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Performance comparison of three passive samplers for monitoring of polar organic contaminants in treated municipal wastewater

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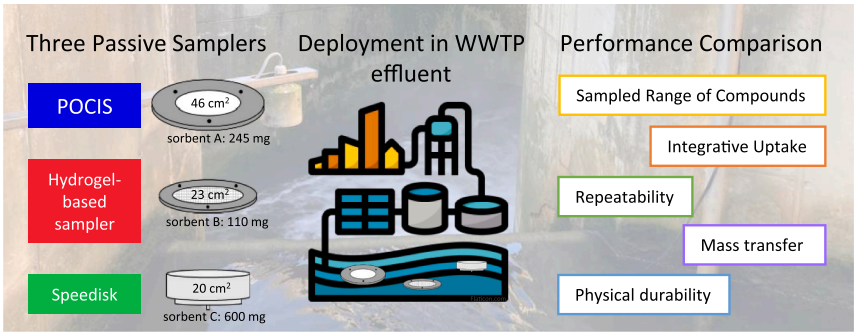
HIGHLIGHTS

- Three co-deployed passive samplers showed consistent surface-specific uptake.
- Differences in sampler design did not affect the overall mass transfer coefficient.
- Water boundary layer was the main barrier controlling the uptake in all three samplers.
- Speedisk seems best suited for the monitoring of a broad range of compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

Over the past decades, several types of passive samplers have been developed and used to monitor polar organic compounds in aquatic environments. These samplers use different sorbents and barriers to control the uptake into the sampler, but their performance comparison is usually not well investigated. This study aimed to directly compare the performance of three samplers, i.e., the Polar Organic Chemical Integrative Sampler (POCIS), the Hydrogel-based Passive Sampler (HPS, an upscaled version of o-DGT), and the Speedisk, on a diverse suite of pharmaceuticals, *per*- and polyfluoroalkylated substances (PFAS), and pesticides and their metabolites. The samplers were deployed side-by-side in the treated effluent of a municipal wastewater treatment plant for different exposure times. All samplers accumulated a comparable number of compounds, and integrative uptake was observed for most compounds detected up to 28 days for POCIS, up to 14 days for HPS, and up to 42 days for Speedisk. In the integrative uptake phase, consistent surface-specific uptake was observed with a significant correlation between samplers ($r \geq 0.76$) despite differences in sampler construction, diffusion barrier, and sorbent material used. The low sampling rates compared to the literature and the low estimated overall mass transfer coefficient suggests that the water boundary layer was the main barrier controlling the uptake for all samplers. Although all devices provided comparable performance, Speedisk overcomes POCIS and HPS in several criteria, including time-integrative sampling over a long period and physical durability.

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1. Introduction

Passive sampling has been developed to complement or replace spot sampling in order to improve the monitoring of contaminants in the aquatic environment (Greenwood et al., 2007; Vrana et al., 2005). Passive sampling has several advantages over spot sampling, including spontaneous in situ preconcentration of analytes, estimation of time-weighted average concentration (TWAC) over the sampling period, low cost, and ease of deployment. However, an accurate TWAC estimation from passive sampling data requires robust, well-defined sampling rates (R_s), i.e., the equivalent volume of water extracted by the sampler per unit of time.

The current TWAC estimation approach typically involves laboratory calibration of samplers under defined conditions. The laboratory-derived R_s are then applied for TWAC calculation. However, their use for TWAC estimation may lead to significant uncertainty (Harman et al., 2011b; Miège et al., 2015) since for some sampler designs, such as the Polar Organic Chemical Integrative Sampler (POCIS), R_s values are known to be affected by environmental conditions (Harman et al., 2012). The most common driver of R_s variability in the field is that the accumulation of substances into the passive sampler is controlled by diffusion through the water boundary layer (WBL), which is dependent on local hydrodynamic conditions (Endo et al., 2019; Li et al., 2010b; Mutzner et al., 2019). For hydrophobic compounds, the in situ R_s can be corrected for the effect of variable hydrodynamic conditions using the dissipation of performance reference compounds (PRCs) (Booij and Smedes, 2010). However, this approach does not apply to commonly used passive samplers of polar compounds, i.e., POCIS and Chemcatcher (Booij and Chen, 2018; Mills et al., 2014). An alternative method to assess the effect of WBL on R_s is based on monitoring the mass transfer coefficient (MTC) in the WBL (Fauvelle et al., 2017; Glanzmann et al., 2022). The effect of WBL on compound uptake can also be minimised by the addition of an extra diffusion limiting barrier, e.g., hydrogel in organic diffusive gradients in thin films (o-DGT) passive sampler (Guibal et al., 2019) or a glass fibre filter in Speedisk-based sampler (de Weert et al., 2020). The additional diffusion barrier often makes these passive samplers fairly independent of water flow; however, it also ultimately decreases the observed R_s (Challis et al., 2016).

The overall MTC of the chemical uptake into the passive sampler can also be compared using side-by-side deployed passive samplers, and several studies have recently compared different types of side-by-side deployed passive samplers for polar compounds (Bonnaud et al., 2023; Challis et al., 2018; Chen et al., 2018; Guibal et al., 2017; Kaserzon et al., 2014; Martins de Barros et al., 2023; Vermeirssen et al., 2012). However, most of them compare the TWAC estimated using published R_s values, introducing uncertainty into the comparison. Only a few studies have compared the overall MTC of side-by-side deployed passive samplers with varying results. While Vermeirssen et al. (2012) observed good agreement in the overall MTC for POCIS and Chemcatcher, Kaserzon et al. (2014) and Bonnaud et al. (2023) found no agreement for POCIS and Chemcatcher or POCIS and o-DGT. Therefore, there is insufficient evidence for the comparability and interchangeability of passive samplers.

In this study, three types of passive samplers for polar compounds, i.e., POCIS (pesticide variant), hydrogel-based passive sampler (HPS, an upscaled o-DGT variant (Urík and Vrana, 2019)), and Speedisk (hydrophilic variant), were deployed side-by-side in the treated effluent of a municipal wastewater treatment plant (WWTP). The main study objective was to directly compare the three co-deployed passive samplers regarding uptake characteristics, such as the range of compounds sampled, time-integrative sampling behaviour, and performance stability over time. In addition, the comparability and interchangeability of these passive samplers are discussed. Observed differences in the compound uptake to the three samplers are critically assessed. Finally, practical recommendations are given for selecting and applying passive samplers to monitor polar organic contaminants in aquatic environments.

2. Material and methods

2.1. Reagents and chemicals

All chemicals were obtained in LC or MS grade purity: acetone and dichloromethane from Fisher Scientific (UK), methanol from Sigma-Aldrich (Germany), acetonitrile, toluene, formic acid, and ammonium acetate from Merck (Germany), aqueous ammonia solution 24–28 % from Mikrochem (Slovakia). Ultra-pure water was obtained from Aqua-MAX-Ultra System (Younglin, Kyounggi-do, Korea) and MilliQ water from the MilliQ water system (Millipore, France). Details of the standards used are given in Table S1–4.

POCIS (Pest-POCIS) samplers were purchased from Nya Exposmeter AB (Tavelsjö, Sweden), and Bakerbond Speedisks® H20-Philic J.T. Baker® were purchased from Avantor Performance Materials, Inc., USA. Agarose with a gel strength of 3200 g cm^{-2} (1.5 % gel) and a transition point of 36.0 °C ± 1.5 °C (Sigma-Aldrich, Germany), demineralised water (Aqua Osmotic, Czech Republic), Oasis HLB® 30 μm sorbent (Waters, USA), and nylon mesh (insect screen for windows, Easy Life GmbH, Germany) were used for HPS preparation.

The investigated chemicals included 78 pharmaceuticals and metabolites, 29 PFAS, 110 pesticides and metabolites, and anticorrosives. The list of compounds and their physicochemical properties are given in Tables S1–1 to S1–3.

2.2. Passive samplers

Dimensions of applied samplers and their construction materials are listed in Table 1.

2.2.1. POCIS

The Pest-POCIS consists of a triphasic mixture of a hydroxylated polystyrene-divinylbenzene resin (Isolute ENV+) and a carbonaceous adsorbent (Carboxen 572) dispersed on a styrene-divinylbenzene copolymer (S-X3 Bio Beads) held between two microporous PES membranes and stainless-steel rings (Fig. S2–1). Its surface area is 45.8 cm^2.

Table 1
Parameters of used samplers.

Parameter	POCIS	HPS	SD
Sorbent	Triphasic mixture: Isolute ENV+, Carboxen 572, and S-X3 Bio Beads	Oasis HLB dispersed in agarose hydrogel	Hydrophilic divinylbenzene
Mass of the sorbent (mg)	245	110	600
Diffusion layer material	Polyethersulphone (PES) membrane with 0.1 μm pore size	Agarose hydrogel with embedded nylon mesh	Glass fibre filter
Diffusion layer thickness (mm)	0.11–0.13	1	0.5
Surface area (cm^2)	45.8	22.7	19.6
Equipment used for field exposure	Perforated sheet steel canister	Wireframe	Wireframe

2.2.2. Hydrogel-based passive sampler (HPS)

HPS is a passive sampler based on diffusive gradients in thin films described by Urík and Vrana (2019) and characterised by Fialová et al. (2023). HPS consists of agarose sorptive hydrogel disks with dispersed Oasis HLB sorbent (110 mg sorbent, 3.8 cm diameter, and 0.1 cm thickness) and two outer agarose diffusive hydrogel disks with embedded nylon mesh (5.5 cm diameter and 0.1 cm thickness). All gel layers are assembled between two stainless-steel rings secured by stainless-steel bolts and nuts (Fig. S2–2). Its surface area is 22.7 cm^2.

2.2.3. Speedisk (SD)

The Speedisk (Bakerbond Speedisk® H20-Philic) was originally designed for the solid-phase extraction of organic compounds from water. It comprises a 5 cm wide open polypropylene cylinder with a thin bed of 600 mg of hydrophilic divinylbenzene sorbent on the bottom, held between a nylon mesh and a glass fibre filter (Fig. S2–3). For use as a passive sampler, the top half of the plastic cylinder rim was cut off, and small holes were drilled in the plastic casing to allow its attachment to a wireframe deployment device in water. Its surface area is 19.6 cm^2. Prior to deployment, the sorbent was cleaned with 2 × 5 mL acetone, 2 × 5 mL dichloromethane, 2 × 5 mL methanol, and 5 mL MilliQ water. The prepared SDs were stored in a 2 L glass bottle immersed in MilliQ water at 4 °C. They were transported in polyethylene zip-lock bags filled with MilliQ water for deployment.

2.3. Deployment of samplers

The study was conducted on the treated effluent from the Modřice municipal WWTP, which serves the city of Brno (Czech Republic) with a capacity of approximately 500,000 population equivalents. The WWTP combines mechanical and biological (conventional activated sludge) treatment technologies.

The samplers were deployed in the WWTP effluent discharge weir tank from 6 November to 18 December 2018. All samplers were deployed in triplicate. Deployment time was 7, 14, 21, 28, and 42 days from time 0 for SDs. HPS and POCIS were deployed from day 14 for 7, 14, 21 or 23, and 28 days (Table S3–1). The deployment period of HPS and POCIS was shortened compared to SD because degradation or compound distribution equilibrium attainment was expected. Samplers were attached with colour-coded cable ties to stainless steel wire frames (HPS and SD) or stainless-steel holders inserted into a perforated sheet steel canister (POCIS) and deployed in the effluent with ropes approximately 1 m below the water surface (Figs. S3–1 to S3–3). After retrieval, the samplers were transported to the laboratory in polyethylene zip-lock bags in a refrigerated container. POCISes were stored in zip-lock bags, HPSs were disassembled, and sorptive layers were placed in glass vials. SDs were placed in glass containers with screw caps. All samplers were kept frozen at −20 °C.

Composite 24-hour water samples were prepared from subsamples collected at 2-hour sampling intervals. 150 mL water samples in 250 mL Nalgene® polycarbonate bottles were stored at −20 °C until further processing. Parameters measured in the water, such as temperature, pH, discharge, conductivity, and total suspended solids, were provided by the WWTP operator and are listed in Table S3–2.

2.4. Sample processing

2.4.1. POCIS

Analytes were extracted from POCISes according to the procedure described in our previous work (Vrana et al., 2021). POCISes were disassembled, and the sorbent was transferred to a glass chromatography column plugged with glass wool. The retained compounds were eluted with 50 mL of dichloromethane/methanol/toluene mixture (8:1:1, *v/v/v*). The extracts were evaporated below 1 mL on a rotary evaporator and transferred to 2 mL vials. The volume was adjusted to 2 mL, and the extracts were weighed. Before analysis, 250 μL of the extract was diluted with 250 μL of ultra-pure water, and a mixture of isotopically labelled internal standards (2.5 ng of each compound per sample, Table S1–4) was added.

2.4.2. HPS

Analyte extraction from HPS was described by Fialová et al. (2023). Briefly, sorptive hydrogel disks were freeze-dried for 24 h (Freeze Dryer L10–55 PRO, GREGOR Instruments, Czech Republic) and extracted first with 10 mL of 0.5 % ammonia in methanol and then with 10 mL of methanol shaken on an orbital shaker at 60 rpm for 24 h. The extracts were combined in a glass vial and evaporated under a stream of nitrogen to approximately 0.5 mL. The extracts were filtered through a nylon syringe filter (0.20 μm, Macherey-Nagel, Germany), and the volume was adjusted to 1 mL. The extracts were stored at 4 °C. Before analysis, 250 μL of the extract was diluted with 250 μL of ultra-pure water, and a mixture of isotopically labelled internal standards (2.5 ng of each compound per sample, Table S1–4) was added.

2.4.3. Speedisk

SDs were freeze-dried for 24 h (Freeze Dryer L10–55 PRO, GREGOR Instruments, Czech Republic). Stainless-steel capillary needles were attached to the elution channel at the bottom of the SDs, and retained compounds were eluted with 5 mL of methanol, followed by 5 mL of 0.5 % ammonia in methanol and 50 mL of dichloromethane. The extracts were collected in Syncore flasks and evaporated to approximately 2 mL using a Syncore® Analyst six-position vacuum rotary evaporator. The extracts were quantitatively transferred to 8 mL vials and the volume was adjusted to 5 mL. Prior to analysis, 250 μL of the extract was diluted with 250 μL ultra-pure water, and a mixture of isotopically labelled internal standards (2.5 ng of each compound per sample, Table S1–4) was added.

2.4.4. Water samples

Composite 24-hour water samples were thawed to laboratory temperature and homogenised by shaking. 10 mL of water was filtered through a regenerated cellulose filter (0.2 μm, Minisart, purchased from HPST) and a mixture of isotopically labelled internal standards (2.5 ng of each compound per sample, Table S1–4) was added.

2.4.5. Extraction recoveries

Samplers were not spiked with any recovery standards prior to extraction, but extraction recoveries of target analytes from samplers were estimated in a separate experiment as described in Section S4. The results are presented in Tables S4–1 to S4–3. Compounds with recoveries <40 % and >140 % were considered semiquantitative.

2.5. Instrumental analysis

The analytical method has been described in our earlier work (Fialová et al., 2023). Passive sampler extracts were analysed by liquid chromatography coupled with tandem mass spectrometry. 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 PFAS analysis high-resolution hybrid quadrupole - orbital trap MS QExactive (LC/HRMS), both Thermo Fisher Scientific. Details of the settings and analytical methods can be found in Section S5.1, Fedorova et al. (2013), and Grabic et al. (2012). The passive sampler extracts were also analysed by liquid chromatography with electrospray ionisation full scan combined with data-independent MS^2 in positive and negative modes (LC/HRMS/DIA) for non-targeted screening (for more details, see Nováková et al. (2023)).

Water samples were analysed by 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 for PFAS analysis. Detailed information on settings and validation can be found in Section S5.2, Fedorova et al. (2013), and Lindberg et al. (2014).

2.6. Data analysis

First, it was tested whether compound uptake into each sampler was time-integrative. The accumulated amount in the passive sampler from a single exposure ($N_{\text{single exposure}}$; ng sampler^{-1}) was divided by the sum of the accumulated amounts in co-deployed samplers one after the other for a shorter time ($\sum N_{\text{short exposure}}$), e.g., amounts in samplers exposed for 14 days were divided by the sum of amounts two consecutively deployed samplers for 7 days. The $N_{\text{single exposure}}/\sum N_{\text{short exposure}}$ ratio was calculated for different deployment periods, i.e., 14 days (0–14, 14–28, 28–42), 21 days (0–21, 14–35, 21–42), 28 days (0–28, 14–42), and 42 days (0–42). The acceptable ratio $N_{\text{single exposure}}/\sum N_{\text{short exposure}}$ for integrative uptake was between 0.8 and 1.2.

When the compound uptake is in the linear or integrative uptake phase, the accumulated amount N (ng sampler^{-1}) is described by the following equation:

$$N = R_s C_w t \quad (1)$$

where R_s (mL d^{-1}) is the sampling rate, C_w (ng L^{-1}) is the aqueous concentration during the exposure time t (d). R_s is the product of the overall MTC k_o (m^3 s^{-1}) and surface area A (m^2).

$$R_s = k_o A \quad (2)$$

A combination of Eqs. (1) and (2) shows that the overall MTC k_o (Eq. (3)) is proportional to the surface-specific uptake N/A (ng cm^{-2}) in the integrative uptake phase, which may differ between different types of passive samplers:

$$k_o = N/AC_w t \quad (3)$$

As described above, surface-specific uptake N/A was calculated only for deployment periods when all three co-deployed samplers showed integrative uptake. The correlation between N/A in two compared samplers for the entire set of compounds detected in both samplers after a certain period was assessed using the Pearson correlation coefficient and its significance was tested using Student's t-test ($\alpha = 0.05$). The N/A ratio of the two samplers was calculated for each compound to compare the devices. The N/A ratio was normalised using a decadic logarithm and tested for normality (SigmaPlot Version 12.3, SynStat Software, SanJose, CA, USA) and outliers (Grubbs test, $\alpha = 0.05$, © 2023 GraphPad Software).

R_s for samplers in the integrative uptake phase were calculated from rearranged Eq. (1) using linear regression of uptake data N(t) as a function of exposure time t. Compounds with high variability in aqueous concentration (coefficient of variation CV > 40 %) and low detection frequency (<50 %) were not included in the R_s estimation. The correlation between R_s and physicochemical properties was assessed using the Pearson correlation coefficient and its significance was tested using Student's t-test ($\alpha = 0.05$).

2.7. Evaluation of contaminant pattern in samplers using non-target screening

Samplers deployed for 14 days were selected for the investigation. The targeted analysis confirmed the integrative uptake phase for most of the analysed compounds. The peak areas of the features found by LC/HRMS/DIA in each sample were divided by the surface area of the sampler since the targeted analysis confirmed good comparability of the surface-proportional compound uptake in the integrative phase. The same procedure was applied to the samplers and corresponding blanks to ensure a consistent data treatment. The workflow setting of the Compound Discoverer™ 3.3 software (Thermo Fisher Scientific) is reported in Section S6. The differences among the samplers were investigated using principal component analysis (PCA) and visualised by hierarchical cluster analysis.

3. Results and discussion

3.1. Range of selectivity

We observed that more compounds were detected in samplers than in water when comparing the detection frequency of targeted analysis. Eleven pharmaceuticals and metabolites, one PFAS, and 18 pesticides and metabolites were not detected in water but were detected in all samplers. It shows that the concentration factor of passive sampling was higher than that of the in-line SPE-LC/MSMS method for water analysis. On the other hand, desethyl-2-hydroxy atrazine was the only compound detected in water and not in any of the samplers. It could likely be due to the highly hydrophilic nature of the compound ($\log K_{ow} = -0.96$). On average, all three samplers captured similar numbers and patterns of compounds from water. Only SD was inferior for pesticides, capturing 73 compounds compared to 84 and 81 compounds captured by POCIS and HPS, respectively. The results are presented in Tables S7–1 to S7–3.

3.2. Assessment of integrative uptake and repeatability

The integrative compound uptake into the three investigated samplers was observed for different deployment periods (Table 2 and Fig. S8–1) and the assessment of time integrative uptake is shown in Fig. 1 and Fig. S8–2. POCIS sampling was integrative for up to 14 or 28 days for 38 % and 35 % of the compounds, respectively. HPS sampled most compounds (59 %) integratively for up to 14 days. SD showed integrative properties for 38 % of compounds up to 42 days. Integrative behaviour could not be calculated for many compounds due to data below the detection limit from 7-day exposed samplers, especially for SD (29 %). The lower uptake into SD can be explained by the lower surface-proportional uptake compared to the other two samplers.

The mean repeatability of analyte amounts quantified in triplicate passive samplers was comparable for all passive samplers (Table 3) and remained good throughout the sampling periods, except for HPS for 21 and 28 days exposed passive samplers, where worse repeatability was observed. The degradation of the diffusion hydrogel causes this effect, and it has been discussed in detail in Fialová et al. (2023).

3.3. Comparison of surface-specific compound uptake

The surface-specific compound uptake (N/A ratio) after the integrative sampling period of 14 days spanned over four orders of magnitude, i.e., from <0.1 to >100 ng cm^{-2} (Fig. 2). Comparison of the surface-specific uptake N/A (Fig. 2) in all three co-deployed samplers showed a good correlation ($r \geq 0.76$). In addition, there was a good agreement of N/A between any two of the three compared samplers.

Table 2
Maximum integrative uptake period for compounds sampled by three co-deployed passive samplers, where n is the total number of compounds found above the limit of quantification in a particular sampler. NC "not calculated" means it could not be calculated because some data were below the limit of quantification.

Integrative uptake (days)	POCIS (n = 158)	HPS (n = 155)	SD (n = 137)
NC	8 %	11 %	29 %
0	13 %	7 %	7 %
14	38 %	59 %	6 %
21	6 %	14 %	3 %
28	35 %	9 %	17 %
42	–	–	38 %

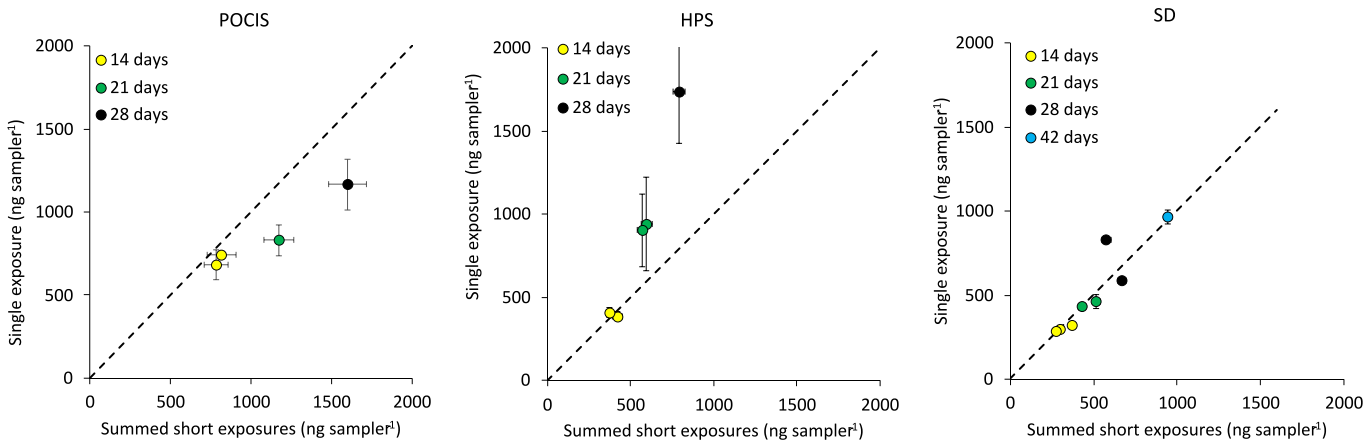

Fig. 1. Assessment of time integrative uptake of carbamazepine in three samplers. The accumulated amount from a single long exposure (y-axis) is compared with the sum of the accumulated amounts from consecutive short 7-day exposures (x-axis). The dashed line represents the unity of the values.

Table 3
Mean repeatability of compound uptake in triplicate passive samplers. Only compounds sampled integratively for at least 14 days were assessed.

Exposure time (days)	POCIS ($n = 125$)	HPS ($n = 127$)	SD ($n = 87$)
7	18 ± 12 %	14 ± 10 %	11 ± 12 %
14	15 ± 14 %	15 ± 12 %	12 ± 13 %
21	20 ± 14 %	27 ± 15 %	11 ± 9 %
28	19 ± 10 %	28 ± 11 %	16 ± 11 %
42	–	–	10 ± 15 %

This observation is in agreement with the theory of passive sampling that the uptake into a passive sampler in the integrative phase does not depend on the mass of sorbent (Eq. (1)). There were only a few compounds where the difference in the *N/A* ratio was higher than a factor of two. The *N/A* ratio for POCIS and HPS was greater than a factor of two for only five compounds. When comparing POCIS and SD, eight compounds fall outside the two-factor range. Comparing HPS to SD, 11 compounds had an *N/A* ratio higher than a factor of two. The *N/A* ratio for all compounds outside the two-factor range was up to a factor of four, except for atrazine-2-hydroxy (POCIS vs. HPS and HPS vs. SD) and PFOA (POCIS vs. SD and HPS vs. SD), where the difference was larger. The *N/A* for atrazine-2-hydroxy was twenty times higher for HPS compared to POCIS and SD, and the *N/A* for PFOA was ten times higher for SD compared to POCIS and HPS.

PFOA (for POCIS/SD and HPS/SD) and atrazine-2-hydroxy (for POCIS/HPS and HPS/SD) were also assessed as significant outliers ($p < 0.05$) for log-normalised data of *N/A* ratio data together with valsartan for POCIS/HPS and 1H-benzotriazole for POCIS/SD (Table S10–1). The test for normal distribution of the data excluding outliers showed that the data for POCIS/HPS and POCIS/SD are log-normally distributed. Two other non-significant outliers, valsartan and 1H-benzotriazole, had to be excluded from passing the normality test ($p > 0.05$) for the log*N/A* ratio of HPS and SD. The mean log*N/A* ratio of all sampler comparisons, excluding outliers, was close to zero and ranged from 0.006 to 0.060. The standard deviation was comparable in all cases and ranged from 0.14 to 0.18. The distribution of the data is shown in Fig. S10–1. In general, it can be concluded that the differences in the comparison of *N/A* in different samplers are likely to be caused by random error, except for the specific outlier compounds mentioned above.

In the case of PFOA, lower uptake in POCIS and HPS compared to SD cannot be explained by sorption to the PES membrane in POCIS or the agarose hydrogel in HPS and consequent slowing of the uptake. PFOA does not accumulate in PES and, as an anionic compound, may be transported through water-filled pores in the PES membrane rather than through the polymer matrix (Gobelius et al., 2019; Kaserzon et al., 2013). The agarose hydrogel also showed no sorption of PFOA from water (Urík et al., 2020). The difference in the observed *N/A* of PFOA in the exposed SD samples may be related to the differences in analyte extraction from the three samplers. Whereas in POCIS and HPS, only the sorbents were separated and extracted, in the case of SD, the extraction included the sorbent and the protective quartz fibre filter and parts of the polypropylene housing inside the sampler cavity. The later parts of the sampler present an additional surface area with potential sorption sites for PFOA. Nevertheless, this hypothesis has not been further tested and needs to be investigated in future research. Surprisingly, PFHxA, a compound structurally similar to PFOA, did not differ in *N/A* in the three compared samplers. For valsartan and other sartan compounds (irbesartan and telmisartan), *N/A* was higher in HPS compared to POCIS and SD. As these molecules are large with molecular weight >429, the uptake into SD and POCIS may be slowed down by diffusion in applied membranes, i.e., the quartz fibre filter and PES, respectively. -atrazine-2-hydroxy may be a selective transformation product of some triazines in the HPS sampler, whereas there is no ready plausible hypothesis that would explain observed differences in surface-specific accumulation of 1H-benztriazole in the three compared samplers.

Very few studies have directly compared the performance of the samplers common to this study. In the study by Challis et al. (2018) , o-DGT (agarose diffusion gel without PES membrane) and POCIS were deployed side-by-side at two sites for multiple deployment times. Still, only aqueous concentrations estimated using previously published R_s were compared. However, we calculated *N/A* from the reported accumulated amount in passive samplers for five compounds analysed (Tables S11–1 and S11–2). *N/A* of POCIS and o-DGT correlated well at both sites (Figs. S11–1 and S11–2; $r = 0.99$ at Red River, $r = 0.97$ at Dead Horse Creek), with *N/A* ratios close to the maximum 2-fold differences for most compounds and periods. Bonnaud et al. (2023) compared the performance of o-DGT and POCIS in a laboratory calibration on 68 compounds, where the median k_o values were four times higher for POCIS than for o-DGT. However, 11 cm^2 was used as the actual exposed surface area for POCIS instead of the 45.8 cm^2 membrane surface area because sorbent sedimentation between membranes was assumed to have reduced the exchange surface area. When membrane surface area is used for k_o calculation, the median k_o values for both passive samplers are similar.

However, for POCIS, R_s is known to be water flow rate dependent. The deployment of POCIS in a perforated steel canister can reduce the water flow around the sampler, causing the mass transfer of chemicals to be mainly controlled by transport through the WBL (Booij and Chen, 2018; Djomte et al., 2018). As POCIS is more susceptible to hydrodynamic changes than HPS and SD, and the sorbent effective surface area can be reduced due to uneven sorbent distribution, higher variability is

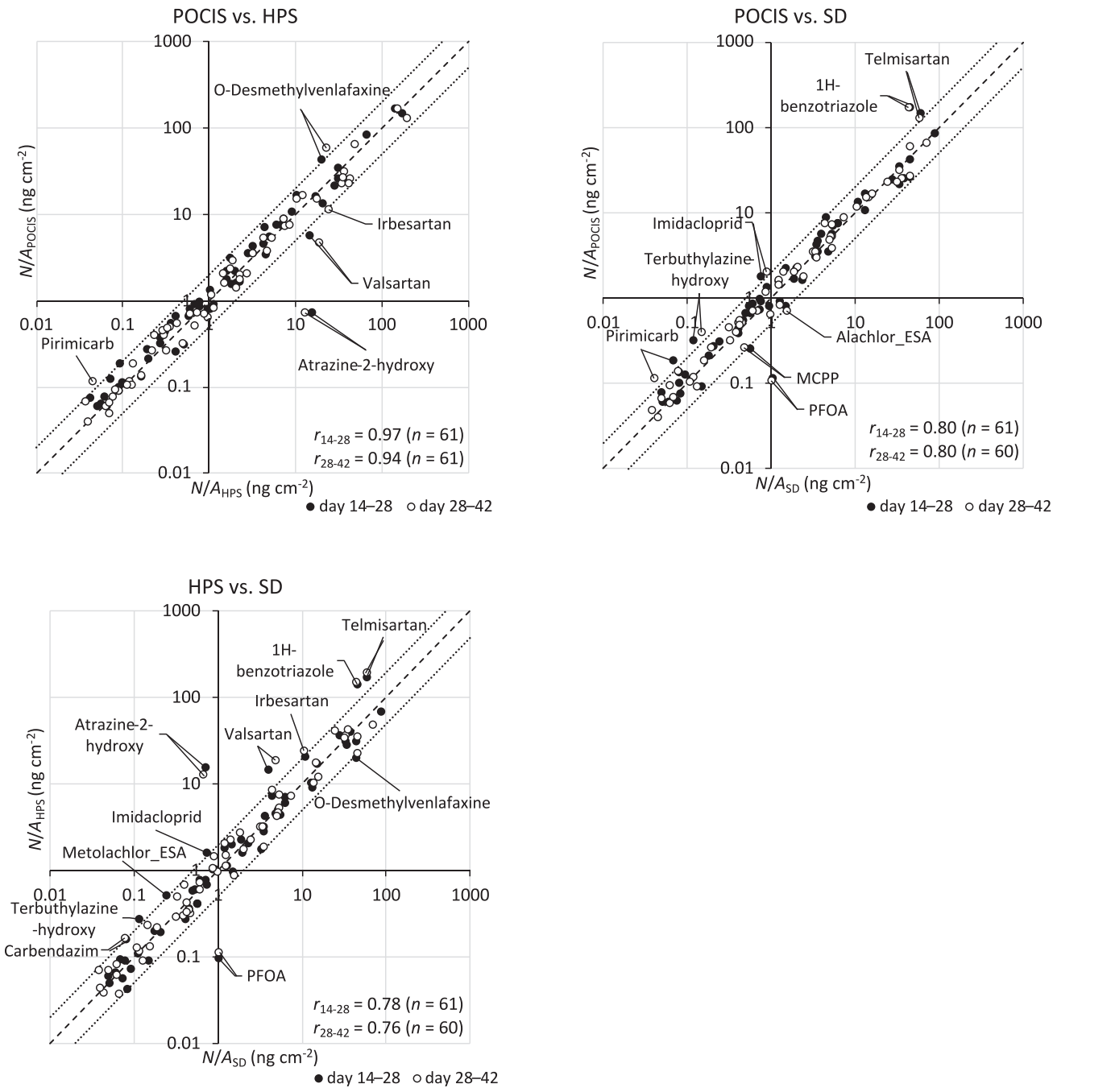

Fig. 2. Comparison of surface-specific uptake N/A for compounds sampled integratively in all three samplers in two consequent 14-day exposures (black and white data points). The dashed line indicates the equality of the two values, and the area between the parallel dotted lines defines the range where the two compared values differ by less than a factor of two. Data points differing by more than a factor of two are labelled with the compound name. The r-value shows the correlation coefficient of the N/A values in both compared samplers and n shows the number of compared compounds.

expected. Therefore, it may be a coincidence that the overall MTC was comparable for all three samplers in our study, and further investigation is needed.

3.4. Evaluation of sampled compounds profile by non-target screening

The data set acquired by the method described in Section 2.5 was processed by the method reported in Section 2.7 in Compound Discoverer™ 3.3 software (Thermo Fisher Scientific). The total number of features in the analysed data was 116,416 in ESI+ ionisation mode and 57,164 in ESI-. A brief comparison of the numbers of detected features across the samplers and ionisation modes in the mass spectrometer is given in Table 4.

There are apparent differences among the samplers. While the number of features detected in ESI- are similar in HPS and POCIS and much higher than in SD, the features detected in exposed samplers in ESI+ are the highest in the HPS, followed by SD and the lowest in POCIS. However, the number of features alone provides little information on qualitative differences among the sampled compound patterns. For this reason, we applied two additional exploratory statistical methods available in the Compound Discoverer software – the principal component analysis (PCA) and the hierarchical cluster analysis visualised as a

Table 4
The numbers of detected features in samplers.

Ionisation mode	Sampler	The average number of features		
		in the exposed sampler	in the corresponding blank	after blank subtraction
ESI-	POCIS	3,686	406	3,280
	HPS	3,897	694	3,203
	SD	1,707	385	1,322
ESI+	POCIS	4,956	1,981	2,975
	HPS	8,614	3,612	5,002
	SD	6,145	2,397	3,748

heat map.

PCA was performed first on the whole sample set, including exposed samplers and associated sampler blanks (Fig. 3) and only on exposed samplers without blanks (Fig. S12–1). When PCA was performed on the complete ESI+ dataset, two principal components were extracted, explaining 55 % (PC1) and 17 % (PC2) of the data variance. The exposed samplers were separated from their blanks in the PCA plot of PC1 and 2 by the PC1. The exposed sampler types were also separated from each other. However, exposed POCIS appeared close to blanks. In general, samples from two consecutive 14-day exposures clustered together for each sampler type, confirming a low variability in effluent composition during the experiment. All sampler groups were also distributed along PC2 but in a different order than along PC1.

In the ESI- performed on the entire sample set, two factors were extracted that explained 50 % (PC1) and 17 % (PC2) of the data variance. The PCA plot separated all exposed samplers from their blanks in the direction of the PC1. Exposed SD was further separated on the PC1 and PC2 from POCIS and HPS, which clustered together. Similar to the ESI+ mode, samples from two consecutive 14-day exposures clustered together for each sampler type. When the analysis was performed only on the exposed passive sampler set, a similar distribution of sampler types appeared in the PCA plot in both ionisation modes (Fig. S12–1).

The findings from PCA analysis were confirmed by the second exploratory statistic tool. The heat maps for ESI+ and ESI- signals of exposed samples, normalised to the sampler surface area, are shown in Figs. S12–2 and S12–3. While ESI+ data of POCIS and SD clustered together, ESI- data of HPS and POCIS clustered closer than POCIS and SD. It is also seen from the heat map of the detected compounds that POCIS samples in ESI+ showed an overall lower signal intensity across the compounds than in SD and HPS, probably due to the signal suppression caused by polyethylene glycol release to the sorbent from the PES membrane, as has been reported by Guibal et al. (2015). The heat map of ESI- (Fig. S12–3) shows a different picture. There are groups of compounds specifically elevated in the SD sampler, with the highest number of high-intensity signals (red colour).

The comparison shows that the HPS sampler presents a variant with the broadest range of accumulated compounds, making it especially attractive for suspect screening or non-targeted analysis and toxicity testing of aquatic contaminants. HPS samplers are equipped with an agarose hydrogel layer, likely permeable for a broader range of compounds than PES in POCIS or quartz filter in SD.

3.5. Sampling rates estimation

For R_s estimation, data from 14-day exposed passive samplers were used. Aqueous concentration was constant for most compounds during the sampling period, enabling R_s estimation. The average aqueous concentration and its standard deviation are shown in Fig. S13.

3.5.1. POCIS

R_s for POCIS were estimated for 47 pharmaceuticals and metabolites, 3 PFAS, 3 anticorrosives, and 20 pesticides and metabolites. R_s ranged from 4 to 371 mL d^{-1} with a median value of 90 mL d^{-1} (Table S14–1). These R_s were compared to published R_s (Table S14–2) in Fig. 4 and were mainly at the lower end of the published values. Unlike HPS and Speedisk, POCIS was deployed in a canister (Fig. S3–1) to protect samplers from debris. However, the canister reduces the water flow around the sampler. Under a low flow rate, the uptake of chemicals into POCIS is typically controlled by MTC in WBL (Booij and Chen, 2018; Djomte et al., 2018). Lower R_s for POCIS observed in this study, compared to published values, indicates that the water velocity around the sampler was low, and consequently, the uptake into POCIS was controlled by the MTC in the WBL.

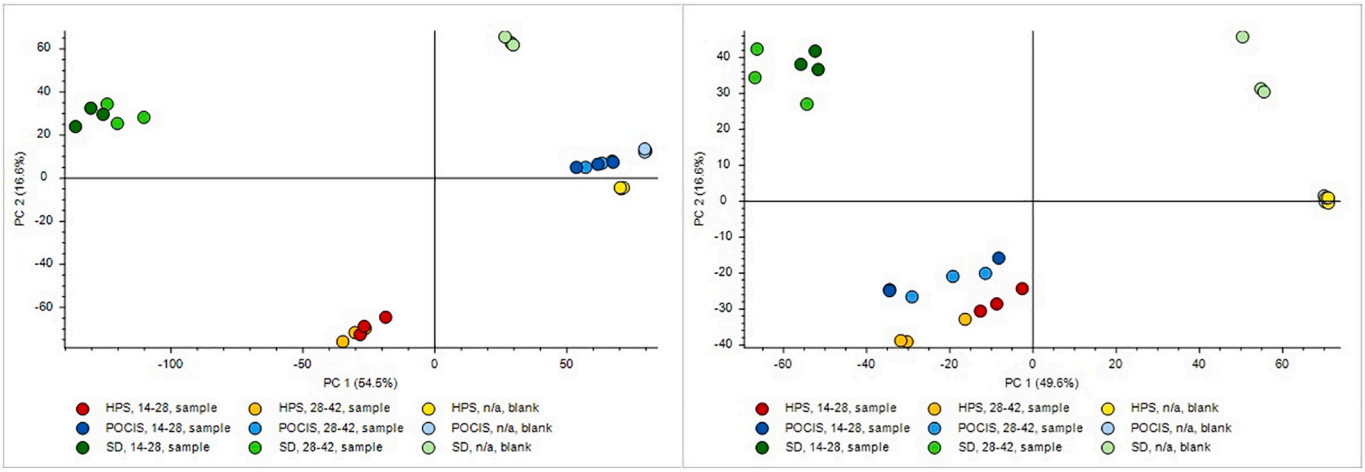

Fig. 3. PCA plots of contaminant patterns in extracts from three co-deployed passive samplers (POCIS, HPS, and SD) after 14 days of exposure and in corresponding blanks, analysed in ESI+ (left-hand plot) and ESI- ionisation mode (right-hand plot). Peak areas normalised to the surface area of the sampler, assuming the time integrative uptake of all compounds, were used for PCA analysis. The points are labelled by the sampler type and deployment period, showing the sample scores along two principal components.

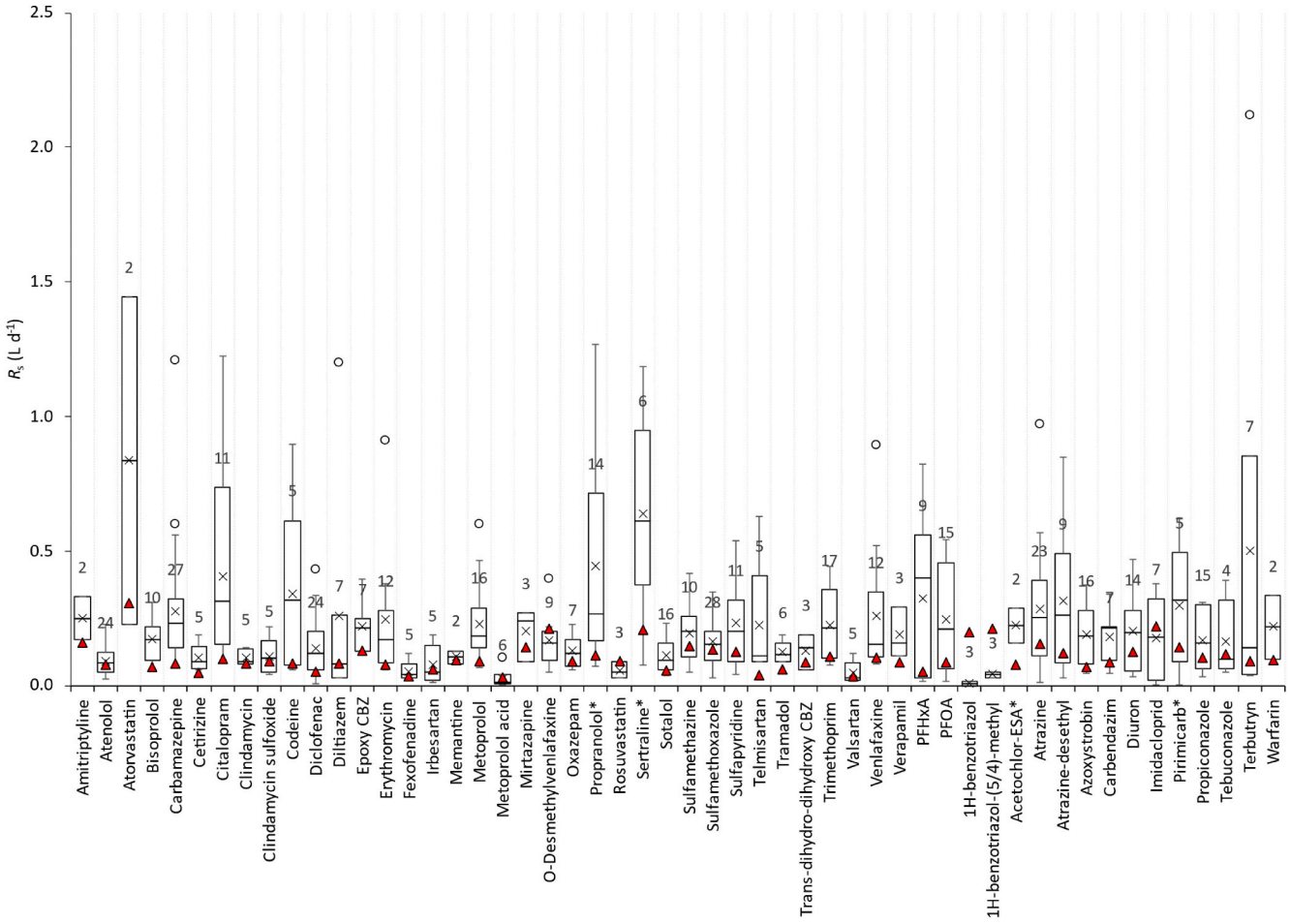

Fig. 4. Comparison of POCIS R_s from this study (Table S14–1) with published values (Table S14–2). Boxplot depicts R_s from literature (Ahrens et al., 2015; Allinson et al., 2023; Bailly et al., 2013; Bartelt-Hunt et al., 2011; Bayen et al., 2014; Baz-Lomba et al., 2017; Berho et al., 2020; Brown, 2010; Di Carro et al., 2014; Djomte et al., 2018; Fauvelle et al., 2014; Fedorova et al., 2013, 2014; Gobelius et al., 2019; Guibal et al., 2020; Harman et al., 2011a; Ibrahim et al., 2013; Kaserzon et al., 2012, 2013, 2014; Li et al., 2010a; Li et al., 2016, 2018; Lissalde et al., 2011; MacLeod et al., 2007; Magi et al., 2018; Martínez Bueno et al., 2009; Mirasole et al., 2016; Morin et al., 2013; Poulier et al., 2015; Vrana et al., 2021), circles represent outlier values (values at least 1.5 interquartile range above the third quartile), and numbers above the boxplot show the number of values from the literature. Red triangles represent R_s estimated in this study.

3.5.2. HPS

R_s for HPS have already been published in Fialová et al. (2023) and ranged from 6 to 132 mL d^{-1}. These estimated R_s were, on average, two times lower than R_s estimated in the field study performed in a membrane bioreactor WWTP effluent by Alygizakis et al. (2020).

3.5.3. Speedisk

SD R_s were estimated for 39 pharmaceuticals and metabolites, 2 PFAS, 2 anticorrosives, and 20 pesticides and metabolites. R_s ranged from 2 to 324 mL day^{-1} with a median value of 35 mL d^{-1} (Table S15). In the study by Hamers et al. (2018), R_s were indirectly estimated from compounds found simultaneously in silicone rubber and SD and ranged from 31 to 471 mL d^{-1} per sampler, depending on water flow at different sampling sites. These R_s represent values for the site only, not for specific compounds. However, the range of R_s is well comparable to the R_s estimated in this study.

3.6. Sampling rates and physicochemical properties

The correlation between R_s and physicochemical properties was assessed (Figs. S16–1 to S16–3, SI of (Fialová et al., 2023)) and a significant negative correlation (p-value <0.05) with molecular weight and molar volume was observed for all three samplers (Table S16). For HPS and SD, a significant negative correlation was also observed with polar surface area. On the other hand, no significant correlation was observed with hydrophobicity (log$P$ and log$D_{7.4}$) and, in the case of POCIS, also with polar surface area.

When the uptake is WBL controlled, R_s is expected to be proportional to $D^{2/3}$, where D is the compound's diffusion coefficient in water (Booij et al., 2007). Rusina et al. (2010) suggested a model that relates R_s to molecular weight M by introducing to the model the known relation of D to M published by Schwarzenbach et al. (2003):

$$R_s = AFM^{-0.47} \quad (4)$$

where A is the sampler surface area and F is an exposure-specific parameter characterising local hydrodynamic conditions. Model Eq. (4) describes an expected linear relationship between logR_s and log$M$, with the slope s equal to the exponent of M (Eq. (5); Fig. 5).

$$logR_s = s \times logM + logAF \quad (5)$$

The s values calculated from the linear regression log$R_s = f$(log$M$) for the three samplers ranged from −0.48 to −0.65 (Fig. 5), and they were not significantly different from the theoretical model value of −0.47 (p-value <0.05). This finding suggests that R_s was at least partially WBL-controlled in all three samplers. The observation agrees with the expected slower diffusion in the WBL of molecules having higher molecular mass. However, the correlations were weak, with correlation coefficients r ranging from 0.34 to 0.36, which does not allow to confirm

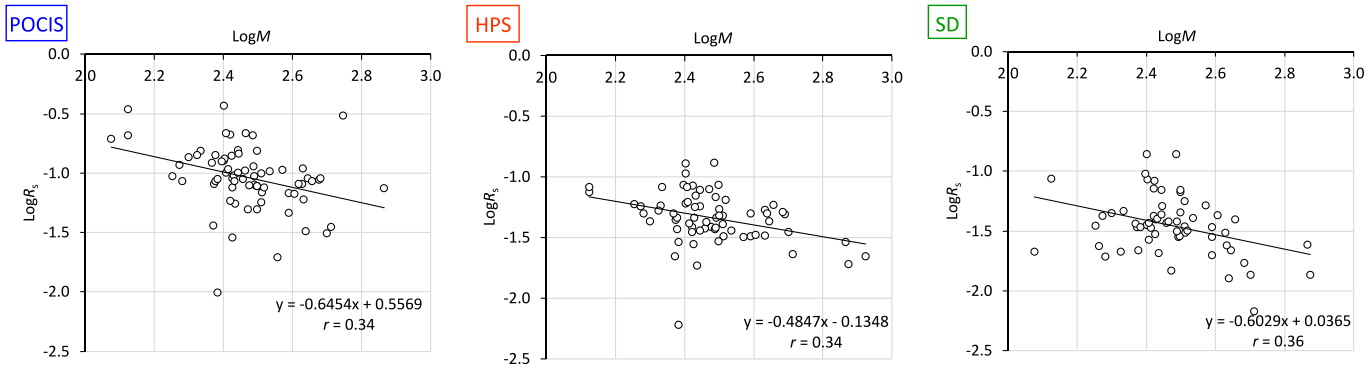

Fig. 5. The graph shows the relationship between logR_s (y-axis) and log$M$ (molecular weight, x-axis) for three co-deployed samplers in the integrative uptake phase (after 14 days of exposure). The solid lines show the linear regression of the data. The linear regression slope corresponds with the exponent in the WBL-controlled uptake model Eq. (4). Data for PFOA and atrazine-2-hydroxy were excluded from the regression.

whether the linear model Eq. (5) is the best for describing the measured data.

The calculated F values from the linear regression were of the same order of magnitude, i.e., 0.03 for HPS, 0.06 for SD, and 0.08 for POCIS. The combination of Eqs. (2) and (5) in the form $R_s = AFM^{-s}$ enables estimating the MTC of a compound with a selected M as $k_o = M^{-s}$ and then comparing its magnitude in the three co-deployed samplers. Selecting a model compound with $M = 300$, i.e., in the middle of the range of tested compounds, results in estimated k_o^{300} values of 0.21, 0.24, and 0.23 μm s^{-1} for HPS, SD, and POCIS, respectively. Thus, the estimated overall mass transfer is equal in the three samplers compared. Substituting k_o^{300} values in Eq. (2) give estimated modelled R_s^{300} values of 0.035, 0.046, and 0.091 L d^{-1} for HPS, SD, and POCIS, respectively. These are well in line with the average experimental R_s values. The difference in sampler surface area causes the difference in R_s among the samplers.

An open question remains whether the observed equality of the overall MTC in the three samplers happened by coincidence in our study or whether it applies in general. Low values of the overall MTC (<1 μm s^{-1}) in combination with their equality in the compared samplers, regardless of the diffusion barrier used (PES membrane, hydrogel, glass fibre filter), suggest that a stagnant WBL indeed controlled the mass transfer in all three samplers. Nevertheless, the R_s reported in this study are challenging to interpret in terms of transport resistances of the WBL, the applied membrane, and the sorbent because these R_s include the combined effects of transport through all these barriers (Booij et al., 2017) and the contribution of individual resistances to the overall mass transfer differs between the three compared samplers. In the case of HPS, the agarose hydrogel essentially behaves as an immobilised WBL. In the case of Speedisk, the pores in the quartz filter are likely filled with water, which behaves similarly to immobilised WBL. In the case of POCIS, it is known that the diffusion limiting barrier is often WBL, although it was initially intended that the PES was the main diffusion barrier. Glanzmann et al. (2023) showed that for passive samplers fitted with PES membrane (Chemcatcher) the MTC strongly depends on the hydrodynamic conditions. The low MTC values observed in our study confirm that the samplers were exposed under conditions where the water flow was limited. This limitation was mainly due to the POCIS deployment in the container (in contrast to HPS and Speedisk). Under limited water flow, the MTC is known to be sensitive to changes in hydrodynamic conditions - e.g., changes in flow rate and variable suspended particle concentration in water. Fialová et al. (2023) found a difference in HPS R_s between two field studies performed with a similar sampling design, suggesting that some WBL effect is still expected.

A separate experiment would be required to characterise the magnitude of the MTC in WBL in the three samplers, for example by co-deploying silicone discs spiked with performance reference compounds (PRCs), as recently demonstrated for the Chemcatcher sampler by Glanzmann et al. (2023) and Reymond et al. (2023).

3.7. Ranking of the performance of passive samplers

When comparing the performance of the samplers in general, SD seems to overcome POCIS and HPS in several criteria (Table 5). With a high amount of sorbent and a small surface area, Speedisk's uptake capacity is high, allowing for long integrative uptake that POCIS or HPS cannot achieve. Regarding the number of compounds accumulated from the target analysis, POCIS and HPS performed slightly better than SD, which still covered a wide range of compounds. In the case of the non-target screening analysis, the number of features was the highest for HPS, followed by POCIS and SD. Repeatability was comparable for all three samplers, at least for 14 days of exposure. The commercial availability of POCIS and SD makes them more likely to be used than HPS. In terms of physical durability, SD can withstand harsh conditions without damage, whereas POCIS and HPS are more susceptible to damage due to the fragile diffusive barrier used. However, several criteria must be considered when selecting a sampler for a particular purpose.

4. Conclusions

We have shown that for most of the compounds investigated (with the exceptions discussed), a consistent surface-specific uptake N/A in the integrative sampling phase was observed, which implies identical MTC despite the differences in sampler design, including used diffusion barriers and sorbent materials. Our study demonstrates the possibility of

Table 5
Ranking of passive samplers compared in this study.

Parameter	POCIS	HPS	Speedisk (SD)
Sample a broad range of compounds (according to target analysis)	++	++	+
Sample a broad range of compounds (according to NTS)	++	+++	+
Integrative sampling over a long time period	–	–	+
Repeatability	+	+	++
Commercial availability	+	–	+
Physical durability	–	–	+

obtaining coherent results with passive samplers despite the differences in their construction. Nevertheless, the independence of the *N/A* from the diffusion barrier material used (hydrogel, PES, quartz filter) suggests that the actual main barrier controlling the uptake was the WBL in all cases. WBL control, in turn, implies that the sampler uptake is sensitive to local hydrodynamic conditions, and a separate monitoring of the effect of hydrodynamics on mass transfer would be desirable. The uptake comparison based on data from non-targeted analysis is complicated because signal intensities are likely affected by various matrix effects and, thus are not strictly proportional to the amount of sampled compounds. It should be stressed that direct mutual comparability of samplers can be assessed for an exposure period when the compound uptake is time integrative; in our case for exposures not longer than two weeks. Longer exposures complicate the sampler uptake comparison, because of gradual compound- and sampler-specific equilibration. Moreover, in some situations, extended exposures may result in deterioration of sampler performance due to sampler fouling, degradation of sampler components and instability of monitored compounds.

CRediT authorship contribution statement

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

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.168153.

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