POSITION PAPER No. 19 - 01

"Sources of contamination of samples for analysis"

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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, their clients, and legal authorities.
If positive findings refer to substances which are listed (EU-harmonised) as active substances for plant protection products (Reg. (EC) No. 1107/2009), then there can be a conflict for the (legal) evaluation of these substances. This is because these substances might not have entered the laboratory sample(s) by deliberate application of plant protection products along the entire food production / processing chain but perhaps by other sources - thus by contamination. Therefore, several substances legally classified as pesticides are referred to as „*multiple source*"-substances.

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

The position paper categorises the multiple-source substances into different groups (chapters 2 to 5) according to the different types of sources (of contamination).

2. Substances deliberately used for other purposes than pesticide applications

These *multiple source*-compounds are deliberately used for other purposes – like f. ex. as biocides (intended to exert a controlling effect on any harmful organism), disinfectants (intended to inactivate or destroy microorganisms on surfaces), repellents (intended to have a repellent effect without causing harm (e.g. fumigants, protective coatings, etc.)), or as additives f.ex. in pesticide or fertiliser formulations.

Source	**Possible compounds (examples)**	**Remarks**
Repellents for personal protection	• DEET • Icaridin	Contamination via skin contact or via air.
Repellents and **insecticides** for protection of goods **/ storage facilities**	• naphthalene • pyrethroids (like permethrin, phenothrin, synergist piperonylbutoxide (PBO)) • chlorpyrifos	Occurrence also in carpets, wool, lambskin etc. possible.
Veterinary biocides against ticks, fleas etc.	biocides such as propoxur, diazinon, imidacloprid, flumethrin, fipronil	For use with pets (dogs, cats), for example as shampoos or in collars.
Antibiotics and veterinary drugs	• tetracyclines • sulfonamides • fipronil	carry-over into plants via manure.

Insecticides, rodenticides, molluscicides, acaricides fumigants etc.	• pyrethroids (such as permethrin, phenothrin) • pyrethrines plus synergist piperonylbutoxide (PBO) • pirimiphos-methyl • metaldehyde • phosphine (phosphane) • ethylene oxide • sulfurylfluoride	Possible uses: • 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. • sterilised centrifuge tubes or urine containers (used as sample containers) → ethylene oxide
Cleansers and disinfectants	• hypochlorite (⇒ chlorate) • chlorine dioxide (→CO_2 pressure disinfection (⇒ chlorate) • quaternary ammonium compounds (DDAC, BAC) • 2-phenyl phenol	Check any cleansers used in factories, transport vessels, labs etc.; 2-phenyl phenol also used in air nebulisers.
Food and feed additives	• 2-phenylphenol, biphenyl (formerly approved as food additives in the EU, now categorised as pesticides) • ethoxyquin (feed additive E 324)	
Fertilisers etc.	• compounds not labelled such as phosphonic acid, perchlorate	
Wood preservatives	• pentachlorophenole (PCP) • fumigation with sulfuryl-fluoride	contamination via air, dust, direct contact
Cosmetics such as hand creams	• preservatives and anti-bacterial compounds such as 2-phenylphenol, benz-alkonium chloride (BAC)	• avoid direct contact with unpacked samples • wearing of lab gloves
Packaging material: Plastics	• perchlorate	Migration into samples possible, also via air.
Packaging material: Paper and cardboard	• anthraquinone (paper additive)	Migration into samples possible, also via air.
Lab gloves / rubber materials	• Dithiocarbamates (DTC) • Diphenylamine (DPA)	• DTC can be used as vulcanising accelerators in the production process of latex gloves [Causton]. • DPA: Antioxidants in the rubber and elastomer industry and additive of perfumes

3. Carry-over of pesticides

Source	Possible compounds (examples)	Annotations
Common pollution of the environment: transport by air, dust and rain	• glyphosate • endosulfan • nicotine • phthalic acid (⇒ phthalimide*)	*The legal residue definition of the fungicide Folpet covers phthalimide.
Contaminated soil	• DDT and metabolites • lindane • HCB	
Residues in perennial plants from former applications	• phosphonic acid • chlormequat	• pome and stone fruits • nuts • etc.
Carry-over contamination via substrates	• chlormequat/mepiquat in mushrooms • nicotine in mushrooms	transfer via contaminated straw or substrate. (f.ex. by presence of tobacco stems or feathers of hens being treated with nicotine).

4. Substances accidently 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	• biphenyl • anthraquinone	high risk products: • dried food and feedstuff (herbs, spices, tea etc.) • products with large surfaces (fresh herbs).
Drinking water/washing irrigation water	• chlorate/perchlorate • bromide	
Metal processing industries	Heavy metals such as cadmium, mercury, lead, and arsenic	
Tobacco users (smoking, chewing), **tobacco cultivation**	nicotine ***	*** 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	• chlorpropham • trimesium in dried herbs and tea • fosetyl in wine	Chlorpropham cross-contamination risk in pack houses

5. Naturally occurring substances

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

Source	Possible compounds	Annotations
Brassicaceae*:** mustard, rape, cabbage species, rucola, broccoli, etc. ***Allium*:** onions, garlic etc ***Caricaceae: papaya ***Capparaceae***: caper ***Moringaceae***: moringa	Naturally occurring CS_2-releasing compounds, thereby pretending the presence of **dithiocarbamates** (DTC).	Judgement of violations of maximum residue levels (MRL) for dithiocarbamates by means of CS_2 analysis are in general critical (indirect parameter).
Plants	indolylacetic acid (auxins) f. ex. present in cereals and rice	Naturally occurring plant hormone
Geogenic compounds: **Bromide** Methyl isothiocyanate	Naturally occurring **bromide** content, pretending residues of the **fumigant methyl bromide**. Certain nuts like Brazil nuts and some varieties of walnuts show high levels of bromide by nature [Furr]. Metabolite of the pesticide "Dazomet"	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. ~~In certain cases, the knowledge of the chloride levels can be helpful to judge samples with elevated bromide levels.~~ Component of mustard oils
Potatoes	• 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.
Finally, the laboratory can only "make pesticides visible" (= detect pesticides) without being able to say how and why the pesticide entered into the sample. There is no sender labelled on the detected pesticide.

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 dithiocarbamates 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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