SUSPECT AND NON-TARGET SCREENING OF ORGANIC MICROPOLLUTANTS IN WASTEWATER THROUGH THE DEVELOPMENT OF A LC-HRMS BASED WORKFLOW

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A large number of organic contaminants and related transformation products (TPs) are present in wastewaters. Target analysis only allows the detection of a very small fraction of these substances, due to the inability to obtain standards for all that substances and the ignorance of the existence of many of them.

Recent advances in high resolution mass spectrometry (HRMS) have opened up new windows of opportunity in the field of complex samples analysis [1]. The application of suspect and non-target screening methods allows the tentative identification of a much larger amount of pollutants and focus efforts on the most relevance substances in terms of environmental concern. However, a balance between extensive target analysis and screening methods is needed.

The aim of the present work is the development and application of an integrated workflow based on liquid chromatography coupled to a quadrupole-time-of-flight mass spectrometer (LC–QToF-MS) to detect suspected and formerly unknown organic contaminants in wastewater.

Suspect screening was carried out through the set-up of a large in-house data base including the molecular formula of more than 7000 relevant organic pollutants and TPs (which were not present in our existing target methods). The tentative identification of these compounds was based in the evaluation of criteria such as blank signal presence, mass accuracy or isotopic pattern. Moreover, the chromatographic retention time plausibility (using prediction models) and MS spectra comparisons were also considered. According with the aforementioned criteria, few suspect compounds were tentatively identified in wastewater samples from the wastewater treatment plant (WWTP) of Athens, the largest in Greece.

Full identification of unknown compounds is often difficult and there is no guarantee of a successful outcome. After optimizing the peak peaking procedure using molecular features algorithm, relevant peaks 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, isotopic pattern and even commercial importance through the use of the Seven Golden Rules software [1].

A deep evaluation of the MS spectra was performed for these peaks, using both data bases (e.g. mass bank) and *in silico* fragmentation software (e.g. Metfrag) to find candidates. Chromatographic retention time prediction models were also applied to assess the plausibility of the candidates. This approach allows the obtaining of plausible candidates for most of the selected peaks and the tentative identification for some of them in the evaluated samples.

References

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