

TARGETED, SUSPECTED & NON-TARGET SCREENING WITH HIGH RESOLUTION MASS SPECTROMETRY IN THE MARINE ENVIRONMENT: READY TO GO?

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Introduction

Many organic micropollutants, such as pharmaceuticals, pesticides, **natural and synthetic steroids** have received special attention because of their omnipresence in the environment. Frequently, these compounds find their way to the environment as **water pollutants**, whether or not metabolised or degraded, resulting in some constraints towards environmental monitoring. While triple quadrupole analysers currently enable only a predefined list of compounds in samples, high resolution mass spectrometry (HRMS) make it possible to detect a **virtually unlimited** number of compounds in a single run without preselection. Therefore, an in-house validated UHPLC-HRMS method was used for screening the marine environment on steroidal EDCs. This study included the quantification of **70 targeted** steroidal EDCs, and on top of that the **suspected** screening of 225 EDCs and a **virtually unlimited** number of unknown compounds.

Objectives

Challenges:

- Micropollutants present at **sub ppb-concentrations**
- Different biotic and abiotic processes result in a wide range of **known and unknown** transformation products of the micropollutants

Goals:

- Evaluating an **environmental omics** approach using HRMS
- **Screening** the marine environment on steroidal EDCs
- Performing 3 analytical approaches: targeted, suspected, and untargeted analysis
- Composing a **relevant suspected database**
- Assessing the impact on the marine environment, i.e. toxicity and **potential harm**



Materials & Methods

Instrumentation

Targeted screening: 70 EDCs

- Accurate mass (m/z)
- Isotope profile (¹³C/¹²C-ratio)
- Retention time (min)

(X-Callibur™)
(Huysman et al., ACA, 2017)

Suspected screening: 225 conjugates of the EDCs/*ToxFinder™*

- Accurate mass (m/z)
- Isotope profile (¹³C/¹²C-ratio)

Untargeted screening: unknown compounds/*Sieve™* & *Simca™*

- Accurate mass (m/z)
- ⇔ Online database Pubchem & Chempidder

Fig 1. UHPLC-HRMS.

Sampling, pre-treatment & extraction

Grab samples: 2.5 L

Filtering & pH adjustment to 3

Loading on hydrophillic DVB Speedisk™

Elution with 5 mL ACN & 5 mL of 0.1% FA in ACN

Evaporation & centrifuging

Reconstitution to 150 µL (40/60 v/v% CH₃OH/H₂O)

- Monitoring the Belgian Part of the North Sea (BPNS)
- 2 sampling campaigns, i.e. fall 2016 (1-4) & winter 2017 (5-7), at 4 different sampling locations:

- Harbour of Oostende: (1) & (5)
- Oostende Open Sea: (2) & (6)
- Harbour of Zeebrugge: (3) & (7)
- Zeebrugge Open Sea: (4)

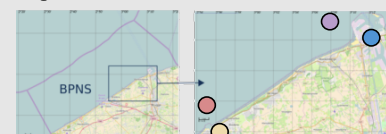


Fig 3. The different sampling locations that were monitored in the BPNS.

Fig 2. Optimised extraction protocol for grab samples obtained from the marine environment.

Results

Targeted screening

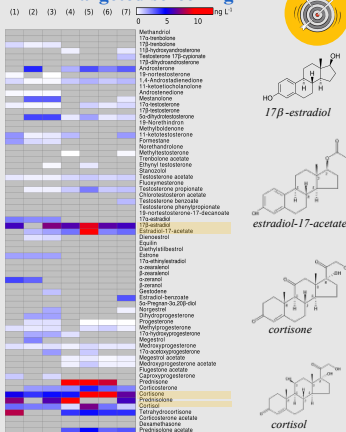


Fig 4. Heatmap illustrating the occurrence of 43 targeted EDCs.

Suspected screening

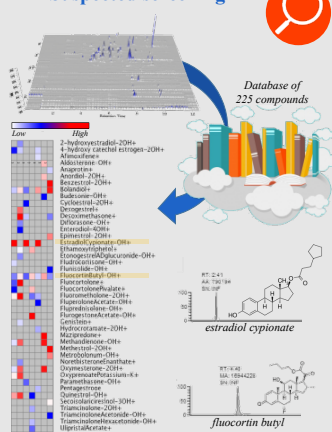


Fig 5. Suspected screening enabling the detection of 44 unique suspected EDCs.

Untargeted screening

Multi-variate analysis

- Scaling: pareto
- Transformation: log
- Compound Intensities > 10⁶

Legend

- (1) & (5): 51.2263°, 2.9357°
- (2) & (6): 51.2468°, 3.1136°
- (3) & (7): 51.3401°, 3.2003°
- (4): 51.3605°, 3.1136°
- Quality control

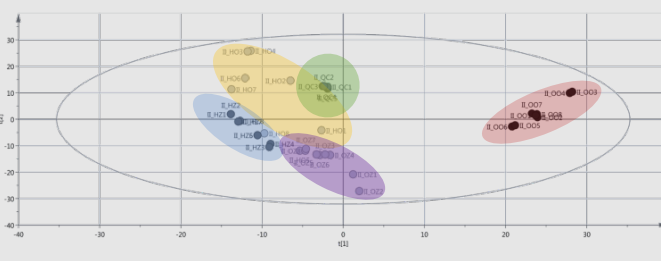


Fig 6. PCA-X Plot displaying the untargeted analysis of different sampling locations and periods in the positive ionization mode.

Conclusion

The marine environment was successfully screened using an environmental omics approach:

- **Targeted** screening: 43 different steroidal EDCs were quantified
- **Suspected** screening: 44 unique suspected EDCs were detected
- **Untargeted** screening: enabled environmental molecular differences according to the sampling locations



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