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Performance comparison of three passive samplers for monitoring of polar organic compounds in wastewater

Pavla Fialová
RECETOX, Faculty of Science, Masaryk University, Kotlarska 2, Brno, Czech Republic
E-mail: pavla.fialova@recetox.muni.cz

Introduction

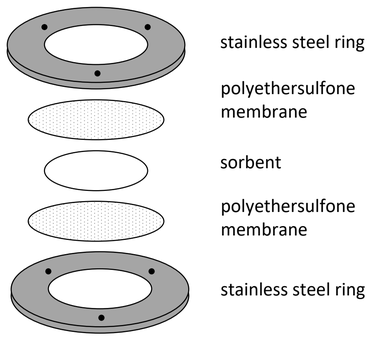
Over the past decades, many different types of passive samplers for monitoring of polar compounds were developed. These passive samplers use different types of sorbents and barriers that should control the uptake of compounds to the sampler. For representative monitoring, passive sampler has to fullfil several criteria; it should accumulate wide range of polar compounds (pharmaceuticals, pesticides, per- and polyfluoroalkyl substances) should be robust (independent on environmental conditions), sample time-integratively for a long time and the uptake mechanism should be fully understood.

For this study, three different types of passive samplers were chosen, i.e. Polar Organic Chemical Integrative Sampler (POCIS), hydrogel-passive sampler (HPS), and Speedisk. These passive samplers use different type of sorbent and different barrier to control the compound uptake. These passive samplers were deployed in effluent of wastewater treatment plant (WWTP) in Brno-Modřice for different periods to assess and compare their performance.

Sampling site and sampling design

- Effluent from municipal WWTP Brno-Modřice
- Sampling performed from 6. 11. to 18. 12. 2018
- POCIS, HPS deployed for 7, 14, 21, and 28 days
- Speedisks deployed for 7, 14, 21, 28, and 42 days
- Passive samplers deployed in triplicates
- Composite 24h water samples were collected, (from subsamples with 2h sampling frequency)
- Temperature: 16.6 ± 1.6 °C
- pH: 7.56 ± 0.12

POCIS

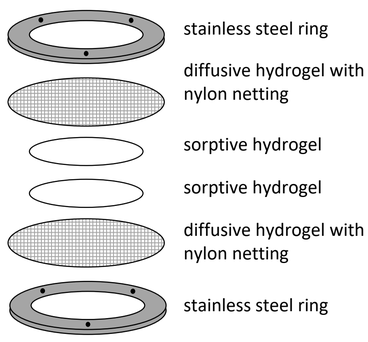


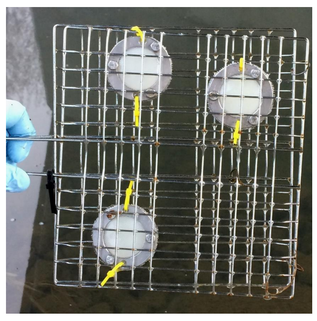
- Surface area A = 41 cm^2
- Sorbent: Triphasic mixture of a hydroxylated polystyrene-divinylbenzene resin and a carbonaceous adsorbent dispersed on a styrene divinylbenzene copolymer ,~200 mg

Processing

- Elution with 50 mL of toluene:methanol:dichloromethane mixture (1:1:8) → evaporation

Hydrogel-passive sampler (HPS)



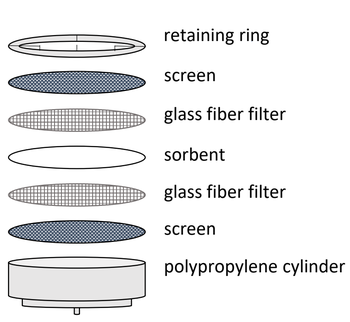


- Surface area A = 22.7 cm^2
- Sorbent: Agarose hydrogel with dispersed Oasis HLB, ~110 mg

Processing

- Freeze-drying of sorptive hydrogel discs
- Extraction in 0.5% NH_3 in methanol (10 mL) and methanol (10 mL) → evaporation
- Filtration through nylon syringe filter (pore size 0.20 µm)

Speedisk

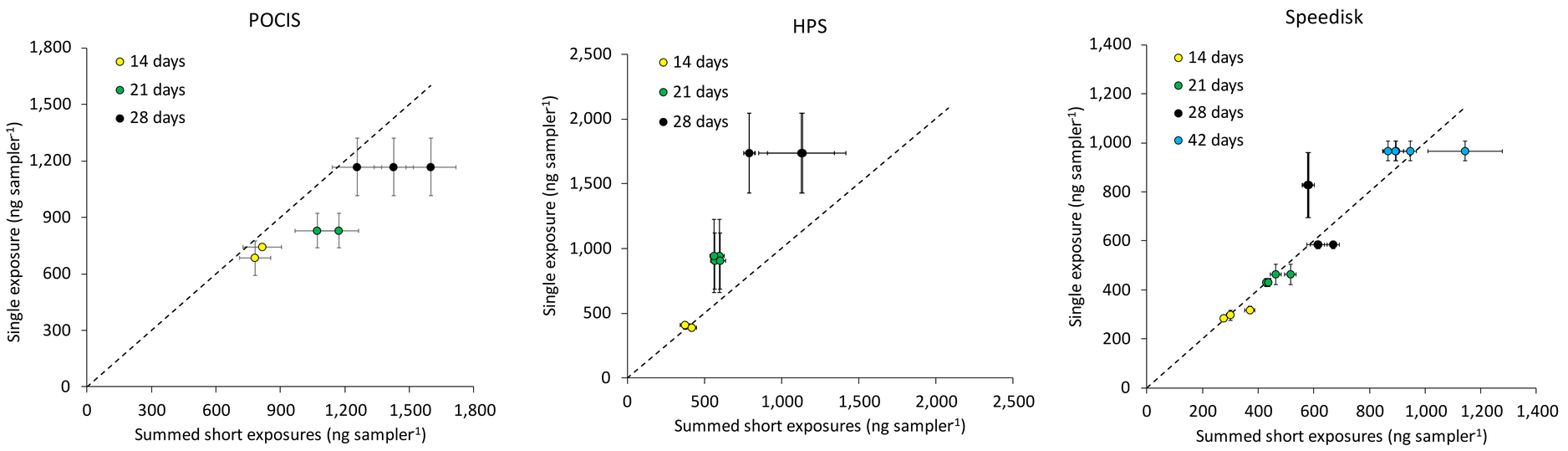


- Surface area A = 19.6 cm^2
- Sorbent: hydrophilic divinylbenzene, ~600 mg

Processing

- Freeze-drying of speedisks
- Elution with 5 mL methanol, 5 mL 0.5% NH_3 in methanol, 50 mL of dichloromethane → evaporation
- Filtration through nylon syringe filter (pore size 0.20 µm)

Assessment of integrative uptake – example for carbamazepine



Comparison of compound uptake in several subsequent short sampler exposures (x-axis) versus uptake into one sampler deployed for a longer time (y-axis). The dashed line represent equality of both values. The uptake was integrative up to 14 days for POCIS and HPS, and up to 42 days for Speedisk.

Instrumental analysis

Analyzed compounds

- Pharmaceuticals and metabolites
- Per- and polyfluroalkyl substances (PFASs)
- Anticorrosives, pesticides, and metabolites

Passive sampler extracts

- LC-MS/MS

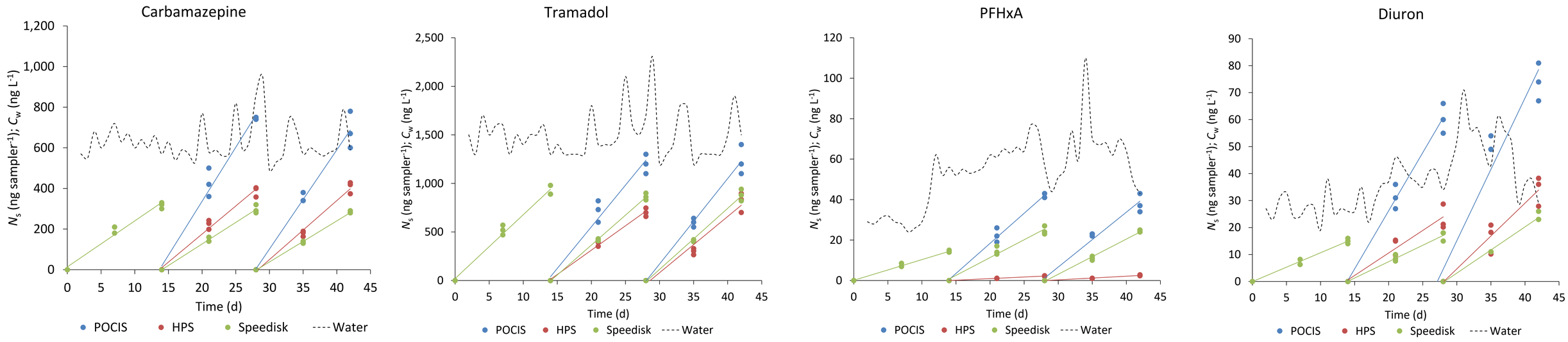
Composite 24h water samples

- Filtration through regenerated celulose filter
- In-line SPE-LC-MS/MS

Data analysis

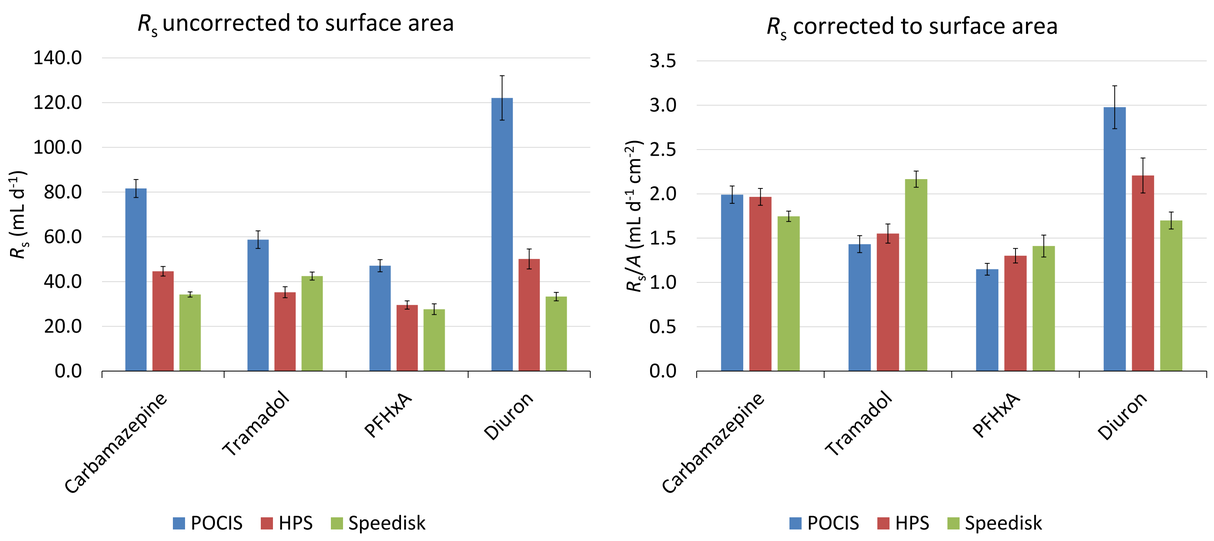
- Aqueous concentration C_w was constant over the whole sampling period
- Sampling rates R_s were calculated for 14 days exposure from linear regression
- $R_s = N_s / C_w t$

Uptake of four compounds in three passive samplers



Uptake of four exemplary compounds in passive samplers. The dashed line represent the aqueous concentration C_w. The full lines represent linear regression for accumulated amount N_s in the sampler.

Comparison of sampling rates R_s



Conclusions

Criterion	POCIS	HPS	Speedisk
Robustness	-	-	+
Time-integrativity over long period	-	-	+
High sampling rates	+	-	-
Commercial availability	+	-	+
Repeatibility	-	+	+
Understood uptake mechanism	-	+	+
Physical durability	-	-	+

- Sampling rates corrected to surface area were for most compounds similar for all three passive samplers.
- Speedisk seems to be the most suitable passive sampler for monitoring of polar organic compounds.