ABSTRACT

In recent years, fate, occurrence and potential adverse effect of emerging contaminants (ECs) in the environment have received an increased attention by scientific community. The ECs are a broad category of chemicals, mainly organic compounds, that are not currently covered by existing regulations but they may be candidates for future regulation, as they may be potential threats to human health and environmental safety. The ECs are mainly substances of anthropogenic origin, introduced continuously into the environment in large quantities and distributed ubiquitously in the ecosystem, due to their wide consumption. Recent studies have indicated that most of them are environmentally persistent, bioactive, and certain have a high potential for bioaccumulation. In literature data are still too few regarding their toxicity, distribution and fate and consequently, it is not still possible to assess their real impact on the environment and on human health. For these reasons it is important to design analytical procedures for monitoring specific environmental compartments and to provide the basis for drawing conclusions about the occurrence, the persistence and hazard of ECs in the environment. Currently, the main objectives of the research and monitoring of ECs are the development of accurate and sensitive analytical methods able to simultaneously analyze multiple chemical classes of ECs in different environmental compartments with different complexity. In line with these requirements, in this PhD project, three multi-residue methods were developed for the determination of three different classes of ECs in different and complex environmental matrices.

The pharmaceutical and personal care products (PPCPs) were the first studied class of ECs and a multi-residue method for their determination in different environmental matrices has been developed. The main challenge of this work was to determine simultaneously twenty-two selected PPCPs belonging to different families. The proposed analytical procedure combines solid phase extraction (SPE) and dispersive liquid-liquid microextraction techniques (DLLME) to perform the extraction (water)/purification (solid matrices) and the ultra-concentration of target PPCPs. An UHPLC-MS/MS multi-residue method was developed for the sensitive and selective quantification

and confirmatory analysis of the target analytes with different chemical characteristics. Finally, the proposed methodologies were validated for different aqueous matrices (tap water, sea water, river water and wastewater).

Subsequently, a novel and advantageous analytical procedure, suitable to investigate the presence of eight Organophosphate esters (OPEs) in sludge samples, was developed. Matrix solid-phase dispersion (MSPD) was selected as an extraction technique considering its low cost, reasonable selectivity and previous successful applications dealing with emerging compounds extraction from sludge. OPEs were determined by LC using, for the first time, a hybrid quadrupole time-of-flight MS system, as an alternative to triploquadrupole instruments. Furthermore, the information contained in accurate, scan MS spectra were used to screen the presence of additional OPEs, which had not been included in the quantitative method, in sludge samples.

Finally, a multi-residue method was developed for environmental monitoring of 18 analytes, corresponding to a wide range of drugs of abuse (DAs) and some of their major urinary metabolites, in wastewater samples. The proposed analytical methodology combines the use of mixed-mode solid phase extraction (Oasis MCX) with fractioned elution strategy, to improve the sensitivity of the overall procedure. A selective UHPLC-MS/MS method was developed for a quantitative and confirmatory analysis and the stable isotope dilution assay (SIDA) was used to compensate the matrix effects and losses of DAs during the sample preparation, ensuring a high accuracy and precision to the method. Furthermore, this method was applied to wastewater samples and it was used as tool to estimate the consumption of DAs in Avellino province by sewage epidemiology approach.