Application of passive sampling to evaluate the chemical pollution of treated wastewater intended for reuse

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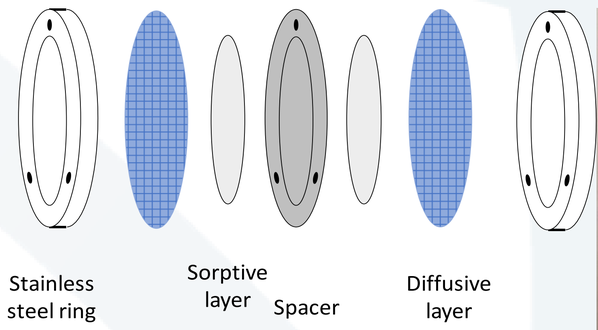
Introduction

Development of novel monitoring methods such as passive sampling (PS) as a promising tool for future application should be pursued according to the Environmental Quality Standards Directive (EQS) issued under the European Union's Water Framework Directive (WFD). This recommendation derives from the fact that compounds of emerging concern (CECs) are often present at trace but toxic concentration levels in the environment. Their low concentration (as low as few pg L^{-1}) makes them difficult to detect with traditional sampling and sample preparation protocols. PS is a novel approach offering detection of CECs in ultra-trace concentration levels. PS is cost-effective, offers an representative image of pollution over a period of several weeks, does not require transport of big volume samples to the laboratory and can be easily integrated into a variety of monitoring programs.



- Two-sided exposure
- 22.7 cm^2 total sampling area
- 2 × 0.1 cm agarose diffusive layer
- 2 × 0.1 cm sorbent gel layer
- Oasis HLB sorbent (5 mg/cm^2)

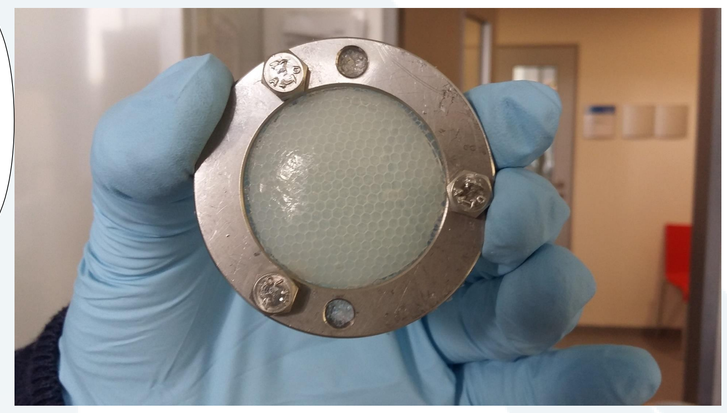


Figure 1. Design of the hydrogel-based passive sampler

Results

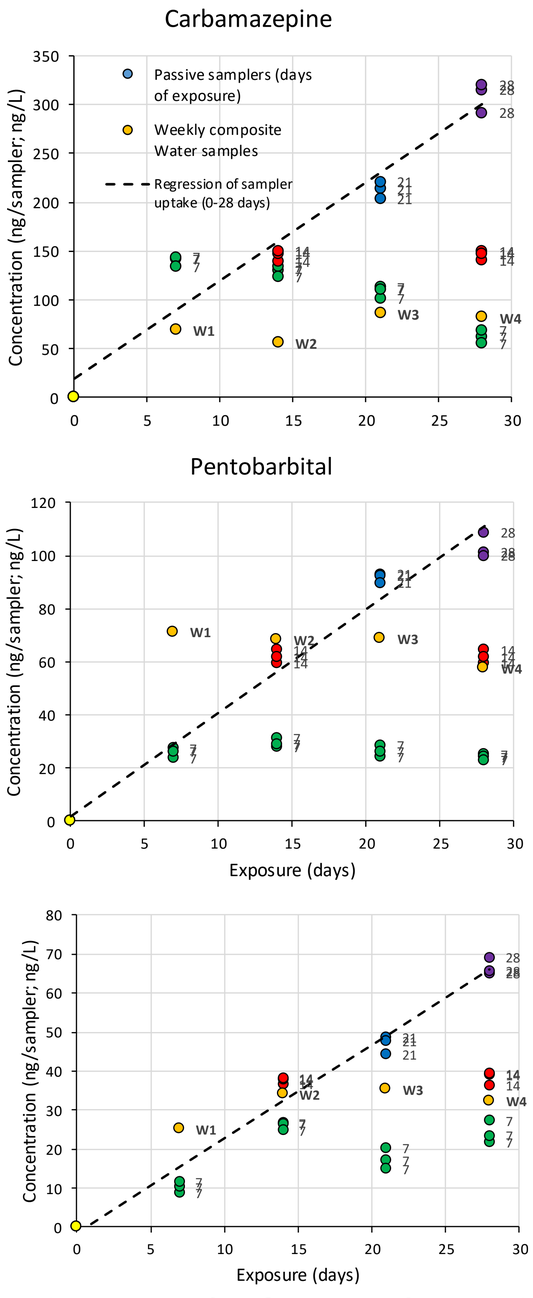


Figure 4. Uptake of compounds to passive samplers and concentrations in weekly composite water samples

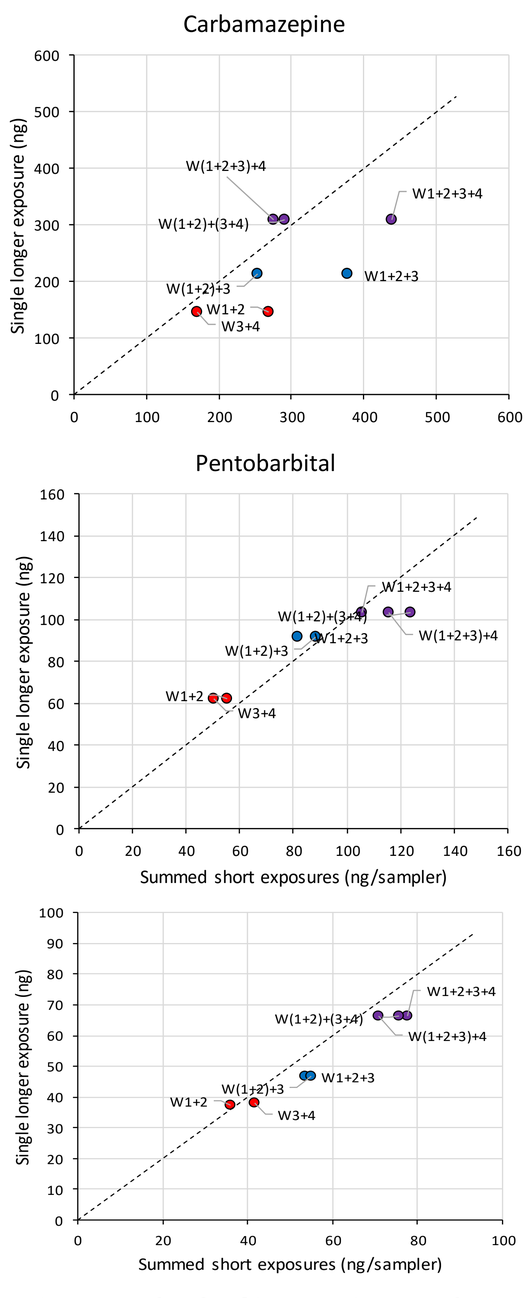


Figure 5. Check of integrative uptake : comparing summed up uptake during short vs. longer sampler exposures

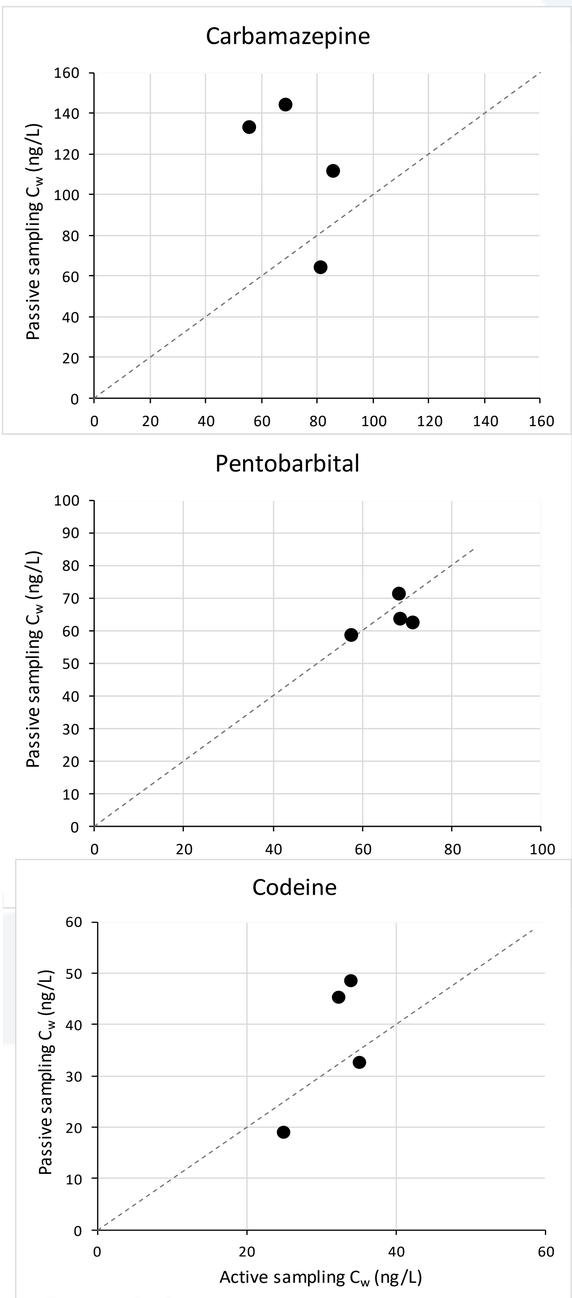


Figure 6. Comparing passive sampler - derived aqueous concentrations exposure with composite water samples (7-day data)

- A set of 171 drugs was analysed including many pharmaceuticals, antibiotics and psychoactive substances
- 115 compondswere detected in all weekly composite samples and in PS extracts.
- Additional 16 compounds were captured only in the passive sampling extracts at sub-ppb concentration levels.
- Most of the detected substances followed integrative behavior until the end of the deployment (Figure 5)
- Relative standard deviations (RSDs) of triplicates did not exceed 20% including sampling and analysis.
- For the compounds detected by both methods, the substance specific sampling rates were calculated (Rs). Average Rs was calculated 0.08 L day^{-1}.
- The passive sampler data verified concentration levels of the targeted substances as revealed from the traditional SPE method of composite water samples (Figure 6)
- Passive sampler - derived aqueous concentrations allowed to identify a number of compounds causing potential risk in water intended for reuse (Figure 7)

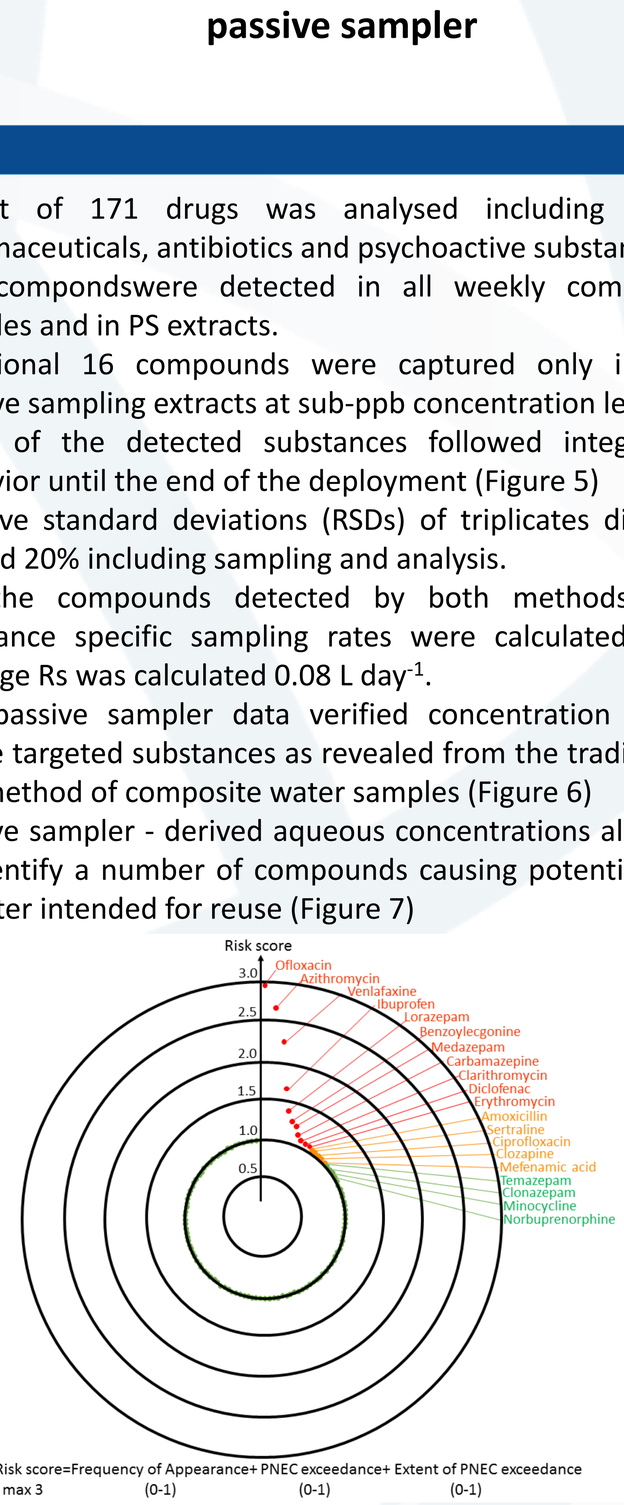


Figure 7. Risk assessment of compounds in WWTP effluent from passive sampler data

Methods

- Agarose hydrogel-based passive sampler (**Figure 1**)
- Deployment in effluent of a wastewater treatment plant (WWTP, **Figure 2**), equipped with membrane bioreactor in Cyprus; the treated wastewater was intended to be reused in the agriculture
- Composite flow-proportional water samples were collected and analyzed by HORIZON SPE-DEX 4790 using OASIS HLB sorbent
- Extracts were analyzed together in one-batch by liquid chromatography tandem MS/MS (LC-QQQ)
- **Field-scale calibration of the sampler** by calculation of the substance specific sampling rates.

Sampler ID	9-15 Nov 2017	16-21 Nov 2017	22-27 Nov 2017	28 Nov-4 Dec 2017
1				
2				
3				
4				
5				
6				
7				
8				

Figure 2. Passive sampler deployment scheme in WWTP effluent in Cyprus

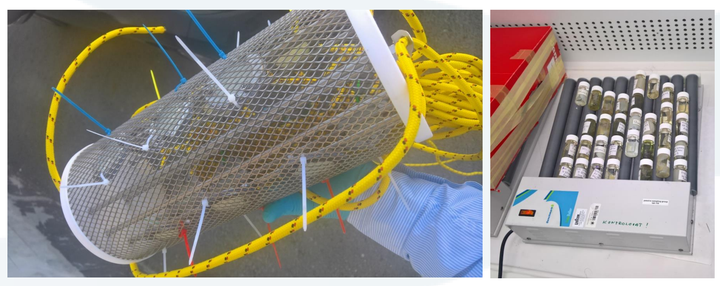


Figure 3. Passive sampler deployment device (left) and sampler extraction (right)

Acknowledgement

This research was supported by the RECETOX Research Infrastructure (LM2015051 and CZ.02.1.01/0.0/0.0/16 013/0001761.It has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 675530.

Conclusions

Hydrogel-based passive sampler proved to be capable of detecting chemicals of emerging concern (CECs) at trace-level concentrations that were missed by traditional sample preparation methods.

The demonstrated advantages include:

- High efficiency (low cost, saves time)
- High preconcentration factors
- Time integrative sampling
- Low sampler sensitivity to flow velocity fluctuations
- Sampling of freely dissolved bioavailable compounds

The limitations include

- Limited stability of hydrogel layer over extended time periods
- Unknown uptake capacity of many compounds