Título: ¿AGRICULTURE-RELATED ORGANIC CONTAMINANTS: OCCURRENCE IN EDIBLE CROPS, POTENTIAL TRANSFER FROM RECLAIMED WATER USED FOR IRRIGATION AND BIOREMEDIATION APPROACHES¿

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Resumen: This doctoral thesis aims at providing novel analytical tools for the environmental control of CECs in waters and crops and generating new knowledge about i) the occurrence and fate of CECs in the agricultural environment, and ii) the efficiency of bioremediation approaches to remove pesticides from water.
Firstly, analytical methodologies for the determination of up to 42 pesticides in five different plant origin food matrices (viz. corn, grapes, alfalfa, olives, and sunflower seeds) were developed and validated reaching high sensitivity and selectivity. Moreover, Maximum Residue Levels (MRLs), the legal limits for pesticide residues in food and feed established by the Regulation (EC) 396/2005 are, in most cases, in the range of the low µg/kg, enforcing analytical methodologies to reach limits of detection below these values. The methods developed, based on QuEChERS extraction and liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) determination, allowed detecting most of the target pesticides below their corresponding MRLs. Moreover, to the

authors¿ knowledge, these were the first analytical methodologies described for eleven (sunflower seeds), eighteen (olives), five (corn), thirteen (grapes), and twenty-four (alfalfa) pesticides in each indicated matrix. The analysis of real samples harvested at different locations along the Iberian Peninsula revealed the presence of a few insecticides and herbicides, some of them included in the PAN International List of Highly Hazardous Pesticides and/or currently banned for use in the European Union.

However, many other CECs may be occurring in the agricultural environment, such as those coming from the reclaimed water used for irrigation. In this context, the need of targeting the right substances at the various environmental and food matrices is clear. To address this need, a wide-scope suspect screening workflow and a prioritization procedure was developed and applied to identify the most relevant contaminants present in a reclaimed water-based irrigation system from a specific agricultural area in Catalonia, Spain. More than one hundred CECs were found in the water used for irrigation. Based on their occurrence and ecotoxicity, CECs were prioritized in the investigated area. This approach allows a more rationale selection of the relevant organic contaminants than classical approaches, normally based on the CEC chemical class, in force legislation, toxic potency, physical-chemical properties, or volumes of usage, that may result in a CEC list that deviates from the real contamination footprint in a specific area. Moreover, the approach developed can be easily implemented in any location to detect site-specific pollutants that could be missed with the national or European regulations, rationally design monitoring and attenuation programs, and support legislators and water managers in their way to extend the safe application of water reuse.

Bearing in mind that CECs are not completely removed during conventional wastewater treatment, it is crucial to evaluate alternative treatment technologies, such as bioremediation technologies. In this doctoral thesis, the feasibility of white-rot fungi Trametes versicolor and microalgae-based systems to remove selected pesticides (bentazone, acetamiprid, and propanil) was investigated. The removal efficiencies were assessed, and the biodegradation pathways characterized, by identifying the TPs formed in each process using an UPLC-HRMS non-target screening approach. The degradation processes involved did not end up in the complete mineralization of the compounds (with the exception of propanil) and 19 TPs were formed during bentazone biodegradation by Trametes versicolor (eight of them tentatively identified), and two and four TPs were identified for propanil and acetamiprid, respectively, during the microalgae-based treatment. QSAR-based ecotoxicological risk assessment of the TPs generated during the biodegradation processes revealed a few TPs, in the case of propanil and bentazone, to be more toxic for the aquatic environment than the parent compound.

Although further research is needed in this field, it is clear that there is not a unique wastewater treatment technology that efficiently removes all CECs and, thus, the combination of complementary treatments is suggested to remove a wider spectrum of CECs. In this context, bioremediation approaches, such as those studied in this doctoral thesis, have shown a good performance in terms of CEC removal, added to the benefits of using nature-based treatment technologies, and present a promising future to be implemented at real scale.

CEC TPs formed during water treatment or natural biotic and abiotic processes (hydrolysis, biodegradation and photodegradation reactions) are still unknown to a large extent and are relevant components of the CEC mixtures in the environment. Their identification and their inclusion in spectral libraries and compound databases are critical to advance in the characterization of the environmental contamination footprint using wide-scope screening approaches based on HRMS technologies.