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Biopesticides Analysis: An Editorial

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It is generally acknowledged that the use of pesticides has resulted in increase in crop yield and helped decisively the agriculture sector. Notwithstanding, a rising concern in recent years about excessive usage of pesticides and their metabolites and impact on nature and human-aquatic organisms health is triggered. In this context organic agriculture is a production system that tends to circumvent the use of synthetic pesticides, fertilizers, and other additives [1]. For this reason natural products have been studied extensively as sources for new pesticides [2]. In US the organic section of the food industry has been emerging strongly and had an average annual sales growth rate of 20% for many years [3]. Even with the economic recession, U.S. sales of organic products, food and non-food, in 2008 were still 17.1% over that of 2007 for a total of $24.6 billion [3].

Biopesticides are certain types of compounds, derived from natural materials such as plants and microorganisms [4]. Among them pyrethrins I and II, cinerins, jasmolins, azadirachtin, spinosad and rotenone are some of the key molecules. Nonetheless the chemical portfolio of these compounds is constantly expanding as evidenced by recent literature. Indicatively, olive mill wastewater extracts which contain mixture of polyphenolic substances have been tested as biopesticides against two pests [5]. In this regard, both public and private bodieson global basis were and are involved in rigorous biopesticide research programmes [6]. The latter was an outcome of negative effects of synthetic origin pesticides and the reported advantages of biopesticides.

The use of biopesticides in the European Union (EU) is controlled by the EEC regulation 2092/91on organic production of agricultural products and indications referring thereto on agricultural products and foodstuffs. The United States Environmental Protection Agency (EPA) has identified three major classes of Biopesticides that are microbial pesticides, plant-incorporated protectants and biochemical pesticides. Additional agents encompassed in this category are entomopathogenic nematodes, parasites, plant extracts and other secondary metabolites [7]. Biopesticides may also be classified according to the target organism such as bioinsecticides, bioherbicides, and biofungicides.

Pyrethrum extract is of utmost importance and exemplifies botanical non-systemic insecticides. It is made from the flower heads of *Chrysanthenum cinerariaefolium* L. and *Chrysanthenumcoccineum* L. and it contains six chemically related esters of chrysanthemic acid (pyrethrin I, jasmolin I, cinerin I) and three esters of pyrethric acid (pyrethrin II, jasmolin II, cinerin II). Finally, piperonyl butoxide is commonly used as synergist compound when it is mixed with some biopesticides (e.g., pyrethrins) to increase toxicity and produce longer residual action, although in general it is not certified to be used on organic crops.

Analysis of biopesticides and organic insecticides can be performed individually or as a broad set with other synthetic organic pesticides or contaminants. High performance liquid chromatography (HPLC) and gas chromatography (GC) in conjunction with various detectors such as diode array detector (DAD) for HPLC or mass spectrometry detector (MSD) in simple or tandem mode for both HPLC and GC are the main techniques used for the determination of Biopesticides [8]. These techniques are in line with the growing demand on rapid and robust analytical methods which can detect low concentrations of analytes. The combination between modern sample preparation procedures and fast GC and HPLC techniques promises unquestionable benefits, such as high throughput, low instrumental operating cost, and higher sensitivity. Noteworthy, the thermal liability (decomposition at elevated temperatures of these compounds) has rendered the HPLC analysis preferable than GC. Ultra HPLC coupled to triple quadrupole tandem mass spectrometry (UHPLC-MS/MS) constitutes a principal analytical technique which emerged rapidly the last fifteen years and is suitable for analysis of residues and organic contaminants in food and environmental samples [9].

Sample preparation steps depend on the matrix of interest. For soil, Solid Liquid Extraction (SLE), Soxhlet, Supercritical Fluid Extraction (SFE), Pressurized Liquid Extraction (PLE), ultrasonic extraction or microwave-assisted extraction have been applied in many extraction endeavors. Recently the well-known QuEChERS technique has been implemented in biopesticides analysis in soils superseding in terms of performance other conventional techniques [9]. Fast and versatile methods with a simple organic solvent extraction step have been also reported in fruits and vegetables [10]. In another case a non-tedious purification step was required for the analysis of azadirachtin in fish tissue involving a maceration step and an ethanolic/methanolic extraction prior to HPLC injection [11]. The latter signifies that biopesticides are comprised of molecules that can be extracted from various matrices by the majority of existing techniques. Thus any update on the extraction techniques/steps which might lead to acceleration of experimental procedures should be carefully considered and applied to biopesticides as well. Apart from chromatographic methods there are scarce applications of sensitive Enzyme-linked Immunosorbent Assay (ELISA) for biopesticides analysis. Indicatively ELISA was applied in 2008 for the determination of toosendanin, a triterpenoid isolated molecule with insecticidal activity.

Therefore, an overview on the analytical techniques and their parameters (sample preparation, validation etc) would be of great interest since the recent tendency on the use of biopesticides should be accompanied by detailed analytical protocols. The latter will aim the sufficient detection of these compounds assuring low levels of detection which sometimes are important for the evaluation of possible biological actions that these compounds might elicit, including their insecticidal activity.

The sensitivity in detection is also related to the Maximum Residue Limits (MRLs) of these active substances. MRLs are defined

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by European Food Safety Authority (EFSA) as the upper legal levels of a concentration for pesticide residues in or on food or feed based on good agricultural practices (GAPs) and to ensure the lowest possible consumer exposure [12]. Hence analytical techniques constitute the backbone on which control of biopesticides is supported and GAPs-if adopted-are reflected. Therefore research community should be aware of new emerging techniques which set basis for a more efficient extraction and analysis of biopesticides in various compartments.

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