

## Authentication strategy for organic food products

### Partnership between Europe – China

The project “EU-China-Safe” aims at reducing food fraud and supporting food safety through focusing on improvement of food legislation, food inspection and increasing access to relevant information for stakeholders across Europe and China. As illegal use of synthetic pesticides represents one of fraudulent practices on organic crops, the availability of authentication strategy developed within this project enables improved authentication of such products both at European and Chinese market.

The methodology for authentication of organic food (developed by UCT Prague) was shared with the Chinese partner (CAIQ) who was provided a detailed Standard operation procedure "*Authentication of Organic Fruits and Vegetable: Rapid UHPLC-HRMS method for pesticide metabolites screening*". The proof of concept was demonstrated also through publications "*Can Occurrence of Pesticide Metabolites Detected in Crops Provide the Evidence on Illegal Practices in Organic Farming?*" (DOI: <https://doi.org/10.1021/acs.jafc.8b06999>), "*Pesticide residues and their metabolites in grapes and wines from conventional and organic farming system*" (DOI: 10.3390/foods10020307). The available documentation also involves the database of identified pesticide metabolites. The approach to organic fruits/vegetables products authentication was successfully demonstrated using test material for interlaboratory comparison (case study on apples).

### Definition of problem

In conventional farming system, the use of plant protection products is a common practice. The benefits associated with their applications are reduced crop yield losses and improved quality of food commodities. However, pesticide residue can be present in crops at the harvest time and thus entering human food chain. The possible adverse health effect set due to dietary exposure to residues has to be taken into consideration even in case when maximum limits are not exceeded. Under these conditions, it is not surprising that consumer's demand on organic food is rapidly growing worldwide. Organic farming is an agriculture system that, apart of other restrictions, eliminates the use of synthetic pesticides and fertilizers, thus reducing possible impact both on human health and environment.

The levels of pesticide residues in treated food commodities decrease relatively quickly after application undergoing various (bio)transformation reactions resulting in a number of various typically less toxic products. The common practice of food inspection authorities / certification bodies is to tolerate residues at or below the level 0.01 mg/kg in organic food. Nevertheless, documentation of illegal pesticide use in organic farming is complicated, especially in case, when parent pesticide rapidly degrades and low or undetectable residues levels are left in tested food commodities. On the other hand, number of transformation products / metabolites are unavoidably present in the treated crop, thus their presence in organic products could be utilized as a marker of an unauthorized pesticide application.

### Pathway to solution

The proposed strategy for authentication of organic food was based on simultaneous analysis of pesticide residues and their metabolites. The extraction procedure for isolation of both analyte groups was based on QuEChERS method. The instrumental analyses were performed using an ultra-high-performance liquid chromatography coupled with tandem high-resolution mass spectrometry (UHPLC-HRMS/MS). The records were screened against in-house library using accurate mass,  $m/z$  value of protonated or deprotonated molecular ions of conceivable pesticide (spectral database was created on the basis of various literature sources). The detected ions were further investigated to confirm their identity. As the outcome the set of identified pesticide metabolites was created. This database includes mass spectrometric data including high

resolution fragmentation spectra (when possible to be obtained) for 52 metabolites in grapes and wine, 17 metabolites in apples and 9 metabolites in citrus fruits. The potential of this methodology was demonstrated on food samples containing pesticide residues of parent compound below the quantification limit 0.01 mg/kg (tolerable limit for organic products), and in which their metabolites were unequivocally found. These observations were made for pesticides in grapes, wine (treated e.g. by pesticide preparation containing as an active ingredient fenhexamid, penconazole, cyprodinil, benalaxy, fluopyram or mepanipyrim) and apples (treated e.g. by acetamiprid, penthiopyrad or thiacloprid). The control strategy of analyzing pesticide metabolites as markers of unauthorized practices in organic farming was applied on a set of organic grapes, wines, apples and citrus fruits. In total, 25% of tested organic samples contained quantifiable pesticide residues or detectable metabolites what indicates possibility of illegal practices, thus importance to authenticate such products.

### Long-term impact

The simultaneous analysis of parent pesticides and their metabolites represents a promising tool for tracing history of pesticide application on various crops; moreover, it enables obtaining the evidence on an unauthorized application of plant protection products in organic production. This methodology was successfully applied on several food commodities (grapes, wines, apples and citrus fruits) and it could generically be employed for other various fruits, vegetables or processed food. The availability of new authentication strategy will support the credibility of organic crops and contribute to misdeclaration fraud.