

NON-TARGET SCREENING OF ORGANIC MICROPOLLUTANTS WITH A DEVELOPED LC-HRMS-BASED WORKFLOW

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Wastewater contains a high number of organic micropollutants and transformation products of environmental concern. Recent approaches, combining methodologies based on target and suspect screening (for suspected substances based on prior information but with no reference standard) are important for the comprehensive characterization of environmental samples. Nevertheless, samples still contain many chromatographic peaks which do not correspond to substances included in target and suspect screening lists. These substances may be potentially relevant (e.g. due to their concentration or potential effects) and thus the identification of selected non-targets is important. However, full identification of unknown compounds is often difficult and there is no guarantee of a successful outcome.

The first objective of the present work was the development of an integrated workflow based on liquid chromatography – quadrupole-time-of-flight mass spectrometry (LC–QToF-MS) to detect and identify unknown organic contaminants in wastewater. Relevant peaks (not present in the blank and the target and suspect lists) were selected based on the intensity and the presence of distinctive isotopic patterns (the most relevant substances with reasonable identification possibilities). For the selected peaks, the most plausible molecular formula(s) were determined by applying thresholds of mass accuracy and isotopic pattern. Then, a deep evaluation of the MS/MS spectra was conducted, using both MS libraries and *in silico* fragmentation platforms (such as MetFusion) to find candidates. To assess the plausibility of the candidates, a chromatographic retention time prediction model was also applied as well as commercial importance criteria such as the number of references, data sources or patents. The developed workflow was successfully applied to wastewater samples collected from the wastewater treatment plant of Athens (Greece). Several compounds in both positive and negative ionization mode were tentatively identified and in some cases confirmed. Among these compounds, the sulfonated surfactant 2-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]ethyl hydrogen sulfate was first identified and then other homologues, which have not been previously reported in wastewater. A high number (29) of tentatively identified surfactants of different types (e.g. Linear Alkylbenzyl Sulfonates (LAS), PolyEthylene Glycols (PEGs)) were among the most intense peaks. In view of these results, the presence of surfactants, originally found as non-targets, was studied in detail through retrospective suspect screening by the use of an extensive surfactants database [1] in order to obtain a broader picture on the occurrence of these compounds in wastewater. Up to 91 compounds were detected, with SulfoPhenyl Alkyl Carboxylic Acids (SPACs) and Alkyl Ethoxy Sulfates (AES) being the most frequently detected classes.

Keywords: Non-target, High resolution mass spectrometry, QTOF, emerging pollutants, transformation products, surfactants.

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