Performance evaluation of hydrogel-based passive sampler for monitoring of polar organic compounds in wastewater

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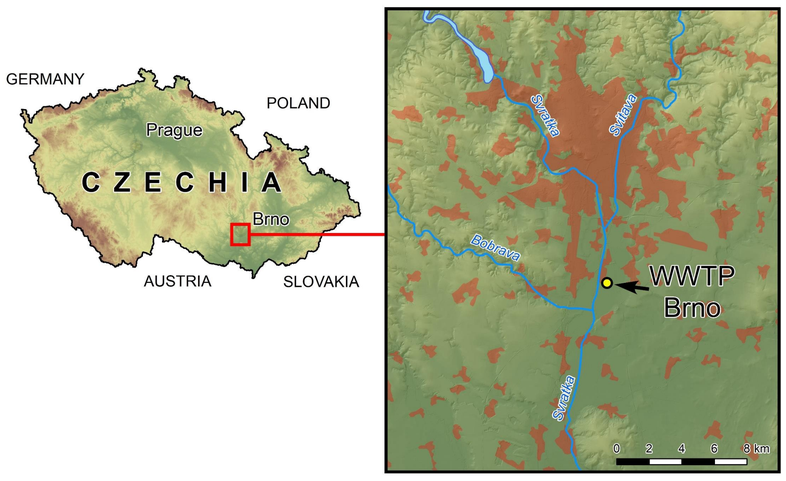
Methods

Sampling site:

- WWTP Brno-Modřice, Czech Republic (49°07'N,16°37'E)
- Effluent of municipal WWTP (500,000 equivalent inhabitants)



Sampler deployment design:

- Different exposure time periods (7, 14, 21, 28 days)
- Samplers deployed in triplicates
- Temperature: 15.6 ± 0.7 °C, pH: 7.6 ± 0.1

Sampler set	Exposure time in weeks			
	w1	w2	w3	w4
1				
2				
3				
4				
5				
6				
7				
8				
9				

Processing and analysis of passive samplers:

- Freeze-drying of sorptive hydrogel discs 24 h
- Extraction 0.5% NH_3 in methanol (10 mL), methanol (10 mL)
- Filtration through nylon syringe filter (pore size 0.20 µm)
- LC-MS/MS analysis

Daily composite water samples (collected every day):

- filtration through regenerated celulose
- in-line SPE-LC-MS/MS analysis

Conclusions

- We analyzed 102 pharmaceuticals, 29 PFASs, 111 pesticides, and their metabolites in exposed passive sampler and treated wastewater.
- In water, we detected 69 pharmaceuticals, 6 PFASs and 58 pesticides.
- In passive sampler, we detected 64 pharmaceuticals, 11 PFASs and 87 pesticides.
- R_s was estimated for compounds present simultaneously in passive sampler and water in at least 50% of the samples. These criteria fulfilled 51 pharmaceuticals, 3 PFASs, and 24 pesticides.
- We observed integrative uptake to the sampler up to 14 days in the effluent and up to 7 days in the influent of WWTP.
- R_s for 28-day exposure were in most cases significantly different from those for 14-day exposure. Meanwhile, R_s for both 14-day exposure did not differ significantly.
- We recommend to shorten the sampler exposure to 14 days.
- Compared to other studies, estimated R_s were comparable for 10 pharmaceuticals, 2 PFASs, and 4 pesticides.

References

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Booij, K. *et al. Environ. Sci. Technol.* 37, 361–366 (2003)

Urík, J. *et al. Environ. Sci. Pollut. Res.* 26, 15273–15284 (2019)

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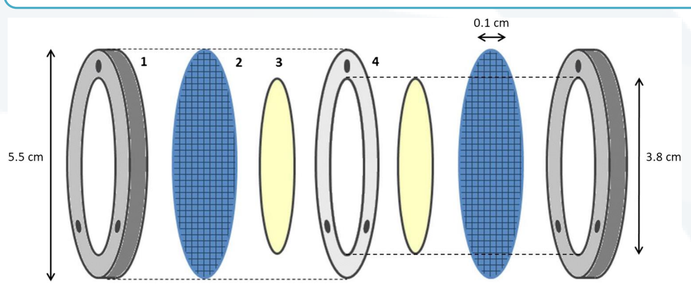
Introduction

Several configurations of passive samplers based on diffusive gradients in thin films for polar organic compounds (o-DTG) were developed in last few years. The uptake of compounds to most samplers is influenced by water boundary layer (WBL), but in case of o-DGT, the layer of diffusive gel is thicker than typical thickness of WBL. As a result, the diffusion process through the diffusive gel to the binding gel with sorbent presents the limiting factor for compound uptake to sampler. Therefore, performance of o-DGT sampler is typically independent on hydrodynamic conditions, unlike other passive samplers used for polar compounds.
Recently, a new version of o-DGT sampler comprising agarose diffusive gel and Oasis HLB binding gel was proposed and calibrated in our laboratory for water monitoring of pharmaceuticals, polar pesticides and poly- and perfluoroalkylated substances (PFASs) (Urík and Vrana, 2019). We tested this passive sampler in the effluent of a municipal wastewater treatment plant (WWTP). We aimed to characterisation of uptake kinetics and passive sampler robustness for monitoring of a broad range of compounds.

Hydrogel-based passive sampler design



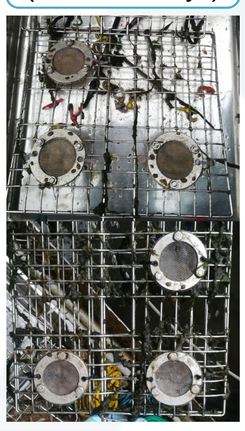
1. Stainless steel rings
2. Diffusive gel layers with netting (1.5% agarose hydrogel, nylon net)
3. Sorptive gel layers (1.5% agarose hydrogel with Oasis HLB sorbent)
4. Spacer

Active surface area: 22.7 cm^2, sorbent mass: 0.1 g

Before exposure

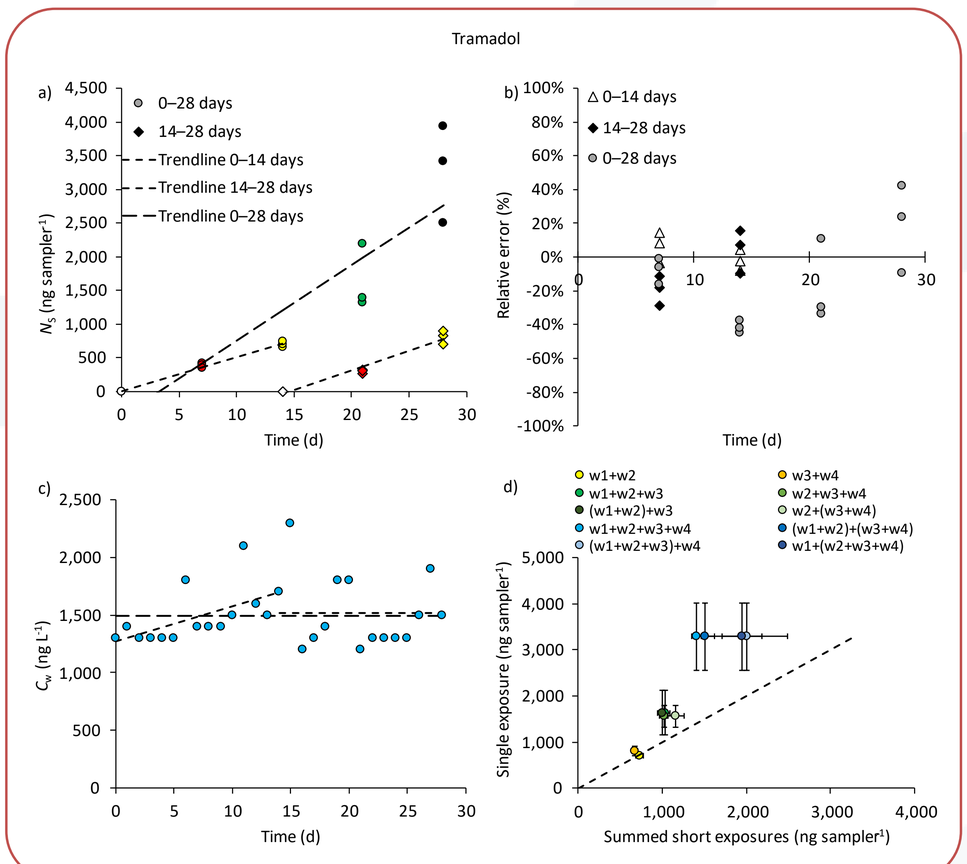
After exposure (7 and 14 days)

After exposure (21 and 28 days)



Sorptive hydrogel discs after exposure

Results



a) Accumulated amount N_s of tramadol to the passive sampler after 7, 14, 21, and 28 days of exposure is shown according to deployment time. Data from samplers deployed from day 0 or day 14 are depicted by a circle or a square. Point colours are set according to exposure duration in alignment to colours used in the sampler deployment design. The dashed lines represent linear regression of tramadol uptake for time periods 0–14, 14–28, and 0–28 days.

b) Repeatability of the accumulated amount of tramadol in the passive sampler in triplicates as a function of deployment time. The difference of measured N_s and N_s calculated from linear regression divided by calculated N_s i.e. relative error, is depicted according to the time exposure of the sampler. Triangles, squares, and circles represent exposure periods 0–14, 14–28, and 0–28 days.

c) Aqueous concentration of tramadol during exposure of passive samplers. The dashed lines indicate an average concentration or linear regression of time trend for periods of 0–14, 14–28, and 0–28 days.

d) Integrative uptake check where summed up N_s of several short sampler exposures is compared to N_s in a simultaneous single long exposure. E.g. w1+(w2+w3) means the sum of 7-day exposure in the first week (w1) and a 14-day exposure in the following two weeks (w2+w3). The summed-up N_s of short exposures (on the x-axis) is depicted versus a single longer exposure (on the y-axis). Error bars represent SD calculated according to the rules for error propagation. The dashed line shows the unity (y=x). Points close to the line indicate an ideal integrative uptake.

Sampling rate (R_s) calculation for three time periods (0–14, 14–28, 0–28 days)

Constant water concentration

$$R_s = \frac{N_s}{C_w t}$$

R_s – sampling rate (L day^{-1})

N_s - accumulated amount in passive sampler (ng sampler^{-1})

t - exposure time (d)

N_s/t - slope of linear regression

C_w - average water concentration (ng L^{-1})

Linear concetration trend (Booij et al., 2003)

$$C_w = C_{w0} + C't$$

$$R_s = \frac{N_s}{\left(C_{w0} + \frac{C't}{2}\right) t}$$

C_{w0} - aqueous concentration at time t = 0

C' - concentration rate of change

Comparison of estimated R_s

One-way ANOVA and pos hoc Holm-Sidak test

R_s comparison with other studies