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CONCERNS, CHALLENGES & POSSIBLE SOLUTIONS

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A SURVEY ON CHLORPYRIFOS RESIDUES IN SARDINIAN EXTRAVIRGIN OLIVE OILS

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INTRODUCTION

Chlorpyrifos ethyl (CPF) is a broad-spectrum organophosphate insecticide currently used in the defense of many crops. Numerous studies highlight its high-risk toxicological profile [1, 2]. Chronic effects have been reported in professional workers repeatedly exposed to the CPF [3]. Currently, various US associations are putting pressure on the Environmental Protection Agency (EPA) for the complete elimination of CPF-based products [4]. In Europe, the use of CPF is authorized on many crops but not on the olive tree. The Italian Ministry of Health, taking into consideration its high liposolubility and environmental stability, and the consequent risk of chronic exposure in the Mediterranean diet [5], has prohibited its use on the olive crown starting from 12 June 2012, limiting it to the soil using granular formulations. In 2016, Italian official control on pesticide residues in food found CPF above its LOQ on fruit samples (9.2%), vegetables (1%), and olive oil (2.3%) [6]. The aim of this work was to assess whether CPF-based treatments on the soil could leave residues on EVOO. To this end, in 2017-2018 84 EVOO samples coming from an olive-growing vocation area of central-western Sardinia (Montiferru) have been collected and analyzed for 41 active ingredients (a.i.) using a GC-QqQ-MS/MS system and a modified QuEChERS method for extraction [7].

METHODOLOGY

Method validation was carried out by spiking an EVOO blank with 41 pesticides and carrying out the extraction with a modified QuEChERS based on Vazquez *et al.* extraction method [7]. The extracts were analyzed in GC-QqQ-MS / MS with MRM mode (LOQ = 10 µg kg^{-1}). The recoveries were between 70 and 120% for all compounds (Table 1); quantification was performed by matrix calibration curves with correlation coefficients higher than 0.99.

GC-MS/MS specifications

7890 GC System coupled to a 7000 GC/MS Triple Quad (Agilent)

GC parameters: Injection volume: 2 µL MMI injector mode.

Column: HP5MS (30 m x 250 µm x 0.25 µm) Agilent

MRM acquisition mode

Extraction method

5 g of samples and 10 mL of AcN were shaked for 4 minutes and added with 6 g of $MgSO_4$ + 1.5g NaCl + 1.5 g NaCit·2H_2O + 0.75 g NaCit·1.5 H_2O, then centrifugated for 5 minutes at 3500 rpm. 5 mL of upper layer were transferred into a d-SPE tube (EMR-Lipid) for purification, centrifugated for 5 minutes at 3500 rpm and analyzed.

FINDINGS

Acrinathrin	Cyhalothrin I (lambda)	Fenamiphos	Myclobutanil	Tetraconazole
Azoxystrobin	Cyproconazole	Fenarimol	Penconazole	Tolclofos-methyl
Benalaxyl	Cyprodinil	Fenbuconazole	Propiconazole	Triadimefon
Bifenthrin	Deltamethrin	Fludioxonil	Pyridaben	Triadimenol
Bitertanol	Difenoconazol	Fluvalinate	Pyrimethanil	Zoxamide
Boscalid	Ethofenprox	Iprodione	Spirodiclofen	
Bupirimate	Etoxazole	Mepanipirim 2 idrossipropil	Tebuconazole	
Chlorpyrifos	Famoxadone	Mepanipyrim	Tebufenpyrad	
Chlorpyrifos Methyl	Fenamidone	Metalaxyl	Teflutrhin, cis-	

Table 1. Investigated active ingredients.

The method allowed the determination of the a.i. reported in tab. 1. Residues were found on about 20% of samples, almost all of them <LOQ except for three cases in which CPF was found above 10 µg kg^{-1}.

Particularly, Chlorpyrifos was responsible for 16.6% of residues, followed by Lambda cyalothrin (2.4%) and Deltamethrin (1.2%). Only one case showed the presence of two residues at the same time. For all other a.i. no residues were found above the analytical determination limit (LOD = 1 µg kg^{-1}).

CONCLUSIONS

Chlorpyrifos was found above its LOQ on 3.5% of EVOO samples, while 16.6% of samples showed CPF residues including those less than 10 µg kg^{-1}. Our data showed a higher contamination comparing those reported by the Italian Ministry of Health [4]. The survey also showed that the prohibition of the use of CPF-based formulations on the olive crown, does not exclude contaminations transferable to the EVOO, even in very low concentrations. The contact of the drupes with a contaminated soil during the harvest or illicit use of CFP-based products on the foliage could explain the residues found.

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