Passive sampling of polar organic compounds in water: POCIS vs hydrogel sampler

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Introduction

Passive samplers are nowadays commonly used for sampling of different compounds in water. However, the sampling process can be unpredictably affected by changes in environmental conditions, e.g. temperature, pH, or water flow rate. While application of correction tools such as performance reference compounds is well investigated for partitioning-based samplers used for hydrophobic compounds, their use in adsorption-based samplers for polar organic compounds is limited. Efficacy of these samplers highly relies on their proper calibration as well as characterisation of environmental conditions.

The most popular sampler for polar organic compounds to this date, POCIS, is often criticized for the water flow rate impact on its performance[1]. When the layer of water near the sampler's surface (the water boundary layer, WBL) becomes the limiting factor of the compound's uptake into the sampler, changes in its thickness affect the sampling rate (R_S). Therefore, new passive sampler designs are investigated: Most notably the hydrogel-based samplers such as DGT. This sampler includes a thick diffusive hydrogel layer, which provides much higher resistance to mass-transfer than the WBL. Uptake is then controlled by the diffusive layer and, in theory, effect of WBL thickness change on sampling rate is negligible. However, this comes at a cost of lowering the sampling rate.

In-situ calibration of both POCIS and a novel hydrogel-based sampler design was performed for pharmaceuticals on Svratka River in Rajhrad from 9.2. to 8.3. 2016. Results allow for a direct comparison of these samplers' performances.

POCIS

Polar organic compounds integrative sampler, or POCIS[3], consists of two stainless steel rings compressed together by three bolts and nuts and holding two polyethersulfone membranes enclosing a sorptive medium: Triphasic mixture of hydroxylated polystyrene-divinylbenzene resin and a carbonaceous adsorbent dispersed on a styrene-divinylbenzene copolymer. The total sampling area is 41 cm².

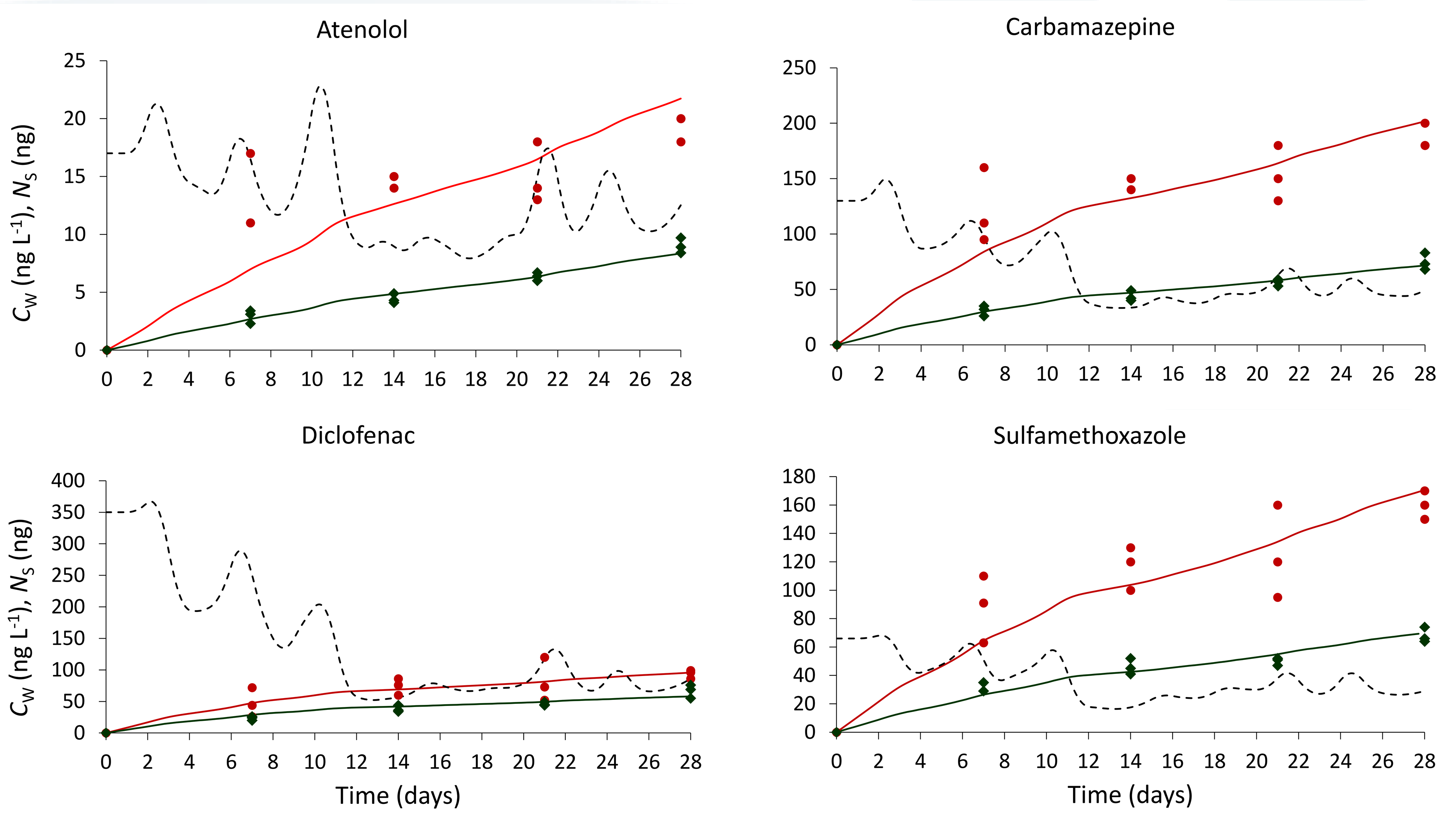
+ Easy processing
+ Commercially available
+ Popular and widely used

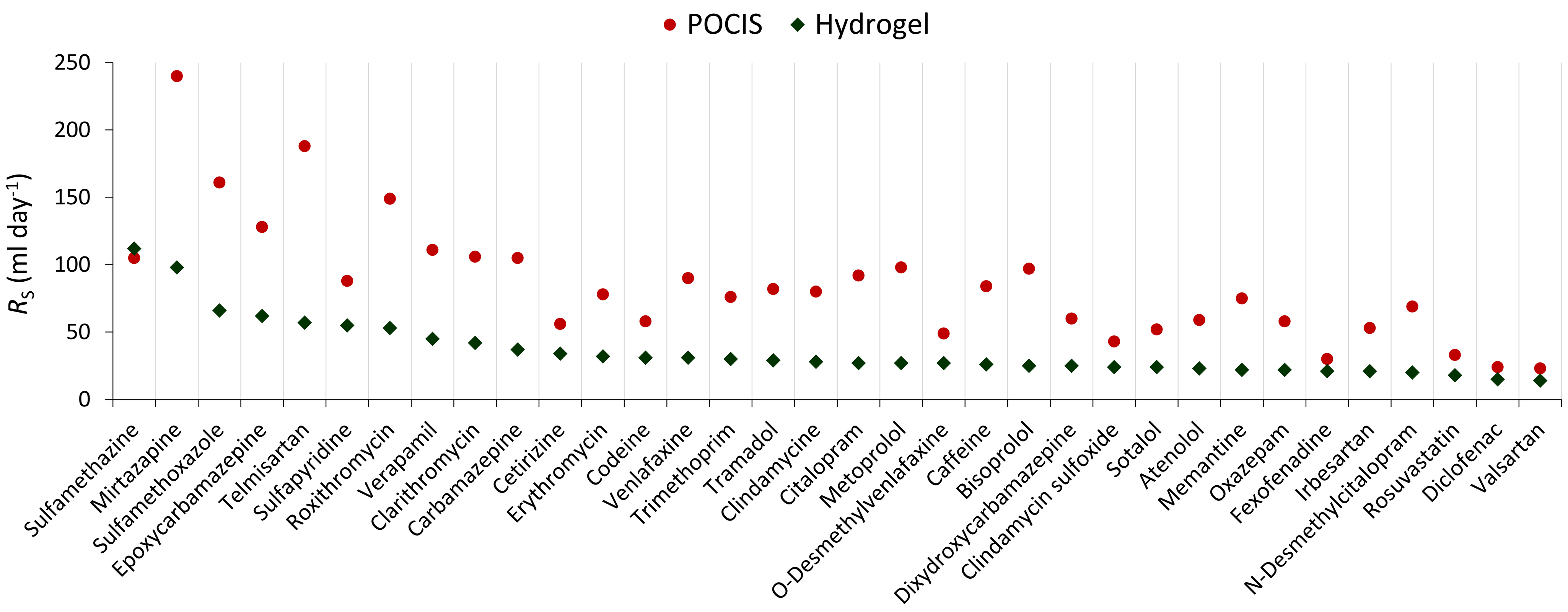
- Membrane sorbs compounds
- Potential sorbent loss
- Sorbent may fall to one side

Sampling method

Samplers were exposed for 7, 14, 21 and 27 days, always in triplicate. Daily composite sample was also prepared using an automatic sampler collecting 50 mL of water every 30 minutes. Average water temperature was 4.9 °C and the water discharge 27.7 m³ s⁻¹. However, river flow was changing considerably during the sampling period due to rain and snowmelt.

Results





The upper four figures show exemplary uptake of four compounds into the samplers. The dashed line represents aqueous concentration of daily composite samples (C_W), full lines represent model fits for amount of compound adsorbed (N_S) into POCIS (red) and the hydrogel sampler (green).

The lower figure shows comparison of sampling rates (R_S) for POCIS and Hydrogel samplers (uncorrected for effective sampling area). In all figures, red circles denote POCIS data, while green squares denote hydrogel sampler data.

Conclusions

Only one compound undetected by the hydrogel sampler while detected by POCIS after 4 weeks

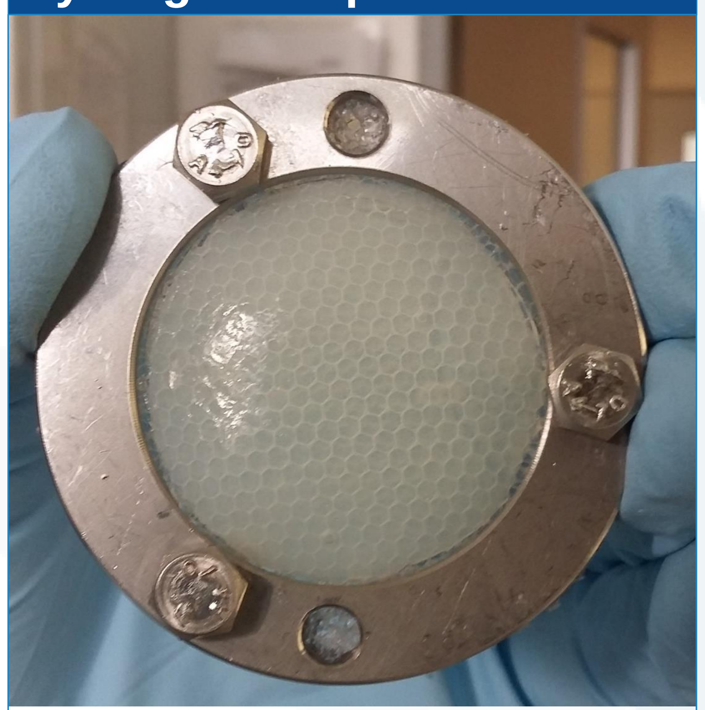
Hydrogel sampler shows better repeatability of triplicates

Lower R_S of hydrogel sampler but only by 20% in average when corrected for sampling area

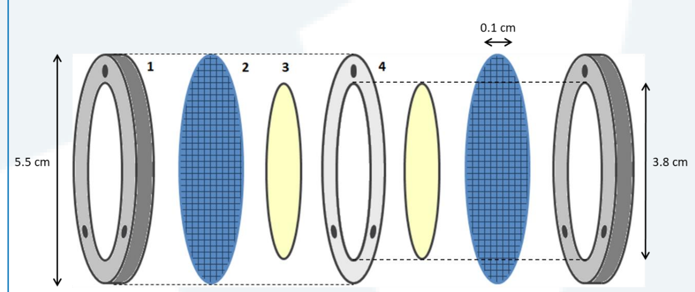
Models better fit the hydrogel sampler data, suggesting lower impact of changes in conditions on R_S

R_S values for POCIS and the hydrogel sampler correlate well (r = 0.76)

Hydrogel sampler



The hydrogel sampler is based on an original diffusive gradient in thin films for organic compounds (o-DGT)[3], with a sandwich design structure similar to POCIS[4]. It has a sampling area of 23 cm² and does not contain any membrane, only a diffusive agarose hydrogel layer strengthened by a nylon mesh netting. The inner hydrogel layers contain a dispersed Oasis HLB sorbent.



+ Sorbent fixed in hydrogel
+ Durable against damage
+ Allows prediction of R_S

- More difficult preparation
- Hydrogel may degrade in time
- Needs to be always moisturised

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3. Alvarez, D. A. *et al.* Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. *Environ. Toxicol. Chem.* **23**, 1640–1648 (2004).
4. Chen, C. E., Zhang, H. & Jones, K. C. A novel passive water sampler for in situ sampling of antibiotics. *J. Environ. Monit.* **14**, 1523–1530 (2012).
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