

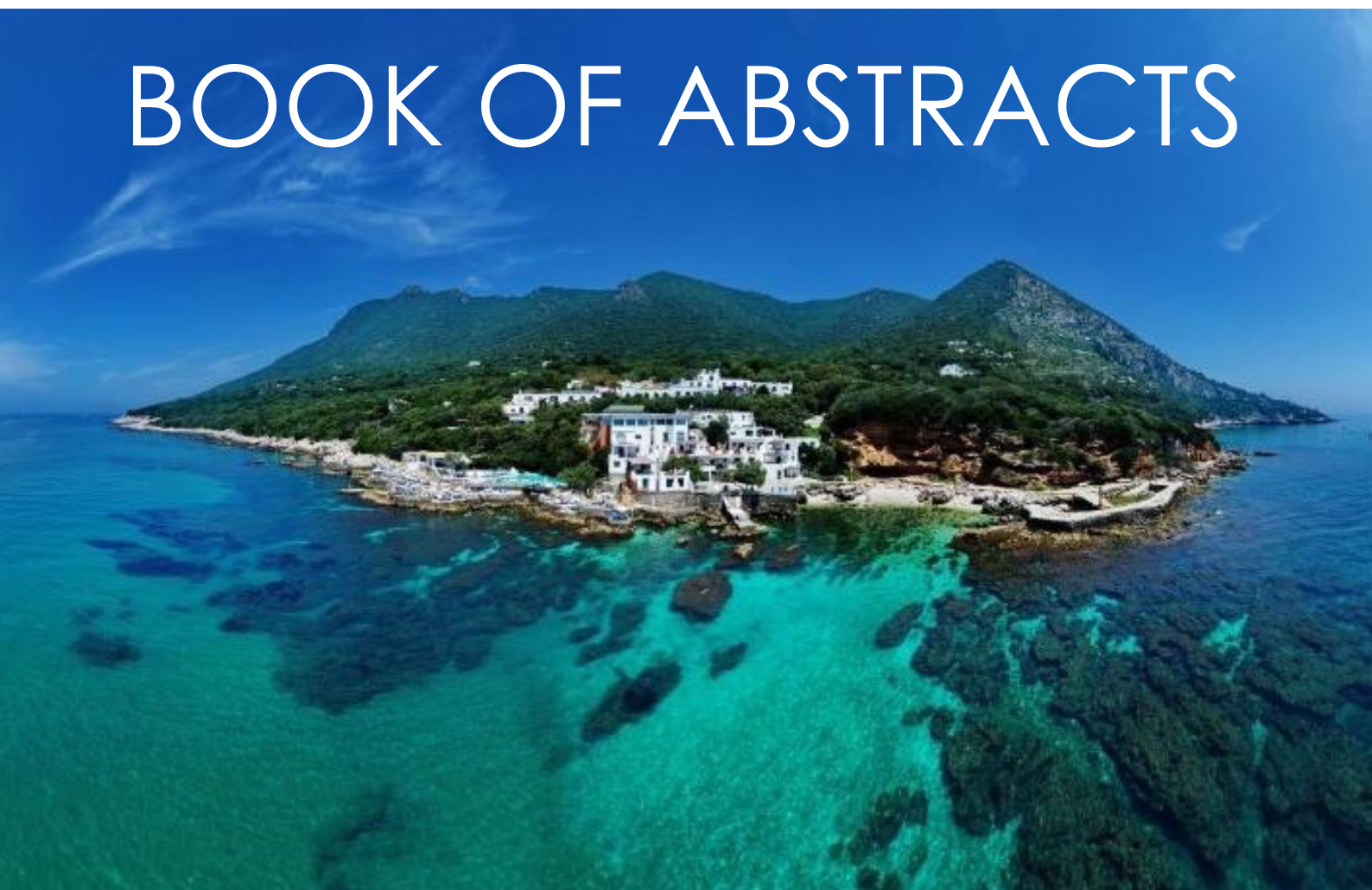
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BOOK OF ABSTRACTS



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Characterization of co-formulants in plant protection products by LC-Q-Orbitrap-HRMS using a polymeric stationary phase

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Co-formulants are part of the mixture contained in plant protection products (PPPs) that serve to improve their efficiency and stability. These are mainly surfactants, antifoam agents, solvents or wetting agents and can make up more than 50% of a product formulation. Many of these substances possess a high toxicity and others may increase the toxic effect of the active ingredient. However, there is no adequate regulation for these types of substances. In 2021, the European Commission established a list of "unacceptable co-formulants", which contains 144 substances that must be banned due to their dangerous properties. Even so, many of the co-formulants used in PPPs are unknown as they are not reported on the product label. In this study, a new method for the identification of co-formulants in 20 plant protection products (PPPs) was carried out using a polyhydroxy methacrylate based stationary reversed phase. These samples were analyzed by liquid chromatography coupled with Quadrupole-Orbitrap high-resolution mass spectrometry (LC-Q-Orbitrap-HRMS) in full-scan Mass spectrometry and data-dependent acquisition (ddMS²) modes. A total of 92 co-formulants were tentatively identified in these formulations by two strategies of analysis (non-targeted and unknown). Among them, 48 compounds were detected for the first time in the selected PPPs. These compounds may be largely classified in anionic surfactants, such as sulfates of ethylene glycol alkyl ethers and alkyl benzenes, amphoteric surfactants, and other non-ionic surfactants, including; alkyl phenoxyethanols, alkyl alcohols, ethoxy ethyl amines, ethanol amines, amino alcohols, ethylene glycol ether, fatty amides, fatty acids such as oleic acid and other compounds. Furthermore, the methodology based on LC-HRMS has allowed for the confirmation as well as the quantification of twelve compounds after the acquisition of standards. The most concentrated co-formulant was the anionic surfactant dodecylbenzenesulfonic acid, whose highest content was obtained in 'Score 25' sample (6.87%, w/v). Furthermore, triethyleneglycol mono methyl ether, 4-sec-butyl-2,6-di-tertbutylphenol, 1-ethyl-2-pyrrolidone, sorbitan monostearate, 2,6-dimethylaniline, palmitamide and N-lauryldiethanolamine were quantified for the first time in these products. Among them, 1-ethyl-2-pyrrolidone is classified as very toxic and has a median lethal dose LD₅₀ of 1.44 g/kg, which is lower than certain active ingredients used in PPPs such as chlorantraniliprole (2.56 g/kg) and tebuconazole (3.12 g/kg). Therefore, the content of this type of co-formulant should be controlled to avoid adverse effects on human health. Hence, polyhydroxy methacrylate based stationary phase increased the identification of new co-formulants in PPPs, being complementary to conventional C18. This strategy could be applied in future studies to estimate potential co-formulant residues from PPPs applied to crops.

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