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Monitoring of organic contaminants in raw wastewater by targeted and non-targeted screening: an effective tool for assessing urban metabolism

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Abstract

Wastewater represents rich and complex matrix, highly contaminated with a broad range of organic molecules. By targeting raw influents close to excretion where degradation is slightly limited, sample collection can afford estimation on uses and expositions of the population within the catchment area. This approach, so called **Wastewater-Based-Epidemiology**, has been initially developed to monitor, in an objective and non-intrusive way illicit drug consumption (Daughton, 2001). Nowadays, it has been extended to several other class of compounds that may provide useful information in order to assess human health in various ways within a population.

Here we present the development of a **analytical set-up** relying on solid phase extraction and liquid chromatography mass spectrometry (LC-MS/MS) for the quantitative monitoring of about 50 selected compounds at trace levels (ng/L). This list includes well-established WBE markers (**drugs, pharmaceutical products**) and others (**dietary or stress tracers**) which might serve this purpose on future WBE studies (Choi et al., 2018).

Workflow

Casual procedure for quantification of organic contaminants such as drugs and pharmaceuticals involve a solid phase extraction (SPE) using a hydrophilic-lipophilic balanced copolymer resin (HLB cf. fig. 1 A) followed by a reversed phase chromatography (RPLC) before mass spectrometry.

→ Such workflow shows limited SPE recovery and poor chromatographic retention for polar compounds

Therefore, due to our compounds large variety of physico-chemical properties (i.e., hydrophilic nature, with log K_{ow} ranging from ≈ -5 to 5), a wider protocol covering all types of analytes might be required to ensure satisfying recoveries and elutions even for polar compounds.

→ A **homemade multilayer cartridge** (fig. 1 B) developed by Kern et al., 2009 (adapted in Huynh et al., 2021) and made of Oasis® HLB, Isolute® Env+, Strata® X-AW and Strata® X-CW (200/150/100/100 mg), was tested for SPE step.

→ Several silica-based reversed-phase C18 column, optimized to enhance retention of polar analytes were tested in order to allow satisfying elution of all targeted compounds in a unique chromatographic run.

Absolute recoveries in different matrix (spiked ultrapure water, IWW samples) for both methods were calculated in order to choose the more suitable extraction protocol. Concerning chromatography, possible retention of all targeted compounds using a hybrid column was also explored, while specificity was the main factor for choosing between available columns.

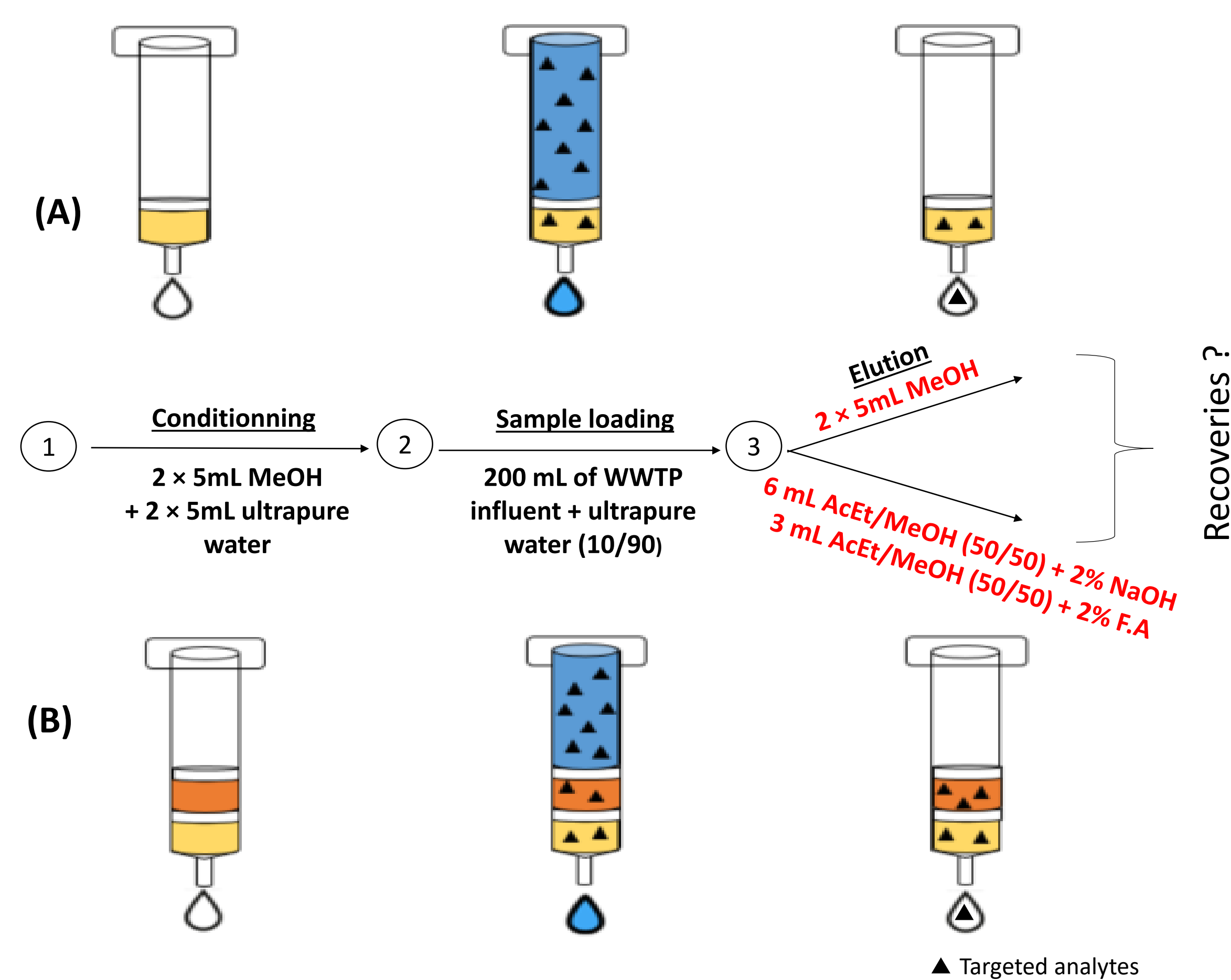


Figure 1 : Solid-Phase-Extraction protocols

Results

Mass spectrometry : dMRM transitions for all compounds were acquired using source optimizer functionality of a Ultivo® triple quadrupole MS (Agilent) with a electrospray ionization probe working in polarity-switching mode (ESI^{+/−}).

Solid-phase extraction (SPE) :

As expected, recovery of highly polar compounds was very low (ex : < 5% for Acesulfame, Log K_{ow} = -1,33) with HLB while the multilayer cartridge enhance this result ($\approx 15-20\%$)(see figures 2 and 3).

Less polar compounds were globally slightly better retained on HLB (ex : Fexofenadine, log K_{ow} = 2,86, recovery > 60%, figures 2 and 4) rather than on the multilayer cartridge ($\approx 55\%$).

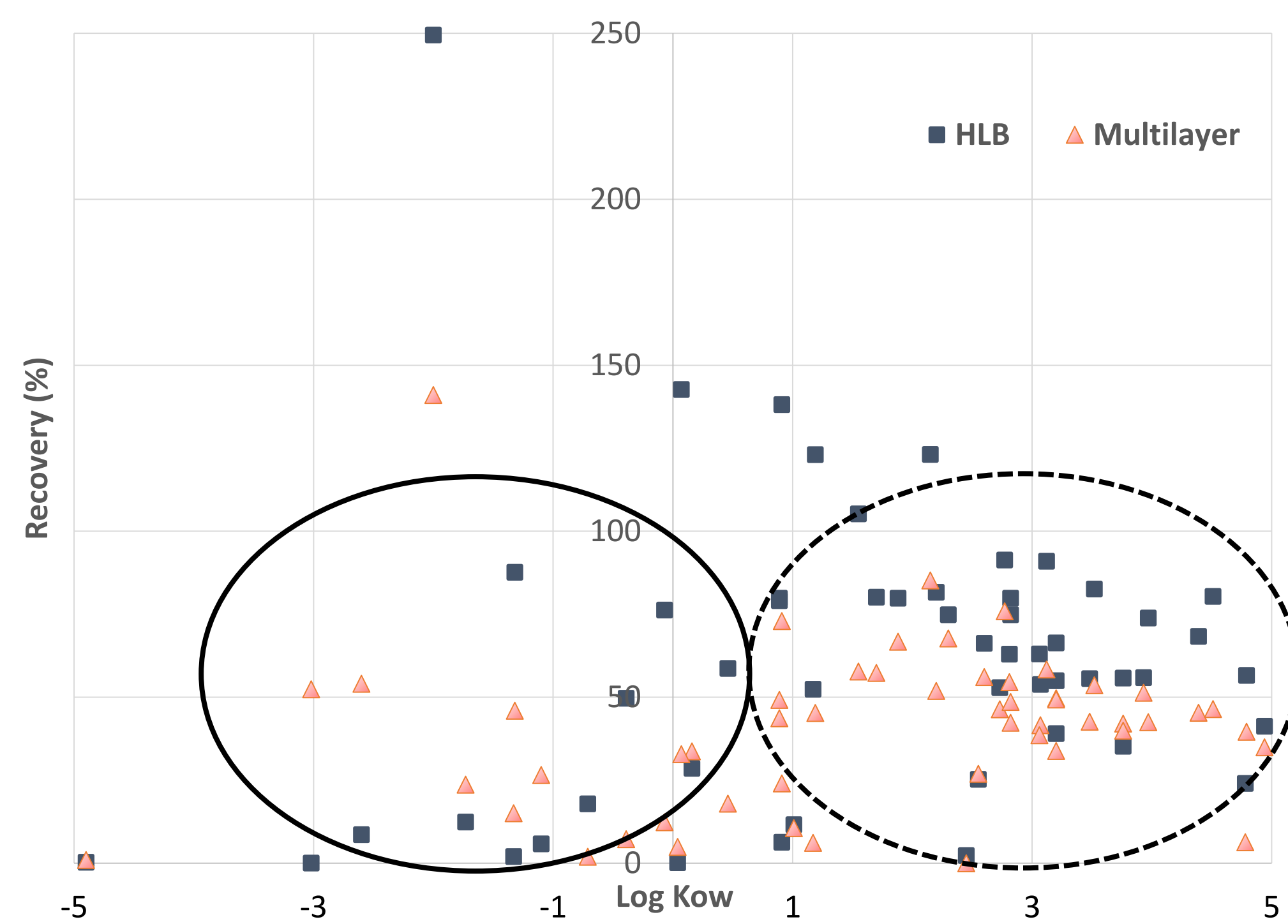


Figure 2 : Absolute recoveries (%) in ultrapure water for all targeted compounds according to both cartridge.

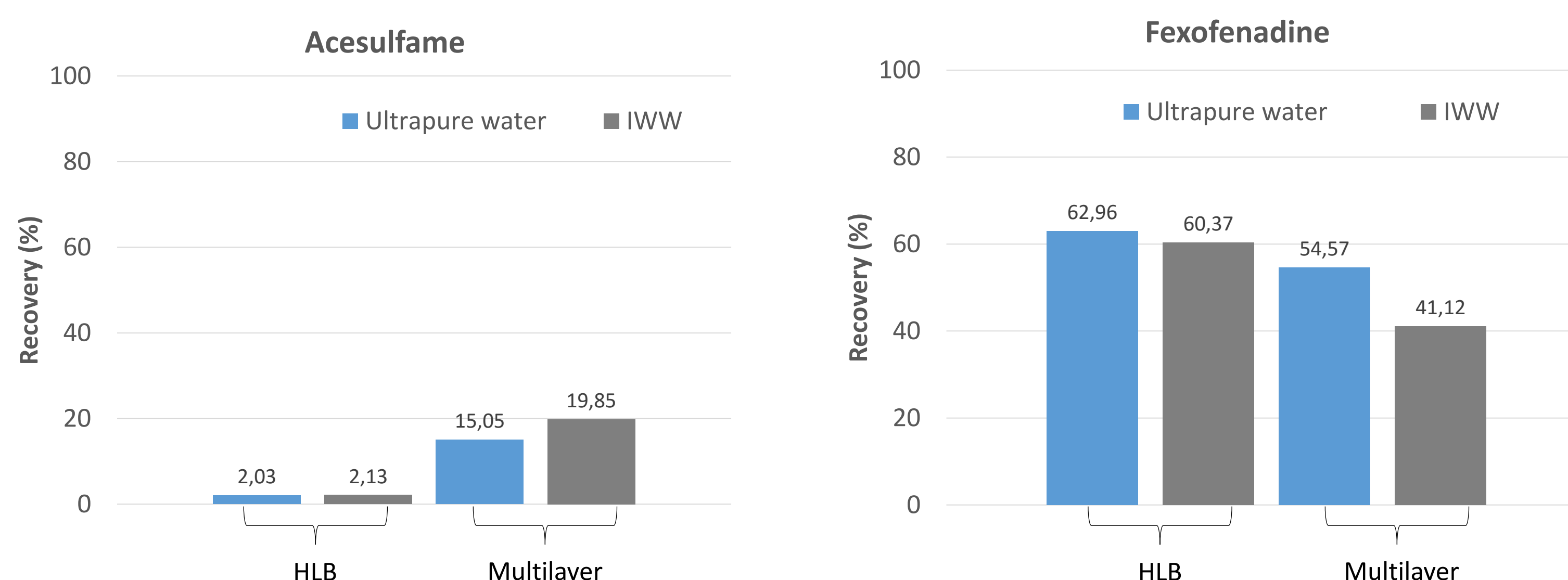


Figure 3 (left) and 4 (right) : Comparison of absolute recoveries (%) for HLB and a multilayer cartridge in ultrapure water and IWW

Liquid chromatography (LC) :

Almost all highly polar compounds (i.e., Metformin, log K_{ow} = -2,6, RT = 0,371 min) were retained on the tested hybrid C18 column. Among all tested, the Atlantis T3 hybrid (Waters®) showed better resolution for most of the targeted analytes. Finally, mobile phase gradient and injection flow were optimized (table 1).

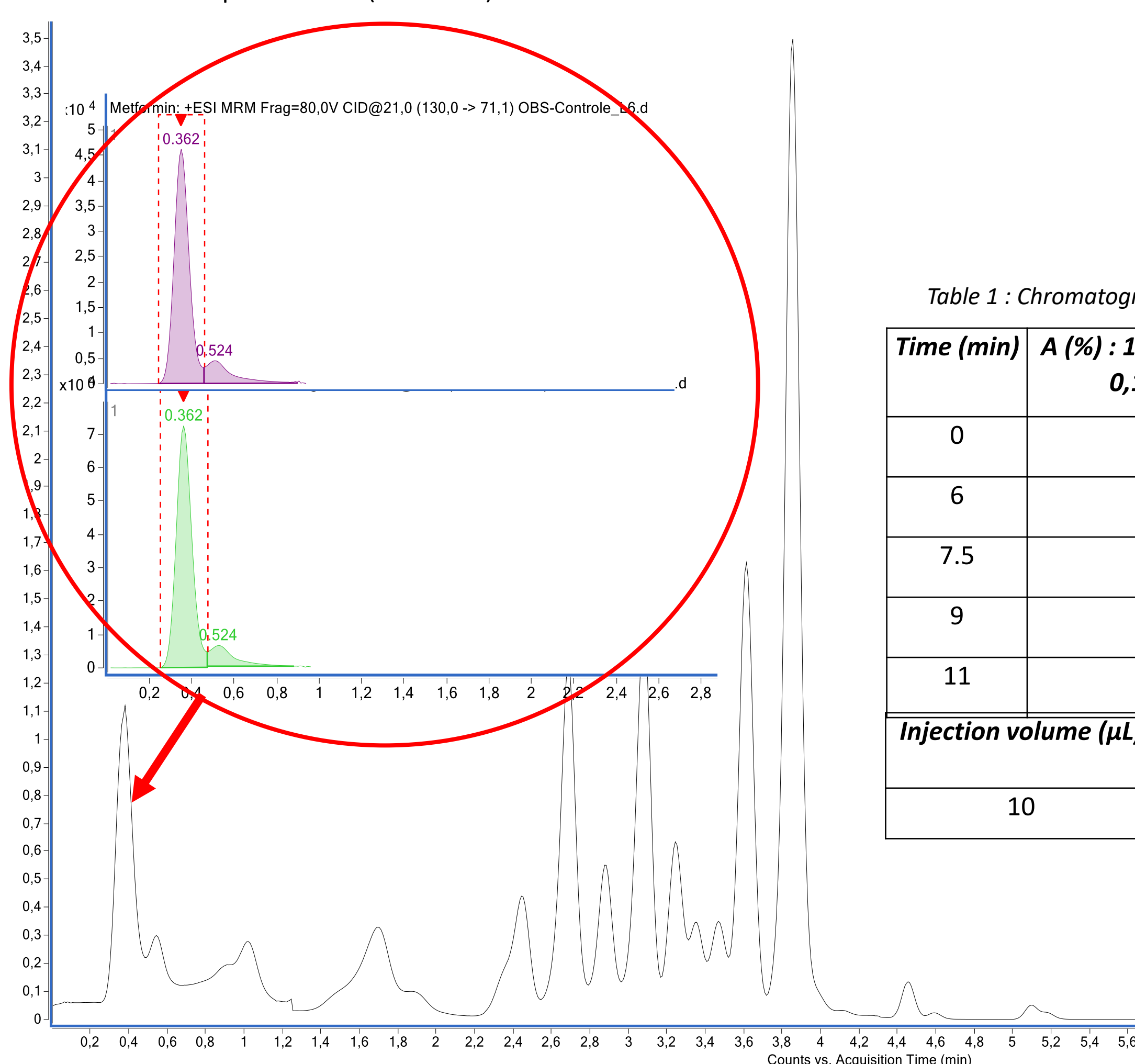


Figure 5 : TIC of a 50 ng control sample using method parameters as described in table 1 and 2

Table 1 : Chromatographic conditions for sample injection

Time (min)	A (%) : 100% Water + 0,1% A. F	B (%) : 100% AcN + 0,1% A. F
0	90	10
6	0	100
7.5	0	100
9	90	10
11	90	10
Injection volume (μL)		Flow rate (mL/min)
10		0,7

Conclusion & Future works

- Low recovery of highly polar compounds using HLB might be overcome by high concentration expected in wastewater samples
- A single chromatographic run is enough to eluate almost all of our compounds
- Explore compatibility of both methods to a **non-targeted** HRMS approach
- Realize quantitative analysis on IWW samples in order to build temporal chronic (in daily loads) for each compounds and look for **temporal trends**
- Change the scale of focus (thinner spatial frame) to assess **spatial disparities**

