Calibration of the Chemcatcher® Passive Sampler and Derivation of Generic Sampling Rates for a Broad Application in Monitoring of Surface Waters

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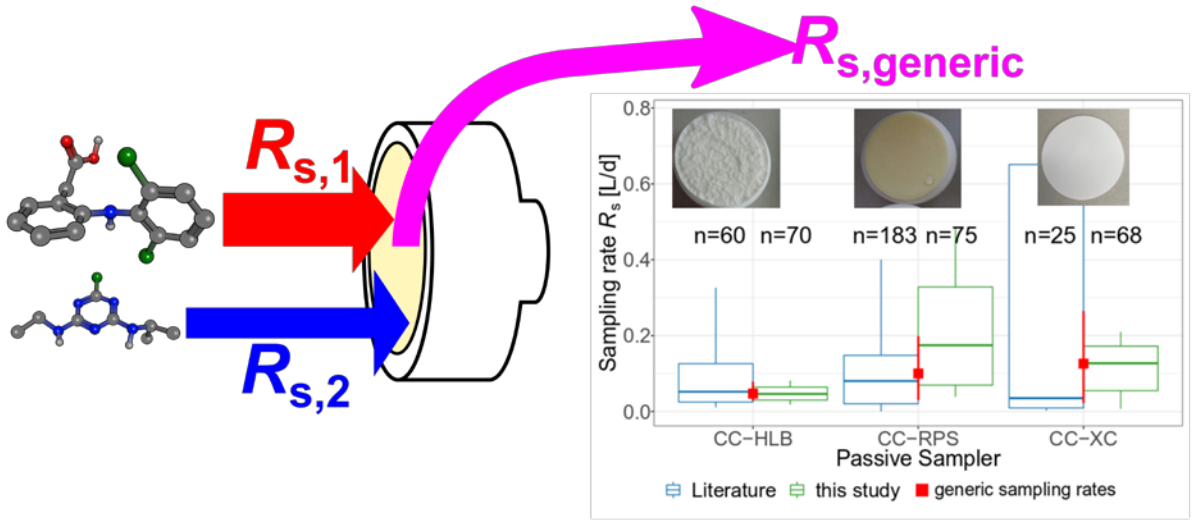
ABSTRACT We determined sampling rates for 34 pesticides, five pesticide transformation products, and 34 pharmaceutical compounds with the Chemcatcher (CC) passive sampler in a laboratory-based continuous-flow system at 40 cm/s and ambient temperature. Three different sampling phases were used: styrene divinylbenzene disks (SDB-XC), styrene divinylbenzene reversed phase sulfonate disks (SDB-RPS), and hydrophilic lipophilic balance disks (HLB), in all cases covered with a diffusion-limiting polyethersulfone membrane. The measured sampling rates range from 0.007 L/d to 0.193 L/d for CC with SDB-XC (CC-XC), from 0.055 L/d to 0.796 L/d for CC with SDB-RPS (CC-RPS), and from 0.018 L/d to 0.073 L/d for CC equipped with HLB (CC-HLB). Comparison with sampling rates from literature enabled to derive generic sampling rates that can be used for compounds with unknown uptake kinetics such as transformations products and new compounds of interest. Field trial results demonstrate that the presently derived generic sampling rates are suitable for estimating time-weighted average concentrations within reasonable uncertainty limits. In this way, Chemcatcher passive sampling can be applied approximately to a broad range of solutes without the need for deriving compound-specific sampling rates, which enable compliance checks against environmental quality standards and further risk assessment.

33 GRAPHICAL ABSTRACT



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1. Introduction

Environmental monitoring is important to ensure clean resources for future generations. In this context, techniques for a low-cost regular sampling followed by high-throughput chemical analysis would enable governmental authorities to react early on possible threats for human and environmental health.

So far, regulatory surveillance of surface waters proceeds through grab sampling to determine concentrations of various micropollutants such as pesticides and pharmaceuticals. Passive sampling provides a low-cost alternative to conventional grab sampling, building on numerous techniques developed in the last 30 years.[1–4] The aim of passive sampling is twofold: First, it facilitates the sampling process by accumulating analytes in synthetic matrices over a specific period of time, thus yielding time-averaged rather than punctual information about the waterborne contamination profile. Second, the built-in accumulation of contaminants lowers the detection limit down to the ng/L-range, thus overcoming sensitivity limits of grab sampling.[5]

Different designs have been developed for passive water sampling, generally targeting different polarity ranges. For nonpolar contaminants polydimethylsiloxane (PDMS) is a well-studied sampler that can also be applied in biota sampling.[3, 6] Polar organic compounds can be detected with the Polar Organic Chemicals Integrative Sampler (POCIS)[2] or the Chemcatcher passive sampler (CC). [7, 8] POCIS is generally applied with hydrophilic lipophilic balance (HLB), but CC can be used with a wide variety of more or less polar receiving phases. Styrene divinylbenzene reversed phase sulfonate (SDB-RPS) is commonly applied, because it offers good accumulating properties for polar pesticides and pharmaceuticals.[9, 10] Other membranes such as styrene divinylbenzene (SDB-XC),[11] HLB,[12] or C_{18}[13] were tested as well.

The uptake into a passive sampler can be described with an empirical two-compartment model: [1, 14, 15]

$$\frac{dc_s}{dt} = k_u c_w - k_e c_s \quad (1)$$

In eq. 1, $\frac{dcs}{dt}$ is the change of analyte concentration in the sampler [ng/(L d)], k_u [1/d] and k_e [1/d] are the uptake and the elimination rate constants, and c_w and c_s are the analyte concentrations in the water phase [ng/L] and the receiving phase [ng/L], respectively. An integration of (1) yields the nonlinear equation (2).

$$c_s(t) = \frac{k_u}{k_e} \cdot c_w[1 - \exp(-k_e \cdot t)] \quad (2)$$

For short exposure times (i.e., kinetic sampling) the term $k_e c_s$ in (1) can be neglected, because c_s is very small at the beginning of the uptake process. In this case, (1) can be reduced to (3). An integration of (3) yields (4). This model can only be applied in the beginning of the accumulation as it only describes the initial velocity of the uptake into the passive sampler. By definition this is up to t_{50}.[16] t_{50} can be derived from (5)

$$\frac{dc_s}{dt} = k_u c_w \quad (3)$$

$$c_s = k_u c_w t \quad (4)$$

$$t_{50} = \frac{\ln(2)}{k_e} \quad (5)$$

Often the mass of analyte on a passive sampler m_s [ng] is not converted to the concentration c_s [ng/L]. Thus, (4) can be rewritten as (6). The uptake in the passive

sampler is now proportional to the sampling rate R_s [L/d] instead of the uptake rate constant k_u (7).

$$m_s = c_s \cdot V_s = k_u \cdot V_s \cdot c_w \cdot t \quad (6)$$

$$R_s = k_u \cdot V_s \quad (7)$$

It should be noted that this model only works if analyte exchange between water and receiving phase is isotropic. Isotropic exchange was confirmed for silicon samplers and for nonpolar Chemcatcher configurations. For polar applications of the Chemcatcher and POCIS monophasic uptake could not be shown.[17] Especially for adsorbing passive samplers, sorption on the receiving polymer might be followed by diffusion into the polymer. Therefore, it is possible that the uptake in the outer receiving phase is followed by uptake in one (or more) inner receiving phases. If uptake in the inner receiving phase (k_u') is faster than ke, the sampler will appear as a quasi-infinite sink.[18, 19] Additionally, it is possible that elimination from the passive sampler is insufficient, which could be shown for PES as a passive sampler for nonpolar analytes by Chepchirchir et al. (2020).[20] If passive samplers act as quasi-infinite sinks, uptake kinetics may be described with (6).

If samplers are deployed in the field during the integrative sampling phase (usually a time frame of two to three weeks), it is assumed that the passive sampler will not release analyte. From this assumption the TWA concentration at a sampling site is derived with (8) (rearranged (6)).

$$c_w^{twa} = \frac{m_s}{R_s t} \quad (8)$$

With knowledge of the average compound concentration c_w [ng/L], the compound-specific sampling rate can be derived from a calibration experiment (9).

$$R_s = \frac{m_s}{c_w \cdot t} \quad (9)$$

It has been attempted to determine sampling rates from physicochemical parameters of analytes and from *in silico* approaches.[9, 21, 22] For polar passive samplers this correlation could not be found. Besides being compound-specific, R_s also depends on external sampling parameters such as the flow velocity of a stream. Laboratory calibration experiments could show that the effect is quite strong.[23, 24] Therefore, the applicability of polar passive samplers is difficult, because flow conditions may vary depending on the season, sampling site, or frequency of rain events.

To reduce the effect of the flow rate for polar passive samplers, Fauvelle et al. (2017) suggest to determine flow-dependent R_s or to determine the mass transfer coefficient k_w directly.[25] Alternatively in situ sampling rates may be derived from field calibrations. Moschet *et al.* (2015) conducted an extensive field calibration study to determine field sampling rates for 123 compounds. However, this approach is time-intensive and only successful for target analytes, which can be found at the site of interest in sufficiently stable concentrations in the water phase.[26]

In other studies, generic sampling rates were applied to overcome uncertainties that affect the uptake rate, like flow conditions or biofouling.[27–29] These universally applicable sampling rates take into account that local uptake conditions likely differ from laboratory data and close a gap between the laboratory calibration of passive samplers and the hesitant application in regulatory monitoring programs. However, resultant time-weighted average (TWA) concentrations have a higher uncertainty due to fact, that individual compound properties are not taken into account.

In this study, sampling rates are derived from laboratory calibration experiments for three different Chemcatcher configurations (CC equipped with HLB, SDB-RPS, and

SDB-XC). For SDB-RPS two different manufacturers are compared, as the often used Empore disk was not available for some time in 2018. This raised the question, whether sampling rates can be transferred to other passive samplers of the same composition, such as the Attract SDB-RPS disk (Attract disk), provided by Affinisep. To examine the uptake kinetics of the Chemcatcher equipped with the Attract SDB-RPS disk (CC-RPS (AD)), calibration experiments are conducted at three different temperatures (10°C, 14°C, and 18°C). Subsequently, generic sampling rates are determined by augmenting the data set derived in this study with literature data to increase applicability of the laboratory sampling rates in field exposure experiments. Generic sampling rates are verified by comparing time weighted average (TWA) concentrations calculated with sampling rates from different studies. They should be more robust towards local field conditions due to the fact that many different sampler exposure scenarios are covered during R_s data generation.

2. Material and Methods

2.1 Chemicals and Materials

Solvents (methanol and acetonitrile) were purchased from VWR. Water was bidistilled prior to use. A list of all analytes, including some physicochemical properties, can be found in the supplementary material (**Table SM-1**). Imidacloprid-d4 and mecoprop-d3 where used as internal standards. Atlantic HLB (hydrophilic lipophilic balance)-L Disks were purchased from Biotage (Uppsala, Sweden). SDB-RPS (styrene divinylbenzene reversed phase sulfonate) disks were purchased from 3M (Empore Disks, St. Paul/USA) and Affinisep (Attract Disks, Petit-Couronne/France). SDB-XC (styrene divinylbenzene exchange) disks were purchased from Affinisep. Polyethersulfone (PES) membranes (pore size: 0.45 µm), which were used as diffusion limiting membranes, were purchased from Pall (Port Washington/USA). Chemcatchers® (d = 47 mm) were ordered from AT Engineering Technology, Tadley/UK.

2.2 Calibration Experiments

Sampling rates were determined in laboratory calibration experiments. Three week and eight week calibration experiments were conducted for CC-RPS and CC-HLB. CC-XC was calibrated for eight weeks.

A continuous flow experiment with passive overflow was conducted: The tank (30 L) was placed in a climate chamber to control the temperature and spiked continuously with analyte solution to yield constant analyte input. Additionally, tap water was pumped through the tank (See also **Figure SM-1**). The system was left to equilibrate for three days before adding passive samplers. Prepared Chemcatchers were mounted to a two-story stainless steel carousel which was stirred with a laboratory stirrer (Heidolph) to simulate water flow ($v \approx 40$ cm/s). This flow rate represents a

relatively fast flow rate in small streams.[15] These fast flow rates are not often considered in calibration experiments. Water was sampled daily during the experiments to monitor the analyte concentrations. During the calibration experiment, passive samplers were removed from the calibration device regularly to yield time-dependent uptake curves. One sampler was taken from the top row, and one sampler from the bottom row to yield duplicates. The respective exposure times can be found in the supplementary material (Table SM-16 – Table SM-20)

The experimental setup is easy to use and three Chemcatcher designs could be calibrated for 34 pesticides, five transformation products and 34 pharmaceuticals (**Table 1**)

2.3 Passive Sampler Preparation and Extraction

Passive samplers were conditioned before deployment to wet the surface thoroughly. PES membranes, SDB-RPS disks, and SDB-XC disks were shaken in methanol (technical grade) for 30 min and subsequently in bidistilled water for 30 min. Atlantic HLB-L disks may lose sorbent material when shaken, which is why these samplers were conditioned gravimetrically with 50 mL methanol (technical grade) and subsequently with 50 mL bidistilled water. After conditioning, samplers were placed in clean and dry Chemcatcher housing and covered with a PES membrane. The set-up is similar to studies conducted by Münze *et al.* (2015 & 2017), and by Moschet *et al*. (2015).[26, 29, 30] The samplers were stored up to one day before deployment in the calibration tank.

After deployment, passive samplers were extracted using different extraction methods as shown in **Table SM-3**. Internal standard (c=10 µg/mL, 10 µL) was added to the extract and the volume was evaporated to 1 mL (0.5 mL for samples that were

deployed for less than 10 days) under a gentle nitrogen stream in a water bath (40°C). Extracts were stored at -20°C until analysis.

2.3.1 Water Samples

Water samples were taken on weekdays during the calibration experiments. The pH of the tap water was measured from every water sample using a Prolab 2000 pH meter (SI Analytics) and ranged from 7.9 to 8.3. A solid phase extraction (SPE) cartridge (Chromabond HLB, 6 mL/500 mg, Macherey Nagel, Düren/Germany) was conditioned with 10 mL methanol (technical grade) and 10 mL bidistilled water. Subsequently, a 1 L water sample was run over the cartridge. It was left to dry for 30 min and eluted with 10 mL methanol (with 1% formic acid) and 10 mL acetonitrile. Internal standard was added (c=10 µg/mL, 10 µL) and the sample was evaporated to 1 mL under a gentle nitrogen stream in a water bath (40°C). Samples were stored at -20°C until analysis with HPLC-MS/MS. Mass transitions and HPLC-methods are described in the supplementary material (**section SM-3**).

2.3.2 Field Samples

The applicability of derived generic sampling rates was tested by comparing time-weighted average (TWA) concentrations derived from different literature references and this study for the herbicides atrazine and diuron, and the pharmaceuticals diclophenac and carbamazepine. Additionally, the empiric generic sampling rates were used to determine TWA concentrations.

Samplers were deployed in duplicates in the small stream Parthe, near Leipzig (51.2122°N, 12.7032°E) for eight periods of two to three weeks in 2020. The site is surrounded by fields, but also receives cleared waste water 50 m upstream. Trip blanks

were used to monitor background contaminations during sampling and the extraction process.

After exposure samplers were disassembled and stored for up to 24 h before extraction.

2.4 Determination of Sampling Rates

For three weeks calibration experiments, sampling rates were determined from the linear uptake by rearranging equation (9). This equation was chosen because the linear uptake phase was generally not left during this time frame. During eight week exposures, most compounds reached the curvilinear uptake phase. Equation (10) was used to fit the data with a nonlinear model. If data were sufficiently linear for eight weeks of exposure (i.e. $r^2 \geq 0.8$, or lower residual standard error), sampling rates were derived from a linear fit. Uncertainties of the sampling rates were calculated by the Gaussian law of error propagation (for details see Supplementary Material **SM-4.3**).

$$m_s = V_s K_{sw} c_w \cdot [1 - \exp\left(-\frac{R_s}{K_{sw} V_s} \cdot t\right)] \quad (10)$$

3. Results and Discussion

3.1 Calibration Experiments

3.1.1 Sampling Rates of the Empore SDB-RPS Disk

The Chemcatcher equipped with the Empore SDB-RPS disk (CC-RPS (ED)) was calibrated for 38 pesticides and transformation products. The concentration in the water phase ranged from 6.5 ng/L to 56 ng/L. The standard deviations of c_w ranged from 19% to 46%, depending on the compound. The relatively large uncertainties are caused by an increase in c_w in the third week of the experiment. Reasons for the increase can be either errors during preparation of the stock solution or inconsistencies in the pumping speed. This directly increases the uncertainty of the sampling rates.

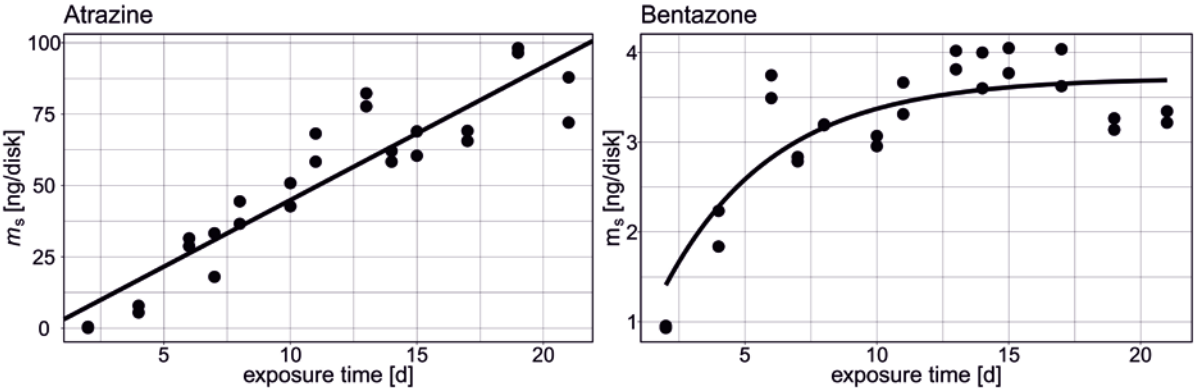

Figure 1: Uptake of the herbicides atrazine (left) and bentazone (right) in the Chemcatcher equipped with Empore SDB-RPS disks over a calibration time of 21 days at 18°C. Sampling rates were determined from a linear model for atrazine and using a nonlinear model for bentazone.

The uptake of the herbicides atrazine and bentazone is plotted in **Figure 1**. Bentazone reached equilibrium within six days, which is why a nonlinear model was used to derive R_s. For all other compounds, except for quinmerac which reached equilibrium within 4 d, a linear model was applied. 37 sampling rates were determined, ranging from 0.026 L/d to 0.36 L/d with an average standard error of 29% (**Table SM-6**).

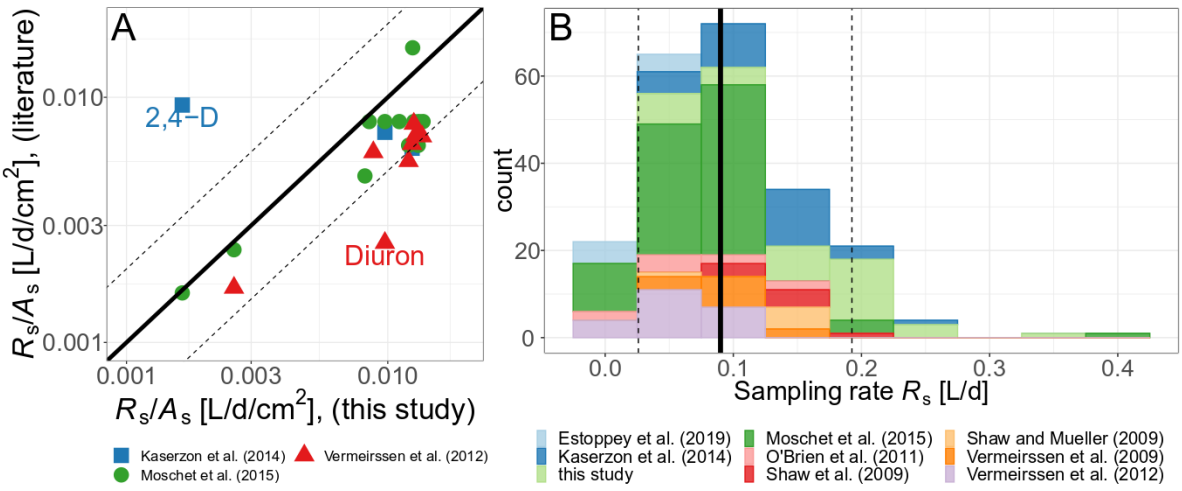

Figure 2 A: Normalized sampling rates R_s of Chemcatcher equipped with Empore SDB-RPS disks (CC-RPS (ED)) compared to literature data [26, 31, 32] (compounds are listed in Table SM-13). Sampling rates were normalized by dividing the sampling rates by the surface area of the passive samplers. The bold line represents the 1:1-line and the dashed lines the 2:1- and 1:2-lines. **B**: Histogram of CC-RPS (ED) sampling rates derived from this study and from different literature references.[10, 24, 26, 31–35] The bold vertical line represents the median sampling rate and the dashed vertical lines the 10% and the 90% quantile.

Figure 2 A shows the sampling rates derived for CC-RPS (ED) in this study compared to literature data from different references.[26, 31, 32] Generally, sampling rates are within a factor of 2 of each other, *i.e.*, within the dashed lines in the figure. This is a reasonable range which was also used by Vrana *et al.* (2016) to compare uptake in different passive samplers.[36] The data were normalized to the exposed surface area of the passive samplers, because the diameter of the applied passive samplers may vary due to in-house sampler designs. Larger deviations from the 1:1-line can be observed for the herbicides 2,4-D and diuron. 2,4-D is a phenoxyacid derivative with pK_a = 2.98. The experiment of Kaserzon *et al.* (2014) was conducted at a lower pH (6.5) than this experiment (pH 8).[31] At the lower pH, more 2,4-D is undissociated, which is why more can be accumulated in the receiving phase. Diuron is a neutral herbicide. It shows a high affinity to the diffusion limiting PES membrane. Vermeirssen *et al.* (2012) used PES membranes with a smaller pore diameter (0.1 µm instead of 0.45 µm).[32] Though

the molecule is much smaller than the pore diameter (D_{eff} = 7.6 Å), this might already impact the uptake kinetics of compounds like diuron which have a high affinity for the PES membrane.[37] R_s from literature references are mostly below the 1:1-line, since higher flow rates were applied in this study compared to literature experiments.

Figure 2 B shows the sampling rates derived in this study and data compiled from eight literature references plotted in a histogram.[10, 24, 26, 31–35] Sampling rates derived in this study are generally higher than literature data with a mean R_s of 0.156 L/d compared to a mean R_s of 0.085 L/d, respectively. This can be ascribed to i) higher flow velocities in this study and ii) the use of PES membranes with a larger pore diameter(0.45 µm instead of 0.1 µm/0.2 µm). An effect of PES membrane pore width on the uptake rate was shown by Kaserzon *et al.* (2014).[31] An average increase of R_s by a factor of 1.4 with a 0.45 µm membrane instead of 0.2 µm pore width was observed.

3.1.2 Sampling Rates of the Attract SDB-RPS Disk

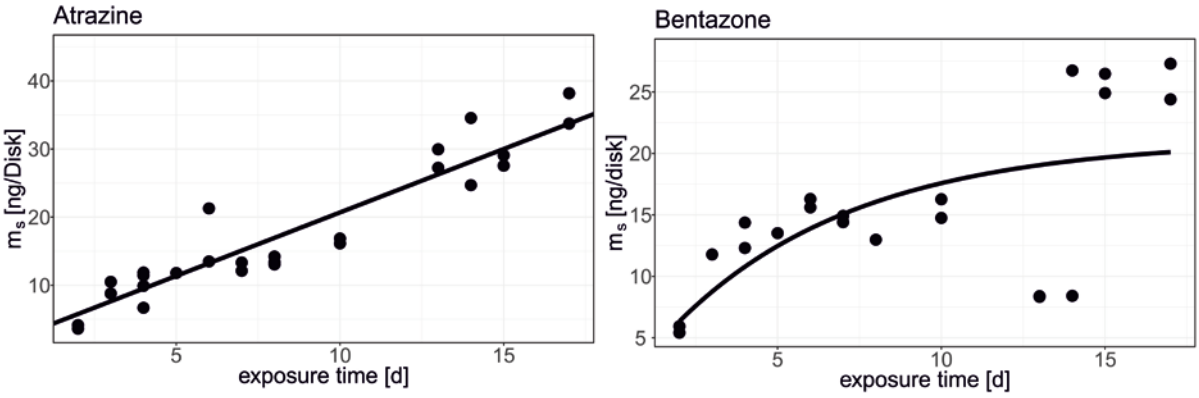

Figure 3: Uptake of atrazine (left) and bentazone (right) in Chemcatcher equipped with Attract SDB-RPS disk for an exposure period of 21 d at 14°C. Sampling rates were determined from a linear model for atrazine and using a nonlinear model for bentazone.

The Chemcatcher equipped with the Attract SDB-RPS disk (CC-RPS(AD)) was calibrated at 10°C, 14°C, and 18°C. At 14°C, the concentration of analytes in the water phase was fairly constant over the whole experiment, ranging from 8.1 ng/L to 29.0

ng/L with a mean standard error of 21%. **Figure 3** shows the uptake of atrazine and bentazone in CC-RPS (AD). Compared to CC-RPS (ED), the uptake of atrazine is decreased and only reaches 40 ng in three weeks instead of to 100 ng. The uptake of bentazone on the other hand is increased from 4 ng to 25 ng (**Figure 1**). Since bentazone reaches equilibrium within five days, the increased concentrations in the sampler at the last three sampling points suggest that c_w increased during the last days of the experiment. In the other experiments (10°C and 18°C), the concentration of the standard mix was increased to nominally 100 ng/L instead of 25 ng/L, because pharmaceuticals were analysed in these experiments, besides pesticides. These compounds are commonly detected in higher concentrations than pesticides in environmental water samples. [38, 39]

At 10°C, the mean concentration in the water phase ranged from 18 ng/L for the antiepileptic oxcarbazepine to 110 ng/L for the pesticide lenacil. At 18°C, the concentration in the water phase ranged from 20 ng/L for the pesticide simazine to 220 ng/L for the betablocker atenolol. c_w were therefore similar in both experiments. The sampling rates derived at both temperatures are comparable, which can be seen in **Figure SM-2** ranging from 0.025 L/d to 0.537 L/d at 10°C, 0.011 L/d to 0.178 L/d at 14°C, and 0.003 L/d to 0.512 L/d at 18°C. The uncertainty is similar to the standard deviation of c_w (**Table SM-8** and **Table SM-9**).

Figure SM-2 shows the sampling rates of pesticides derived from the five different calibration experiments for CC-RPS with disks from different manufacturers. In most cases, the uncertainty of the sampling rates overlap. This suggests that the sampling rates do not differ significantly. However, in some cases sampling rates range up to a factor of 3, *e.g.,* for atrazine. This shows that the determination of reliable sampling rates in the selected experimental setup is challenging. Sampling rates from the eight-

week calibration experiment are generally larger than sampling rates from three-week calibrations. This may be due to higher fluctuations of c_w. For dichlorvos and quinmerac larger sampling rates were calculated for CC-RPS (ED) compared to CC-RPS (AD). Therefore, the slightly different disk composition affects the sampling rate of these compounds. A general trend cannot be observed which is in line with results by Becker *et al.* (2021),[12] who compared the uptake into naked (*i.e.*, without diffusion limiting membrane) Attract disks and Empore disks directly in a flow channel system.

3.1.3 Sampling Rates of the Atlantic HLB-L Disk

The Atlantic HLB-L disk (Atlantic disk) contains HLB (hydrophilic lipophilic balance) as sorbent material which is fixed in a glass fiber filter. Due to that the sampler is thicker compared to PTFE-based samplers. The uptake of pesticides in the Chemcatcher equipped with the Atlantic disk (CC-HLB) has been discussed elsewhere.[15] Calculated sampling rates for the uptake of polar and semipolar pesticides and pharmaceuticals range from 0.018 L/d to 0.073 L/d in an eight week calibration experiment (**Table SM-11**). The mean standard error of R_s is 55% (20% to 140%). The higher error compared to CC-RPS can be attributed to the higher fluctuation in c_w in the experiment.

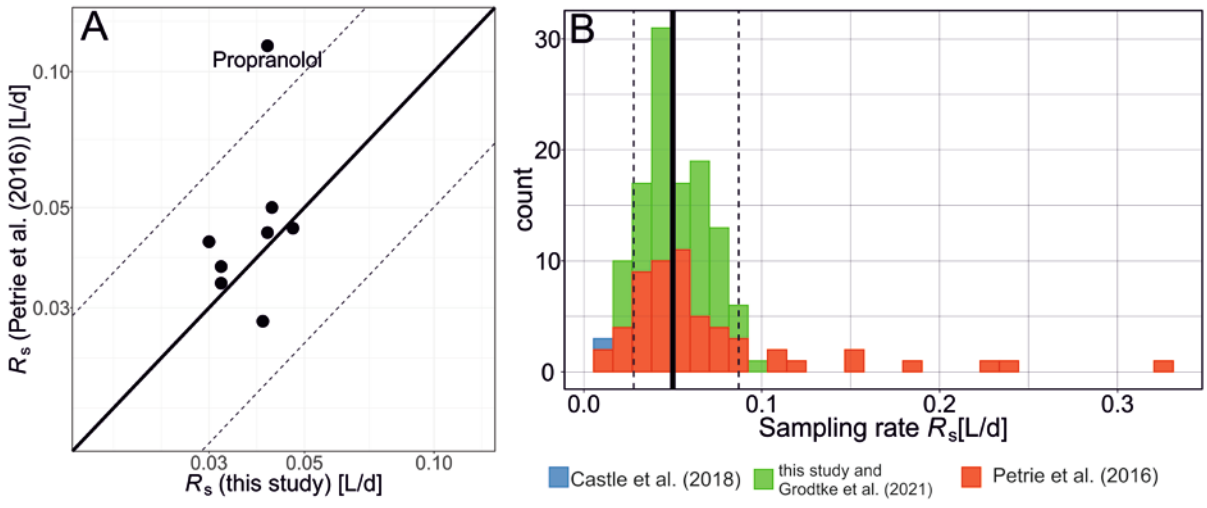

Figure 4 A: Sampling rates for CC-HLB (this study) compared to sampling rates published by Petrie *et al.* (2016) (compounds are listed in Table SM-14).[40] The bold line represents the 1:1-line. The dashed

lines represent the 2:1- and 1:2-lines respectively. **B**: Histogram of Atlantic HLB-L disk sampling rates derived from this study and different literature references.[15, 40, 41] The bold vertical line represents the median sampling rate and the dashed vertical lines represent the 10% quantile and the 90% quantile.

Sampling rates of the Atlantic disk are plotted against literature data published by Petrie *et al.* (2016)[40] in **Figure 4 A**. Seven of eight sampling rates are within a factor of 2 of each other. Only the sampling rate of the beta blocker propranolol in this study is much lower than in Petrie *et al.* (2016) with 0.045 L/d instead of 0.114 L/d (outlier in **Figure 4 A**). During the field exposure by Petrie *et al.*, the concentration of propranolol increased from 80 ng/L to 100 ng/L. Possibly, the concentration gradient during the course of the (comparably short) study increased the uptake rate.

Up to now, only three papers have been published which calibrated CC-HLB as a passive sampler for polar organic compounds and calculated sampling rates. Petrie *et al.* (2016) calibrated the disk in an eight-day field calibration and Castle *et al.* (2018) calibrated it for the molluscicide methaldehyde over 14 d.[40, 41] Recently, we calibrated CC-HLB for polar organic pesticides.[15] **Figure 4 B** shows the histogram of the literature sampling rates (blue, red) compared to the sampling rates derived by our group (green). Uptake in CC-HLB is generally slower than uptake in CC-RPS (ED), which shows in the lower sampling rates for CC-HLB compared to CC-RPS (ED) (90% quantile of 0.078 L/d in CC-HLB (**Figure 4 B**) compared to 0.198 L/d in CC-RPS (ED) (**Figure 2 B**)). The slower uptake compared to CC-RPS may be an effect of the glass fiber membrane which fills with stagnant water during conditioning. Due to the slower uptake, some compounds even showed a linear uptake for an exposure time of eight weeks. However, it also results in lower sensitivity of CC-HLB compared to CC-RPS. On the other hand, the integrative sampling phase of CC-HLB is longer. This would allow for a longer depletion in the field. The results show that the selection of the receiving phase is crucial and should depend on the aim of a study. If a screening is

performed, CC-RPS may be the better choice, because it is more sensitive towards polar organic analytes. It can be deployed for up to two weeks for integrative passive sampling of a wide range of analytes. Sensitivity could even be increased by deploying 'naked' disks to cover short concentrations peaks, *e.g.*, in rain-overflow sewers.[42] If long integrative sampling phases were needed, CC-HLB would be a good selection. However, the sampler will be less sensitive than CC-RPS and for most applications deployment times within a timeframe of one to two weeks are sufficient.

3.1.4 Sampling rates of the Attract SDB-XC disk

For the Chemcatcher equipped with the SDB-XC disk (CC-XC), the concentration in the average water phase ranges from 14 ng/L (simazine) to 235 ng/L ethinylestradiol. The standard deviation of the concentrations in the water phase is relatively large, ranging from 7% to 95%. In the median, the water concentration was relatively stable with a standard error of 27%. The resulting sampling rates range from 0.007 ng/L for clotrimazole to 0.193 ng/L for carbamazepine. The very low uptake of clotrimazole can be attributed to the low polarity of the compound(log K_{ow} = 6.26). This lead to significant retention in the PES membrane.

As for the Atlantic HLB-L disk, only limited literature data are available for the Chemcatcher equipped with the Attract SDB-XC disk (CC-XC). While the order of magnitude of the sampling rates determined in this study is in line with data by Allinson *et al.* (2015), Tran *et al.* (2006), and Schäfer *et al.* (2008), sampling rates are much lower than calculated by Kaserzon *et al.* (2014) and much higher than derived by Allinson *et al.* (2014), as shown in **Figure 5 A**.[11, 31, 43–45] Since not all experimental parameters (flow rate, temperature) are stated clearly in the references, a comparison is difficult. The data show that depending on the experimental design sampling rates may differ quite a lot. The high sampling rates derived by Kaserzon *et al.* (2014) might

be a result of the water temperature during the study (27°C).[31] Uptake experiments by Tran *et al.* (2006) were conducted at almost stagnant flow (0.04 cm/s).[44] Since sampling rates decrease significantly under stagnant flow conditions, this may explain the low uptake rates in their study. **Figure 5 B** shows the strong variation of sampling rates obtained from different studies. To conclude, the data base for CC-XC is poor: While sampling rates within studies are similar, they cover several orders of magnitude when comparing different studies. It appears that the sampler is very sensitive to the experimental conditions it is calibrated with. CC-XC can be applied as an integrative passive sampler, but for polar organic pollutants CC-RPS may be the better choice due to the better literature data basis and the general comparability of results from different research groups.

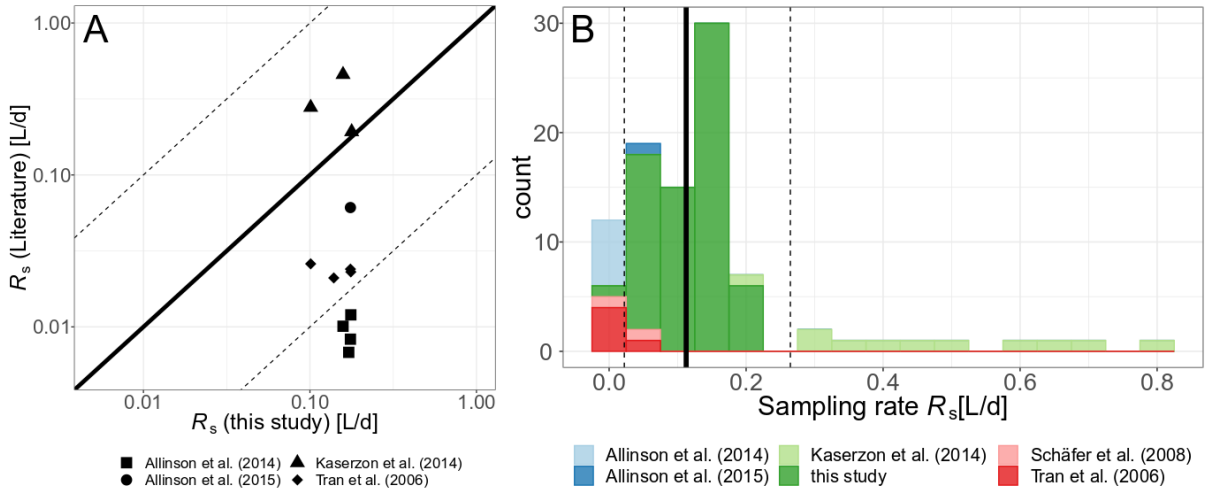

Figure 5 A: Sampling rates for Chemcatcher equipped with SDB-XC disks (CC-XC) compared to sampling rates published in different literature references) (compounds are listed in Table SM-15).[31, 43–45] The bold line represents the 1:1-line. The dashed lines represent the 2:1- and 1:2-lines respectively. **B**: Histogram of CC-XC sampling rates derived from this study and different literature references.[31, 43–46] The bold vertical line represents the median sampling rate and the dashed vertical lines represent the 10% quantile and the 90% quantile.

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400 3.2 Determination of Generic Sampling Rates

401 No correlations could be found between R_s and different physicochemical properties
402 (log K_{ow}, log K_{aw}, log K_{oc}, water solubility S_w, **Figure SM-3**). This also becomes
403 apparent when comparing the sampling rates of the herbicide atrazine (log K_{ow} = 2.82)
404 and its transformation products hydroxyatrazine (log K_{ow} = 2.09), deethylatrazine
405 (log K_{ow} = 1.78), and deisopropylatrazine (log K_{ow} = 1.36). Though log K_{ow} range
406 several orders of magnitude, sampling rates are fairly similar for CC-HLB, ranging from
407 0.043 L/d to 0.051 L/d. For CC-RPS and CC-XC R_s cover a wider range (0.092 L/d to
408 0.188 L/d and 0.106 L/d to 0.176 L/d, respectively). Additionally, LSER modeling
409 (linear solvation energy relationships) was tested to correlate R_s with physicochemical
410 properties. However, it was unsuccessful. This suggests that the sampling rate does
411 not depend on the physicochemical properties of an analyte. Uptake may rather be
412 governed by flow velocities and properties of the sampling phases.

413 **Figure SM-4** shows sampling rates from different studies plotted against the flow
414 velocity [cm/s] of the experiments. Most data are available for CC-RPS which is why
415 the effect of the flow velocity is more prominent for this sampler. The figure shows that
416 the sampling rates generally increase with flow velocity, which is in line with
417 experiments conducted by Vermeirssen *et al.* (2008) with naked CC-RPS.[23] An
418 increase of R_s with flow velocity can be observed up to 14 cm/s. At higher flow rates
419 sampling rates appear to stagnate at approximately 0.2 L/d. Sampling rates derived for
420 CC-XC by Kaserzon *et al.* (2014) at flow velocities of 23 cm/s are considerably higher
421 than 0.2 L/d.[31] As discussed above the experiment was conducted at 27°C which might
422 result in faster uptake. Sampling rates in this study were derived from flow velocities at
423 approximately 40 cm/s and generally did not exceed 0.3 L/d. However, some

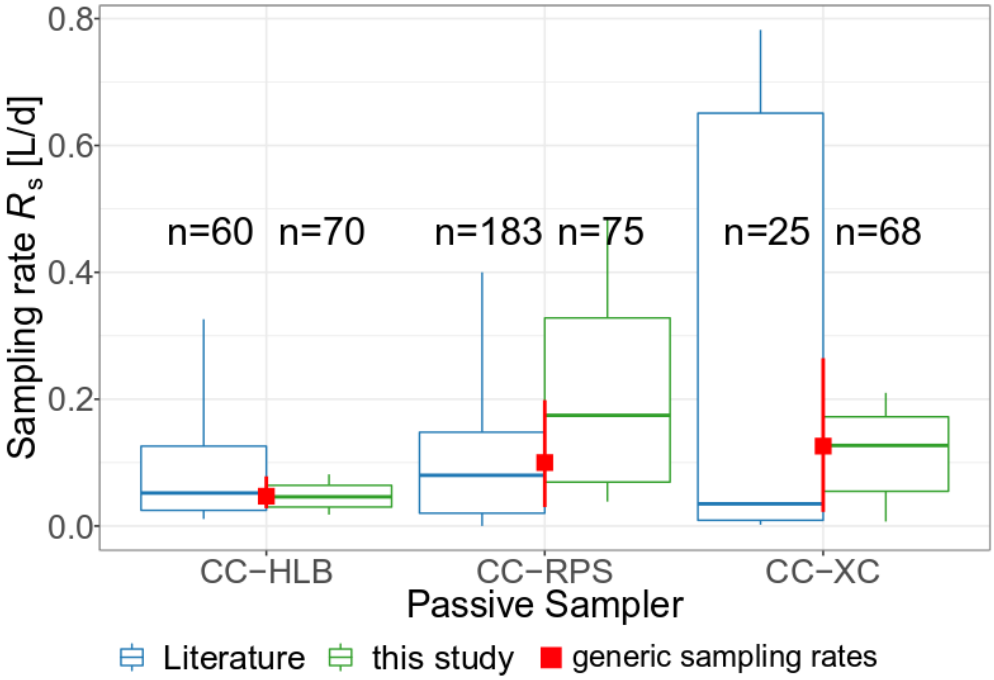
pharmaceuticals showed higher sampling rates in CC-RPS (propyphenazone, atenolol, sulfadimethoxin, phenazone, trimetoprim, carbamazepine, lidocaine, sulfadimidin, nadolol, pentoxifylline, benzotriazole, tiamulin, and caffeine). These compounds do not share structural similarities but are relatively polar (log K_{ow} < 2.25), except for tiamulin (log K_{ow} = 4.75). The laboratory calibration experiments showed, that very polar compounds equilibrate quickly with the selected sampling matrices. This might be a driver for the elevated sampling rates of these compounds.

We suggest to use generic sampling rates, which are derived from the median sampling rate of compiled literature data, to calculate TWA concentrations of compounds with unknown uptake kinetics or for sampling sites with unknown hydrodynamics. Median sampling rates are suggested, because the median is independent of outliers and compiled sampling rates from literature are not normally distributed. The 10% quantile and the 90% quantile are selected as uncertainty boundaries to include most of the generated data available. Generic sampling rates and their quantiles are marked with a bold line and dashed lines, respectively, in **Figure 2 B**, **Figure 4 B** and **Figure 5 B**. This approach regards that most laboratory calibration experiments can only simulate the uptake in the field to a limited extend, because one generally has to compromise on the experimental design, the matrix, the flow velocity, or the temperature. This study used a carousel approach, which probably overestimated the water flow rate, as the water phase moves as well as the carousel to which the passive samplers are mounted. Measuring the correct flow velocity is a challenge in other calibration approaches as well, *e.g.*, when the water phase is stirred directly. It is likely that flow channel systems represent the uptake of analytes in the field best, but the installation and maintenance is cost-intensive.

448 **Figure 6** displays the distribution of sampling rates from different Chemcatcher
449 configurations (CC-HLB, CC-RPS, and CC-XC, green boxes) compared to literature
450 data (blue boxes). Generic sampling rates were derived from all available data for the
451 respective Chemcatcher configurations (red squares). For CC-HLB sampling rates
452 from this study correspond well with the available literature data. Therefore, TWA
453 concentrations derived from generic sampling rates will likely yield similar results as
454 specific sampling rates.

455 Compared to the other Chemcatcher configurations, uptake in CC-HLB is slow. As
456 discussed above, this results in lower sensitivity of this Chemcatcher configuration
457 compared to CC-RPS and CC-XC. For CC-RPS the literature basis is good. Sampling
458 rates from this study extend the applicability of the generic sampling rates to a wider
459 flow velocity since most literature experiments were conducted at flow velocities below
460 20 cm/s. Due to the large literature basis of sampling rates the generic sampling rate
461 is not affected strongly by inclusion of the data from this study. For CC-XC the data set
462 could be extended strongly with the calibration experiments from this study. Sampling
463 rates in literature studies cover several orders of magnitude which is why generic
464 sampling rates show the highest uncertainties of all Chemcatcher configurations.
465 Sampling rates for individual compounds and generic sampling rates are shown in
466 **Table 1.** Since most studies were conducted with flow velocities between 0.1 m/s and
467 0.5 m/s this should be regarded as the application domain of the derived generic
468 sampling rates. For lower flow velocities and quiescent lakes we suggest the 10%
469 quantile to estimate TWA concentrations.

470



471

472 **Figure 6**: Boxplots of sampling rates R_s [L/d] derived from carousel calibration experiments in this study
473 (green) compared to literature data (blue). The bar in the middle of each box represents the median
474 sampling rate of the respective data set. The length of the box is defined as the interquantile range
475 between the 10% quantile and the 90% quantile. The distance of the furthest outlier is shown by the
476 whiskers. Red squares represent the median sampling rate from all data for the respective Chemcatcher
477 configuration (CC-HLB, CC-RPS, or CC-XC). Red lines represent the uncertainty of these generic
478 sampling rates, which is derived from the 10% quantile and the 90% quantile of each data set. n
479 represents the size of each data set.
480

481 **Table 1**: Mean sampling rates R_s [L/d] derived from laboratory calibrations for CC-HLB, CC-RPS, and
482 CC-XC, including generic sampling rates.

Compound	CC-HLB		CC-RPS		CC-XC	
	R_s	s(R_s)	R_s	s(R_s)	R_s	s(R_s)
Pesticides						
2,4-D	0.043	0.037	0.055	0.052	0.049	0.024
2,4-DB	0.037	0.006	0.114	0.095		
Atrazine	0.052	0.030	0.188	0.162	0.176	0.106
Bentazone	0.047	0.028	0.113	0.109	0.091	0.061
Carbendazim	0.036	0.023	0.121	0.109	0.137	0.062
Chloridazon	0.066	0.037	0.139	0.121	0.138	0.075
Clothianidin	0.046	0.024	0.163	0.138	0.118	0.057
Cybutryne	0.044	0.014	0.087	0.049	0.122	0.061
Dichlorprop	0.032	0.023	0.064	0.060	0.057	0.026
Dichlorvos	0.045	0.030	0.173	0.189	0.139	0.083
Dimethachlor	0.041	0.025	0.193	0.181	0.130	0.060
Diuron	0.032	0.019	0.150	0.140	0.085	0.039
Ethofumesate	0.056	0.036	0.197	0.186	0.135	0.058
Fenuron	0.049	0.027	0.097	0.085	0.112	0.058
Flufenacet	0.038	0.023	0.175	0.165	0.126	0.056
Imidacloprid	0.050	0.028	0.156	0.135	0.124	0.057
Isoproturon	0.036	0.020	0.190	0.161	0.122	0.051
Lenacil	0.052	0.031	0.206	0.184	0.170	0.125
MCPA	0.046	0.035	0.063	0.056	0.051	0.026
MCPB	0.042	0.024	0.132	0.108	0.095	0.035
Mecoprop	0.029	0.019	0.068	0.058	0.054	0.025
Metamitron	0.053	0.027	0.132	0.112	0.135	0.074
Metazachlor	0.042	0.024	0.188	0.163	0.132	0.059
Metolachlor	0.049	0.034	0.197	0.070	0.139	0.061
Metribuzine	0.052	0.027	0.172	0.149	0.171	0.095
Pirimicarb	0.042	0.025	0.182	0.166	0.145	0.066
Propazine	0.053	0.030	0.192	0.181	0.139	0.074
Quinmerac	0.057	0.014	0.096	0.108	0.057	0.036
Sebuthylazine	0.049	0.029	0.194	0.173	0.131	0.068
Simazine	0.051	0.029	0.180	0.151	0.175	0.101
Terbuthylazine	0.049	0.029	0.205	0.180	0.146	0.080
Terbutryn	0.043	0.025	0.178	0.180	0.160	0.074
Thiacloprid	0.069	0.038	0.190	0.163	0.163	0.077
Thiamethoxam	0.052	0.030	0.164	0.142	0.136	0.069
Pesticide Transformation Products						
OH-ATZ	0.037	0.022	0.092	0.085	0.123	0.057
DE-ATZ	0.053	0.031	0.161	0.147	0.177	0.115
DIP-ATZ	0.044	0.027	0.156	0.144	0.106	0.089
OH-TBZ	0.042	0.025	0.168	0.163	0.158	0.081
DE-TBZ	0.058	0.034	0.158	0.144	0.158	0.081
Pharmaceuticals						

17-α-Ethinylestradiol	0.031	0.007	0.111	0.458	0.127	0.041
17-β-Estradiol	0.040	0.011	0.140	0.190	0.127	0.046
AMDOPH	0.039	0.012	0.213	0.072	0.132	0.106
Amoxicillin	0.022	0.007	0.238	0.187	0.071	0.033
Atenolol	0.033	0.013	0.463	0.274	0.094	0.055
Benzotriazol	0.050	0.024	0.305	0.074	0.096	0.039
Bezafibrate	0.030	0.014	0.130	0.030	0.113	0.053
Caffeine	0.030	0.010	0.292	0.080	0.065	0.048
Carbamazepine	0.052	0.014	0.385	0.084	0.193	0.083
Chloramphenicol	0.030	0.007	0.180	0.150	0.115	0.050
Clofibric acid	0.037	0.012	0.073	0.122	0.038	0.023
Clotrimazole	0.018	0.023	0.121	0.151	0.007	0.005
Diclofenac	0.038	0.009	0.174	0.262	0.112	0.044
Ibuprofen	0.038	0.021	0.070	0.925	0.087	0.051
Indometacin	0.024	0.006	0.119	0.014	0.097	0.040
Iopromide	0.020	0.013	0.197	0.190	0.058	0.039
Lidocaine	0.040	0.012	0.358	0.035	0.114	0.059
Lincomycin	0.055	0.074	0.796	0.032	0.152	0.135
Metoprolol	0.042	0.023	0.173	0.107	0.068	0.035
Metronidazole	0.043	0.020	0.179	0.121	0.032	0.026
Nadolol	0.029	0.033	0.329	0.227	0.067	0.036
Oxcarbazepine			0.022	0.040	0.091	0.075
Paracetamol			0.175	0.101		
Pentoxifylline	0.041	0.012	0.316	0.169	0.159	0.081
Phenazone	0.064	0.042	0.427	0.306	0.179	0.170
Primidone	0.045	0.017	0.182	0.095	0.055	0.038
Propranolol	0.045	0.073	0.223	0.189	0.127	0.064
Propyphenazone	0.060	0.023	0.484	0.286	0.167	0.088
Roxithromycin	0.030	0.010	0.225	0.160	0.072	0.038
Sulfadimethoxin	0.041	0.032	0.451	0.293	0.084	0.078
Sulfadimidin	0.023	0.010	0.327	0.227	0.067	0.061
Sulfamethoxazole	0.023	0.032	0.215	0.133	0.026	0.018
Tiamulin	0.045	0.029	0.298	0.262	0.111	0.060
Trimethoprim	0.040	0.032	0.394	0.275	0.092	0.050
Generic Sampling rates from this study						
10% quantile	0.029		0.088		0.055	
Median generic R_s	0.042		0.178		0.122	
90% quantile	0.055		0.352		0.167	
Median R_s (Lit)	0.052		0.080		0.035	
Combined generic R_s from this study and literature data						
10% quantile	0.028		0.030		0.022	
Median R_s	0.047		0.100		0.126	
90% quantile	0.078		0.198		0.265	

CC-HLB: Chemcatcher equipped with Atlantic HLB-L disk, CC-RPS: Chemcatcher equipped with Attract/Empore SDB-RPS disk, CC-XC: Chemcatcher equipped with Attract SDB-RPS disk, OH-ATZ: Hydroxyatrazine, DE-ATZ: Deethylatrazine, DIP-ATZ: Deisopropylatrazine, OH-TBZ: Hydroxyterbuthylazine, DE-TBZ: Deethylterbuthylazine.

3.3 Application of Generic Sampling Rates

Sampling rates for four compounds were compiled from different literature references to calculate TWA concentrations in field samples derived at the small stream Parthe in Saxony. Since most data were available for CC-RPS, these results are discussed here. TWA concentrations derived from generic sampling rates (boxes) and data from different references and this study (data points) are plotted in **Figure 7**.

TWA concentrations of atrazine were calculated with sampling rates from five different references and **Table 1**.[24, 32–35] Highest TWA concentrations were derived with sampling rates obtained by O'Brien *et al.* (2011), who calibrated CC-RPS at different flow velocities. TWA concentrations with R_s from low flow velocities are a factor of 2 larger than TWA concentrations from other flow velocities. In general, the data overlap well and show results within the same order of magnitude.

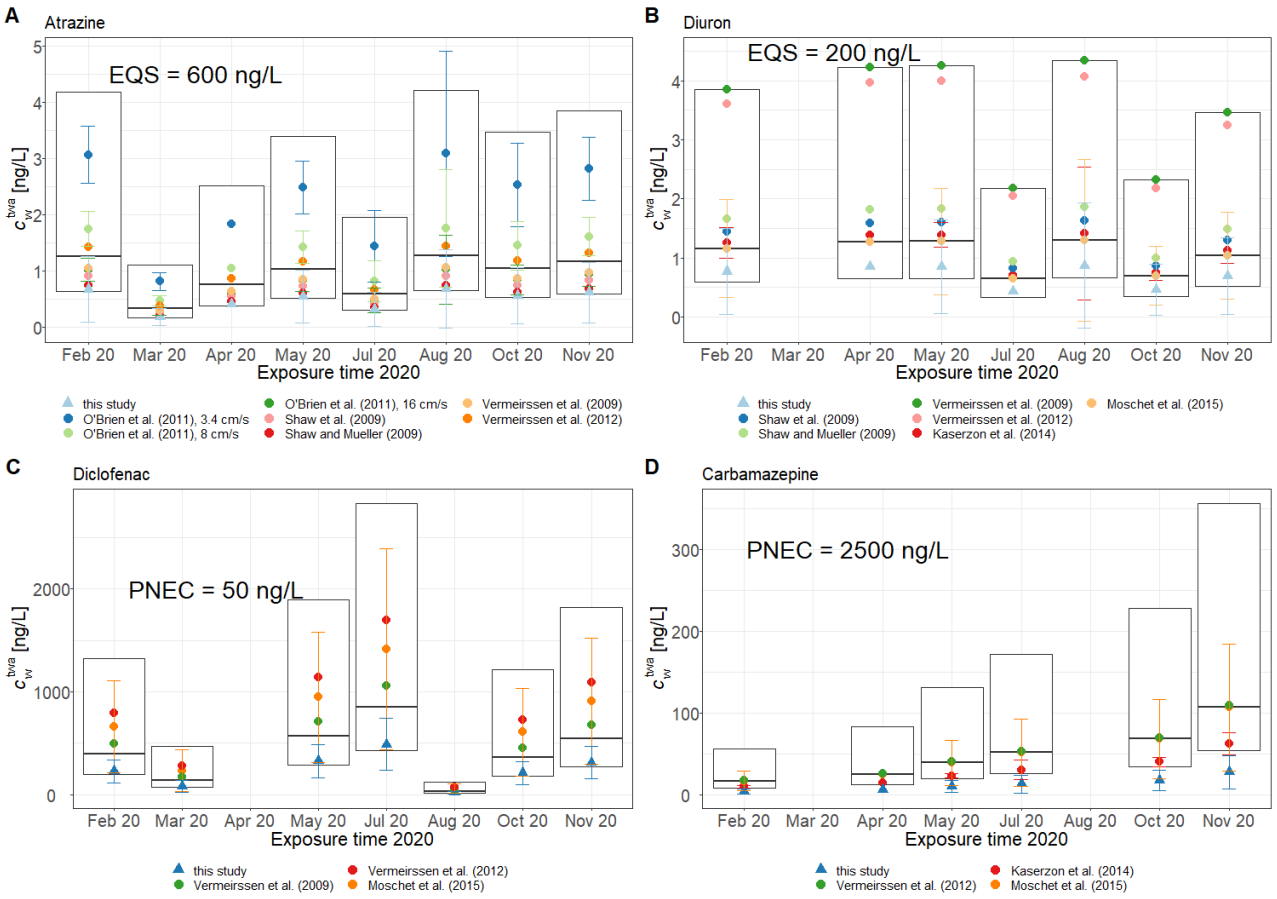
For carbamazepine, only three literature references were found.[26, 31, 32] Due to the generally larger concentration, the uncertainty of calculated TWA concentrations is more visible than for atrazine. The same applies to diclofenac, whose TWA concentration were calculated with three literature references.[26, 32, 35] TWA concentrations calculated with sampling rates from this study are a factor of 3 below concentrations calculated with the R_s derived by Moschet *et al.* (2015).

Diuron shows a good agreement of sampling rates from different references,[26, 31, 33, 34] but sampling rates derived by Vermeirssen *et al.* in 2009 and 2012 are considerably

lower than other sampling rates.[32, 35] This corresponds to twice as high TWA concentrations for these references.

Though individual sampling rates may vary, most TWA are within the range of TWA derived with generic sampling rates. This shows that the method is robust regarding different environmental conditions. Sampling rates derived from this study are at the lower end of the uncertainty range of the generic sampling rates. This can be attributed to the fact that calibration experiments were conducted at higher flow velocities. The dependence on the flow velocity was not considered in this study, as generic sampling rates were applied to determine TWA concentrations. Despite the high uncertainty, it can be shown, that EQSs of atrazine (600 ng/L) and diuron (200 ng/L) are not exceed during the field sampling campaign. For the pain reliever diclofenac and the antiepileptic drug carbamazepine EQSs are not available. However, so-called predicted no effect concentrations (PNECs) have been derived by the German Environmental Agency (UBA).[47] For carbamazepine no exceedences can be found with the applied method (PNEC = 2.5 µg/L). On the other hand, the PNEC of diclofenac (0.05 µg/L) are generally exceeded in the field samples.

For CC-XC and CC-HLB the generic sampling rates perform similarly well. Since only few literature references are available a profound analysis is not possible. However, TWA concentrations from generic sampling rates still cover the wide variety within the literature data. The figures can be found in the Supplementary Material (**Figures SM-5** and **Figure SM-6**).



526

527 **Figure 7**: TWA concentrations of field samples calculated with R_s from different references
528 for the Chemcatcher equipped with SDB-RPS disks. The bar represents the TWA
529 concentration derived with the generic sampling rate. The length of the box represents the
530 uncertainty of the generic sampling rate.
531

532

4. Conclusion

This study determined sampling rates for a wide variety of polar organic compounds using different Chemcatcher configurations. Depending on the sampling phase, sampling rates may vary up to one order of magnitude. While the Chemcatcher equipped with Atlantic HLB-L disk (CC-HLB) showed relatively similar uptake conditions for a wide polarity range, sampling rates varied stronger for other Chemcatcher configurations. For CC equipped with SDB-RPS disks, the available literature data could be extended regarding higher flow velocities.

Time weighted-average (TWA) concentrations resulting from generic sampling rates overlap well with most TWA concentrations derived from other references. The proposed generic sampling rates can be used to estimate TWA concentrations of compounds with unknown uptake kinetics. However, due to the relatively high uncertainty, integrative passive sampling should only be considered as a semi-quantitative monitoring tool. However, due to their high detection power (low LODs) the Chemcatcher may complement traditional grab sampling as an early warning tool in tiered monitoring approaches and for long-term trend analysis, as it could be shown, that the rough estimation of TWA concentrations (with known uncertainty limits) suffices to determine EQS of PNEC exceedances in the investigated small stream. In future studies, we will apply the new approach to substances with unknown uptake kinetics, such as emerging aqueous micropollutants and their transformation products.

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ABBREVIATIONS

SDB-RPS: styrene divinyl benzene reversed phase sulfonate, SDB-XC: styrene divinyl benzene exchange, HLB: hydrophilic lipophilic balance, CC-RPS: Chemcatcher equipped with SDB-RPS disk, CC-XC: Chemcatcher equipped with SDB-XC disk, CC-HLB: Chemcatcher equipped with Atlantic HLB-L disk, EQS: Environmental Quality Standard, PNEC: Predicted no effect concentration, RAC: Regulatory acceptable concentration.

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