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How solid phase extraction conditions affect suspect and non-target screening for the evaluation of surface water contamination

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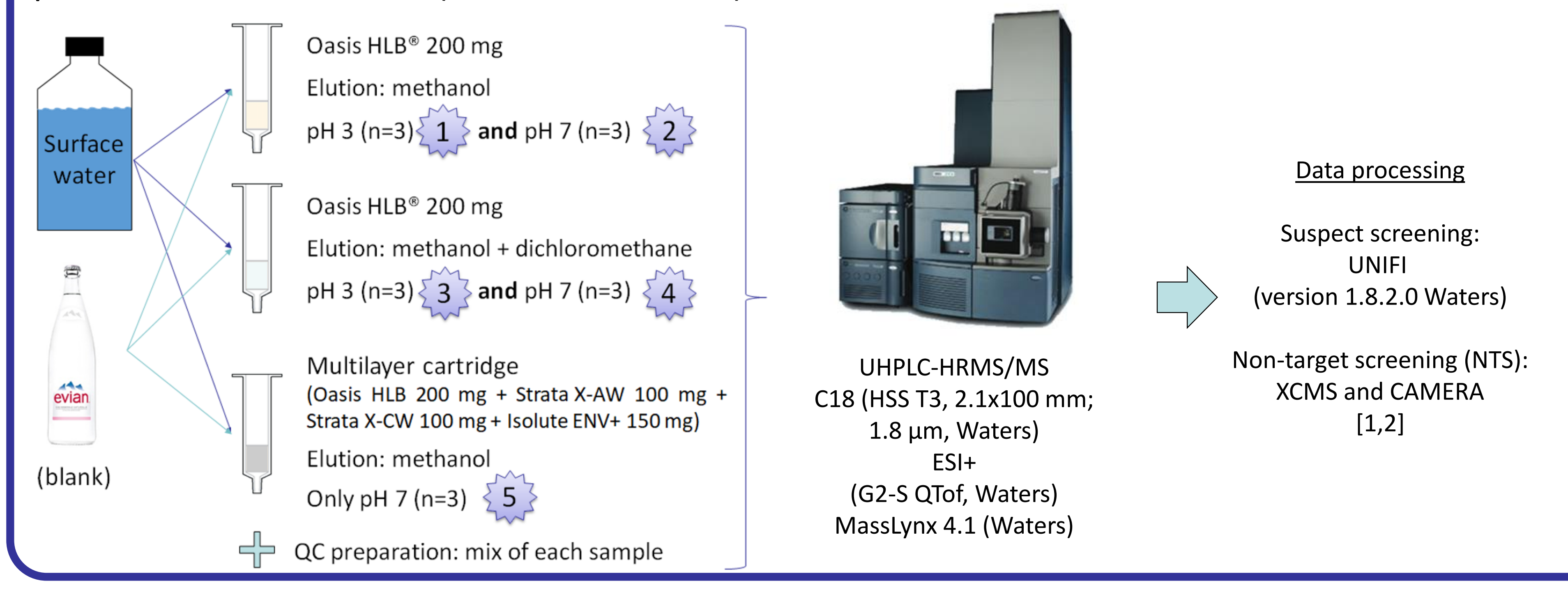
Introduction & Objectives

Identifying organic contaminants present at trace level concentration in aquatic environments is of major concern for water quality monitoring. Suspect and non-target analyses are increasingly applied to study the presence of emerging contaminants and their transformation products in waters. The sample preparation is the first crucial step to be optimized before using suspect and non-target-screening (NTS) approaches for qualitative evaluation of water contamination by organic compounds.

As part of the action of AQUAREF (French reference laboratory for environmental monitoring in the Water Framework Directive), the main objective of our study was to assess the influence of sample preparation on suspect and non-target screening results.

Material & Methods

A **surface water sample** collected in a French river (Gier, Rhône, France) was extracted following five different **solid phase extraction** (SPE) methods. Analytical blanks, SPE blanks, and quality controls (QC) were also prepared. **Chemical fingerprints** were generated by ultra-high performance liquid chromatography coupled to high resolution mass spectrometry in positive ionization mode (UHPLC-HRMS/MS).



Oasis HLB® 200 mg
Elution: methanol
pH 3 (n=3) ① **and** pH 7 (n=3) ②

Oasis HLB® 200 mg
Elution: methanol + dichloromethane
pH 3 (n=3) ③ **and** pH 7 (n=3) ④

Multilayer cartridge
(Oasis HLB 200 mg + Strata X-AW 100 mg + Strata X-CW 100 mg + Isolute ENV+ 150 mg)
Elution: methanol
Only pH 7 (n=3) ⑤

QC preparation: mix of each sample

UHPLC-HRMS/MS
C18 (HSS T3, 2.1x100 mm; 1.8 µm, Waters)
ESI+
(G2-S QTof, Waters)
MassLynx 4.1 (Waters)

Data processing

Suspect screening:
UNIFI
(version 1.8.2.0 Waters)

Non-target screening (NTS):
XCMS and CAMERA
[1,2]

The data were processed to perform suspect screening and NTS.

Suspect screening was performed by comparison of the data with a list of **28 compounds**, including compounds such as pesticides, pharmaceuticals, sweeteners. Suspect compounds screening was performed by comparison of their measured and theoretical monoisotopic mass $[M+H]^+$ and their fragments (Δ = ± 5 ppm).

To evaluate by **non-target analysis** the **SPE methods repeatability, informativity, and specificity**, the signals satisfying the following criteria were retained:

- Quality control (QC) signals coefficient of variation (CV) <30% (⇔analytical repeatability assessment is good if >70% of the signals in all QC injections have a CV <30% [3]) (n=11)
- SPE signals CV <30% (extraction repeatability, n=3 per method)
- Signal-to-noise ratio (S/N) compared to analytical blank > 3
- S/N compared to SPE blanks > 3

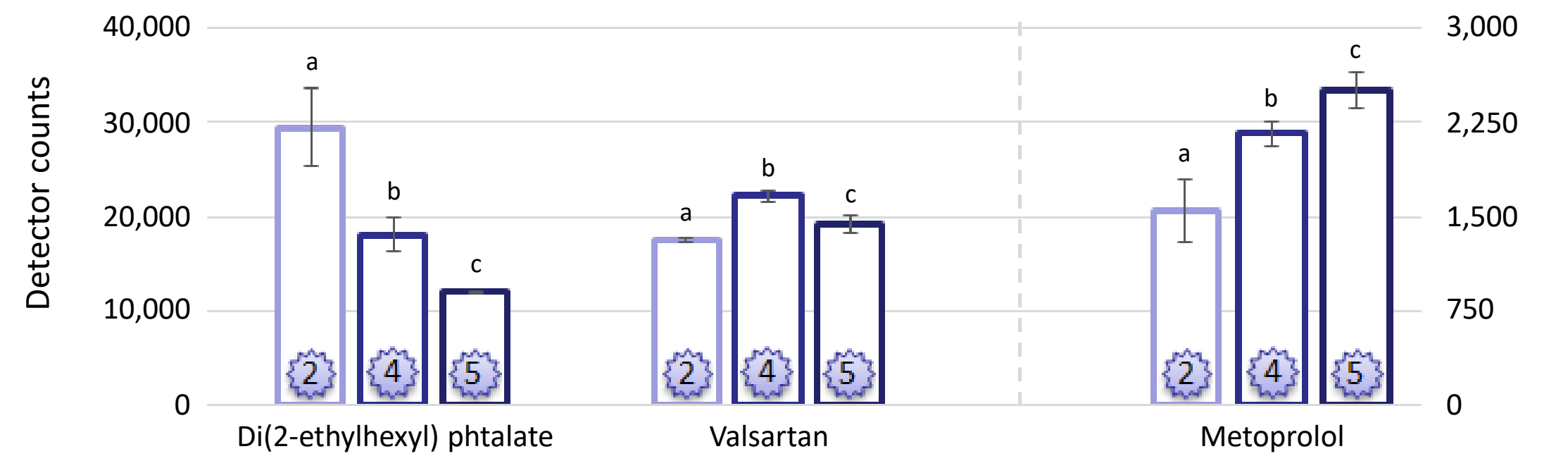
Results

Suspect screening

- Among the 28 suspect compounds, 4 were not detected in any extract (cotinine, methylparaben, metolachlor-ESA, and paracetamol).
- Based on the detector counts of the suspect compounds, the methods ① & ③ provide a lower extraction efficiency than the other methods. On the opposite, **the methods** ② **&** ④ **allowed a higher extraction efficiency** for most of the 28 suspect compounds than the other methods.
- Most of the pesticides detected in the sample extracts are currently banned (e.g. diuron, terbutryn).
- Concerning the pharmaceuticals, drugs acting on the nervous system were the most commonly detected (e.g. oxazepam, venlafaxine), as well as betablockers (e.g. atenolol, metoprolol).

Examples of suspect compounds detected in the SPE extracts

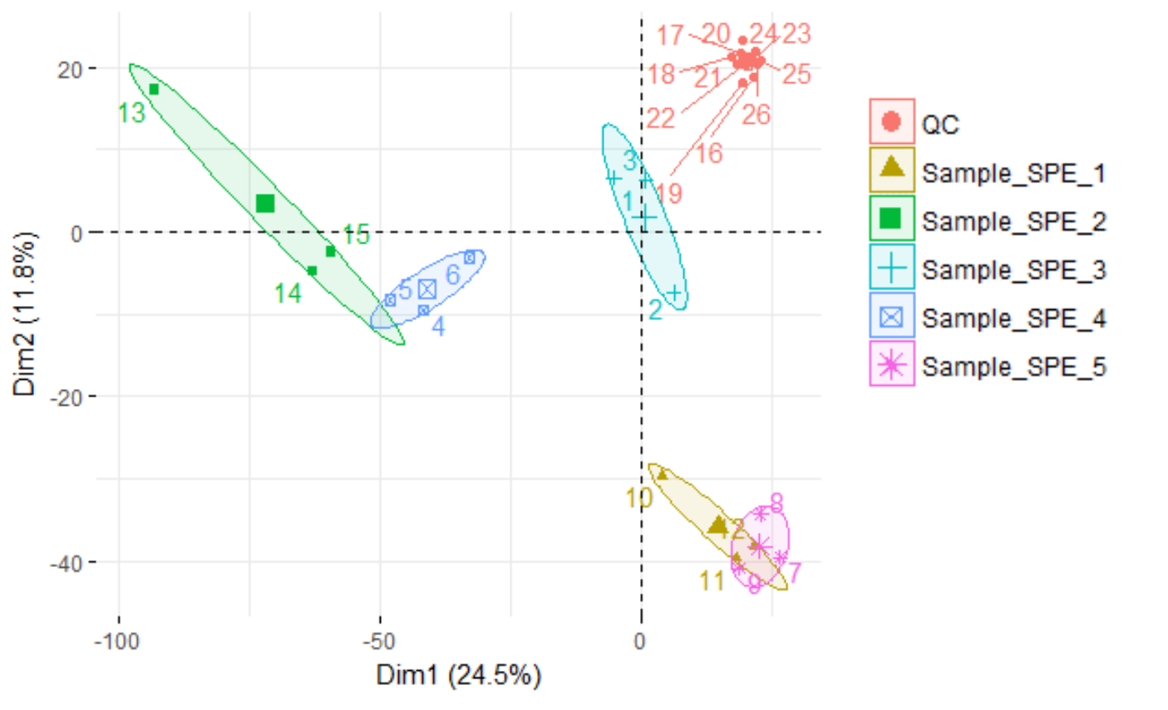
SPE method	①	②	③	④	⑤
Number of total detected compounds	23/28	24/28	22/28	24/28	22/28
Specific compounds to each SPE method	Metformin	–	Metformin	–	2-OH-atrazine Benzoylecgonine
Compounds better extracted by one of the SPE methods	–	Caffeine Diclofenac Di(2-ethylhexyl) phtalate	–	Acebutolol Lidocaine Oxazepam Valsartan	Benzotriazole Metformine Metoprolol



Examples of suspect compounds better extracted by one of the SPE methods tested

Non-target screening

1/ Repeatability of the whole analytical sequence



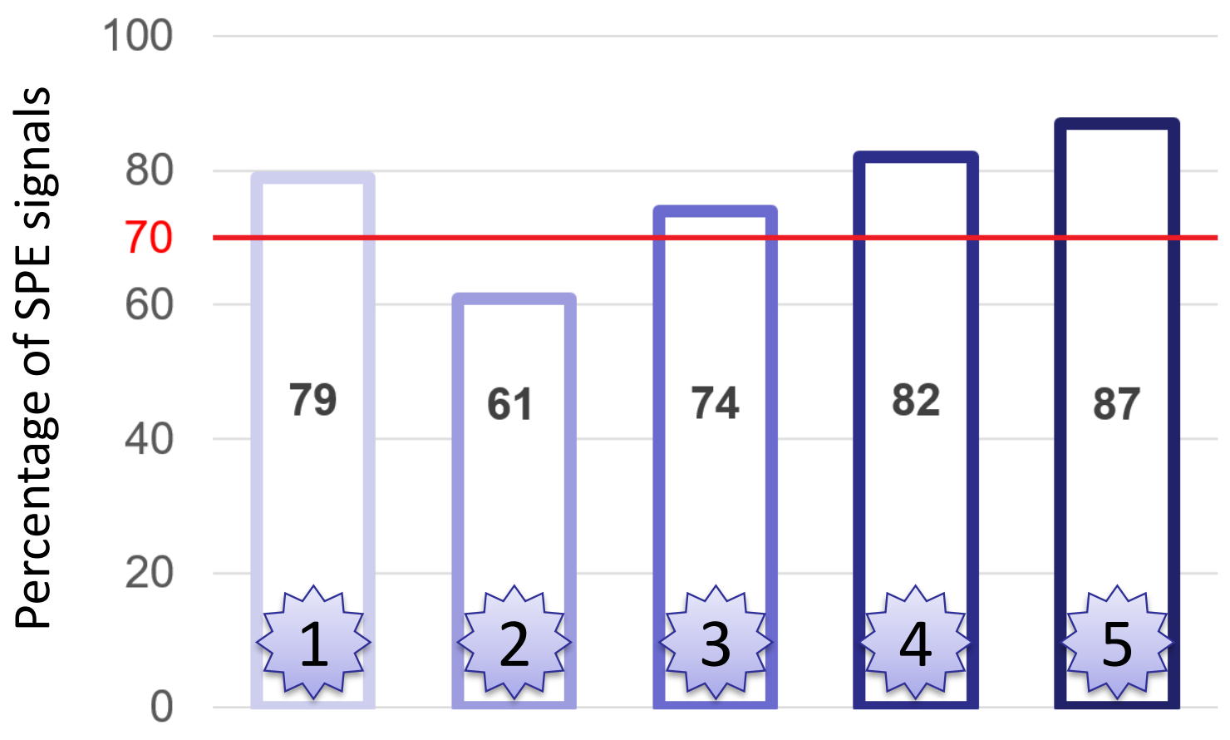
PCA score plot of the full-scan data obtained after SPE and before sorting data according to their CV QC

- The PCA score plot reveal that QC injections are clustered together (in red).
- The CV calculation of the QC signals revealed that 82% of the signals present a CV <30%.

→ **The analytical repeatability was good.**

The data processing can therefore be further investigated.

2/ Repeatability of the SPE methods

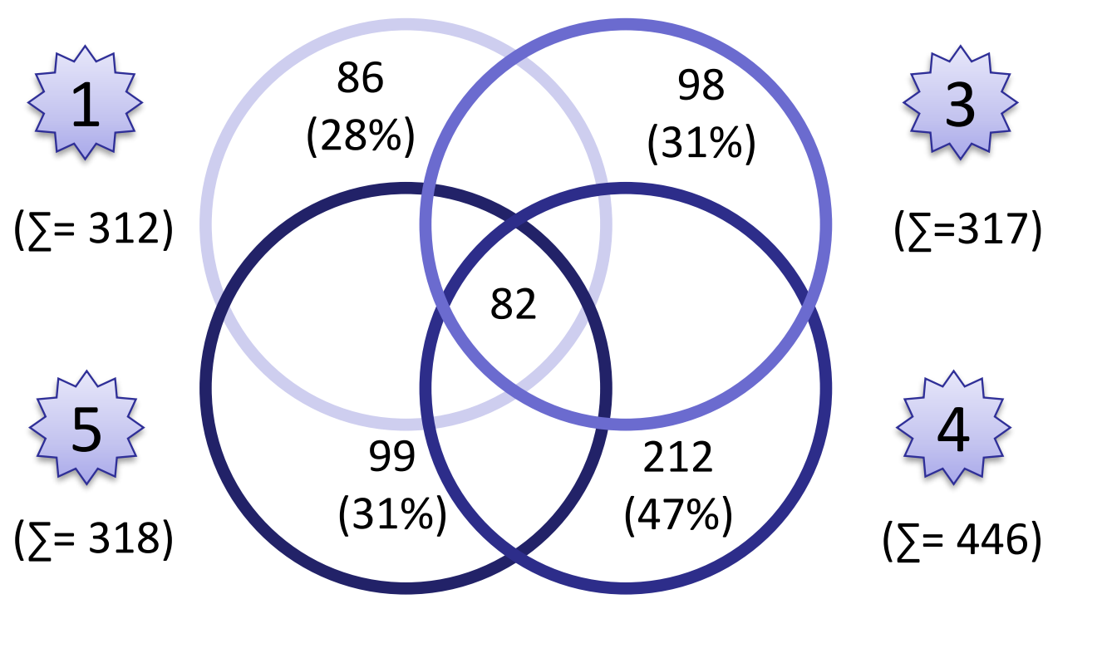


Percentage of SPE signals presenting a CV < 30% for each SPE method

- Extraction methods with more than 70% SPE signals presenting a CV lower than 30% are considered as repeatable.

→ **The methods ① / ③ / ④ / ⑤ are retained for the next steps of this study.**

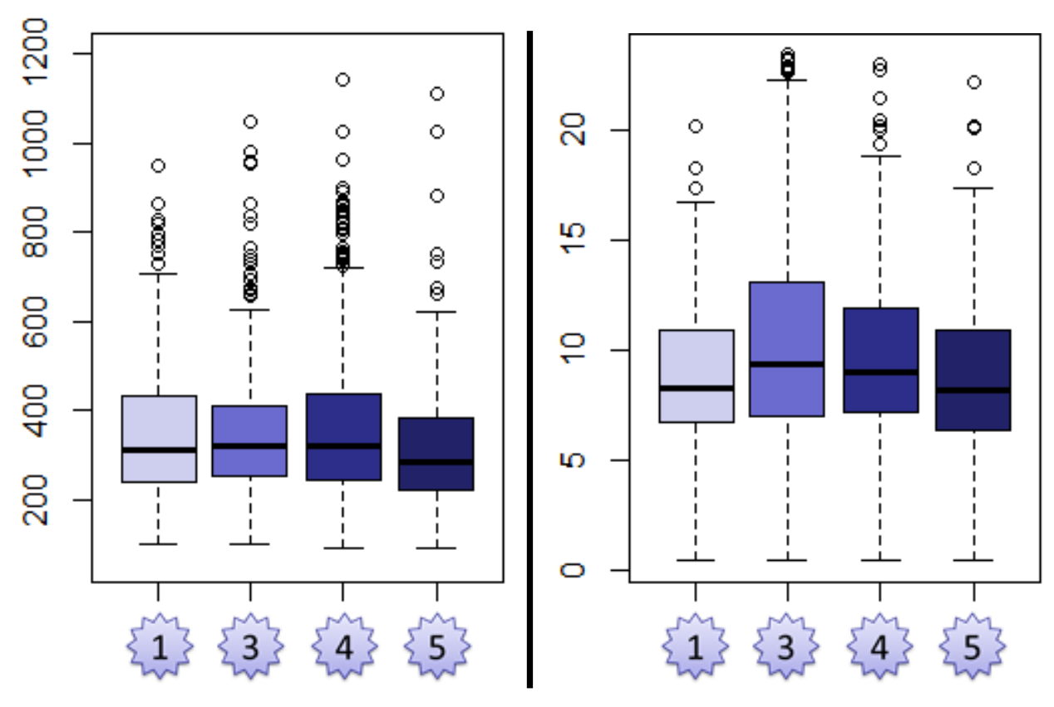
3/ Informativity and specificity of the SPE methods



Number of common and specific signals detected in water extracts, depending on the SPE method. Performed on sorted data.

- The method ④ allowed the detection of more signals in water extracts than other methods, with about 100 additional signals.
- Each SPE method allowed several specific signals detection, particularly the method ④.
- The method ④ allowed the extraction of compounds with higher m/z in contrast to the method ⑤.
- The method ⑤ allowed the extraction of more polar compounds, considering retention time distribution.

→ **The best compromise between data repeatability and informativity is obtained with the method ④.**



Distribution of m/z (left) and retention time (right) of signals detected. Performed on sorted data.

Conclusion & Perspectives

This study highlights that the sample preparation influences the chemical fingerprints obtained by non-target analyses of surface water samples. Each sample preparation tested allows the detection of specific and common signals. Nevertheless, both the suspect and the non-target approaches reveal the method ④ is the most suitable regarding the informativity, the specificity, and especially the repeatability of the sample preparation methods tested.

The assessment of the sample preparation is a pre-requisite to evaluate surface water contamination without any *a priori*.

To go further, analyses in negative ionization mode have to be realized to confirm the SPE method ④ selection. Moreover, a structural elucidation process of common and specific signals may highlight other SPE method specificities.

References

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