Science of the Total Environment 864 (2023) 161071

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

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

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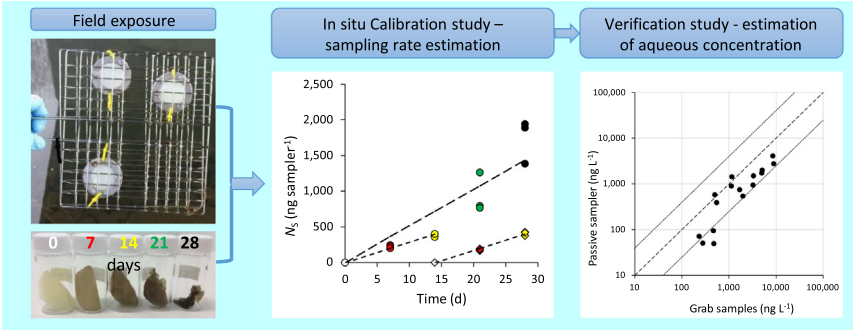
HIGHLIGHTS

- In situ calibration of hydrogel-based sampler for (HPS) 70 compounds in the effluent
- Sampling robustness and repeatability worsened after 14 days of exposure.
- Agarose diffusive layer is prone to microbial degradation and fouling in wastewater.
- HPS-derived aqueous concentrations were within a factor of 4 of grab sample data.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Damià Barceló

Keywords:
o-DGT
Sampling rate
In situ calibration
Pharmaceuticals
Currently used pesticides
Perfluoroalkyl substances

ABSTRACT

An upscaled passive sampler variant (diffusive hydrogel-based passive sampler; HPS) based on diffusive gradients in thin films for polar organic compounds (o-DGT) with seven times higher surface area (22.7 cm^2) than a typical o-DGT sampler (3.14 cm^2) was tested in several field studies. HPS performance was tested in situ within a calibration study in the treated effluent of a municipal wastewater treatment plant and in a verification study in the raw municipal wastewater influent. HPS sampled integratively for up to 14 days in the effluent, and 8 days in the influent. Sampling rates (R_s) were derived for 44 pharmaceuticals and personal care products, 3 perfluoroalkyl substances, 2 anticorrosives, and 21 pesticides and metabolites, ranging from 6 to 132 mL d^{-1}. Robustness and repeatability of HPS deteriorated after exposures longer than 14 days due to microbial and physical damage of the diffusive agarose layer. In situ R_s values for the HPS can be applied to estimate the aqueous concentration of the calibrated polar organic compounds in wastewater within an uncertainty factor of four. When accepting this level of accuracy, the HPS can be applied for monitoring trends of organic micropollutants in wastewater.

1. Introduction

Over the past decades, more and more chemicals have been emitted into the aquatic environment via effluents from municipal wastewater treatment plants (WWTP). Chemicals that end up in waterways include compounds that are regulated by authorities as well as compounds of emerging concern such as pharmaceuticals and personal care products (PPCPs), per- and polyfluoroalkyl substances (PFASs), pesticides, and their transformation products (de Souza et al., 2020; Richardson and Kimura, 2019). Many of these chemicals are not sufficiently removed during wastewater treatment (Golovko et al., 2014; Zhang et al., 2014).

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http://dx.doi.org/10.1016/j.scitotenv.2022.161071
Received 13 November 2022; Received in revised form 15 December 2022; Accepted 16 December 2022
Available online 22 December 2022

Typically, they are continuously emitted from WWTPs in low concentrations, which causes their pseudo-persistence and results in chronic organism exposure in recipient ecosystems (Ebele et al., 2017; Hughes et al., 2013). Since many of these chemicals are designed to possess specific physiological effects on organisms, complex mixtures present in wastewater can adversely affect aquatic life (Cleuvers, 2003; Hernando et al., 2006; Malaj et al., 2014) and even pose a risk to human health (Sharpe and Irvine, 2004). Understanding the occurrence and fate of the chemicals mentioned above and their transformation products is essential for their successful management in the future. Therefore, there is a growing need for efficient and representative monitoring of their emissions and levels in wastewater and receiving water bodies.

Over the past decades, passive sampling techniques have been developed for representative monitoring of trace contaminants. Their advantages over conventional sampling methods include time integrative sampling, simple operation, low cost, and low detection limits (Alvarez et al., 2005; Górecki and Namieśnik, 2002; Kot et al., 2000; Vrana et al., 2005).

In passive sampling, compounds accumulate by diffusion from the sampled medium onto a sorbent that is typically used for solid-phase extraction. During the initial stage, the passive sampler accumulates compounds integratively, and the sampled compound mass is proportional to the time-weighted average concentration in water (Booij et al., 2007). Sorbent powder can be compressed between diffusive membranes as in Polar Organic Chemical Integrative Sampler (POCIS) (Alvarez et al., 2004) or dispersed in a porous supporting disk as in Chemcatcher (Kingston et al., 2000) or Speedisk (de Weert et al., 2020). The compound uptake into the passive sampler is typically affected by environmental conditions such as hydrodynamics, temperature, or pH (Charlestra et al., 2012; Mills et al., 2014). Among these factors, hydrodynamics has a significant effect on passive sampling uptake kinetics due to the flow-dependent mass transfer resistance in the water boundary layer (WBL) (Harman et al., 2012). Inserting a diffusion-limiting barrier between water and the sorbent phase can minimize or even eliminate the effect of hydrodynamics (Challis et al., 2016; Zhang and Davison, 1995). POCIS and Chemcatcher use a microporous polyethersulfone (PES) membrane, but the uptake of many compounds is still partially controlled by mass transfer through WBL (Djomte et al., 2018; Li et al., 2010; O'Brien et al., 2011; Vermeirssen et al., 2008). Alternatively, the effect of WBL resistance to mass transfer can be greatly reduced, e.g., by using a several mm thick microporous polyethylene tube (Fauvelle et al., 2017) or a diffusive hydrogel layer (Chen et al., 2012; Davison and Zhang, 1994).

A passive sampler based on diffusive gradients in thin films (DGT) was first applied for monitoring labile metal species in water (Davison and Zhang, 1994) and later adapted for polar organic compounds (Chen et al., 2012). DGT for organic compounds (o-DGT) was applied for passive sampling of PPCPs, pesticides, organophosphate flame retardants, and PFASs (Challis et al., 2016; Chen et al., 2018; Guan et al., 2018; Guibal et al., 2017; Guo et al., 2017; Wang et al., 2020a). However, there are several limitations concerning using the o-DGT sampler. Most o-DGT designs include a PES membrane for mechanical protection, which can sorb some compounds and complicate uptake modeling (Vermeirssen et al., 2012). Another issue of o-DGT is its small surface area (3.14 cm^2). It is 5–10 times smaller than that of Chemcatcher or POCIS, resulting in low surface-proportional sampling rates (Challis et al., 2016; Guibal et al., 2017; Li et al., 2019; Wang et al., 2020a; Zheng et al., 2015, Booij et al., 2007) and related sensitivity. Therefore, several upscaled o-DGT sampler variants with 4 to 25 times larger surface area were recently developed (Belles et al., 2017; Martins de Barros et al., 2022; Mechelke et al., 2019; Urík and Vrana, 2019; Yang et al., 2022).

The passive sampler design introduced by Urík and Vrana (2019), further denoted here as the diffusive hydrogel-based passive sampler (HPS), has a surface area of 22.7 cm^2 and uses 1.5 % agarose hydrogel as an outer diffusive layer without any additional membrane protection. The HPS was recently tested in a laboratory and several field studies (Alygizakis et al., 2020; Urík and Vrana, 2019), showing integrative chemical uptake over several weeks (Alygizakis et al., 2020). However, when considering the deployment of the sampler under harsh environmental conditions, e.g., in raw sewage, the diffusive layer and, consequently, compound uptake might be affected beyond control. Therefore, it is necessary to test in situ the sampler's robustness under different exposure conditions and characterize its performance and limitations.

The main objective of this study was to assess the robustness of the HPS performance under various exposure conditions and prove the comparability of sampling rates (R_s) derived under different conditions (laboratory, wastewater effluent) for the estimation of aqueous concentration. The HPS is expected to resist changes in water flow rate and show robust R_s. The HPS performance was tested in two case studies: treated wastewater effluent and raw influent. The parameters assessed included the integrativeness of HPS over the deployment in two scenarios, namely treated wastewater effluent and raw influent, and the reproducibility of R_s values compared to previously published studies (Alygizakis et al., 2020; Urík and Vrana, 2019). R_s for PPCPs, PFASs, anticorrosives, pesticides, and metabolites were estimated in situ in the treated wastewater effluent. Their applicability for estimating aqueous concentration was tested in a verification study in the raw influent (Fig. 1).

2. Materials and methods

2.1. Reagents and chemicals

A range of chemicals from different classes was selected, including 78 pharmaceuticals, personal care products and their metabolites (further denoted as PPCPs), 29 PFASs, and 110 pesticides, their metabolites, and anticorrosives in the calibration study (see Section 2.3.1); and 28 PPCPs, and 53 pesticides in the verification study (see Section 2.3.2). These compounds were selected due to their toxicological relevance and frequent occurrence in municipal wastewater. The list of all investigated compounds and their physicochemical properties is given in Tables S1–1 to S1–3. The list of used chemicals and analytical standards is given in Tables S2–1 and S2–2.

For HPS preparation, agarose with a gel strength of 3200 g cm^{-2} and a transition point of 36.0 °C ± 1.5 °C (Sigma-Aldrich, Germany), demineralized water (Aqua Osmotic, Czech Republic), Oasis HLB® 30 μm sorbent (Waters, USA), and nylon netting (insect screen for windows, Easy Life GmbH, Germany) were used.

2.2. Passive sampler

We applied a HPS design based on diffusive gradients in thin hydrogel films, as described previously by Urík and Vrana (2019). The passive sampler consists of two sorptive agarose hydrogel disks containing dispersed Oasis HLB sorbent (110 mg sorbent per disk, diameter of 3.8 cm and 0.1 cm thick) and two outer diffusive hydrogel disks made of 1.5 % (*w/v*) agarose with embedded strengthening nylon netting (disk diameter of 5.5 cm and 0.1 cm thickness). The sampler was assembled with all gel layers held together between two stainless steel rings using stainless steel bolts and nuts (Fig. S3). This two-sided sampler surface area active for compound uptake from water is 22.7 cm^2, and the ratio of surface area to sorbent mass is the same as in POCIS, i.e., 200 cm^2 g^{-1}.

2.3. Sampling site and deployment design

2.3.1. In situ calibration study

The in situ sampler calibration study was performed in the treated wastewater effluent from a large municipal WWTP in Modřice, serving the city of Brno (Czech Republic), with a capacity of approximately 500,000 equivalent inhabitants. The WWTP utilizes mechanical and biological (conventional activated sludge) treatment technologies.

The sampling campaign was carried out from 20 November to 18 December 2018 in the WWTP effluent discharge weir tank used to measure the effluent flow. Passive samplers were deployed for 7, 14, 21, and 28 days in triplicates according to the deployment design shown in Table 1. Passive samplers were fixed with color-labeled cable ties to a stainless-steel

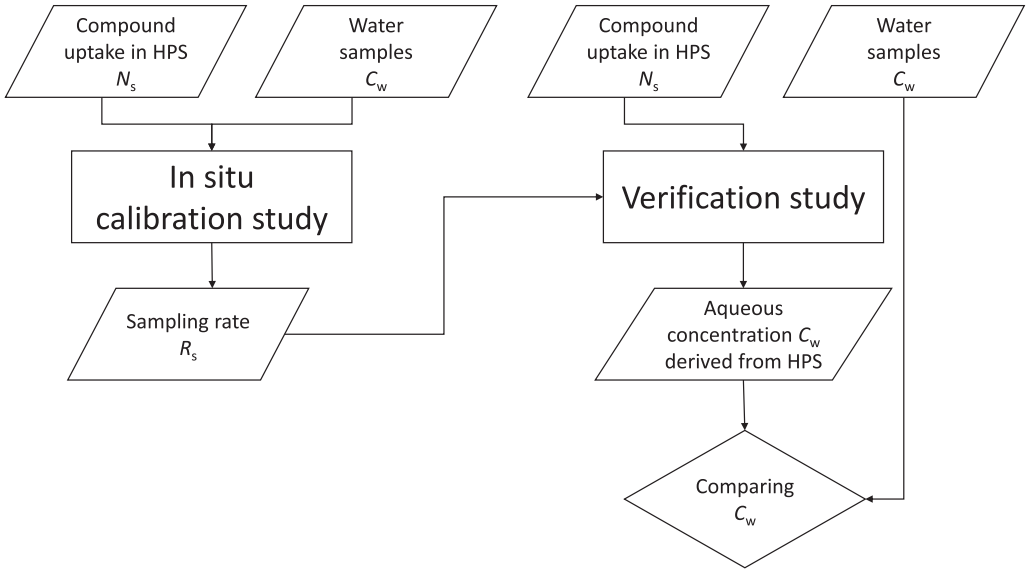

Fig. 1. A flowchart explaining the testing HPS performance for monitoring contaminants in wastewater.

wireframe and deployed in treated wastewater using ropes around 1 m below water level (Fig. S4–1). After retrieval, they were immediately transported in a cooled container to the laboratory and further processed. The WWTP operator provided daily composite 24 h water samples, prepared from subsamples collected with 2 h sampling frequency. 150 mL daily composite water samples were stored frozen at −20 °C in 250 mL Nalgene® polycarbonate bottles until processing in the laboratory. Wastewater parameters are provided in Table S4.

2.3.2. Verification study

In the verification study, passive samplers were deployed in the raw influent of a municipal WWTP in the Brisbane area, Queensland, Australia, from 26 July to 10 August 2017. Passive samplers were deployed in duplicates in time series up to 15 days according to the deployment design shown in Table 2 and Fig. S4–2. On days 6, 8, 12, and 15, composite 24 h water samples were collected and analyzed for comparison with passive samplers. Water samples were stored frozen at −20 °C at the laboratory until analysis was done.

2.4. Sample processing

2.4.1. Passive samplers

Exposed passive samplers were photographed and inspected for signs of physical damage or diffusive gel layer decomposition (Figs. S5–1 and S5–2). In the laboratory, samplers were disassembled, diffusive hydrogel disks were discarded, and the sorptive hydrogel disks were collected into 20 mL vials with screw caps. Extraction solvent was added, i.e., 10 mL of methanol with 0.5 % ammonia (calibration study) or pure methanol (verification study). Compounds were extracted from the sorptive hydrogel to the organic solvent by shaking on an orbital shaker at 60 rpm for 24 h. Subsequently, the extraction was repeated with 10 mL of methanol for another 24 h. The extracts were collected, combined, and evaporated under gentle nitrogen flow to a volume of <2.5 mL. The extracts were filtered through a 0.20 μm syringe filter, evaporated under nitrogen to the last drop, and redissolved in 1 mL of methanol. Details are described in Section S5.

Extraction recoveries of methods used in the calibration and the verification study were tested separately. The procedure is given in Section S6 and results in Tables S6–1 to S6–3. Compounds with recoveries <40 % were excluded from R_s estimation.

2.4.2. Water samples

The daily composite water samples from both studies were thawed, homogenized by shaking, an aliquot of the sample was filtered through a regenerated cellulose filter, and a mixture of isotopically labeled standards was added. An aliquot of water samples was directly injected into the instrument for analysis (Section 2.5). Details are provided in Section S5.

Table 1
Passive sampler deployment design in the calibration study performed in the treated wastewater effluent in municipal WWTP in Modřice, Brno, Czech Republic. Color bars represent the sampling periods; the deployment duration in days is noted inside the bars. Triplicate passive samplers were deployed during each sampling period.

Sampler set	From	To	Exposure time in days			
			0–7 days	7–14 days	14–21 days	21–28 days
1	20-Nov-18	27-Nov-18	7			
2	27-Nov-18	4-Dec-18		7		
3	4-Dec-18	11-Dec-18			7	
4	11-Dec-18	18-Dec-18				7
5	20-Nov-18	4-Dec-18	14			
6	4-Dec-18	18-Dec-18			14	
7	20-Nov-18	11-Dec-18	21			
8	27-Nov-18	18-Dec-18		21		
9	20-Nov-18	18-Dec-18	28			

Table 2
Passive sampler deployment design in the verification study performed in the raw influent of municipal WWTP in the Brisbane area, Queensland, Australia. Color bars represent the sampling periods; the deployment duration in days is noted inside the bars. Duplicate passive samplers were deployed during each sampling period.

Sampler set	From	To	Exposure time in days			
			0–5days	5–8 days	8–12 days	12–15 days
1	26-Jul-17	31-Jul-17	5			
2	31-Jul-17	3-Aug-17		3		
3	3-Aug-17	7-Aug-17			4	
4	7-Aug-17	10-Aug-17				3
5	26-Jul-17	3-Aug-17	8			
6	3-Aug-17	10-Aug-17			7	
7	26-Jul-17	7-Aug-17	12			
8	26-Jul-17	10-Aug-17	15			

2.5. Instrumental analysis

In the calibration study, passive sampler extracts were diluted with ultra-pure water 1:1, and an isotopically labeled standard mixture was added (2.5 ng of each compound, Table S2–1). Samples were analyzed by LC/MSMS. The analytical system consisted of LC pump Accela 1250 (Thermo Fisher Scientific, USA), mass spectrometers – triple stage quadrupole TSQ Quantiva (LC/MSMS; for PPCPs and pesticides analysis), and for PFASs analysis high-resolution hybrid quadrupole - orbital trap MS QExactive (LC/HRMS), both Thermo Fisher Scientific. Details of settings and methods of analysis can be found in Section S7.1.1, Fedorova et al. (2013), and Grabic et al. (2012).

PPCPs and pesticides in water samples from the calibration study were analyzed using in-line solid-phase extraction with tandem mass spectrometry (SPE-LC/MSMS). The in-line SPE/LC-QqQ MS system was the same, but the second LC pump Accela 600 (Thermo Fisher Scientific, USA), operating extraction HPLC column was used. According to our previously published method (Lindberg et al., 2014), 1 mL of water was injected and transferred to the extraction column. LC/HRMS (QExactive) with 100 μL direct water injection was used to analyze PFASs. Detailed information on settings and methods validation is given in Section S7.1.2, Fedorova et al. (2013), and Lindberg et al. (2014).

In the verification study, passive sampler extracts were evaporated under nitrogen to 200 μL and 800 μL of MQ water was added. Passive sampler extracts and grab samples of water were analyzed using the Shimadzu Nexera HPLC system (Kyoto, Japan) with a Phenomenex biphenyl column (50 mm × 2.1 mm × 2.6 μm particle size) and a Kinetex EVO C18 pre-injector column. Analytes were quantified using an AB/SCIEX (Ontario, Canada) 6500 QTRAP system with electrospray ionization in positive and negative ionization mode with a scheduled multiple reaction monitoring (MRM) switching process. All other details about the instrumental method are given in Section S7.2 and Kaserzon et al. (2017).

2.6. Data analysis

The uptake kinetics of a compound from water to the passive sampler can, in general, be described by a differential equation (Booij et al., 2007).

$$\frac{dC_s}{dt} = \frac{Ak_o}{m_s}\left(C_w - \frac{C_s}{K_{sw}}\right) \quad (1)$$

where C_s (ng kg^{-1}) is the concentration of a compound in the sampler sorbent, t (days) is the sampling time, k_o (L m^{-2} d^{-1}) is the overall mass-transfer coefficient, A (m^2) is the sampler surface area, m_s (kg) is the sorbent mass, C_w (ng L^{-1}) is the compound concentration in water and K_{sw} (L kg^{-1}) is the compound-specific sorbent-water distribution coefficient. The product $A \times k_o$ is the sampling rate (R_s; L d^{-1}) and may be interpreted as a compound-specific volume of water extracted by the sampler per day.

In general, when K_{sw} value of analyzed compounds is on average log K_{sw} of 4 (L kg^{-1}) and the sampling rate R_s 50 mL d^{-1} as estimated in Urík and Vrana (2019), it can be assumed that the Oasis HLB sorbent uptake capacity is sufficiently high to integratively sample investigated compounds for up to 14 days deployment. In such a case, the sampling rate is the only calibration parameter needed to estimate the aqueous concentration. When assuming integrative sampling, a constant compound aqueous concentration and zero initial concentration in the sampler, Eq. (1) can be integrated:

$$C_s = \frac{C_w R_s t}{m_s} \quad (2)$$

The product of $C_s \times m_s$ represents the accumulated amount of a compound in the passive sampler N_s (ng sampler^{-1}).

In the calibration study, N_s was calculated from the mass fraction of compounds in the dried sorptive gel layer (ng g^{-1}) multiplied by the nominal dry sorptive gel mass, determined as the mean value of sorptive gel mass from blank samplers (0.13 ± 0.01 g). Sampling rates R_s (L d^{-1}) were calculated for sampler deployment periods of 0–14, 14–28, and 0–28 days. Different approaches were used to calculate R_s depending on the temporal trend of chemical concentrations measured in daily composite water samples C_w during sampler exposure. When C_w was constant, R_S was estimated from linear regression of compound uptake to sampler using a rearranged Eq. (2):

$$R_s = \frac{N_s}{C_w t} \quad (3)$$

where C_w (ng L^{-1}) is the mean concentration of a compound in 24 h composite samples during the investigated period, and N_s/t (ng day^{-1}) is the slope of a linear regression of sampler uptake as a function of exposure time.

In case when the concentration in the sampled water had a linear increasing or decreasing temporal trend, the time course of aqueous concentration was described by parameters of a linear regression

$$C_w = C_{w0} + C't \quad (4)$$

where C_{w0} is the aqueous concentration at $t = 0$ and C' is the concentration rate of change. In such case, R_s was calculated according to Booij et al. (2003):

$$R_s = \frac{N_s}{(C_{w0} + \frac{C't}{2})t} \quad (5)$$

The calculation of corresponding uncertainties is shown in Section S8.

Time integrative properties of the sampler were assessed starting from the previous evidence that a 7-day time exposure is fully time-integrative for a broad range of investigated compounds (Alygizakis et al., 2020).

The sum of amounts accumulated in samplers exposed for several consecutive short time intervals was compared with the amount in a sampler exposed in parallel for a longer time, i.e., 2 × 7-day against 14-day exposures, 3 × 7-day against 21-day exposures, 4 × 7-day against 28-day exposures and other possible combinations. Time-integrative uptake is confirmed for a long exposure, if N_s does not differ from the N_s sum in parallel consecutive short exposures.

For statistical tests, normal data distribution was assumed. Linear regression of sampler uptake data was performed in Microsoft Excel for Microsoft 365 MSO Version 2202 (Microsoft Corporation). The linear regression intercept was forced through the origin because all compound concentrations in the analyzed field blanks were below limit of quantification (LOQ), and no lag phase was observed in the uptake curves. Statistical analyses were performed in SigmaPlot Version 12.3 (SynStat Software, San Jose, CA, USA). Sampling rates were compared using one-way ANOVA ($p < 0.05$) and post hoc Holm-Sidak test ($p < 0.05$). Correlation between sampling rates and compound properties was assessed using the Pearson correlation coefficient, and linear regression slope difference from zero was tested by Student's t-test ($p < 0.05$).

In the verification study, C_w was estimated for compounds that showed time-integrative uptake to the sampler. C_w was calculated from the accumulated amount in the exposed passive sampler N_s using R_s derived in the calibration study applying a rearranged Eq. (3).

3. Results and discussion

3.1. Calibration study

3.1.1. Concentrations of compounds in wastewater

During the calibration study, 55 PPCPs, 6 PFASs, and 58 anticorrosives, pesticides, and metabolites were detected in treated wastewater effluent from WWTP in Brno, Czech Republic. The compounds' occurrence during three sampling intervals (0–14, 14–28, 0–28 days) in the daily composite 24 h water samples is summarized in S9, Tables S9–1 to S9–3. The average concentration in water was calculated for compounds detected in at least 50 % of the 29 composite water samples. The compounds' average concentrations in water are given in Table S10. The concentration of 87 % of compounds was constant without any large fluctuations (CV < 40 %) during the entire sampler exposure (Table S10). Aqueous concentrations with variability <40 % were used for further R_s estimation, accepting a precision of 40 % for compounds at μg L^{-1} or lower level according to the Horwitz function (Taverniers et al., 2004).

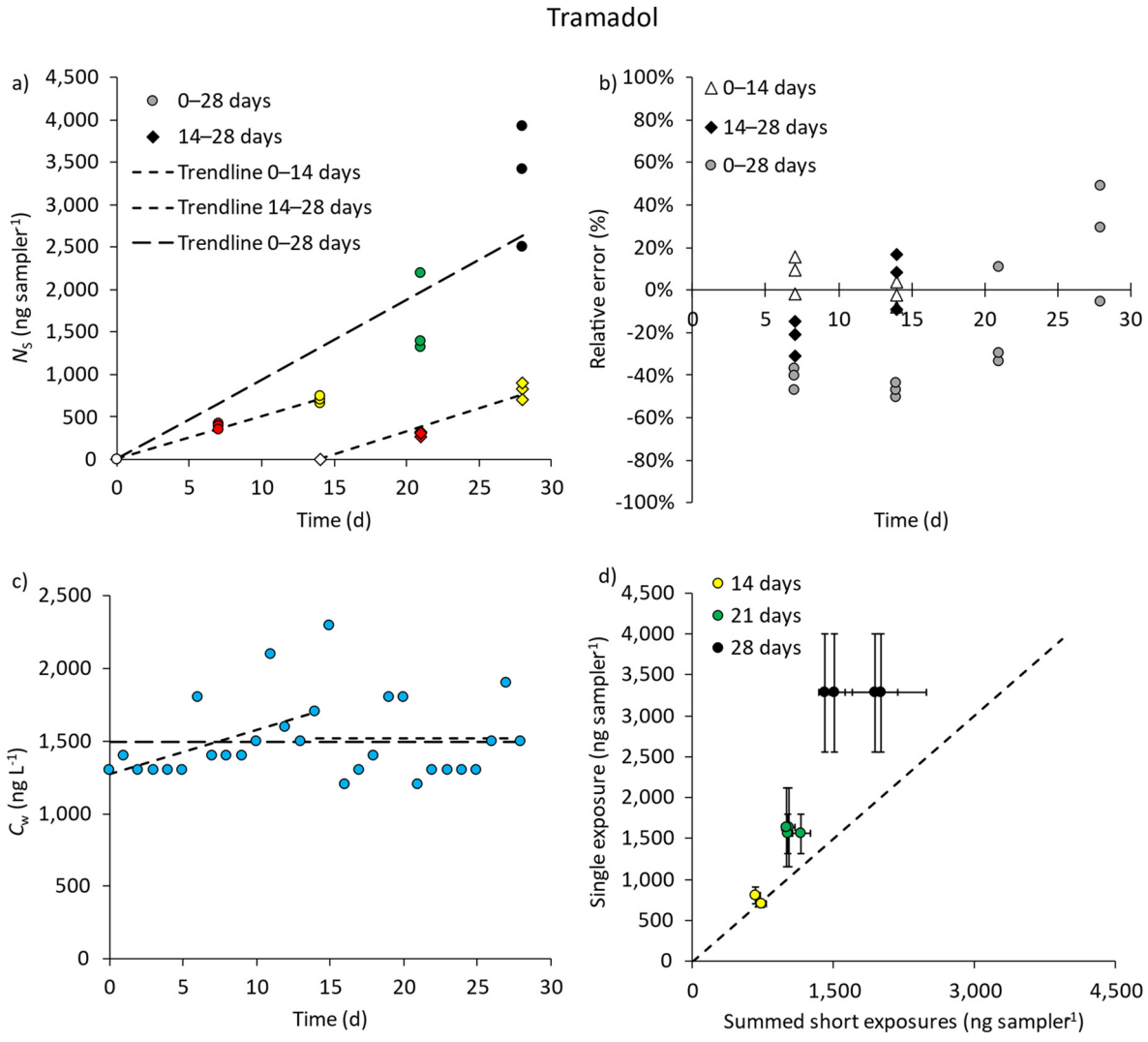

Fig. 2. Exemplary results of tramadol from the calibration study: a) compound uptake to the passive sampler, red, yellow, green, and black color represent 7, 14, 21, and 28 days of exposure; b) the difference between modeled and measured compound uptake; c) the aqueous concentration in daily composite water samples and their modeled time trends (lines) during sampler deployment; d) assessment of time-integrative uptake, comparing compound uptake in several subsequent short sampler exposures (x-axis) versus uptake into one sampler deployed in parallel for a longer time (y-axis). More detailed graph description is provided in Section S11.

Table 3
Tramadol sampling rates (R_s) estimation over three periods of passive sampler exposure. The number of samples above their respective LOQ is *n*. C_w in time describes the temporal variability during sampler exposure (constant, linear time trend, or fluctuating), the *p*-value from the Student's *t*-test documents whether the uptake line slope is significantly different from zero, C_w is the mean aqueous concentration, and its standard deviation (SD), C_{w0} denotes C_w at $t = 0$ and the slope describes the rate of concentration change. The number of samples used for R_s estimation (*n*), R_s, and its standard error (SE) were calculated as described in Section S8.

Tramadol	Water							Passive sampler		
Exposure time	*n*	C_w in time	*p*-Value	C_w (ng L^{-1})	SD	C_{w0} (ng L^{-1})	Slope (ng L^{-1} d^{-1})	*n*	R_s (mL d^{-1})	SE
0–14 days	15	Linear	0.02	–	–	1270	30	9	35	4
14–28 days	15	Constant	0.46	1520	320	–	–	9	36	3
0–28 days	29	Constant	0.53	1500	270	–	–	15	63	6

3.1.2. Passive sampler uptake

Together, 64 PPCPs, 11 PFASs, and 87 anticorrosives, pesticides, and metabolites were detected in exposed passive samplers. Details of the compounds' occurrence in the passive sampler are given in Tables S9–1 to S9–3. Compounds present simultaneously in water and passive sampler in at least 50 % of the samples comprised 44 PPCPs, 3 PFASs, and 23 anticorrosives, pesticides, and metabolites. For those compounds, R_s estimation was performed.

3.1.3. Assessment of linearity and integrative range of uptake

Integrative uptake to the passive sampler was demonstrated for up to 14 days (shown in Figs. 2d and S11). After 21 and 28 days of deployment, data points were far from the unity line, indicating a deviation from time integrative uptake. The uptake during the sampler exposure was linear, but the linear regression slope for the exposure of 28 days was steeper than the slopes of 14 days of exposure (Fig. 2a).

3.1.4. Calculation of in situ sampling rates

We estimated R_s for three time periods, i.e., 0–14, 14–28, and 0–28 days. Depending on the time trend of compound concentration in water during the period of interest, sampling rates were calculated using approaches as described in Section 2.6.

An example evaluation of the results of the calibration study for tramadol is given in Table 3 and Fig. 2. Equivalent information for the remaining investigated compounds is provided in Table S11 and Fig. S11.

3.1.5. Sampling rate stability during passive sampler exposure

Estimated R_s for periods 0–14, 14–28 days, and 28-day exposure (0–28 days) were mutually compared using one-way ANOVA. The results (Table S12–1) showed that R_s for 28-day exposure were significantly higher ($p < 0.05$) in most cases than those for 14-day exposures, while R_s for subsequent 14-day exposures did not differ significantly from each other. These results were observed for 34 PPCPs, two PFASs, and two anticorrosives, pesticides, and their metabolites. However, ANOVA showed no significant difference among the three calculated R_s for 23 compounds (11 PPCPs, one PFAS, 11 anticorrosives, pesticides, and metabolites). This uniformity can be, in most cases, explained by elevated variability in aqueous concentration and worsened repeatability in passive sampler uptake data after longer exposure. This results in lower R_s precision causing a problem with the identification of statistical differences in mean R_s values.

In addition to R_s values increasing in exposures exceeding 14 days, the sampling repeatability also deteriorates, as shown in Fig. 2b. The average repeatability of passive sampler triplicates exposed for 7, 14, 21, and 28 days was 12 ± 7 %, 11 ± 8 %, 25 ± 11 %, and 27 ± 11 %, respectively. The repeatability of individual compounds is shown in Table S12–2.

The increase in R_s, combined with a worsened sampling repeatability, in sampler exposures longer than 14 days can be explained by the effect of harsh exposure conditions in effluent with a high activity of microorganisms and invertebrates. The diffusive layer got visibly thinner and showed signs of physical damage (Fig. S5–1), but no passive sampler was destroyed (nylon netting incorporated in the diffusive layer prevents physical damage). When the diffusive layer is damaged, e.g., by bacterial degradation or by colonizing biota, it becomes more permeable and less homogeneous. Consequently, compound uptake speeds up beyond the expected control by diffusion in the hydrogel. In such a situation, R_s do not remain constant, and thus they cannot be applied for an accurate calculation of aqueous concentrations. The durability could in the future be improved by using a different type of diffusion hydrogel, e.g., polyacrylamide gel which has been shown to be more resistant to degradation compared to agarose gel (Stroski et al., 2018). However, it has also been shown that polyacrylamide gel exhibits some undesirable sorption of some compounds (Chen et al., 2012).

In the work of Alygizakis et al. (2020), integrative uptake with constant R_s to the identical HPS deployed in the WWTP effluent was observed for up to 28 days. Alygizakis et al. (2020) study was performed in effluent from a membrane bioreactor (MBR) combining activated sludge and membrane filtration. This type of WWTP technology likely yields less biological activity in treated water than the activated sludge technology in our experiment. Results of a single field study do not seem to provide sufficient evidence of the general sampler applicability. Our study showed that for exposures longer than 14 days, there is a significant risk of bias caused by potential

Table 4
R_s values and SE estimated in the calibration study at temperature 15.5 ± 0.7 °C. For most compounds, R_s was calculated as an average from two subsequent 14-day exposure values. SE denotes the standard error of the mean.

Compound	R_S ± SE (mL d^{-1})	Compound	R_S ± SE (mL d^{-1})
Alfuzosin	33 ± 2	Sulfapyridine	87 ± 12
Alprazolam	68 ± 4	Telmisartan	23 ± 1
Amitriptyline	57 ± 4	Tramadol	35 ± 3
Atenolol	28 ± 2	Trans-dihydro-dihydroxy CBZ	70 ± 5
Bisoprolol	32 ± 2	Trazodone	32 ± 1
Carbamazepine (CBZ)	45 ± 2	Trimethoprim	42 ± 5
Cetirizine	50 ± 3	Valsartan	50 ± 3
Citalopram	48 ± 3	Venlafaxine	36 ± 2
Clarithromycin	19 ± 2	Verapamil	59 ± 5
Clindamycin sulfoxide	43 ± 3	62FTS	33 ± 2
Clomipramine	87 ± 3	PFHxA	30 ± 2
Codeine	39 ± 3	PFOA	39 ± 2
Diclofenac	79 ± 5	1H-benzotriazol-(5/4)-methyl	76 ± 4
Dihydro CBZ	46 ± 2	1H-benzotriazol-1-methyl	83 ± 4
Epoxy CBZ	61 ± 4	2.4-Dichlorphenoxypropionic acid	22 ± 2
Erythromycin	29 ± 3	Acetochlor ESA	54 ± 6
Fexofenadine	35 ± 2	Alachlor ESA	48 ± 5
Glimepiride	49 ± 4	Atrazine	83 ± 9
Irbesartan	54 ± 3	Atrazine-2-hydroxy	39 ± 3
Lamotrigine	62 ± 4	Atrazine-desethyl	57 ± 6
Memantine	60 ± 4	Azoxystrobin	33 ± 2
Metoprolol	46 ± 2	Carbendazim	50 ± 3
Mirtazapine	85 ± 8	Diuron	50 ± 5
N-Desmethylcitalopram	46 ± 3	Imidacloprid	83 ± 8
O-Desmethylvenlafaxine	39 ± 3	Metazachlor ESA	41 ± 3
Orphenadrine	57 ± 3	Metolachlor ESA	65 ± 6
Oxazepam	38 ± 2	Metribuzin	59 ± 3
Oxcarbazepine	129 ± 16	Picloram	6 ± 1
Propranolol	42 ± 2	Pirimicarb	37 ± 2
Rosuvastatin	52 ± 7	Propiconazole	36 ± 3
Roxithromycin	22 ± 2	Pyrimethanil	44 ± 2
Sertraline	132 ± 10	Tebuconazole	37 ± 2
Sotalol	19 ± 1	Terbuthylazine-hydroxy	53 ± 6
Sulfamethazine	79 ± 10	Terbutryn	29 ± 2
Sulfamethoxazole	108 ± 5	Warfarin	38 ± 2

sampler wearing. Therefore, we generally do not recommend the HPS for deployment longer than two weeks. Based on the above observations, we consider R_s average from both 14-day exposures as sufficiently robust and applicable for estimations of aqueous concentrations. All R_s are summarized in Table 4. The values ranged from 8.7 to 132 mL d^{-1} for PPCPs, from 29.6 to 38.6 mL d^{-1} for PFASs, and from 6.1 to 83.3 mL d^{-1} for anticorrosives, pesticides, and metabolites.

3.1.6. Sampling rate comparison

Several studies published the R_s values for the HPS design for compounds common to those investigated in this study. We compared the R_s values from our field calibration study to those published by Urík and Vrana (2019) obtained under laboratory conditions and to R_s values in Alygizakis et al. (2020) estimated in WWTP effluent (Table S13–1, Fig. S13). The R_s values were compared using one-way ANOVA and post hoc Holm-Sidak test. Eight of twenty-nine R_s values by Alygizakis et al. (2020) did not differ significantly from R_s reported in this study including alprazolam, clomipramine, diclofenac, oxcarbazepine, sertraline, sulfapyridine, imidacloprid, and metolachlor-ESA. Two of ten R_s, for metribuzin and tebuconazole, reported by Urík and Vrana (2019) also showed no significant difference. The summary results of ANOVA are given in Table S13–2. Overall, R_s estimated in this study were for most compounds lower than those published in previous works. On average, the ratio of R_s values reported by Alygizakis et al. (2020) and R_s values estimated in this study was 0.6 ± 0.3, and the ratio of R_s values from Urík and Vrana (2019) and this study was 1.0 ± 0.7. When inspecting uptake data from Alygizakis et al. (2020), we observed that the uptake for most compounds was not integrative for the entire 28 days. Recalculation of R_s using uptake data from 14 day passive sampler exposures (corresponding with the sampling period in our calibration study) resulted in lower R_s values for most compounds (Table S13–1, Fig. S13). The linear regression of R_s (14 days data) from Alygizakis et al. (2020) against R_s from this study is shown in Fig. 3. The linear regression forced through the origin has a slope of 0.53 ± 0.03 (n = 30, r = 0.96, SE = 19 mL d^{-1}; the linear regression yielded an intercept that was not significantly different from zero). The good correlation between the two datasets means that R_s in our study are systematically lower by a factor of 2 in comparison with the study of Alygizakis et al. (2020).

Different exposure conditions (Table S13–3), especially the temperature and biofouling can explain differences in R_S between the studies. Using the published data on the Arrhenius temperature dependence of diffusion coefficients in agarose hydrogel (Section S14, Urík et al., 2020), the decrease in temperature from 19.7 °C (average temperature in the study by Alygizakis et al., 2020), or 20 °C (average temperature from the study of Urík and Vrana, 2019) to 15.5 °C (this study) is expected to result in a decrease of R_s controlled by diffusion in the hydrogel by 13 % to 14 %. This indicates that the temperature effect alone cannot fully explain the observed R_S decrease. The effect of pH was likely negligible since water pH across studies was similar. The effect of flow rate is also considered negligible since the diffusion hydrogel presents a rate-limiting barrier on compound uptake (Urík and Vrana, 2019).

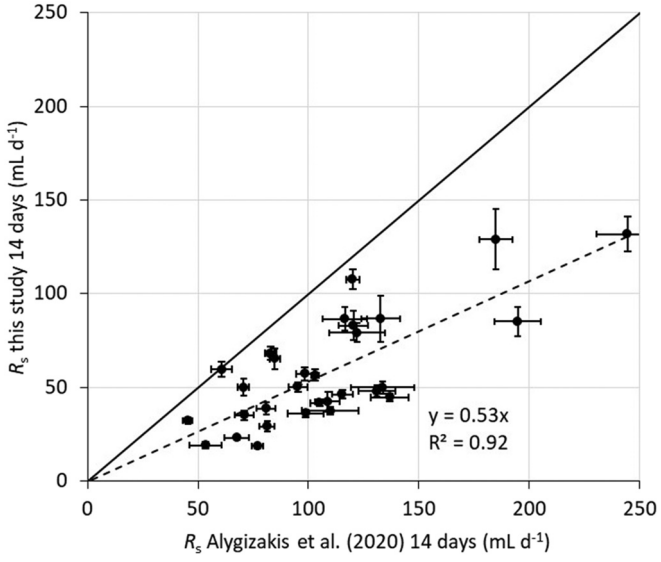

Fig. 3. Comparison of R_s values from this study (on the y-axis) and the study of Alygizakis et al. (2020) (on the x-axis) for 14 day passive sampler exposure. The dashed line represents the linear regression of the data, and the solid line indicates the unity (y = x). The error bars show SE of the R_s values.

It seems that fouling has the most significant impact on the observed R_S difference, but its measurement and quantitative assessment are difficult. The two in situ calibration studies were performed at WWTPs that differed in treatment technology. Whereas our study was performed in a WWTP with the activated sludge process, Alygizakis et al. (2020) study was conducted in a WWTP with a membrane bioreactor (MBR). Effluent from the activated sludge process possesses a higher microbial activity than the MBR effluent since solids and microorganisms are better retained by MBR. Elevated microbial activity in our study could result in faster sampler colonization by microorganisms associated with biofouling buildup in the initial period, resulting in increased resistance to mass transfer and related R_S decrease. The effluent from our study also contained a higher average concentration of total suspended solids (7.4 mg L^{-1}) than the effluent from MBR in the study by Alygizakis et al. (2020) (3.1 mg L^{-1}), which also indicates a higher potential for sampler fouling in our study. There are few studies (Challis et al., 2016; Wang et al., 2022; Wang et al., 2020b) that observed a limited effect of biofouling on sampler uptake but only Challis et al. (2016) used agarose diffusive layer without any additional protective membrane. Moreover, some compounds may sorb to biofouling and degrade by microorganisms in the fouling layer before they reach the binding phase. Since the passive sampler used in our study has a higher surface area than o-DGT, the effect biofouling on R_s may be better detectable. A quantitative evaluation of the effect of biofouling on HPS performance requires further research.

3.1.7. Sampling rates and compounds' properties

In addition to environmental factors, R_S is related to compound properties. We assessed the correlation between estimated R_S and compounds' properties (log K_{ow}, octanol-water distribution coefficient at pH 7.4 log $D_{7.4}$, molecular weight, and molar volume). The graphs showing the relation between the compound properties and R_s are reported in Fig. S15.

Since the sampler has been designed to control the compound uptake by diffusion in gel, R_s should be proportional to the diffusion coefficient in hydrogel D (cm^2 s^{-1})

$$R_s = \frac{DA}{\Delta g} \tag{6}$$

where A (cm^2) is the sampler surface area, and Δg (cm) is the thickness of the diffusive gel.

Since diffusion coefficients decrease with molecular size, large molecules are expected to diffuse through the gel slower than small molecules. Indeed, R_s values decrease with increasing molecular weight and molar volume, with linear regression slopes significantly different from zero (t-test, Fig. S15). R_s is expected to be controlled by diffusion in the hydrogel, and thus it should not be directly related to the compound's hydrophobicity (represented by log K_{ow} or log $D_{7.4}$). In agreement with the expectation, no significant correlation between R_s and log K_{ow} or log $D_{7.4}$ was observed.

3.2. Verification study

3.2.1. Assessment of time integrative uptake

In the verification study conducted in raw influent, 21 PPCPs and four pesticides were detected in all passive samplers. The sum of N_s from two short exposures was compared with N_s of a single long exposure to assess

the sampler uptake. Time integrative uptake was confirmed for 12 PPCPs (atenolol, atorvastatin, carbamazepine, codeine, furosemide, ibuprofen, naproxen, nicotine, temazepam, tramadol, triclosan, and venlafaxine) and three pesticides (DEET, diuron, and imidacloprid) for periods 0–8 and 8–15 days (see Figs. 4 and S16–1). For these 15 compounds, we calculated an average ratio between the sum of N_s from two short exposures (5 and 3 days or 4 and 3 days) and N_s from a single long exposure (8 or 7 days). The average ratio of 1.1 ± 0.4 is close to 1, indicating that the overall uptake was time integrative up to 8 days.

Unfortunately, time integrative uptake could not be confirmed for exposure extended to 15 days. The average ratio of 2.0 ± 0.5 was found between the sum of N_s from two consecutive one-week exposures (8 and 7 days) and N_s from two-week exposure (15 days). Lower uptake in the 15-day deployment may be related to the sampler fouling in raw influent that increases with the increasing exposure time. In addition, slower uptake may be associated with a partial sorbent saturation by co-extracted matrix components from wastewater, as suggested by the coloring of the disks getting more intense with increasing exposure time (Fig. S5–2). Both hypotheses require further investigation.

For the remaining compounds: acesulfame, caffeine, cotinine, hydrochlorothiazide, hydroxycotinine, iopromide, paraxanthine, paracetamol, salicylic acid, and MCPA, we could not confirm time integrative uptake (Fig. S16–2). The average ratio of 2.9 ± 0.4 was found between the sum of N_s from two consecutive deployments (5 and 3 days or 4 and 3 days) and N_s from more extended deployments (8 or 7 days). An even higher average ratio of 7.6 ± 4.3 was found between the sum of N_s from two consecutive one-week deployments (7 and 8 days) and N_s during the two-week deployment (15 days).

The different time integrative behavior of the two substance groups can be partially explained by their physicochemical properties. Whereas compounds from the group that was integratively sampled for up to 8 days had log $K_{ow} > 0$ and were present as neutral species at wastewater pH of 7.5, the remaining compounds were either more hydrophilic with log $K_{ow} < 0$ or present in anionic form (low pK_a values). For those compounds, the Oasis HLB sorbent applied in sampler construction likely has a limited capacity. Stroski et al. (2018) also observed reduced capacity of HLB sorbent for charged compounds. This results in a fast sorbent-water equilibration and consequently in the absence of time integrative sampling. Moreover, the sampler capacity may have been further reduced by the competitive sorption of matrix components from sewage. Uptake capacity can be increased by increasing the mass of Oasis HLB sorbent in the sampler design. When monitoring specific groups of compounds, adsorbents with a higher sorption capacity for a specific binding mode (e.g. ion exchange resins, complex binding agents, etc.) may also be utilized. In addition to a low sorptive capacity, some compounds such as cotinine and hydroxycotinine have low half-lives in wastewater (in the range of hours) (Buerge et al., 2008). These compounds may be degraded by microbial communities colonizing the sampler surface during biofouling buildup.

3.2.2. Estimation of the aqueous concentration

Among the 15 compounds sampled integratively in sewage up to 8 days of sampler deployment, there were 7 with R_s values derived during in situ calibration in WWTP effluent in Modřice, including atenolol, carbamazepine, codeine, diuron, imidacloprid, tramadol, and venlafaxine. For these substances, we estimated C_w from the uptake to passive samplers for the deployment periods 0–8 and 8–15 days, applying the R_s values from the calibration study. Estimated C_w from passive samplers were compared to C_w obtained from water samples. The inspection of Fig. 5 shows that for the investigated compounds most data points fall within the range $0.25 \leq C_{w\ \text{passive sampler}}/C_{w\ \text{water sample}} \leq 4$. When applying R_s values from Alygizakis et al. (2020), points move further from the unity line than in the case of R_s values derived in our calibration study (Fig. S17).

It appears that passive sampling generally underestimates the concentrations in raw sewage measured by active sampling. Several factors may affect the observed difference between active and passive sampling techniques applied to raw sewage. Sewage presents a complex matrix that complicates both sampling and chemical analysis. In raw sewage, some analytes may be partially bound to suspended solids or colloids. Passive samplers enrich only the dissolved fraction of compounds, whereas analysis of whole water samples may also include bound or colloidal analyte residues. Passive sampling efficiency may be further reduced by partial degradation of analytes and the physical fouling, which is more pronounced in sewage than in WWTP effluents. Besides biofouling, partial coverage of the sampler surface by debris present in sewage may cause a reduction in sampling rates.

4. Conclusions

Samplers that utilize diffusion in hydrogel to control the mass transfer of monitored compounds present a promising approach because sampling rates are less prone to the effect of hydrodynamics compared to other passive samplers such as POCIS. Our work showed the derivation of in situ

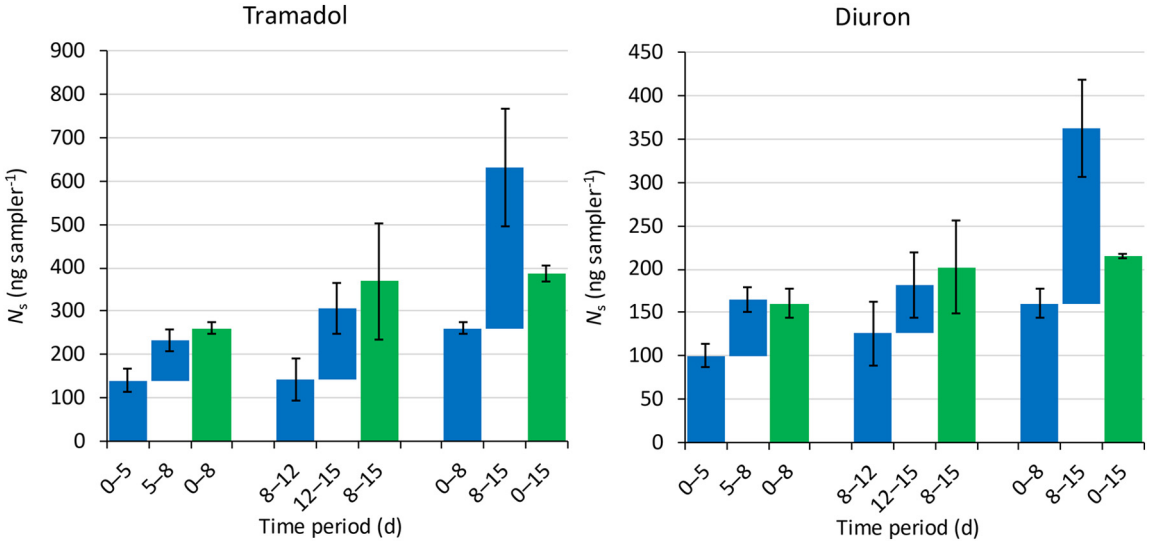

Fig. 4. Uptake of tramadol and diuron in consecutively and in parallel exposed passive samplers in sewage at the WWTP in the Brisbane area, Queensland, Australia is shown as the accumulated amount N_s on the sampler (ng sampler^{-1}) during periods indicated at the x-axis. The summed-up N_s of short exposures (stacked blue bars) is depicted versus a single longer exposure (green bars). Error bars indicate the standard deviation of replicate exposures for direct measurements and propagated standard deviation for the cumulative results.

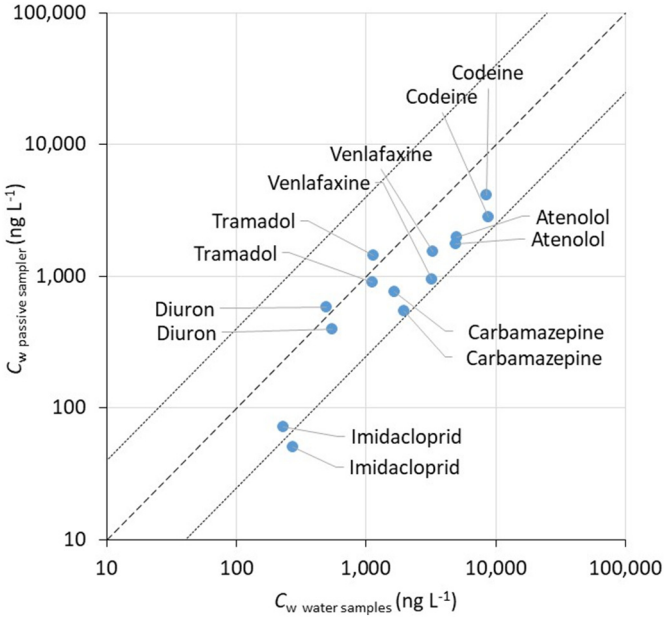

Fig. 5. The comparison of raw sewage C_w using water sampling (x-axis; median value of multiple measurements) and corresponding passive sampling (y-axis) for eight compounds. $C_{w\ passive\ sampler}$ was calculated applying R_s values from the calibration study and is shown for sampler deployments 0–8 and 8–15 days. The diagonal dashed line indicates the equality of both values, and the area between the parallel dotted lines delimits the range where both compared values differ less than a factor of 4.

R_s values for the HPS that can be applied for determining aqueous concentrations of a range of polar organic compounds, including pharmaceuticals, currently used pesticides, and PFAS with an uncertainty factor of four even in extreme sampler exposure conditions of raw municipal sewage. The identified weaknesses of the HPS design include worsening repeatability and poor robustness of the agarose-gel-fitted HPS when deployed in WWTP effluent or raw municipal sewage for >2 weeks. Deteriorating HPS robustness with increasing deployment time is most likely caused by microbial disruption of the diffusive agarose layer, resulting in its gradual physical degradation. Another important factor reducing the sampler efficiency and stability of compounds accumulated in HPS is fouling in the presence of debris and/or high microbial activity in wastewater. In the future, these factors should be investigated in more detail, especially when considering the application of passive samplers as monitoring tools in wastewater-based epidemiology. Future development would benefit from using samplers more resistant to hydrogel degradation. This can be achieved by applying a less biodegradable hydrogel, e.g. based on polyacrylamide, or by protecting the diffusive gel layer with a membrane that does not adsorb chemicals of interest, such as a quartz fiber filter.

CRediT authorship contribution statement

Pavla Fialová: Investigation, Formal analysis, Visualization, Validation, Writing – original draft. **Roman Grabic:** Funding acquisition, Data curation, Writing – review & editing. **Kateřina Grabicová:** Investigation, Data curation, Validation, Writing – review & editing. **Petra Nováková:** Investigation. **Helena Švecová:** Investigation. **Sarit Kaserzon:** Supervision, Writing – review & editing. **Kristie Thompson:** Investigation, Data curation, Writing – review & editing. **Branislav Vrana:** Conceptualization, Methodology, Investigation, Supervision, Project administration, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Authors thank Research Infrastructure RECETOX RI (No LM2018121) financed by The Ministry of Education, Youth and Sports, and Operational Programme Research, Development and Innovation – project CETOCOEN EXCELLENCE (No CZ.02.1.01/0.0/0.0/17_043/0009632) for supportive background. This work was supported from European Union's Horizon 2020 research and innovation programme under grant agreement No 857560 and under the Marie Sklodowska-Curie grant agreement No 734522. The project results were created with the financial support of the provider Czech Science Foundation within the project 'Holistic exposure and effect potential assessment of complex chemical mixtures in the aquatic environment' no. 20-04676X. Personnel of both WWTPs, Sarah MacKay and Sean Van Niekerk from the Queensland Alliance for Environmental Health Sciences are acknowledged for assisting with field sampling and Jakub Urík from RECETOX, Masaryk University is acknowledged for the advice on passive sampler construction and valuable comments on the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.161071.

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