

A Metabolomics Approach Towards Identification of Unknown Emerging Pollutants in Marine Waters

Huysman Steve¹, Vanryckeghem Francis², Demeestere Kristof² and Vanhaecke Lynn^{1,3}

¹ Department of Veterinary Public Health and Food Safety, Ghent University, Ghent, Belgium

² Department of Green Chemistry and Technology, Ghent, Belgium

³ Institute for Global Food Security, School of Biological Sciences, Queen's University, Belfast, United Kingdom

E-mail: Steve.Huysman@UGent.be and Lynn.Vanhaecke@UGent.be

1. Introduction

The potential prevalence of emerging organic micropollutants in the aquatic environment has become a significant risk for public and ecological health, which is stressed by different regulatory bodies. Despite this, legislation so far mainly focuses on a few priority pollutants, thereby missing a substantial fraction of the water exposome (i.e. known and unknown compounds). Hence, the occurrence and identity of most compounds in the exposome remains unexplored. Therefore, this study presents a novel analytical strategy for elucidating structurally related emerging organic pollutants in the aquatic environment.

2. Approach

In-house developed and validated UHPLC-HR-Q-Orbitrap-MS methods targeting 70 steroids (i.e. 32 androgens, 14 oestrogens, 13 progestins and 11 corticosteroids; *Huysman et al., 2017*) and 27 plasticizers (i.e. 7 alkylphenols and 20 phthalates; *Huysman et al., 2018 (submitted)*) were used to enable the detection of unknown emerging organic pollutants. To elucidate typical fragmentation profiles and identify characteristic fragments of the above-mentioned chemical pollutants, the target standards were respectively fragmented at 35 and 20 eV.

To demonstrate the applicability of the novel analytical strategy, 24 seawater samples (obtained from the Belgian Part of the North Sea, BPNS) were screened in full-scan at a resolution of 70,000 FWHM. Thereafter, unknowns were fragmented, using parallel reaction monitoring, and tentatively identified using the tier 3 confidence level (according to the Chemical Analysis Working Group & Metabolomics Standards initiative).

3. Results and discussion

Optimal collision energy (CE) of 35 eV (steroids) and 20 eV (plasticizers) allowed the simultaneous detection of the pseudo-molecular ion and its associated fragments. Lower collision energies caused little to no fragmentation of pseudo-molecular ions, whereas higher collision energies resulted in the absence of the pseudo-molecular ions. As a result, typical fragmentation profiles were obtained for the androgens, oestrogens, progestins, corticosteroids (Figure 1), alkylphenols and phthalates.

To this end, data of the full-scan analysis were subjected to the extraction of relevant unknown components (Compound Discoverer 2.1), which resulted in the detection of 1292 unique components. To elucidate the chemical identity of these unknowns, each extracted component was fragmented. The generated fragments were screened – using a newly written Python code – on their agreement with characteristic fragments and neutral losses obtained from the target standards. In total, 13% (n=173) of the unknowns present in water could be tentatively identified, i.e. 125 steroids, 21 alkylphenols and 27 phthalates, at a confidence level of Tier 3. Finally, during untargeted screening of seawater samples, all target analytes were successfully detected, confirming that fragmentation occurred also in a salty aqueous matrix.

4. Conclusion

In conclusion, fragmentation of target compounds lead to a typical profile for steroids and plasticizers. The latter was used for the successful tentative identification of 173 unknown compounds (in seawater samples obtained from BPNS) with a backbone related to the target emerging organic pollutants.

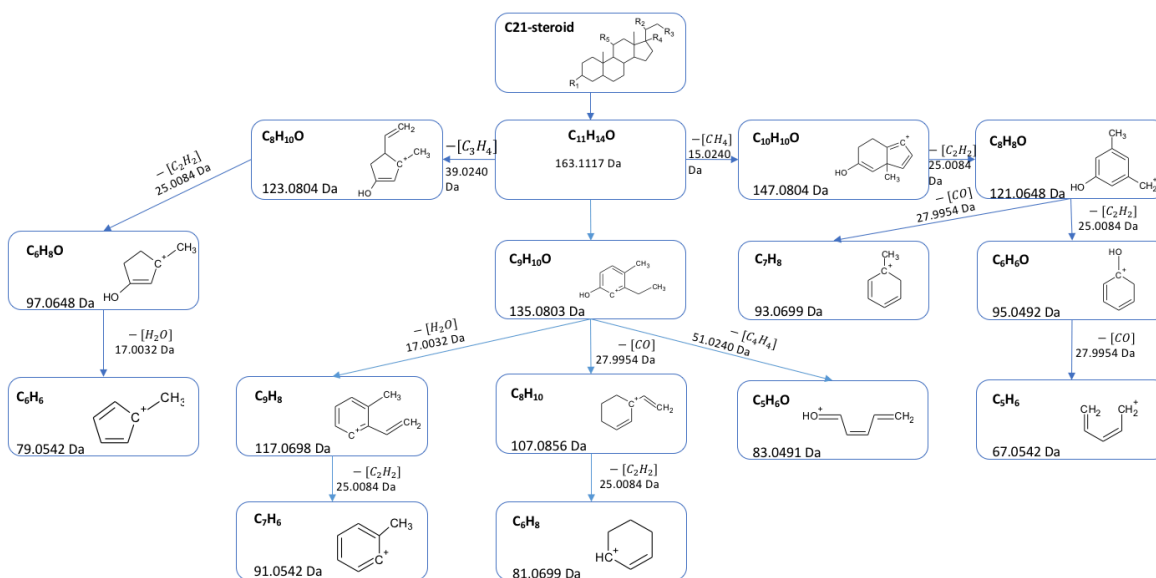


Figure 1. The observed fragmentation patterns for corticosteroids in ultrapure water at a CE of 35 eV.