DEVELOPMENT OF MULTI-RESIDUE METHODS FOR PESTICIDE SCREENING IN ORGANIC FOOD SAMPLES

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AUTHENTIC FOOD

Introduction and objectives

Over the last decade, there has been an ever-increasing demand for foods cultivated using organic practices. However, the sector is becoming dominated by corporate players that might not strictly fulfil all the requirements of organic farming, with or without fraud intentions. The AuthenticFood project aims to combine novel analytical techniques discriminating between the cropping systems to improve the reliability of organic authentication.

This study describes the development of multi-residue analytical methods for the determination of pesticides in food products. The main challenge was to reach the highest sensitivity allowing the detection of very low contaminations, while keeping a wide range of target molecules.

Material and methods

Samples

Food items (tomato, tomato sauce, wheat flour, durum, pasta) were collected from conventional and organic crops and from processing plants, located in Denmark and in Italy (Figure 1), over two years.

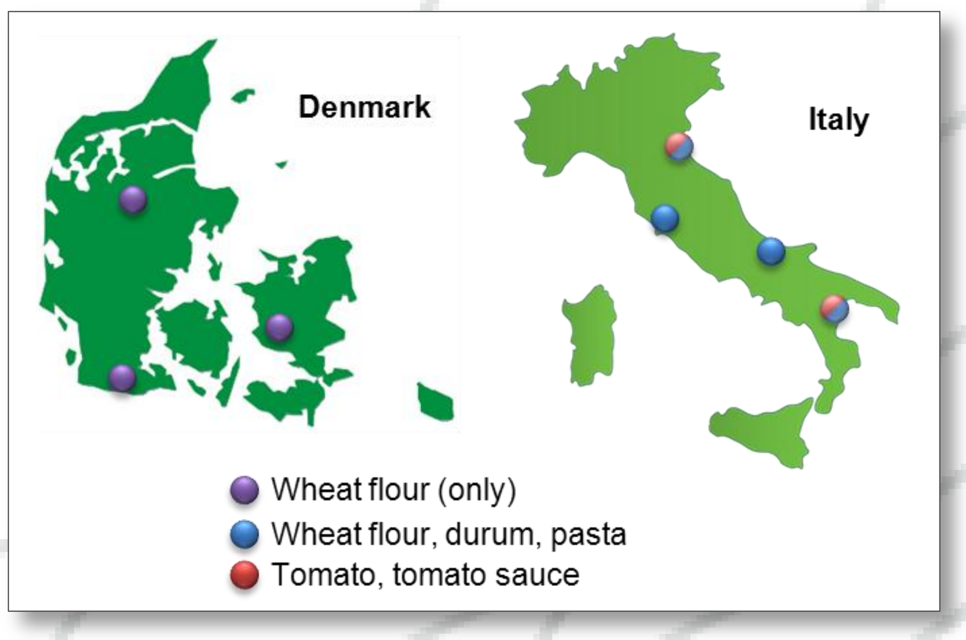

Figure 1: Origin of analysed samples

Preparation and extraction

The samples were finely ground and homogenized, then kept at -20°C (tomato) or at ambient temperature (wheat) until extraction.
Pesticides were extracted using a generic method based on the QuEChERS[1-3] protocol. The extraction/cleanup parameters were optimised for each matrix (Figure 2).

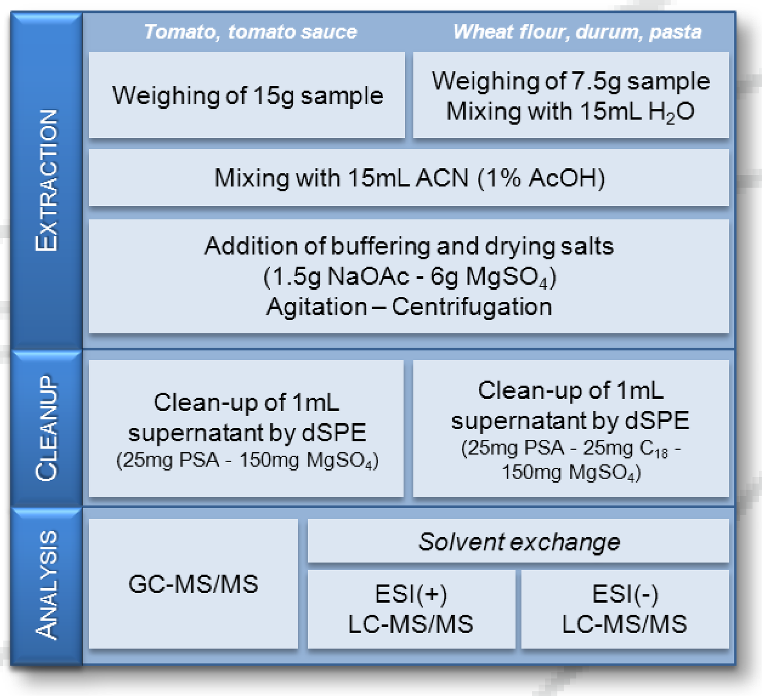

Figure 2: Extraction protocols

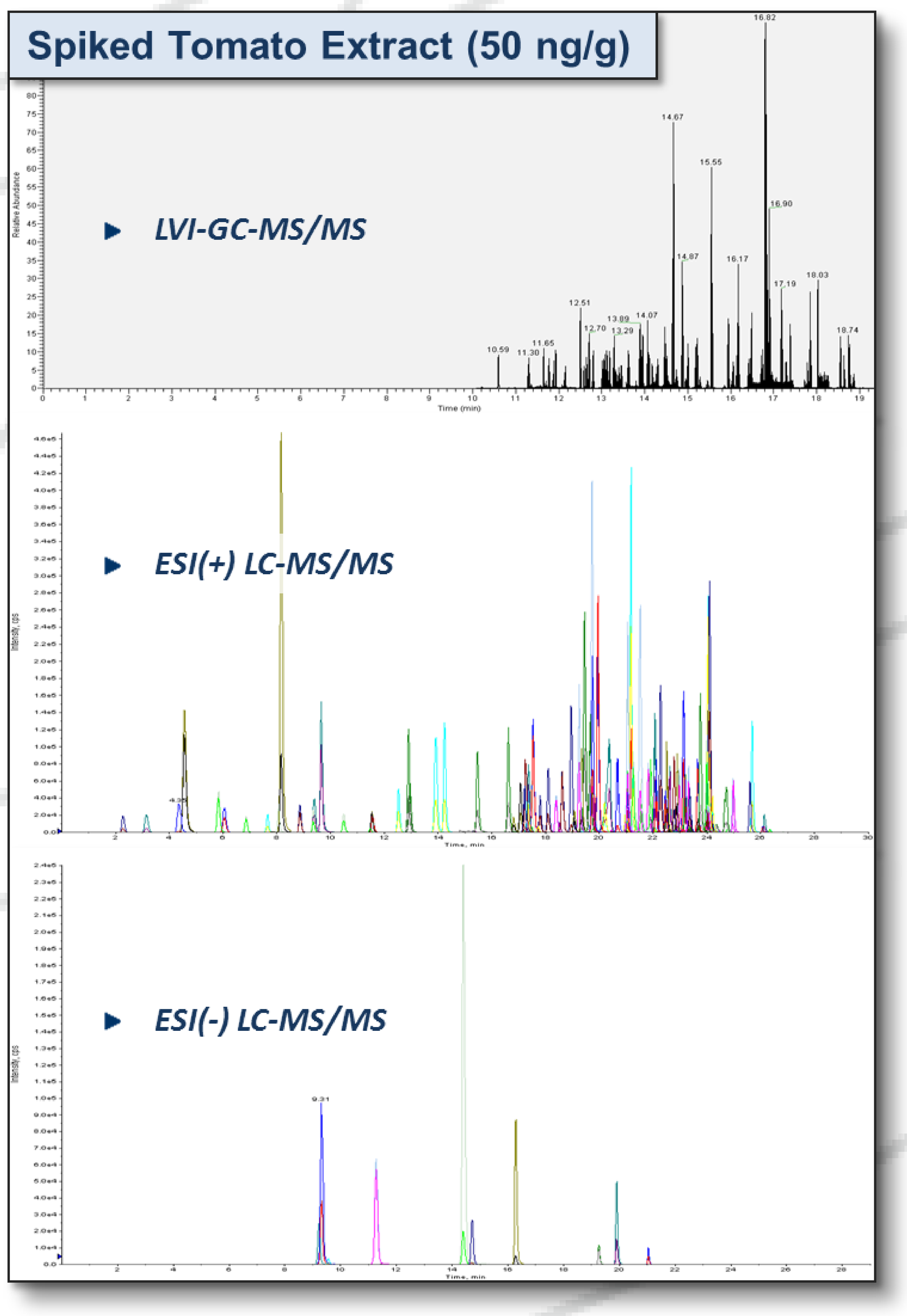

Figure 3: GC-MS/MS and LC-MS/MS Chromatograms from a spiked tomato extract (spiking level 50 ng.g^{-1}, 150 pesticides + 8 IS)

Analysis

The extracts were analyzed in parallel using Liquid Chromatography coupled to triple-quadrupole tandem Mass Spectrometry (LC-MS/MS) in positive and negative Electrospray, and Gas Chromatography coupled to triple-quadrupole tandem Mass Spectrometry (GC-MS/MS) with large volume injection. The MS/MS were operated in Multiple Reaction Monitoring. A summary of the analysed pesticides is given in Table 1 and representative chromatograms are shown in Figure 3.

Chemical family	Number of analytes (/150)	Activity	Analytical technique
Anilides	15	Herbicides, fungicides	GC-MS/MS ESI(+)LC-MS/MS
Carbamates	14	Insecticides, herbicides, fungicides	ESI(+)LC-MS/MS
Chlorotriazines	8	Herbicides	ESI(+)LC-MS/MS
Conazoles	14	Fungicides	GC-MS/MS ESI(+)LC-MS/MS
Nicotinoides	5	Insecticides	ESI(+)LC-MS/MS
Organochlorides	23	Insecticides, fungicides	GC-MS/MS
Organophosphorus	20	Insecticides	GC-MS/MS ESI(+)LC-MS/MS
Phenylureas	8	Herbicides	ESI(+)LC-MS/MS
Pyrethroids	9	Insecticides	GC-MS/MS
Strobilurines	7	Fungicides	GC-MS/MS ESI(+)LC-MS/MS
Sulfonylureas	7	Herbicides	ESI(+)LC-MS/MS
Others	20	Insecticides, herbicides, fungicides	GC-MS/MS ESI(+)LC-MS/MS ESI(-)LC-MS/MS

Table 1: Analysed pesticides

Acknowledgements

This work was supported by the Luxembourg's National Research Fund (FNR) and by the European Commission within the ERA-Net (CORE Organic II) program.

References

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2. Lehotay S. J., de Kok A., Hiemstra M., van Bodegraven P., Journal of AOAC International 88 (2), 2005, 595-614.
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Results

Pesticides in organic and conventional food products: System-dependent *vs.* location-dependent contaminations

► In year 2, all the conventional tomato samples contained at least two pesticides (mainly *Chlorpyriphos, Imidacloprid, Permethrin, Tebuconazole* and *Tetramethrin*). On the contrary, all the organic samples appeared to be free of any contamination, which tends to demonstrates a direct effect of the cropping system on the pesticide residues content. This trend was not observed for year 1.

► The distributions of pesticides in tomato samples were clearly location-dependent and were closely related to the pesticides used during cropping and storage. The analysis of tomato sauce samples showed a similar local effect, with significantly lower amounts compared to corresponding tomatoes, certainly due to degradation during processing.

► Wheat flour, durum and pasta samples showed one-time contaminations (*Deltamethrin*, *Tetramethrin*) inconstant within both years, and without any clear relationship with the cropping system, nor any local effect.

Contamination of organic products: potential sources

► ***Uptake from polluted soils***

All the wheat flour samples collected in one specific site in DK contained traces of Lindane (ng/g). Considering the persistence of this pesticide, the origin of this pesticide was strongly suspected to be the uptake from a polluted soil, which was confirmed by the analysis of soil samples from the corresponding crops (ng/g).

► ***Cross-contamination during processing or storage***

Traces of Deltamethrin have been found in four pasta samples, whereas this pesticide was not detected in the corresponding wheat flour samples. The most probable explanation is a cross-contamination between conventional and organic samples, during processing or storage.

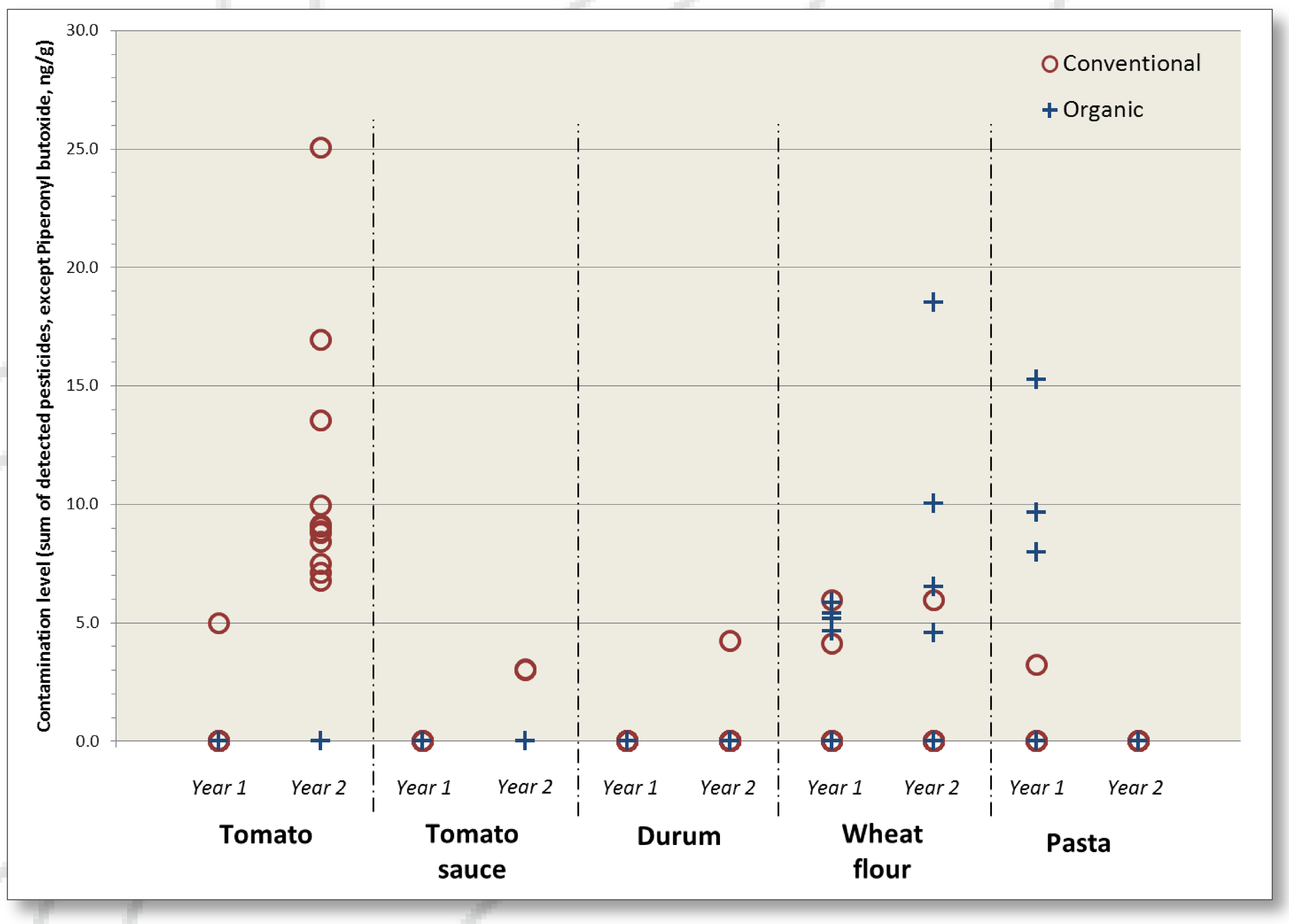

Figure 4: Cumulated concentrations in detected pesticides (excluding Piperonyl Butoxide)

Piperonyl Butoxide (PBO): a special case

► *PBO* is a synergist currently authorised in organic farming to improve the natural defence system of crops against pests or in combination with natural pesticides (pyrethrins family). It is not unusual to find it in organic products and its presence is not considered as being problematic, even if *PBO* becomes increasingly controversial from environmental and toxicological points of view.

► Moderate amounts of *PBO* were found in tomato and tomato sauce samples. Pasta samples showed a general contamination with *PBO*, neither location- nor system-dependent, but certainly due to an intended use during storage.

Conclusions

- The combination of three analytical methods with one extraction protocol allows the determination of trace amounts of 150 pesticides in food products.
- The cropping system (organic vs. conventional) can have a direct effect on the pesticide content and distribution pattern in raw products.
- The influence of cropping system can be hindered by location-dependent effects and by processing or storage.
- Two contamination pathways of organic samples with pesticides were identified: the cross-contamination of organic samples from conventional samples during processing or storage, and the uptake from polluted soil.

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