

# Identification of organic micropollutants transformation products in the aquatic environment

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## *Abstract*

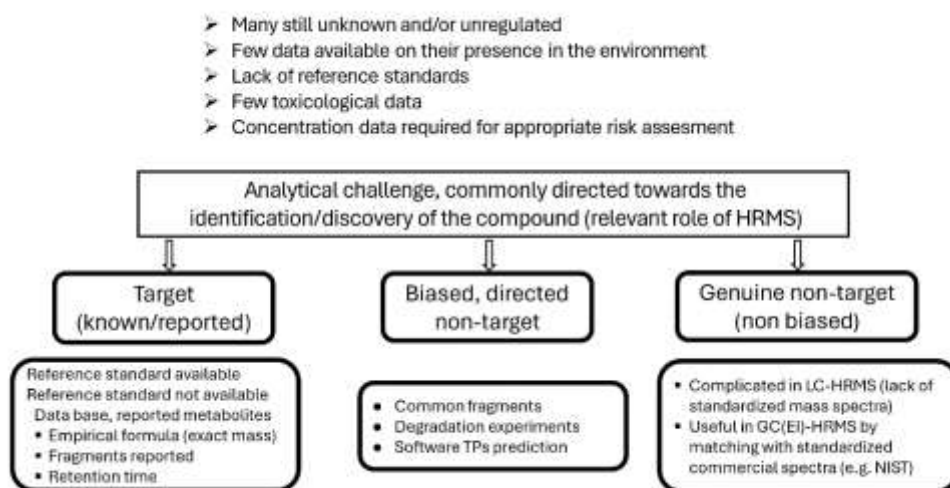
The presence of organic micropollutants in aquatic environments is a topic of current concern, as reflected by the large number of studies reporting the presence of these compounds in environmental and wastewaters around the world. However, most monitoring findings only report data on parent compounds, while their transformation products (TPs) are not commonly included in analysis. TPs include human or animal metabolites, and many other compounds resulting from different processes in the aquatic environment, such as photodegradation, hydrolysis, biodegradation. The investigation of TPs in the aquatic environment is a hot topic, but an analytical challenge as well, due to the huge number of TPs that may be present in waters, their wide occurrence, and the analytical difficulties for their identification (Ibáñez, 2021). In this conference, the potential of High-Resolution Mass Spectrometry (HRMS) coupled to Liquid Chromatography (LC) is explored for the identification of TPs of organic micropollutants. The acquisition of accurate-mass full-spectrum data and the high resolving power of HRMS, combined with the previous chromatographic separation of matrix components, are essential for their identification, both as reported compounds -in a target approach- and as unknown compounds -in a non-target approach. Considering the polar nature of most TPs, LC offers better performance than GC in this field. The identification of TPs is not only required for realistic overview of the actual impact of OMPs in the aquatic environment. It is of great relevance in degradation experiments too (e.g. using AOPs), in order to perform comprehensive studies obtaining information on both the disappearance of the parent compounds and the degradation products formed along the process.

## **INTRODUCTION**

The presence of organic micropollutants (OMPs) in aquatic environments is a matter of current concern widely described in the last decade. OMPs include many different compound families, with pesticides, personal care products, pharmaceuticals, and drugs of abuse among the most widely investigated. Many studies have addressed the presence of these compounds in environmental and waste waters around the world (Botero, 2018; Lopez, 2022; Nieto-Juarez,

2021; Wilkinson, 2022), even in pristine areas such as Amazonia or Antarctic (Fabregat-Safont, 2021; Hernandez, 2019). However, most monitoring studies are focused on the parent compounds, while transformation products are included only in a few cases. The fact that many compounds are excreted in urine and/or faeces after human or veterinary consumption as a mixture of parent compound and metabolites (e.g. pharmaceuticals, drugs of abuse) implies that many metabolites are present in waters. In addition, OMPs suffer different transformation processes in the aquatic environment, such as photodegradation, hydrolysis or biodegradation, notably increasing the number of potential contaminants in waters, including metabolites and transformation products. This means that parent compounds are just the “tip of the iceberg” of the overall problem of organic micropollutants in the aquatic environment.

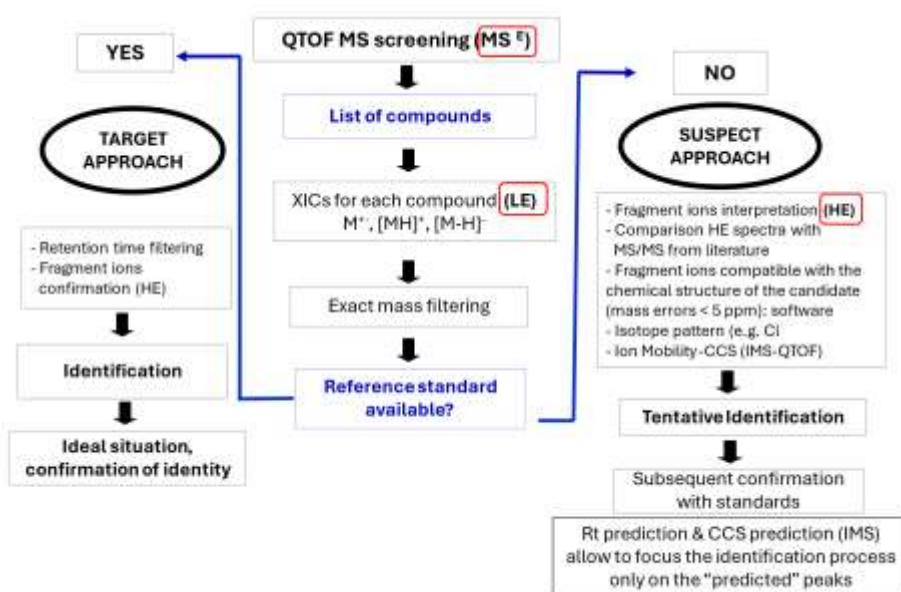
Taking into account all these considerations, the investigation of OMPs TPs in the aquatic environment is a hot topic and an analytical challenge (Ibañez, 2021) (**Figure 1**). The main difficulties come from their identification. One of the major limitations is the lack of reference standards, which impede the confirmation of the identity of the compounds detected in samples. It must be considered that the number of potential TPs in the overall aquatic scenario can be extremely high, and therefore is impossible to have available thousands of reference standards in a laboratory.



**Figure 1.** Investigation of TPs in environmental samples: analytical approaches

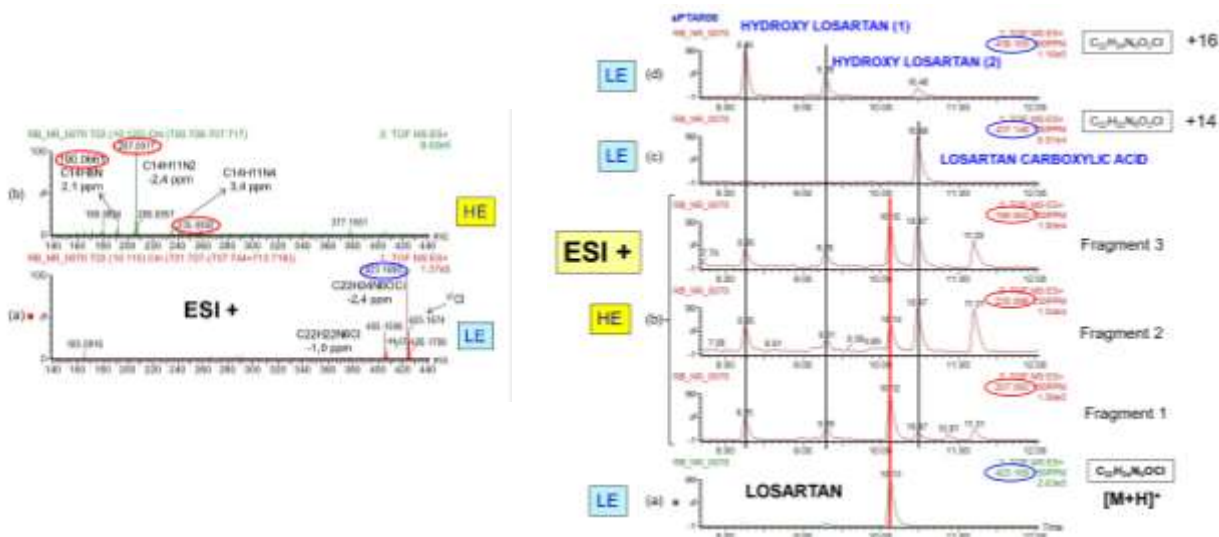
Many TPs are still unknown and/or have been previously reported as tentatively identified but not fully confirmed using reference standards. This means that their discovering/elucidation is commonly the main challenge; their quantification is also very problematic, except for a few

reported/known TPs whose reference standards are commercially available. The role of LC-HRMS is essential in this field. By one side, LC is required for appropriate separation of TPs and sample-matrix components in the samples, due to the medium-high polar nature of most TPs. By other side, HRMS allows the obtention of accurate-mass full-spectrum data at reasonable sensitivity. This information is essential for the reliable identification of TPs. **Figure 2** shows the detection/identification workflow based on HRMS, specifically using QTOF under MS<sup>E</sup> mode.



**Figure 2.** Detection and identification workflow of TPs using HRMS

The analytical investigation of TPs can be addressed by different ways (**Figure 1**): 1) target/suspect approach, when there is a list of reported compounds to be searched independently of reference standards are available (target) or not (suspect); 2) biased/directed non-target, when the investigation of TPs is made in a limited scenario, for example searching TPs in environmental samples for certain compound or searching TPs formed in degradation experiments of selected parent compounds; 3) genuine-non-target approach, when searching is made for any TPs present in samples without restrictions. In this conference, different strategies for investigation of TPs in waters are presented, including illustrative examples of real-world positive cases, and recent improvements such as the use of Ion Mobility in QTOF MS based analysis. Emphasis is made on the strategy of searching for common fragments between TPs and the parent compound (*Ibáñez, 2017*) (**Figure 3**).



**Figure 3.** Discovering of losartan TPs in urban wastewater. Top: Low energy and high energy mass spectra of losartan standard in ESI+. Bottom: Extracted ion chromatograms of a wastewater sample at m/z losartan ion fragments, illustrating the presence of TPs in sample

## CONCLUSIONS

HRMS coupled to LC is nowadays the technique of choice for detection and identification of TPs of OMPs. Its high resolving power together with the large amount of useful information provided (accurate-mass full-spectrum acquisition), allows the reliable identification of TPs even without reference standards (tentative identification). LC-HRMS can be applied to environmental waters making use of different target and non-target approaches, using (Q)TOF and Orbitrap analysers. Investigation of TPs formed in degradation experiments under laboratory conditions (e.g. AOPs) is another area of interest (*Serna-Galvis, 2019*). In these studies, the use of common fragmentation pathway between parent compound and TPs is one of the key approaches applied.

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