Section 5- Monitoring

5.1.P Pesticide Residues and Transformation Products in Honeybees: A 2018 mid-2019 Appraisal

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Abstract

Due to the ongoing reports of numerous death incidents of honeybees, there is still an urge to assess the occurrence of pesticide residues and their transformation products in them. In this context, during the period of 2018 mid-2019, 82 honeybee samples were sent from several areas of Greece and analyzed for the determination of pesticide residues and transformation products. In particular, more than 130 analytes were incorporated and assessed by applying two multi-residue methods (HPLC-ESI-MS/MS and GC-MS/MS) based on modified QuEChERS methodology and clean-up with Z-Sep, PSA, and C18 materials. Both analytical methods were validated for repeatability, reproducibility, specificity, recovery and sensitivity according to SANTE/11813/2017 guideline. The confirmation of the analytes was based on the retention time (RT), retention time relative to the isotope labelled internal standards and ion-ratio of the quantifier and qualifier ion. The limit of quantification (LOQ) for the analytes of both methods were in the range of 1 to 10 ng/g. In addition, quality control (QC) standards (one blank and two honeybee samples spiked at LOQ and 10 LOQ) were analyzed in every batch of samples, controlling in this way the repeatability of the analytical method. The recoveries of the spiked analytes and of the mass-labeled internal standards, added to the sample prior to extraction, were monitored and ranged between 67 and 120% for the different analytes. Moreover, the uncertainty and the expanded uncertainty of the two methods were also assessed and calculated.

According to the results, 78% of the analyzed honeybee samples were contaminated with at least one active substance. In particular, neonicotinoids were the most frequently detected compounds during 2018, while pyrethroids, and especially cypermethrin, were the most predominant ones in the samples of 2019. The relatively high concentrations of cypermethrin (84.1 to 66288 ng/g $_{\text{bee body weight}}$), and in one case of λ-cyhalothrin (1259 ng/g $_{\text{bee body weight}}$) could be attributed to the misuse of plant protection products containing them. In addition, fungicides, such as difenoconazole, trifloxystrobin, cyprodinil, and carbendazim were also frequently detected, mainly in the samples analyzed until mid-2019, with concentrations ranging from 5 to196 ng/g$_{\text{bee body weight}}$. Apart from the aforementioned pesticide residues, transformation products of imidacloprid such as imidacloprid olefin and 5-hydroxy imidacloprid, the oxon metabolites of chlorpyrifos and coumaphos, and the metabolites of amitraz (DMF and DMPF) were also detected. Last but not least, in limited occasions, piperonyl butoxide, a known synergist component of pesticide formulations, was also quantified.

The above information reveals that honeybees frequently accumulate a broad range of concentrations of pesticide residues and their transformation products. To this end, this work's results, indicate that the extended use and the subsequent occurrence of pesticides in honeybees, could potentially cause or be implicated in severe health effects to the latter.