

POSITION PAPER No. 19 - 01**“Sources of contamination of samples for analysis“****Version 2019/04/12**

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1. Introduction

Positive findings of pesticides and certain contaminants in food and feed samples are not always related to a deliberate and documented use. This aspect might lead to conflicts between suppliers and customers of food products as well as between laboratories and their clients.

With this position paper, known sources for contaminations outside analytical laboratories and also contaminations caused by chemical processes during analyses are discussed. Solutions are concluded in terms of how to avoid such contaminations.

2. Substances deliberately used for other purposes

Several substances legally classified as pesticides are so-called „multiple source“-compounds, f. ex. they are deliberately used for other purposes, such as biocides, disinfectants, repellents, or additives f.ex. in pesticide or fertiliser formulations.

Source	Possible compounds (examples)	Remarks
Repellents against mosquitos , midges, ticks	<ul style="list-style-type: none"> • DEET • Icaridin 	<ul style="list-style-type: none"> • Contamination via skin contact or via air.
Repellents and insecticides against moths	<ul style="list-style-type: none"> • naphthalene • pyrethroids (like permethrin, phenothrin, synergist piperonylbutoxide (PBO)) • chlorpyrifos 	<ul style="list-style-type: none"> • Occurrence also in carpets, wool, lambskin etc. possible.
Veterinary biocides against ticks, fleas etc.	<ul style="list-style-type: none"> • biocides such as propoxur, diazinon, imidacloprid, flumethrin, fipronil 	<ul style="list-style-type: none"> • For use with pets (dogs, cats), for example as shampoos or in collars.
Antibiotics and veterinary drugs	<ul style="list-style-type: none"> • tetracyclines • sulfonamides 	<ul style="list-style-type: none"> • carry-over into plants via manure.
Biocides: insecticides rodenticides molluscicides acaricides etc.	<ul style="list-style-type: none"> • pyrethroids (such as permethrin, phenothrin) • pyrethrines plus synergist piperonylbutoxide (PBO) • pirimiphos-methyl • metaldehyde • fipronil • phosphine (phosphane) 	Possible uses: <ul style="list-style-type: none"> • insecticides used against cockroaches, midges, bugs, ants etc. (also used for pets) • rodenticides against rat and mice • Usage in warehouses, silos, transport vessels, households and offices.
Cleansers and disinfectants	<ul style="list-style-type: none"> • hypochlorite (⇒ chlorate) • quaternary ammonium compounds (DDAC, BAC) • 2-phenyl phenol 	<ul style="list-style-type: none"> • Check any cleansers used in factories, transport vessels, labs etc.; 2-phenyl phenol also used in air nebulisers.

Food and feed additives	<ul style="list-style-type: none"> • 2-phenylphenol, biphenyl (formerly approved as food additives in the EU, now categorised as pesticides) 	
Fertilisers etc.	<ul style="list-style-type: none"> • compounds not labelled such as phosphonic acid, perchlorate 	
Wood preservatives	<ul style="list-style-type: none"> • pentachlorophenole (PCP) • PCB • arsenic, chromate • PAH and anthraquinone caused by the use of oil-derivatives for wood protection 	<ul style="list-style-type: none"> • contamination via air, dust, direct contact
Cosmetics such as hand creams	<ul style="list-style-type: none"> • preservatives and antibacterial compounds such as 2-phenylphenol, benzalkonium chloride (BAC) • MOSH/MOAH of petroleum-based ingredients such as Vaseline 	<ul style="list-style-type: none"> • avoid direct contact with unpacked samples • wearing of lab gloves
Packaging material: Plastics	<ul style="list-style-type: none"> • plasticisers (phthalates, ESBO, adipates etc.) • perchlorate • MOSH/MOAH (mineral oil compounds) • further additives 	<ul style="list-style-type: none"> • Migration into samples possible, also via air.
Packaging material: Paper and cardboard	<ul style="list-style-type: none"> • anthraquinone (paper additive) • MOSH/MOAH (of printing inks via recycled paper) • printing inks including photo initiators • primary aromatic amines (PAA) 	<ul style="list-style-type: none"> • Migration into samples possible, also via air.
Packaging material: adhesives	<ul style="list-style-type: none"> • MOSH/MOAH • Solvents (f.ex. aromatic components "BTEX") 	<ul style="list-style-type: none"> • Migration into samples possible, also via air.
Lab gloves	<ul style="list-style-type: none"> • Dithiocarbamates (DTC) 	<ul style="list-style-type: none"> • DTC can be used as vulcanising accelerators in the production process of latex gloves [Causton].

3. Carry-over of pesticides

Source	Possible compounds (examples)	Annotations
Common pollution of the environment: transport by air, dust and rain	<ul style="list-style-type: none"> • glyphosate • endosulfan • nicotine • phthalic acid (⇒ phthalimide*) 	*The legal residue definition of the fungicide Folpet covers phthalimide.
Contaminated soil	<ul style="list-style-type: none"> • DDT and metabolites • PCB • lindane • HCB 	
Residues in perennial plants from former applications	<ul style="list-style-type: none"> • phosphonic acid • chlormequat 	<ul style="list-style-type: none"> • pome and stone fruits • nuts • etc.
Carry-over contamination via substrates	<ul style="list-style-type: none"> • chlormequat/mepiquat in mushrooms • nicotine in mushrooms 	<ul style="list-style-type: none"> • transfer via contaminated straw or substrate. (f.ex. by presence of tobacco stems or feathers of hens being treated with nicotine).

4. Substances accidentally generated or released by other processes

Source	Possible compounds (examples)	Annotations
Open fires , firesides, bonfires, heating, drying with exhaust fumes, open waste incineration incl. waste incinerating plants	<ul style="list-style-type: none"> • PAH • biphenyl • anthraquinone • dioxins • MOSH/MOAH • heavy metals (such as mercury) 	high risk products: <ul style="list-style-type: none"> • dried food and feedstuff (herbs, spices, tea etc.) • products with large surfaces (fresh herbs).
Drinking water/washing irrigation water	<ul style="list-style-type: none"> • chlorate/perchlorate • bromide 	
Waste water	<ul style="list-style-type: none"> • arsenic** • dioxins, PCB • heavy metals 	**contamination of rice cultivated in polluted water.
Metal processing industries	Heavy metals such as cadmium, mercury, lead	
Tobacco users (smoking, chewing), tobacco cultivation	<ul style="list-style-type: none"> • nicotine *** • PAH • cadmium 	*** direct contact with smoke; contamination via hands (especially after rolling of tobacco products for chewing); nicotine through air and dust (if close to tobacco plantations) [Romanotto].

Processing contaminants	<ul style="list-style-type: none"> • chlorpropham • trimesium in dried herbs and tea • fosetyl in wine 	<ul style="list-style-type: none"> • Chlorpropham cross-contamination risk in pack houses
Traffic	<ul style="list-style-type: none"> • benzene • MOSH/MOAH • lead**** 	**** especially in countries where leaded fuel is still in use.

5. Naturally occurring substances

In some cases, naturally occurring substances can counterfeit the presence of pesticides.

Source	Possible compounds	Annotations
<p>Brassicaceae: mustard, rape, cabbage species, rucola, broccoli, etc.</p> <p>Allium: onions, garlic etc</p> <p>Caricaceae: papaya</p> <p>Capparaceae: caper</p> <p>Moringaceae: moringa</p>	<p>Naturally occurring CS₂-releasing compounds, thereby pretending the presence of dithiocarbamates (DTC).</p>	<p>Judgement of violations of maximum residue levels (MRL) for dithiocarbamates by means of CS₂ analysis are in general critical (indirect parameter).</p>
Geogenic compounds: bromide	<p>Naturally occurring bromide content, pretending residues of the fumigant methyl bromide.</p> <p>Certain nuts like Brazil nuts and some varieties of walnuts show high levels of bromide by nature [Furr].</p>	<p>Bromide is present in all food and feed stuffs by nature. The usage of the fumigant methyl bromide in containers or warehouses also leads to the formation of bromide.</p> <p>In certain cases, the knowledge of the chloride levels can be helpful to judge samples with elevated bromide levels.</p>
Geogenic compounds: heavy metals and elements	<ul style="list-style-type: none"> • copper • mercury • cadmium • arsenic, etc. 	
Potatoes	<ul style="list-style-type: none"> • 1,4-dimethylnaphtalene 	Naturally occurring low levels of 1,4-dimethyl-naphtalene

6. Conclusion

As discussed in this position paper, possible sources for contaminations with pesticides and contaminants are abundant. The same applies for the number and types of possible compounds.

Consequently, conspicuous analytical results should be carefully verified in terms of other sources than pesticide applications.

Application of appropriate measures across the entire food chain, during sampling, transport, storage, processing, sample preparation, and analysis, can reduce the risks of possible contaminations. Numerous risks are outside the control of analytical laboratories.

7. Literature (selection)

General:

M. Anastassiades: Overview of pesticide-relevant compounds originating from sources other than pesticide use, presentation at EPRW2018

Single topics:

B.E. Causton et al.: Implications of the presence of dithiocarbamate in latex gloves, Dent Mater. 1993 May;9(3):209-13

A. K. Furr et al.: Elemental composition of tree nuts, Bull. Environm. Contam. Toxicol. 21, 392-396 (1979)

A. Romanotto: Bestimmung der Herkunft von Anthrachinon und Nikotin in Tee, GDCh-Pestizidseminar 2018

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