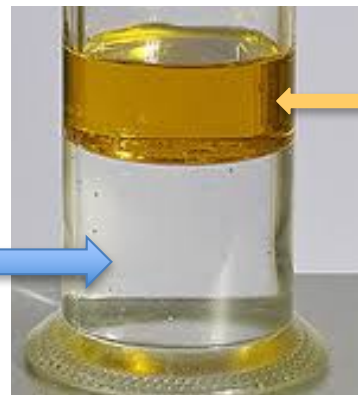
Application of Processing Factors ("PF") on organic products



The pesticides show in general quite different behaviour related to processing steps, strongly depending on their properties like solubility in water and fat, volatility, thermal stability etc.



Water soluble (f. ex.):
Propamocarb,
Glyphosate, Chlormequat



Fat soluble (f. ex.):
DDT, Procymidone,
Bifenthrine





PROCESSING FACTORS

Depending on the chemical-physical properties of the pesticides (water / fat soluble, volatility, thermal stability)



and the processing techniques (peeling, cooking, baking, drying, fermentation, pressing, milling),

the level of a pesticide present in the raw product will increase or decrease in the processed product.



A simultaneous increase and / or a decrease of one or more pesticides during the processing is possible and also quite probable.



PROCESSING FACTORS



For every (!) pesticide/product combination related to every particular processing technique an individual study is necessary to get a reliable knowledge about a possible processing factor.

It is not possible to define a “standard” PF for a processing technique.



Is not possible!



PROCESSING FACTORS

BfR (federal institute for risk assessment) - Approach



Compilation of Processing Factors and Evaluation of Quality Controlled Data
of Food Processing Studies (source: http://www.bfr.bund.de/de/a-z_index/verarbeitungsfaktoren-8400.html)

residue definition (for monitoring)	commodity	processed matrix	median Pf	number of trials	acceptability of study
abamectin (sum of avermectin B1a, avermectinB1b and delta-8,9 isomer of avermectin B1a)	tomatoes	juice	0.29	4	yes
abamectin (sum of avermectin B1a, avermectinB1b and delta-8,9 isomer of avermectin B1a)	tomatoes	fruit, canned	0.20	4	yes
abamectin (sum of avermectin B1a, avermectinB1b and delta-8,9 isomer of avermectin B1a)	tomatoes	puree	1.56	4	yes

$$PF = \frac{\text{Residue in processed product}}{\text{Residue in raw product}}$$

PF > 1 = Enrichment
PF < 1 = Decrease

} in processed food product

PROCESSING FACTORS



Grapes - Raisins



PF > 1 = Enrichment
PF < 1 = Decrease

} in processed food product

residue definition (for monitoring)	commodity	processed matrix	median Pf	number of trials	acceptability of study
carbendazim and benomyl (sum of benomyl and carbendazim expressed as carbendazim)	grapes, red	raisin	3.07	2	indicative
carbendazim and benomyl (sum of benomyl and carbendazim expressed as carbendazim)	grapes, white	raisin	2.53	1	indicative
chlorantraniliprole	grapes, white	raisin	4.92	2	yes
chlorantraniliprole	grapes, red	raisin	3.77	2	yes
chlorothalonil	grapes	raisin	0.47	2	yes
chlorpyrifos	grapes	raisin	0.17	1	indicative
chlorpyrifos	grapes, white	raisin	0.95	1	indicative
chlorpyrifos-methyl	grapes, white	raisin	not applicable	1	no
chlorpyrifos-methyl	grapes, red	raisin	< 0.09	1	indicative
clofentezine	grapes	raisin	0.29	6	yes
clofentezine	grapes	raisin	< 0.67	1	indicative
clofentezine	grapes	raisin	1.00	1	no



PROCESSING FACTORS

BNN - Approach



Conversion factors for pesticide residues in dried organic products (for the evaluation according to the BNN orientation value for pesticides)

Food product	Factor
Dried fruits	
in general	5
Green and black tea, aromatic herbs, medicinal herbs, herbal tea, and tea-like products	
in general	4

These conversion factors are not legally binding and do not replace appendix VI of regulation (EC) No 396/2005. They solely serve as recommendations in order to apply the BNN orientation value for pesticides.



PROCESSING FACTORS

BNN - Approach



Food item (continuation)	Factor
Spices	
It is not reasonable to apply a single conversion factor to the large variety of products, which are covered by the term “spices“. A product-specific conversion factor between 1 and 10 can be applied, when a product is dried for the purpose of preservation.	
The categories below serve for orientation.	
Vegetables and mushrooms (dried), e.g. chilli- or ground paprika	7
Exemption: garlic	3
Leaves and herbs	4
Flowers, e.g. rose flowers, lime flowers, hibiscus, cornflower etc.	4
Roots and rhizomes, e.g. ginger, turmeric, horseradish etc.	4
Seeds and fruits, e.g. fennel, aniseed, caraway, cumin, vanilla bean etc.	1
Exemptions: nutmeg, pepper, cilantro, vanilla powder	4
Bark, e.g. cinnamon	4
Further spices:	
Buds (cloves), style and stigma (saffron) and aril (mace)	4

PROCESSING FACTORS



If possible, make use of **analytical data** of the **raw products** themselves. The presence of certain pesticide levels on processed organic food may be used as a first indicator, to go for further investigations. This should always include the request for analytical data of pesticide testing of the related raw material.



HALOXYFOP



How is the MRL definition of the pesticide?

Does it cover only **one analyte** or also **metabolites / degradation products / conjugates**?

*Example: Phenoxycarboxylic acids like f. ex. **Haloxypop** or **2,4-D***

The **MRL definitions** are complex:

***Haloxypop** = sum of Haloxypop, its' esters, its' salts and its' conjugates*

2,4-D** = sum of 2,4-D, its **salts**, its **esters** and its **conjugates

What influence does this aspect have on the reported laboratory result?

Haloxyfop results reported

Laboratory 1	Laboratory 2	Laboratory 3
n.r. ($< 0,01$ mg/kg)	0,035 mg/kg	0,075 mg/kg

Lab 1: did not analyse for Haloxyfop as it was **NOT part** of the multi-method scope.

Lab 2: analysed for Haloxyfop **within** the multi method scope.

Lab 3: Analysed the sample while applying a specific approach (SRM = single residue method).



Residues of Haloxyfop in food products

Quick degradation of mother compounds?

Example: **Haloxyfop**

Properties of **Haloxyfop-P-methyl** (formulation “Galant Super”)

Half-Life in soil (Disappearance Time 50% = DT 50):

DT50 in soil < 24 h: “In environmental matrices, **rapidly hydrolysed** to **haloxyfop-P**, with nearly **quantitative conversion** in **1 day or less**.

Subsequent degradation then follows the pathways and rates for **haloxyfop-P**.

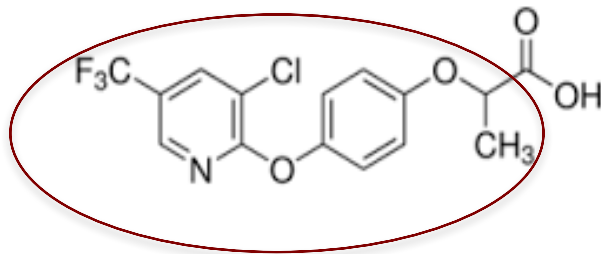
Half-Life of **haloxyfop-P** in soil

ave. DT50 **ca. 9 d**. The major soil metabolite, **haloxyfop-pyridinol**, is more persistent, **DT50 ca. 200 d**.

→ **haloxyfop-pyridinol = Conjugate of Haloxyfop !**

(data from the Pesticide Manual)

Residues of Haloxyfop in food products



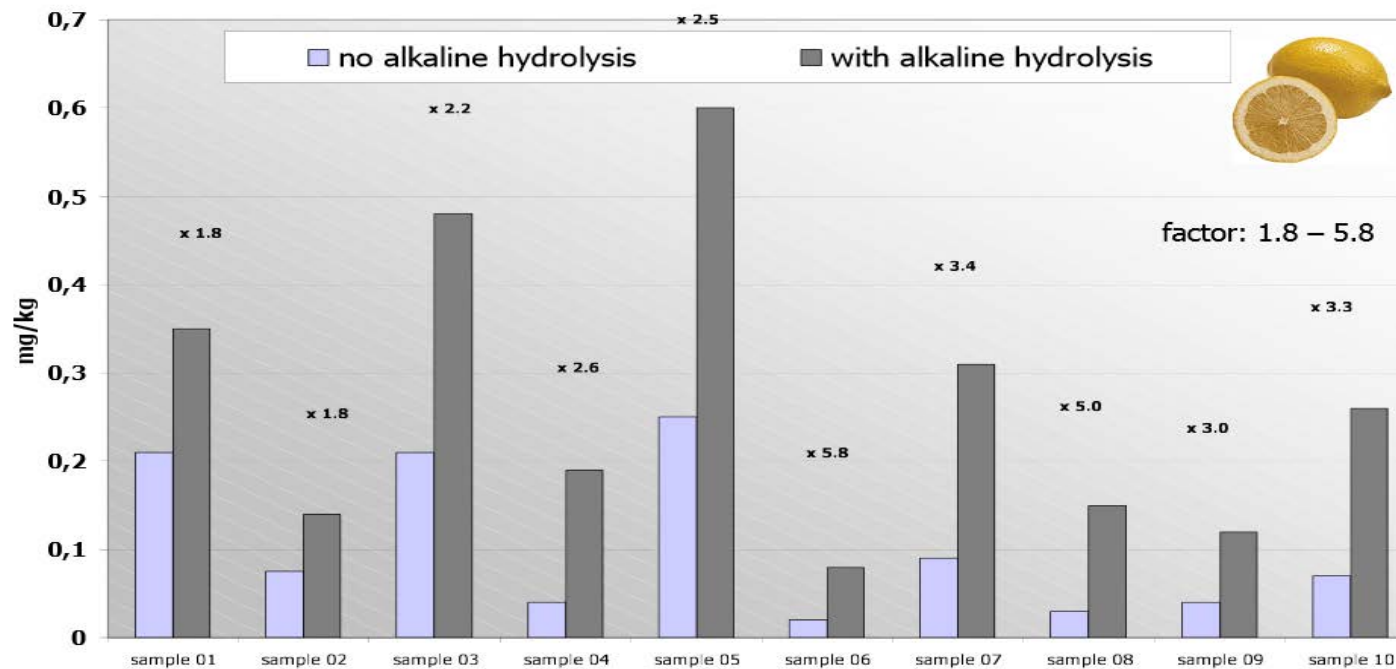
Haloxyfop-moiety

Laboratories are usually able to detect only **Haloxyfop (acid)** and particular **esters** (f.ex. Haloxyfop-methyl).

All other **Haloxyfop-molecules** - mainly the **conjugates** - **cannot be detected** applying a multi residue method (**MRM**) like QuEChERS.

The laboratories are required to analyse the samples in a different way (**hydrolysis**). Then, the **total Haloxyfop-moiety** is detected and of course **with higher quantities** (than Haloxyfop acid only).

Analysis of Acidic Herbicides including a “hydrolysis step”



Levels of 2,4-D in lemons without and with hydrolysis
(Data: Acidic pesticides using QuEChERS method, CVUA Stuttgart)

ANALYTICAL APPROACH

Questioning the analytical results

Can the pesticide be analysed by a multi-method? Or is a single residue method or an additional analytical step necessary?

Example **Haloxyfop**: This pesticide requires an extra step (“**Hydrolysis**”) to **cover all components** which are relevant like free acid, esters, and conjugates.

Challenge: Laboratories sometimes (often?) do not explain in detail, whether they perform extra/additional analyses.

Some labs do – others don't!

Consequence:

At a first glance, results are often not comparable!

PHTHALIMIDE (PI)

Folpet / Phthalimid

Regulation **2016/156** provides a new definition of the MRL of Folpet:

Sum of Folpet and Phthalimide, expressed as Folpet !

BUT: ***Phthalimide (PI)*** is found in all kinds of products. In case of **dried products**, PI is related to contaminations / forming during drying (processing). Only in a very limited number of samples (with positive PI results) also Folpet is detected. In most cases, there is no correlation between Folpet and PI results.

PHTHALIMIDE (PI)

Environmental impact:

→ House dust: ubiquitous presence of “**phthalic anhydride**”



→ **Phthalic acid** and **Phthalic anhydride** are present in

resins



paintings



Plastics (PVC)



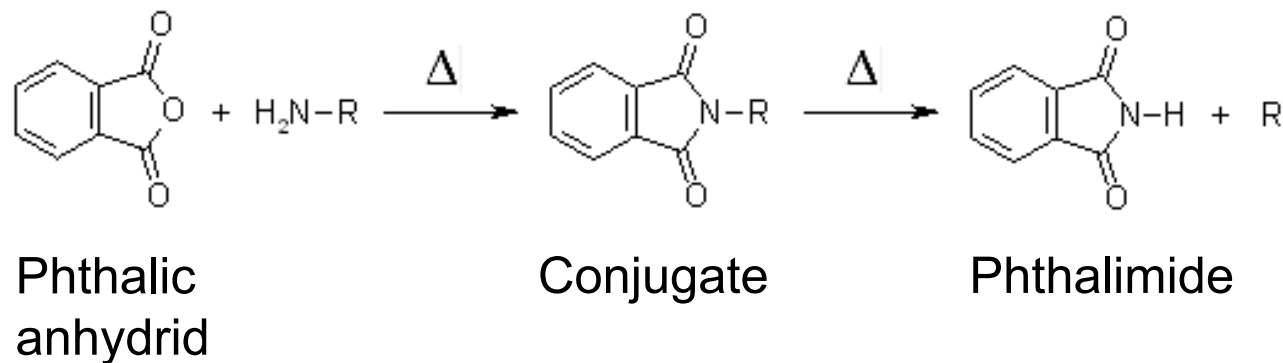
newspaper printings



→ Sources for formation of **Phthalimide** in food stuff!

PHTHALIMIDE (PI)

Reaction equation of **phthalic anhydride** with compounds of the **food matrix** containing **primary amino-groups** (like amino acids, peptides, etc.) under **heating conditions**:



Investigations performed by the relana® member Labor Friedle GmbH

PHTHALIMIDE (PI)

Problem related to organic food products

Regulation 2016/156:

Sum of Folpet and Phthalimide, expressed as Folpet !

In case of PI findings above 0,01 mg/kg (but no Folpet), the related organic food product might be suspected to be in conflict with the organic regulations!

Mainly affected food products are:

- *Tea, Fruit and Herbal Tea*
- *Dried Herbs and Spices*



PHTHALIMIDE (PI)

How to deal with findings of PI?

See BNN Interpretation Guide “Phthalimide”:

http://www.n-bnn.de/sites/default/dateien/bilder/Downloads/interpretation_guide_Phthalimid_English.pdf

See Position Paper to Phthalimid of the Working Group Pesticides of the German Association of Chemists (GDCh) ¹:

“Keine zweifelsfreie Überwachung des Rückstandshöchstgehaltes von Folpet möglich”

“It is not possible to monitor the maximum residue level of Folpet”

¹ Document (German language) available at: magnus.jesussek@lgl.bayern.de

Where to get information about analytical challenges?

<http://www.relana-online.com/position-papers/>





CONTAMINATIONS BY CONTACT





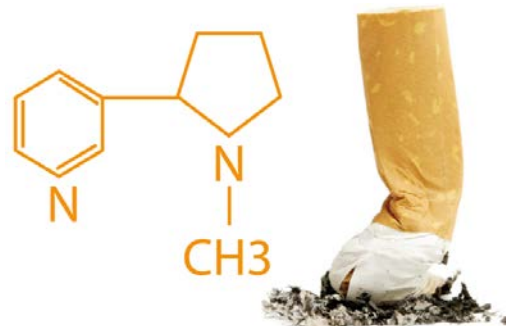
CONTAMINATIONS BY CONTACT



CONTAMINATIONS BY CONTACT

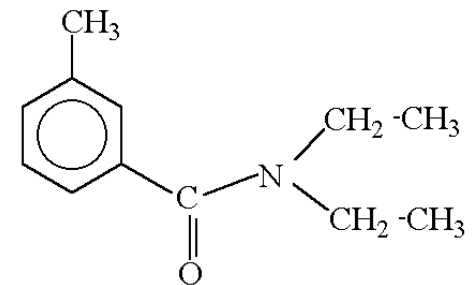
Nicotine

→ Tea, Mushrooms



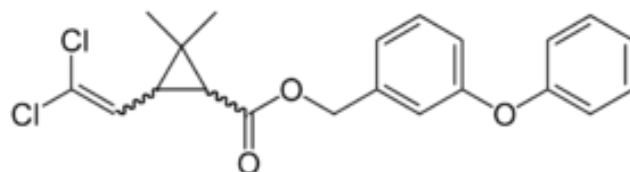
DEET

→ Berries, Mushrooms



Permethrin

→ Several commodities





NICOTINE

Tea samples analysed in the laboratory for pesticides showed detectable Nicotine levels. Repeatedly – across tea produced in different countries across the world.



Investigations gave evidences that no Nicotine was applied at all.

Tea pluckers confirmed that they did not smoke at all. This was also controlled by the tea farm owners.





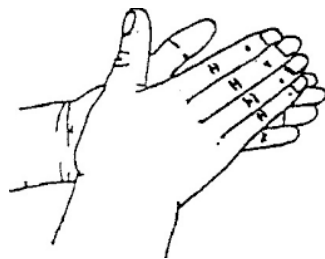
NICOTINE

Source of Nicotine?

Waste found in the tea gardens:
Packaging material of **chewing tobacco**

Paper
waste

How is chewing tobacco usually consumed?
Tobacco is rubbed by hands before consumption.



Take also into consideration, that tea pluckers do not put every single tea leave immediately into the tea basket. They store the leaves in their hands until the hand is full with tea leaves and then throw the leaves into the basket.

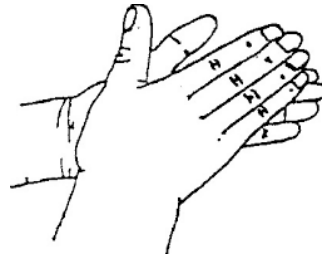
NICOTINE

Source identified!

Nicotine



Nicotine



The tea dust in the factory was highly contaminated as well with Nicotine and increased the levels significantly.

DEET

- Acts as an olfactometric chemical (liquid with own smell)
- Application ONLY direct on the skin or on processing equipment (f.ex. tables)
- Insects smell and taste DEET; as they don't like it, they stay away (“malodour”):

REPELLENT

(not covered by reg. (EC) no. 396/2005 !
in Germany: national regulation “RHmV”)

- DEET is not covered by reg. 889/2008!
As a consequence, **BNN orientation value** is **NOT applicable!**



DEET

Which food products are affected by DEET?

In general ALL products, which are harvested by **manual picking** and /or **processed on tables** etc.:

➔ Berries (mainly Blueberries), mushrooms (chanterelle), spices (f.ex. black pepper), ...



In Germany special permissions are existing for the trading of certain food products with levels of DEET exceeding the national MRL of 0,01 mg/kg. All these permissions are dedicated to single products and companies (Importers)!

PERMETHRIN

- Acts as an **insecticide/acaricide** and **repellent**



Permethrin is EPA approved for use as an insect repellent when applied to clothing and other textiles.

“Not only does this product repel insects, but will actually kill ticks, mosquitoes, chiggers, mites and more than 55 other kinds of insects.”
(from www.SectionHiker.com)



PERMETHRIN

Which food products are affected by Permethrin?

Permethrin is used as a “**Insecticide and Biocide**”:

- *in agriculture, to protect crops*
 - *in agriculture, to kill livestock parasites*
 - *for industrial/domestic insect control*
 - *in the textile industry to prevent insect attack*
 - *in aviation, as aircraft disinfectant*
 - *in timber (wood) treatment*
 - *as a personal protective measure (cloth impregnant, mosquito nets)*
 - *in pet flea preventative collars or treatment*
- In general ALL products **processed** and/or **stored** after harvesting might be affected

BioFach 2018

lach : bruns

Taking a closer look.

***See you again for ...
... Pesticides and
contaminants in
organic products ?***

Dr. Günter Lach - Dr. Silke Bruns