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An improved Chemcatcher-based method for the integrative passive sampling of 44 hydrophilic micropollutants in surface water – Part B: Field implementation and comparison with automated active sampling

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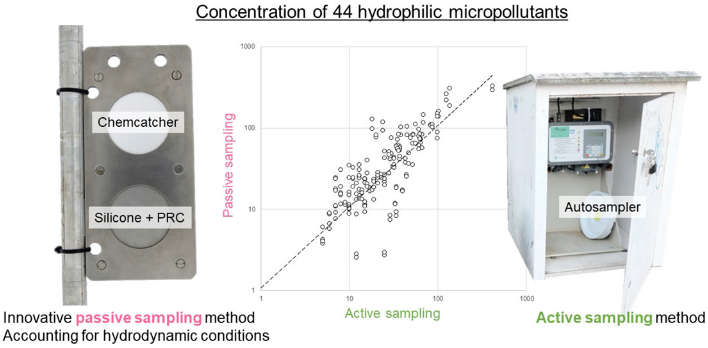
HIGHLIGHTS

- Co-deployment of Chemcatcher-like samplers and hydrodynamic-characterizing silicones
- Data from silicones and calibration allowed to determine in-situ sampling rates R_S
- Good agreement between passive and active automated sampling
- Limited added value of in-situ R_S when velocity > 20 cm s^{-1} for most studied compounds
- To design monitoring programs, errors related to the use of fixed R_S are provided

GRAPHICAL ABSTRACT



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ABSTRACT

Integrative passive sampling is particularly useful in the monitoring of hydrophilic contaminants in surface water, but the impact of hydrodynamics on contaminant uptake still needs to be better considered. In part A (Glanzmann et al., 2023), Chemcatcher-like hydrophilic samplers (i.e., SDB-RPS extraction disks covered by PES microporous membranes) were calibrated to determine the sampling rates R_S of 44 hydrophilic contaminants (pesticides, pharmaceuticals, industrial products) taking into account the hydrodynamic conditions. In this study, Chemcatcher-like passive sampling devices that allowed co-deploying hydrophilic samplers and performance reference compounds (PRC)-spiked silicone disks were tested in a Swiss river with intermediate water velocities (5–50 cm s^{-1}, 23 cm s^{-1} on average) during 11 consecutive 14-day periods. The PRC dissipation from silicone disks – combined with the calibration data from part A – allowed to determine in-situ R_S that took into account hydrodynamic conditions. The obtained aqueous time-weighted average (TWA) concentrations were found to be robust with good concordance between duplicates (mean quotient of 1.16 between the duplicates). For most measurements (76 %), TWA concentrations showed no major difference (<factor 2) from concentrations obtained with automated sampling (14-day composite samples). This observation was also valid for TWA concentrations calculated with extrapolated R_S at infinite water velocity ($R_{S,MAX}$), revealing that the added value of using in-situ R_S compared to $R_{S,MAX}$ is limited above intermediate water velocities (>20 cm s^{-1}). R_S from the literature ($R_{S,LIT}$) – obtained at water velocities between 8 and 37 cm s^{-1} – were also shown to provide comparable TWA concentrations in the studied hydrodynamic conditions (average water velocity of 24 cm s^{-1}). The estimated errors due to the use of $R_{S,MAX}$ or $R_{S,LIT}$ rather than in-situ R_S are given as a function of the water velocity to determine in which conditions the developed method is required (or not) in monitoring programs.

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1. Introduction

The amount of industrial chemicals produced each year increases with rising anthropogenic activities, thus creating many potential entry pathways for micropollutants such as pesticides, pharmaceuticals, and industrial products to be released in aquatic environments (Bataineh et al., 2021). More knowledge about the presence of such compounds in water is needed, and this requires water quality monitoring (Bartram and Ballance, 1996; Behmel et al., 2016; Boyd, 2019). While active grab sampling (GS), is used to obtain a snapshot of the water quality at a given time and location, it is not appropriate when contaminant concentrations fluctuate over time, often related to their input pathways (Brack et al., 2016; Schreiner et al., 2020; Vermeirssen et al., 2008; Vrana et al., 2005). Thus, active automated sampling (AS) is often implemented in monitoring campaigns to increase the sampling frequency: multiple samples are collected during a given period (typically from a few hours to a couple of weeks) and then combined. AS can allow for a better temporal resolution (Goumenou et al., 2021; Spycher et al., 2018), but requires specific and to some extent costly material and infrastructure (e.g., secured site with access to electricity).

Integrative passive sampling (PS) can also be used as an alternative to GS or to extend the monitoring to locations where AS cannot be applied. In Part A (Glanzmann et al., 2023), a method was developed to take into account the hydrodynamic conditions when sampling hydrophilic compounds with Chemcatcher-type devices (i.e., styrenedivinylbenzene-reversed phase sulfonate (SDB-RPS, hereinafter referred to as SDB) extraction disk covered by a polyethersulfone (PES) microporous membrane). The samplers were calibrated for 44 hydrophilic contaminants in a channel system to establish relationships between the sampling rate (R_S) of a contaminant and the mass transfer coefficient of the water boundary layer (WBL) (k_w). The k_w is a parameter that characterizes the hydrodynamics at the sampler's surface, and it can be measured using the dissipation of performance reference compounds (PRC) from silicone disks (Booij et al., 2017; Fauvelle et al., 2017; Glanzmann et al., 2022).

Here, the developed PS method was implemented in parallel to AS in a river. Custom housings allowed the co-deployment of hydrophilic samplers (SDB extraction disk covered by a PES membrane) and PRC-spiked silicone disks. The devices were deployed at one site in a medium-sized Swiss river for 11 consecutive 14-day sampling periods (Spring and Summer 2021) to monitor 44 hydrophilic micropollutants (pesticides, pharmaceuticals, industrial products). The selected river was also monitored for micropollutants using AS (14-day composite samples). Results obtained with the two methods were compared, then the applicability and the added value of the novel PS method were discussed to assess the best strategy when designing or implementing a surface water monitoring program.

2. Materials and methods

2.1. Passive sampling

2.1.1. Sampler preparation and deployment

Silicone sheets (SSP-M823, 0.25 mm thick) (Shielding Solutions Limited, UK) were shaped into 42 mm diameter disks with a round punch. Silicone disks were pre-extracted successively with ethyl acetate and methanol (Sigma-Aldrich, Switzerland) using a Soxhlet for 100 h and 48 h, respectively. Disks were then shaken for 24 h in a methanol solution spiked with the PRC (biphenyl-d10, PCB 1, 2, 3, 10, 14, 21, 30, 50, 55, 78, 104, 145, and 204 (Dr Ehrenstofer, Germany)) to reach 0.2–0.6 μg of PRC per disk. Ultrapure water (Merck Millipore, Germany) was gradually added until a 50 % *v*/v mix was reached (>7 days). Additional details can be found in Glanzmann et al. (2022) and Smedes and Booij (2012).

Solid-phase extraction disks (47 mm diameter) were used as hydrophilic samplers with SDB as a receiving phase (Affinisep, France), covered by a 47 mm diameter PES membrane (132 μm thick, 0.1 μm pores) (PALL Science, USA). The SDB disks and PES membranes were conditioned successively in a methanol solution (30 min) and a water bath (30 min) under gentle stirring (Estoppey et al., 2019; Vermeirssen et al., 2009).

A custom housing for the samplers was laser-cut in stainless steel (Techniques-Laser SA, Switzerland). It consists of two plates (2 mm thick), one of which has two holes (40 mm in diameter), bound together by screws (Fig. 1). For each device, a silicone disk and a hydrophilic sampler were sandwiched between the stainless-steel plates of the housing using 6 screws. The devices were transported in a cooler from the lab to the sampling site in ultrapure water. On-site, each device was attached to an aluminium tube using cable ties (Fig. 1). The tube could freely slide up and down a steel rod vertically embedded in the riverbed to ensure easy deployment and retrieval, and the tube could rotate around the rod to align with the current; a stopper ensured the device did not touch sediments.

The sampling site is located in the river Boiron de Morges, Switzerland. It is a medium-sized river with a mean annual water volumetric flow <0.5 m^3 s^{-1} and a nivo-pluvial regime. The catchment size is 35.5 km^2 with the surrounding land mainly dominated by agriculture. At the site, two devices were deployed on separate rods about 10 cm apart (one with the silicone on top and the other with the silicone on the bottom) for each exposure period of 14 days. A third device was also prepared but not deployed: the silicone acted as a reference for PRC amount before exposure and the hydrophilic sampler as a field blank (exposed to the air on an aluminium sheet during preparation to account for airborne pollution at the sampling site). For each sampling period, four more silicone disks from the same preparation batch were used as a reference for PRC amount before exposure (to have average amounts) but were not brought to the field. On-site water velocity was measured between the two samplers with a current meter (OTT MF Pro, HydroMet, Switzerland) when deploying and retrieving them. The sampling started on March 2nd and finished on August 3rd, 2021 (11 deployments of 2 PS devices, 11 on-site PS references (SDB and silicone), and 44 laboratory silicone references).

At the end of the exposure period, the devices were removed from the water, and the housings were opened on-site to prepare the samplers for transportation to the laboratory. Silicone disks were dried with lint-free wipes and rolled individually in 10 mL amber vials. Excess water was removed from SDB disks and PES membranes with aluminium sheets before being rolled and placed separately in 10 mL amber vials. Samples were transported back to the laboratory in a cooler. In the laboratory, 7 mL of acetone (Sigma-Aldrich, Switzerland) was added to each SDB and PES vial. Silicone and SDB samples were stored in a freezer at −24 °C until extraction. PES samples were also stored in a freezer but not analyzed.

2.2. Extraction and analysis

PRC were solvent-extracted (24 h on a rotary shaker at 30 rpm) with 8 mL hexane (Sigma-Aldrich, Switzerland) (Glanzmann et al., 2022). An aliquot of silicone-disk extract (650 μL out of the 8 mL) was spiked with 100 μL of the internal standard (ISTD) mix (500 ng mL^{-1}) containing ^{13}C-PCB 1, 8, 28, 52, 101, 118, 138, 153, and 180 (Cambridge Isotope Laboratories, United Kingdom). Separation and detection of the PRC were achieved by GC–MS/MS (Agilent 7890A GC coupled to an Agilent 7000 - Triple Quad MS/MS) in multiple reaction monitoring (MRM) mode. The column was an Agilent HP-5MS column (20 m × 0.2 mm × 0.33 μm). The sample (4 μL) was injected in splitless mode with a temperature gradient (50–320 °C). Additional details on the method can be found in Glanzmann et al. (2022).

SDB disks were kept for 30 min to adapt to room temperature and shaken for 30 min on a rotary shaker (30 rpm). The solvent (acetone) extract was transferred to a 20 mL amber vial. SDB disks were shaken again for 30 min on a rotary shaker (30 rpm) with 7 mL of methanol. The methanol extract was added to the acetone extract. Aliquots of the combined extracts (100 μL out of the total 14 mL) were spiked with 100 μL of the ISTD (40 ^{13}C-labeled isotopes (HPC standards, Germany), Supplementary Information (SI), Table S1.2), and 800 μL of ultrapure water was added. Quantification levels ranging from 0.01 ng mL^{-1} to 10 ng mL^{-1}

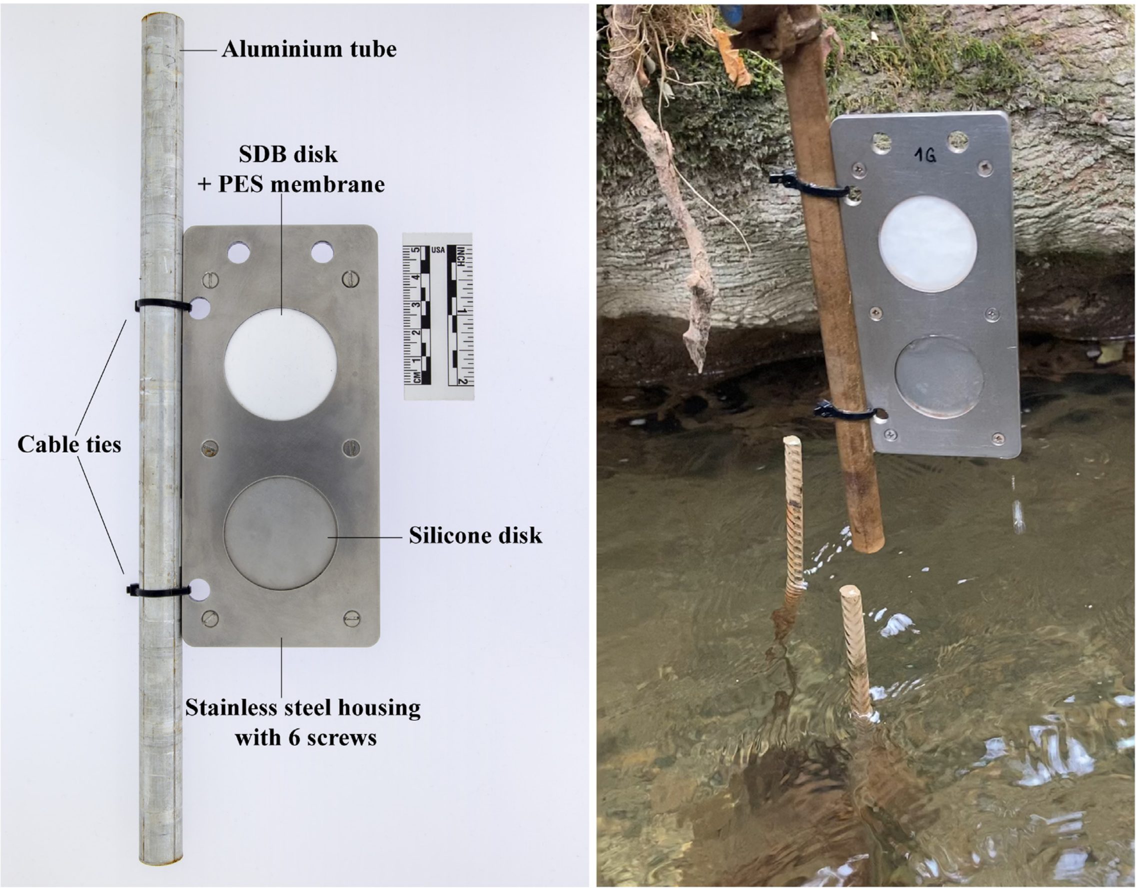

Fig. 1. Left: housing device attached to an aluminium tube using cable ties. The top disk is a hydrophilic sampler (SDB disk + PES membrane), and the bottom one is a PRC-spiked silicone. Right: Sampling device deployed in a river. The aluminium tube slides along the steel rod.

were prepared using the analytical standards (Neochema, Germany) of the 44 selected compounds (SI, Table S1.1). Separation was achieved on a Phenomenex Luna Omega column (C18, 150 mm × 2.1 mm × 1.6 μm, 100 Å). MS/MS detection (AB Sciex QTRAP 6500+) was done in MRM mode using positive and negative electrospray ionization. Additional details on the method can be found in part A (Glanzmann et al., 2023), and SI, Tables S2.1 and S2.2. Samples with decreasing concentrations of compounds were prepared and analyzed to determine the limits of detection (LOD) and quantification (LOQ) empirically (Armbruster and Pry, 2008). The LOQ (SI, Table S2.3) were adjusted to at least 10 times the area of the associated field blank.

2.3. Time-weighted average concentration

First, the retained fractions of PRC (f) were fitted as a function of their sorbent-water partition coefficients K_{SW} (L kg^{-1}) and the McGowan molar volume V_{McG} (cm^3 mol^{-1}) using non-linear least-square (NLS) regression (Glanzmann et al., 2022):

$$f = \frac{C_{PRC}}{C_0} = \exp\left(-\frac{\beta t}{m_s K_{sw} V_{McG}{}^{0.43}}\right) \tag{1}$$

where C_{PRC} is the PRC concentration after exposure, C_0 is the mean initial concentrations in the reference disks, β is a proportionality constant estimated by the NLS, t is the exposure time (days), and m_s is the mass of the sorbent (silicone disk) (kg).

PRC-based in-situ $k_{w,PRC}$ (dm d^{-1}) were then calculated for an arbitrary organic compound with intermediate dissipation (PCB 14) with Eq. (2), using β obtained by NLS from Eq. (1), and A the area of the silicone disk (dm^2) (Glanzmann et al., 2022):

$$k_{w,PRC} = \frac{\beta}{A V_{McG}{}^{0.43}} \tag{2}$$

As k_w is compound-specific, in-situ $k_{w,PRC}$ obtained for PCB 14 were corrected to correspond to the desired contaminant in-situ $k_{w,org}$ (dm d^{-1}) using Eq. (3):

$$k_{w,org} = k_{w,PRC}\left(\frac{D_{w,org}}{D_{w,PRC}}\right)^{2/3} \tag{3}$$

where $D_{w,org}$ and $D_{w,PRC}$ are the diffusion coefficient in water (m^2 s^{-1}) of the contaminant and PCB 14 respectively, both calculated from V_{McG} (Schwarzenbach et al., 2016) and adjusted to experimental temperature using the predicted temperature effect from Hayduk and Laudie (1974).

In part A (Glanzmann et al., 2023), k_w – R_S relationships were established (Fig. 2), and two parameters (a and $R_{S,MAX}$) were determined for each micropollutant. As the in-situ $k_{w,org}$ was calculated from PRC dissipation (Eqs. (1)–(3)), the in-situ R_S can be calculated with Eq. (4):

$$\frac{1}{R_S} = \frac{a}{A k_{w,org}} + \frac{1}{R_{S,MAX}} \tag{4}$$

where a is an adjustable parameter, and $R_{S,MAX}$ (L day^{-1}) is the limiting R_S (L day^{-1}) at an infinite water velocity.

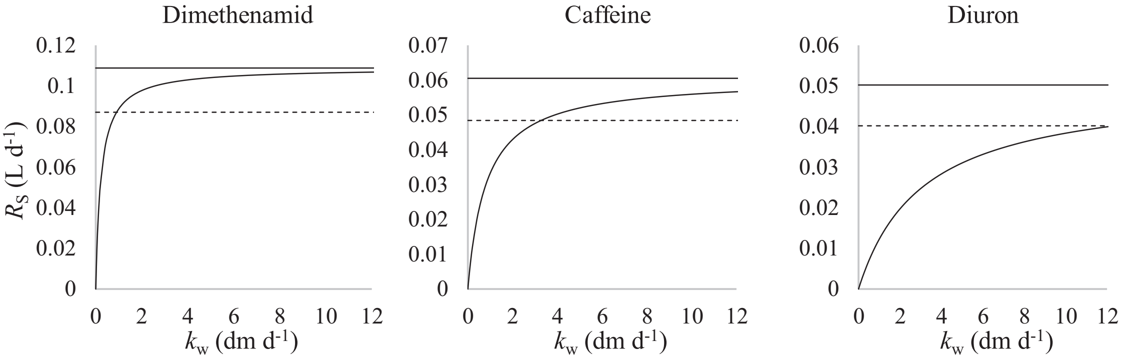

Fig. 2. Examples of sampling rates (R_S) and mass transfer coefficients of the WBL (k_w) relationships as established in part A. Solid lines are $R_{S,MAX}$, and dashed lines are $0.8{*}R_{S,MAX}$.

Finally, Eq. (5) was used to calculate the time-weighted average (TWA) concentration C_{PS} (μg L^{-1}) from the amount of contaminant accumulated in each passive sampler (Ahrens et al., 2015):

$$C_{PS} = \frac{N_S}{R_S t} \tag{5}$$

with N_S (μg) the mass measured in the SDB extraction disk after exposure.

2.4. Automated active sampling

Water was collected and analyzed by the local environmental agency (Direction Générale de l'Environnement (DGE), canton de Vaud, Switzerland). Composite water samples were collected time-proportionally (45 mL every 2 h) by a refrigerated (4 °C) automatic sampling device (ISCO 3710) over the same 14-day periods as PS, and were analyzed by direct injection in an LC-MS/MS (Agilent 1290 Infinity LC coupled to an Agilent 6495 Triple Quad MS/MS) (Tables S2.4 and S2.5). The DGE analyzed 41 contaminants out of the 44 calibrated in part A (36 pesticides, 3 pharmaceuticals, and 2 industrial compounds) (SI, Table S1.1).

2.5. Data analysis

To evaluate the robustness of the PS method, the TWA concentrations of the duplicates were compared by calculating the ratios (C_{PS1}/C_{PS2}), the highest concentration in the numerator (C_{PS1}) and the smallest in the denominator (C_{PS2}). A value of 1 indicates no difference between duplicates. N_S ratios were calculated the same way (N_{S1}/N_{S2}). The relative error was calculated by dividing the difference between the duplicates by their mean. Concentrations obtained with PS and AS were also compared by calculating ratios (C_{PS}/C_{AS}). No major difference between the compared values was considered when the obtained quotients were within a confidence interval below a factor 2, as previously defined in other studies (Bernard et al., 2019; Mathon et al., 2022; Moschet et al., 2015).

To assess the added value of the developed method, TWA concentrations obtained using in-situ R_S (TWA,$R_{S,IN\text{-}SITU}$) were compared to TWA concentrations determined with $R_{S,MAX}$ (TWA,$R_{S,MAX}$) and TWA concentrations calculated with mean R_S from the literature (TWA,$R_{S,LIT}$). All TWA concentrations were tested statistically (paired t-test, p-value = 0.05) with concentrations obtained by AS. $R_{S,MAX}$ were obtained from the relationships between R_S and k_w (Part A (Glanzmann et al., 2023)), whereas $R_{S,LIT}$ normalized by the exposed disk area were obtained for 28 compounds (Table 1, and details in SI, Tables S1.3 and S1.4).

Measurement errors due to the use of $R_{S,MAX}$ and $R_{S,LIT}$ instead of $R_{S,IN\text{-}SITU}$ were calculated as follow, respectively:

$$Error_{R_{S,\,MAX}} = \frac{\left|TWA, R_{S,IN-SITU} - TWA, R_{S,\,MAX}\right|}{TWA, R_{S,IN-SITU}} \tag{6}$$

$$Error_{R_{S,LIT}} = \frac{\left|TWA, R_{S,IN-SITU} - TWA, R_{S,LIT}\right|}{TWA, R_{S,IN-SITU}} \tag{7}$$

Table 1
Water velocities U (cm s^{-1}) at which errors on TWA concentrations are <20 % when $R_{S,MAX}$ or $R_{S,LIT}$ are used. When $R_{S,LIT}$ were missing, no calculation of U were performed.

	Use of $R_{S,MAX}$		Use of $R_{S,LIT}$	
Compound	$R_{S,MAX}$ (L d^{-1})	U at which error is < 20 % (cm s^{-1})	$R_{S,LIT}$ (L d^{-1})	U at which error is < 20 % (cm s^{-1})
2,4-D	0.048	$U > 1.5$	0.02	$0.0 < U < 0.1$
5MethylBenzotriazole	0.076	$U > 1.8$	0.055	$0.2 < U < 5.2$
Atrazine	0.108	$U > 13.8$	0.099	$U > 6.5$
Bentazon	0.053	$U > 1.3$	–	–
Benzotriazole	0.048	$U > 0.5$	0.032	$0.0 < U < 0.5$
Boscalid	0.058	$U > 48.4$	–	–
Caffeine	0.061	$U > 5.4$	0.039	$0.4 < U < 3.9$
Carbamazepine	0.109	$U > 3.0$	0.099	$U > 1.3$
Carbendazim	0.077	$U > 7.6$	0.082	$U > 15.7$
Chloridazon	0.125	$U > 14.6$	0.075	$0.8 < U < 5.9$
Chlorotoluron	0.076	$U > 43.0$	0.09	$U > 882.7$
Cyproconazol	0.091	$U > 9.5$	–	–
DEET	0.104	$U > 0.9$	–	–
Diazinon	0.168	$U > 5530.3$	0.06	$55.3 < U < 194.5$
Diclofenac (acid)	0.085	$U > 8.1$	0.058	$0.7 < U < 11.0$
Dimethenamid	0.109	$U > 0.6$	0.1	$U > 0.3$
Dimethoate	0.100	$U > 0.9$	0.1	$U > 0.9$
Diuron	0.050	$U > 88.8$	0.055	$U > 277.2$
Ethofumesate	0.068	$U > 58.3$	0.08	$U > 1000.2$
Flufenacet	0.075	$U > 11.5$	0.1	$U > 154.4$
Foramsulfuron	0.027	$U > 0.0$	–	–
Imidacloprid	0.109	$U > 11.3$	–	–
Iprovalicarb	0.078	$U > 2.8$	–	–
Isoproturon	0.083	$U > 15.7$	0.076	$U > 7.3$
MCPA	0.049	$U > 1.3$	–	–
Metalaxyl-M	0.137	$U > 148.9$	–	–
Metamitron	0.093	$U > 10.4$	0.06	$0.7 < U < 7.5$
Metazachlor	0.113	$U > 7.2$	0.2	$U > 5.2$
Methoxyfenozid	0.068	$U > 1.9$	–	–
Metolachlor	0.099	$U > 5.2$	0.121	$U > 808.7$
Metribuzin	0.117	$U > 7.1$	–	–
Napropamid	0.070	$U > 30.0$	0.1	$U > 120.4$
Nicosulfuron	0.023	$U > 2.4$	–	–
Pirimicarb	0.106	$U > 7.5$	0.1	$U > 4.3$
Propamocarb	0.024	$U > 7.2$	–	–
Propyzamid	0.079	$U > 34.2$	–	–
Pyrimethanil	0.043	$U > 45.4$	–	–
Spiroxamin	0.038	$U > 0.3$	–	–
Sulfamethoxazole	0.048	$U > 1.5$	0.044	$U > 0.7$
Tebuconazol	0.086	$U > 48.6$	0.09	$U > 85.2$
Terbuthylazine	0.098	$U > 16.0$	0.095	$U > 11.8$
Terbutryn	0.084	$U > 26.3$	0.089	$U > 52.1$
Thiacloprid	0.095	$U > 19.5$	–	–
Thiamethoxam	0.104	$U > 6.6$	0.1	$U > 4.6$

3. Results and discussion

3.1. Qualitative monitoring

From the 41 compounds analyzed with both AS and PS methods, 33 were detected at least once with AS and 35 with PS (SI, Table S3.1) during the sampling period. The same compounds were generally detected using both sampling approaches. However, carbendazim was not detected using PS, while it was detected but not quantified during four sampling periods with the autosampler. Diazinon, napropamid, tebuconazol, and terbuthylazine were also detected more frequently in the water samples than in the passive samples. These compounds are more hydrophobic (log $K_{OW} > 3.2$) than the remaining 37, and they are more retained by the PES membrane than by the SDB disk (see part A (Glanzmann et al., 2023)). Thus, SDB disks with PES membranes may not be appropriate to detect such compounds.

Conversely, carbamazepine, metribuzin, and thiamethoxam were detected seven, eight, and ten times respectively out of all SDB samples but never with the autosampler. Additionally, 2,4-D, chloridazon, imidacloprid, metalaxyl-m, and thiacloprid had much higher detection frequencies with PS than AS. The lower detection frequency for these compounds may be due to matrix effects in the AS water samples (Moschet et al., 2015), or to enrichment on the sampler (pre-concentration factors between 13.3 and 118.3).

These results are in agreement with previous studies that support the use of PS for the qualitative monitoring of hydrophilic micropollutants in surface waters (Harman et al., 2012; Mills et al., 2014; Moschet et al., 2015). The qualitative performance of PS could potentially be improved with the use of a membrane in which compounds are less retained (e.g., polytetrafluoroethylene (Endo et al., 2019; Endo and Matsuura, 2018)). Another possibility would be to use the SDB disks without a membrane, which leads to higher R_S, but it may however shorten the kinetic regime (Charriau et al., 2016; Schreiner et al., 2020; Shaw et al., 2009; Vermeirssen et al., 2009, 2008).

3.2. Quantitative monitoring

3.2.1. Robustness of the PS method

The TWA concentrations were obtained in duplicate (C_{PS1} and C_{PS2}) for 33 of the 44 compounds measured by PS (SI, Table S3.1). All obtained TWA C_{PS1}/C_{PS2} ratios ranged from 1.00 to 1.85 (median at 1.16) (Fig. 3), corresponding to relative errors from 0.1 % to 59 % (median of 15 %). In 1 % of the cases (7 out of 484), a micropollutant was quantified by one duplicate but not by the other one, and the ratio could not be calculated. This showed that the robustness between duplicates was satisfactory despite the relatively high number of steps required by the method (analyses of SDB and PRC-spiked silicone disks).

As duplicates were presumably exposed to the same aqueous concentration, it was hypothesized that differences in mass accumulated in SDB disks ($N_{S1} \neq N_{S2}$) were partly due to slight differences in hydrodynamic conditions ($k_{w,1} \neq k_{w,2}$). So, for duplicates with N_S ratios >1, it was aimed that the use of in-situ R_S (determined from measured k_w) would have given TWA concentration ratios closer to 1. The regression line from TWA concentration ratios plotted against N_S ratios (SI, Fig. S3.1) shows that the developed method allows for a minor improvement only, compared to when no correction for the hydrodynamic conditions was accounted for. In some cases, the mass N_S recovered by the duplicates was similar but the TWA concentrations showed higher differences (SI, Fig. S3.1). This is most likely due to uncertainties associated with the measure of k_w using PRC dissipation where a precision of 10 to 20 % can be expected (Glanzmann et al., 2022; Lohmann et al., 2012; Smedes and Booij, 2012). This assumption can be supported by the fact that the ratio of measured $k_{w,PRC}$ between the two duplicates (SI, Table S3.2) was on average 1.5 for the same sampling period. Thus, it was not possible to show that the developed method allows for major improvements by correcting the impact of hydrodynamics, given that the uncertainty of the k_w measurements was as high as the variation of the hydrodynamic conditions between duplicates. A sampling site with larger hydrodynamic differences should also be tested to better assess the ability of the method to correct for the impact of hydrodynamics.

However, this study shows that correcting for the impact of hydrodynamics may not be so crucial in rivers with similar or higher water velocities than the studied one (average velocity of 24 cm s^{-1}). Indeed, in-situ R_S were shown to approach $R_{S,MAX}$ (mean in-situ R_S at 83 % of $R_{S,MAX}$ for the whole campaign) because the model (for mixed rate control by the WBL and the membrane) governing the relationship between k_w and R_S follows a hyperbolic curve (Fig. 2). Thus, the hydrodynamic conditions of the studied river (SI, Table S3.2) were mostly not in the range where differences in flows significantly impact R_S. These results are in agreement with previous studies that showed a shift of resistance to compound mass transfer from diffusion through the WBL to diffusion in the membrane at an increased water velocity for similar PS designs and analytes (O'Brien

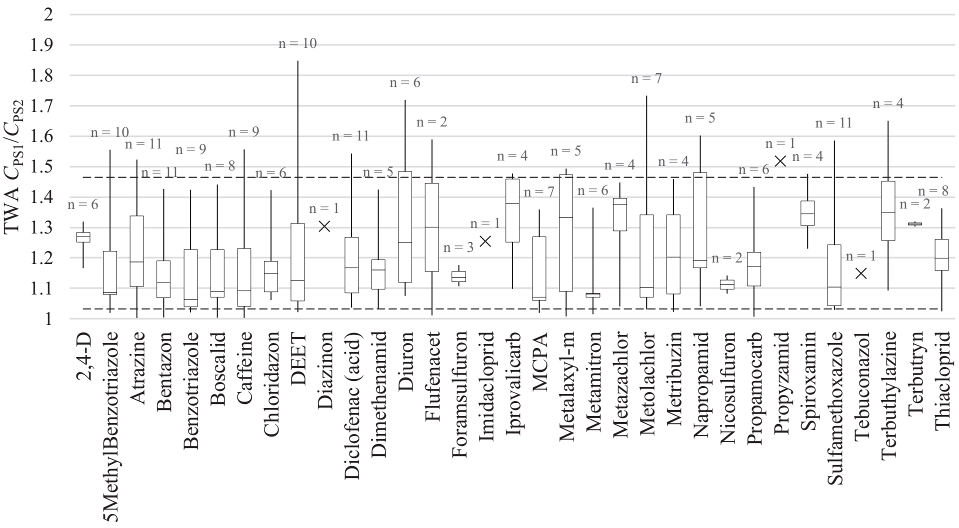

Fig. 3. Ratio between TWA concentrations of replicate 1 and replicate 2 for the 33 detected hydrophilic micropollutants over the 11 sampling periods. Boxes show the 1st and 3rd quartiles (Q1 and Q3) with the horizontal line inside being the median. Whiskers show distance from min/max to Q1/Q3, and dashed lines are the 10th and 90th percentile of the whole data set. The number of sampling periods with detections in both replicates is given by n.

et al., 2011; Vermeirssen et al., 2009, 2008). Additionally, when the water velocity is <5 cm s^{-1}, calibration of the compounds at smaller k_w would be necessary so that the measured k_w are within the range of the laboratory experiments.

3.2.2. Comparison between PS and AS

The number of contaminants quantified (i.e., concentration above the LOQ) at least once over the whole sampling period was higher with PS (33) than with AS (22). This can be explained by the sensitivity of the PS method that achieved lower LOQ (except for methoxyfenozid), because analytes are pre-concentrated in the sorbent, while AS samples were directly injected into the LC-MS/MS (SI, Table S2.3). It must be noted that the analytical sensitivity of both methods could still be improved with more sample preparation steps (for instance concentration).

Overall, measured concentrations with both methods (22 compounds) shared good agreement (Fig. 4). The regression curve between the two sampling methods (C_{PS} plotted versus C_{AS}) shows a slope of 1.074. Comparing PS and AS concentrations, 76 % of the measured concentrations showed no major difference between the two methods (median C_{PS}/C_{AS} at 1.29). The overall agreement between the two methods is particularly good given the inter-laboratory variability and the different analytical methods that add to the effects of the different sampling strategies. However, some C_{PS}/C_{AS} resulted in quotients between 0.11 and 7.07, showing some differences between the two methods.

More particularly, the comparison of PS and AS concentrations shared very good agreement for 12 contaminants (5-methylbenzotriazole, atrazine, bentazone, benzotriazole, boscalid, dimethenamid, foramsulfuron, metamitron, metolachlor, nicosulfuron, sulfamethoxazole, tebuconazol) (interquartile range of the C_{PS}/C_{AS} ratio always between 0.5 and 2 (factor 2 difference), Fig. 5). PS achieved slightly higher concentrations compared to AS for 6 micropollutants (flufenacet, iprovalicarb, metazachlor, napropamid, terbuthylazine, thiacloprid) (upper quartile of the C_{PS}/C_{AS} ratio above 2, Fig. 5). These results are in agreement with previous studies where C_{PS}/C_{AS} ratio is within a factor 2, and PS tends to yield higher concentrations (Birch et al., 2013; Mutzner et al., 2019a; Škodová et al., 2016). For 2,4-D, MCPA, and propamocarb, PS overestimated AS's concentrations (smallest C_{PS}/C_{AS} ratio above 2). Conversely, DEET was slightly underestimated with PS compared to AS (lower quartile of the C_{PS}/C_{AS} ratio below 0.5, Fig. 5).

These differences can be explained by multiple scenarios. First, AS can be subject to errors – e.g., aqueous micropollutant degradation cannot be excluded in the autosampler. Moreover, AS samples were only collected every 2 h, and this sampling frequency might be too low to estimate the true average water concentration of compounds with highly fluctuating concentrations (Mutzner et al., 2019b). In this context, PS could allow for more integrative sampling, and therefore more accurate and representative TWA concentrations. There are also uncertainties due to environmental variables (Ahrens et al., 2015). We hypothesized that differences in temperature between calibration (11 °C, part A (Glanzmann et al., 2023)) and field (3 to 19 °C, SI, Fig. S4.1) experiments could lead to slightly inaccurate R_S. Indeed, R_S increases with temperature because the diffusion in the WBL and the membrane, as well as the uptake rate in the sorbent, increase with higher temperatures (Harman et al., 2012; Kingston et al., 2000; Lissalde et al., 2016). However, no effect related to temperature was observed here (SI, Fig. S4.2).

For 2,4-D, MCPA, and propamocarb, other hypotheses can also be formulated. The pH of the river (filtrate) was measured between 8.2 and 8.6 during the sampling period (SI, Table S3.3). As these 3 analytes have the lowest $\log K_{OW}$ and some of the lowest $\log D_{OW}$ (SI, Table S1.1) of the compounds detected with both AS and PS, the charged chemicals of low hydrophobicity could have transferred very rapidly to the sorbent as observed in a previous study (Vermeirssen et al., 2012). Next, in-situ R_S for these compounds were low (0.01–0.05), possibly because of their dominant ionic form at neutral pH (Tran et al., 2007). Also, it was previously observed that R_S can vary in different matrices, perhaps due to competition for adsorption with other contaminants and dissolved organic carbon (Mutzner et al., 2019a). Therefore, the ionic strength and the different parameters in the water matrices from calibration to field experiments might have affected the accumulation behaviour of these compounds (Mutzner et al., 2019a; Schreiner et al., 2020).

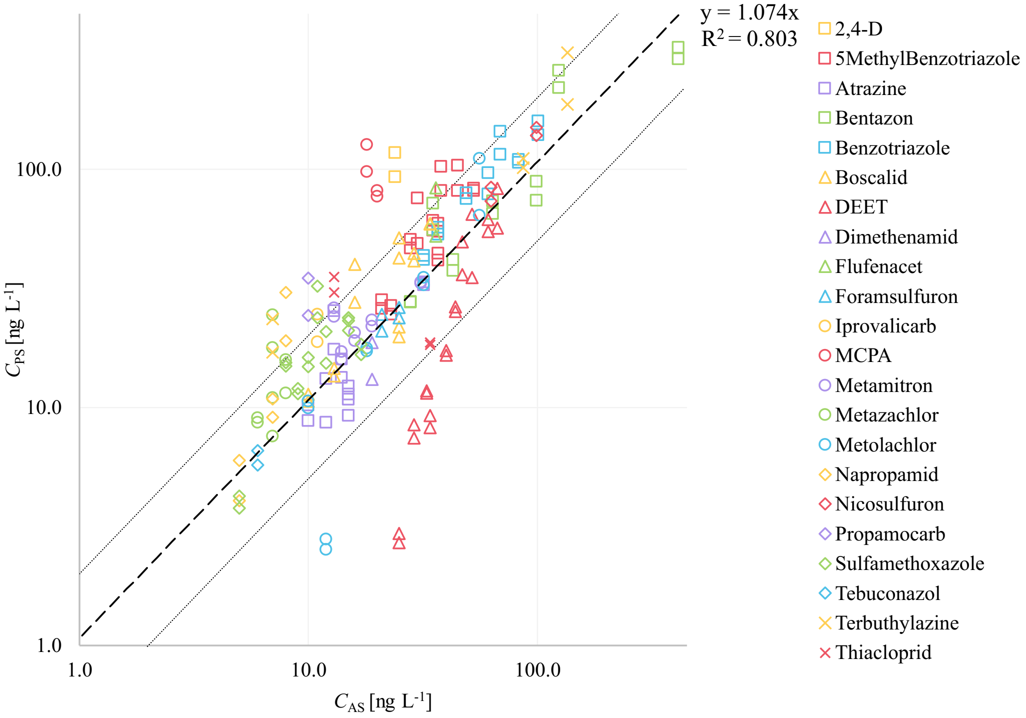

Fig. 4. Concentration of composite samples obtained with AS on the x-axis (logarithmic scale) and TWA concentration with PS on the y-axis (logarithmic scale). The dashed line is a regression curve with a fixed intercept at the origin, dotted lines show a factor 2 confidence interval (y = 2x and y = 0.5x).

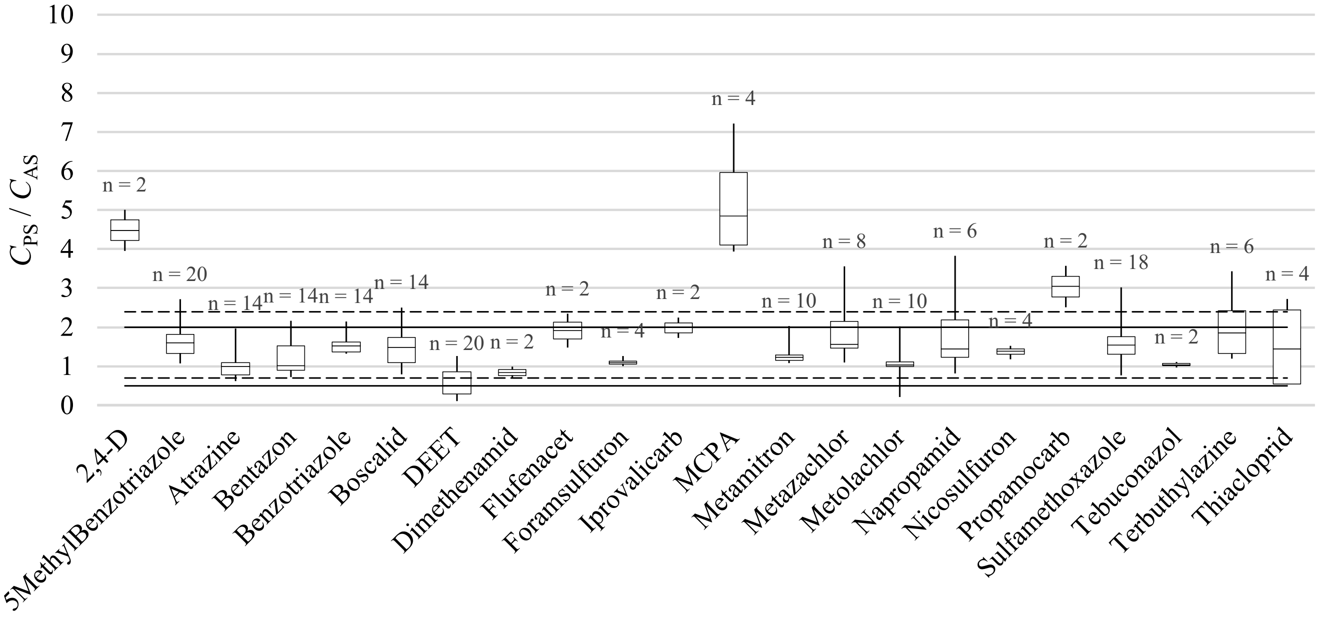

Fig. 5. Ratio between PS TWA and AS concentrations for the hydrophilic micropollutants (22) quantified with both methods over the 11 sampling periods. Boxes show the 1st and 3rd quartiles (Q1 and Q3) with the horizontal line inside being the median. Whiskers show distance from min/max to Q1/Q3, dashed lines are the 10th and 90th percentile of the whole data set, and solid lines show a factor 2 confidence interval. The number of sampling periods with detections in both replicates given by n.

3.2.3. Comparison with TWA concentrations calculated with R_S from the literature and $R_{S,MAX}$

TWA,$R_{S,IN\text{-}SITU}$ and TWA,$R_{S,MAX}$ upper and lower quartiles were within the same range (SI, Fig. S3.2), which is expected considering that the mean in-situ R_S is at 83 % of $R_{S,MAX}$ (8–100 %) (Section 3.2.1). Statistical testing (paired *t*-test, p-value = 0.05) between TWA,$R_{S,IN\text{-}SITU}$ and TWA,$R_{S,MAX}$ with concentrations obtained by AS showed that the differences were not significant for 12 compounds (out of 22) with both methods. The difference with AS was not significant for 2 additional compounds using $R_{S,MAX}$, and for 1 compound using $R_{S,IN\text{-}SITU}$ (SI, Table S3.4). This shows that the added value of the developed method is relatively limited in the studied hydrodynamic conditions, although the measure of integrative k_w (through the dissipation of PRC) was very useful to ensure that $R_{S,MAX}$ were approached for the whole sampling period.

Overall, TWA,$R_{S,LIT}$ were higher than TWA,$R_{S,IN\text{-}SITU}$, and thus overestimated more the concentrations obtained with AS (y = 1.834x). For 4 compounds, the lower and/or the upper quartile of the TWA,$R_{S,IN\text{-}SITU}$/C_{AS} ratios was above 2 (SI, Fig. S3.2), suggesting that it is important to use accurate R_S that best reflects the specific exposure conditions (i.e., R_S based on measured k_w). However, significant difference (paired *t*-test, p-value = 0.05) between TWA,$R_{S,LIT}$ and concentrations obtained by AS were observed in only 5 compounds (SI, Table S3.4), because (average) water velocities used in calibration studies from the literature were between 8 and 37 cm s^{-1} (SI, Table S1.3), a range encompassing the water velocities encountered in the studied river (24 cm s^{-1} on average).

The above suggests that the error on TWA concentrations due to the use of a 'fixed' R_S (the same R_S irrespective of water velocities, i.e., $R_{S,MAX}$ or $R_{S,LIT}$) instead of $R_{S,IN\text{-}SITU}$ may be acceptable when working above a given water velocity (or within a range). Knowing how obtained TWA concentrations vary with k_w (and the water velocity) is useful to determine the approximate values of water velocity below (or above) which the added value of the developed method is significant. The calculated errors (Eqs. (6) and (7)) were plotted against the water velocity U (cm s^{-1}) obtained from k_w using the following semi-empirical model (Glanzmann et al., 2022):

$$U = \frac{\nu}{L}\left(\frac{k_w}{0.52\frac{D_w}{L}\left(\frac{\nu}{D_w}\right)^{\frac{1}{3}}}\right)^2 \qquad (8)$$

with ν the water viscosity (m^2 s^{-1}) at 11 °C, D_W the diffusion coefficient of the contaminant in water (m^2 s^{-1}) at 11 °C, and L the characteristic length of the disk (m). Examples of graphs are given in Fig. 6; the graphs for all compounds are given in SI (Section S5).

The values of the water velocity U above (or between) which Error$R_{S,MAX}$ and Error$R_{S,LIT}$ are <20 % are given in Table 1. Error$R_{S,MAX}$ is <20 % for 33 of the 44 compounds above 20 cm s^{-1}, and >20 % for only 2 compounds above 100 cm s^{-1}, thus confirming that $R_{S,MAX}$ can be used in many situations. The use of $R_{S,LIT}$ appears to be more complicated. In some cases (8 compounds), Error$R_{S,LIT}$ is <20 % in only a range of water velocities. In other cases (9 compounds), Error$R_{S,LIT}$ is still >20 % above 100 cm s^{-1}, because $R_{S,LIT}$ are higher than $R_{S,MAX}$. For these compounds, further studies are needed to determine whether $R_{S,LIT}$ are overestimated or R_S from this study are underestimated.

4. Practical considerations for application in monitoring programs

Overall, the method from sampler preparation to retrieval and analysis was fast and easy to set up. A summarizing flowchart is available in SI (Section S7). Sampler conditioning, mounting, retrieval, and extraction were kept to a minimum (when prepared in batch, total time <5 min per sampler for one operator). The aluminium tube that could freely slide on the steel rod was a valuable asset to spend a minimum amount of time in the water (<1 min). Vermeirssen et al. (2009) emphasized the need for a good fit between the sorbent and the membrane (to avoid a reduced or variable sampling area leading to less reproducible data). In this study, the PES membrane was easily fitted on the sorbent disk. Moreover, it is known that biofouling can be an issue as it can affect the resistance to mass transfer (Vrana et al., 2005). It was suggested that PES membranes were less prone to fouling due to their hydrophilic nature (Aguilar-Martínez et al., 2008; Alvarez et al., 2004). This tended to be confirmed in our study as no to little fouling was observed on the membrane's surface during the sampling periods, though this can also be related to the relatively short deployment period (14 days).

Some other aspects could be improved during the deployment of sampling devices. First, the silicone disks were impractical to align well with the hole in the top plate of the housing, because the diameters of the disks (42 mm) and the holes (40 mm) were quite similar which left very

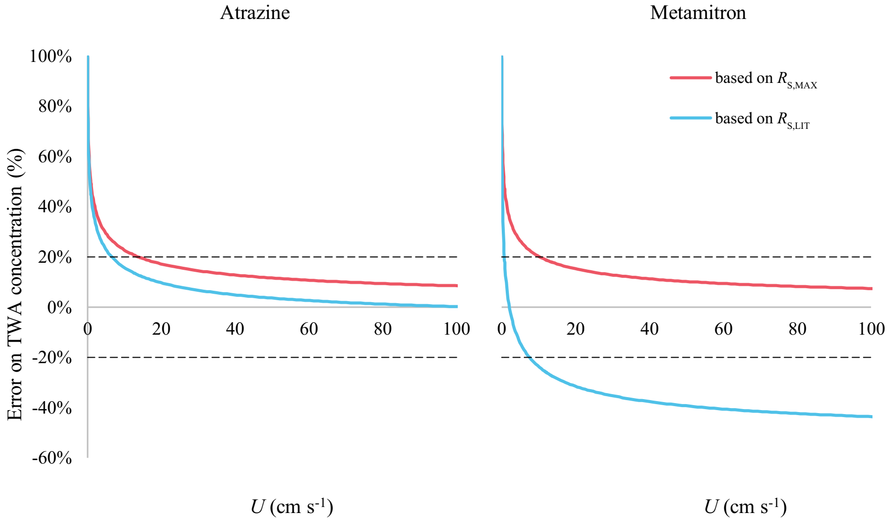

Fig. 6. Example of graphs for the error on TWA concentration plotted against the water velocity U. Error$R_{S,MAX}$ is in red, and Error$R_{S,LIT}$ in blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

little wiggle space. This is because the time scale for lateral diffusion from the rim to the exposed area needs to be negligible compared to the one of PRC dissipation (Glanzmann et al., 2022). An increased diameter of 2 mm for the silicone disks should not be an issue for uniform PRC distribution (SI, Section S6) and could ease the fitting of the disk into the housing. Secondly, special arrangements could be developed or installed to prevent solid items such as branches, leaves, and anthropogenic waste (e.g., plastic bags) from being retained by the steel rods and thus possibly lessening accumulation on the sampler (e.g., protective iron bars upstream of the samplers). Thirdly, some additional water quality parameters (e.g., pH) could also be monitored during deployment, because their variability could affect uptake on the sampler (e.g., for ionisable compounds) and thus reproducibility of the measured data.

Another point is that ideally k_w should be measured at the surface of the hydrophilic sampler. As this has not been achieved in previous studies, this work focused on measuring k_w as close as possible from the sampler (6 cm between the disks' centres). As water velocity can change with depth, a vertical deployment of the housing may not be ideal for every river profile, and care must be taken when deploying samplers in small streams. The best housing position for a given river site could be initially determined by installing PRC-spiked silicone disks in the two holes of housings deployed both vertically and horizontally; the best position being the one producing the smallest difference between the two k_w. In deep water streams, relative differences in water velocity within the 6 cm water column are probably negligible.

While taking into account water velocity for the uptake on the sampler is important, the implications of deploying both a hydrophilic sampler and a silicone disk are major, as they both require different analytical instruments. One of the main advantages often showcased is that PS incurs lower costs than AS (Endo and Matsuura, 2018; Goumenou et al., 2021; Vrana et al., 2005). However, with the proposed methodology, acquiring and maintaining two high-end instruments rather than one will not be cheaper and will require more manpower. To save time and money, it is thus necessary to identify when the use of the PRC-spiked silicone disk is needed and when it is not. Its use is crucial in surface water with low water velocity where uptake is limited by the WBL (below values of U given in Table 1), as well as in sampling sites with unknown water velocities. It is however not essential in water streams where the water velocity is high enough (i.e., >20 cm s^{-1} for 33 of the 44 compounds and 100 cm s^{-1} for 42 compounds if $R_{S,MAX}$ is used, see Table 1) so that the resistance in the WBL is negligible compared to the one in the sampler. Alternatively, it is worth mentioning that the silicone disk has another valuable asset that could be taken advantage of; in addition to the determination of k_w, it could also be used as a passive sampler to monitor hydrophobic compounds (Estoppey et al., 2015; Mills et al., 2014; Rusina et al., 2010; Vrana et al., 2005).

5. Summarizing conclusions of the study

Uptake on a passive sampler can be impacted by the hydrodynamic conditions. These conditions can be characterized by k_w, a parameter that can be measured using the dissipation of PRC. In part A (Glanzmann et al., 2023), Chemcatcher-like passive samplers (SDB disk and PES membrane) were calibrated for 44 hydrophilic contaminants under four k_w to determine condition-specific R_S. Then, relationships were established between k_w and R_S, to determine the most accurate R_S when k_w is measured on-site. This methodology was tested in part B of this study, where SDB disks with PES membranes were co-deployed with silicone disks spiked with PRC. The samplers were exposed in a medium-sized river during 11 consecutive 14-day periods, and the site was also equipped with an autosampler. Results showed that the PS method was robust as minimal variation was obtained between duplicates (median factor at 1.16). Moreover, 76 % of the calculated TWA concentrations showed no major difference with concentrations obtained with AS (median C_{PS}/C_{AS} at 1.29). The method was optimised to be applicable in routine monitoring with minimal preparation and extraction steps, and an easy set-up and deployment system. Additionally, to save time and money, the PRC-spiked silicone disk can be omitted and $R_{S,MAX}$ can be used to calculate TWA concentrations when the water velocity is high enough (alternatively $R_{S,LIT}$ can be used depending on the hydrodynamic conditions). Errors on TWA concentrations due to the use of 'fixed' R_S (instead of $R_{S,\text{IN-SITU}}$) are provided to allow practitioners and project managers to assess the best strategy to adopt in the surface waters to be monitored.

CRediT authorship contribution statement

Naomi Reymond: Methodology, Formal analysis, Investigation, Visualization, Data curation, Writing – original draft, Writing – review & editing. **Vick Glanzmann:** Methodology, Formal analysis, Investigation. **Sofie Huisman:** Investigation. **Cécile Plagellat:** Investigation, Data curation. **Céline Weyermann:** Conceptualization, Supervision, Writing – review & editing. **Nicolas Estoppey:** Conceptualization, Supervision, Writing – original draft, 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.

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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.2023.161937.

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