ICUD-0438 Passive sampling: an efficient way to monitor micropollutants in sewer overflows?

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Summary

High spatio-temporal variability characterizes micropollutants discharged from separate and combined sewers. This challenges monitoring and prediction. We propose passive samplers (Chemcatcher® for polar, organic substances) as an alternative to active water sampling. Our results indicate sufficient sensitivity of passive samplers for short exposures so that typical rain event durations (<30 h) can be sampled integratively. Although time-weighted average concentrations estimated via passive sampling are higher than in composite water samples — on average by a factor 2.7 — we conclude that passive sampling is a cost-effective approach to identify locations with critical concentration ranges.

Keywords

micropollutants, monitoring, passive sampling, polar organic pollutants, SDB, sewer overflows

Introduction

In case of rain events, untreated wastewater can be discharged via sewer overflows to creeks and lakes, since the hydraulic capacity of the sewer system locally or of the wastewater treatment plant can be exceeded. These sewer overflows can negatively impact receiving environments (e.g. Gooré Bi et al. 2015). Due to the temporal variability of rain intensities and the local differences in substance usage, discharged micropollutant concentrations typically show high temporal and spatial variation (e.g. Madoux-Humery et al. 2013). Hence, reliable monitoring of micropollutants in sewer overflows is challenging. As a result, there is only limited data (number of events and catchments) available on micropollutants in sewer overflows.

Monitoring sewer overflows with traditional sampling methods such as grab samples and auto-samplers have short-comings. Grab samples are likely to not properly cover the high fluctuations of rain-driven sewer overflows (Ort et al. 2010). Water collection with auto-samplers is logistically and financially very costly. Passive samplers (PS) have been shown to sample polar organic micropollutants in a time-proportional manner in wastewater treatment plants influents and effluents (Harman et al. 2011; Petrie et al. 2016; Baz-Lomba et al. 2017). PS can be deployed for any defined period, during which the sampler takes up substances from the water phase. Sampling rates depend on PS properties, substances and environmental conditions. Thus, PS have to be calibrated for targeted substances and site-specific environmental conditions. Overall, the advantages of PS – i.e. reduced costs for installation and maintenance (size and no power supply requirements) – outweigh this initial efforts of calibration (Söderström et al. 2009).

Few studies specifically focus on highly variable (peak) concentrations as expected for sewer overflows (Shaw and Mueller 2009; Fernandez et al. 2014; Novic et al. 2017). Further, to the best of our knowledge so far only one study exists for passive sampling micropollutants in highly variably, short duration sewer overflows: Birch et al. (2013) monitored heavy metals in a storm sewer with a
flow-through PS. The results show a good agreement of passive sampling results with volume-proportionally pooled samples and model estimates.

We hypothesize that occurrence or levels of specific micropollutants is related to land use and that monitoring a large number of catchments is needed to identify such a correlation. Thus, passive sampling may be a solution to deal with the monitoring challenges in sewer overflows. The Chemcatcher PS equipped with a styrenedivinylbenzene (SDB) disk and an optional PES membrane is one of two common designs used to sample polar organic micropollutants. For monitoring of short durations below 30 hours a SDB-disk without a PES membrane seems more suitable as higher sampling rates can be achieved. This has not been tested and published so far for the application in sewer overflows.

The motivation of our study is to systematically determine the applicability of passive sampling devices to monitor typical polar organic pollutant concentrations in short, highly dynamic sewer overflows (environmental conditions in sewers and wastewater matrix). The following three main questions are in the foreground of this study:

Can typical (micro)pollutant concentrations during short exposures be measured with PS?

How do average concentrations from PS compare to concentrations in traditionally collected water samples for sewer applications?

What is the effect of temporal variability on concentration estimates from PS?

Methods

Calibration in flow channel

PS (SDB-RPS Empore disks, 47 mm) were exposed in an experimental channel to assess the uptake behaviour in raw wastewater for short exposures. The channel (length: 340 cm, width: 6 cm, water level: 11 cm, velocity: 0.72 – 0.94 m/s) was fed with fresh municipal raw wastewater from a close-by sewer and operated in batch mode by recirculating raw wastewater from a well-mixed 750 L tank. At the beginning of the experiments, 13 substances were spiked to the tank with a target concentration of 2,000 ng/L (Tab. 1). Conditioned, duplicate PS were exposed for a range of different periods. During exposure the PS were mounted between two stainless steel plates (one side with a circular 40-millimeter opening). In Experiment I replicates of pre-conditioned samplers were exposed for 0, 2, 3, 5, 7 hours. In Experiment II PS were also analysed for time periods <2 hours to evaluate the initial uptake behaviour. Duplicate samplers were removed from the flow channel after 5, 15, 30 min and after 1, 2, 4, 8, 14, 24, 30, 36 hours. In both experiments, raw wastewater samples were taken before the start of the experiment in order to assess the background concentration and at all time points when PS were removed (not at 3h in Experiment I).

Field study

A field test was carried out at one location directly in a sewer pipe (diameter 0.6 m, slope 2.2%, catchment characteristics: area 5.7 haimp, population 1,330) to determine the applicability of PS and to compare with traditionally collected wastewater samples. Between April and June 2016 we sampled five rain events (rain sum 6.5 to 25.7 mm, PS exposure duration 2.9 to 17.8 hours and velocities in sewer 1.0 to 1.4 m/s). The monitoring site was equipped with a discharge measurement device (FloDar 4000SR) and a water level sensors (MB7369 HRXL-MaxSonar-WRM). For each discharge event a set of four conditioned PS were exposed. Due to technical reasons not all PS time periods could be matched exactly with corresponding water sampling periods. Therefore, some PS were exposed longer which is accounted for by using the real PS exposure time to determine the time-weighted average (TWA) concentration (Eq. 1 below). Active water sampling was done with
automated sampling devices (Sigma 900MAX). Time-proportional water samples were collected every 5 min and composited over 20 min in a glass bottle (total 24 bottles).

**Micropollutant analysis**

We aimed to consider the two relevant sources of pollution: wastewater-derived and runoff from outdoor surfaces (garden, facade, roof, street). Furthermore, the substances were selected based on the following criteria: i) mainly transported in the water-phase, ii) reported toxicological relevance, iii) omnipresence in urban sewer overflows and iv) preferably low biological degradation in wastewater treatment plants. This resulted in 13 polar, organic substances to be monitored (pharmaceuticals, pesticides with logKow < 4.5, Tab. 1).

Before being exposed in the flow channel, the PS were pre-conditioned in MeOH and in nanopure water (Vermeirssen et al. 2009). After exposure, the disks were extracted as described in Vermeirssen et al. (2013). The extracts from the experiments were evaporated to 0.1 mL and filled with nanopure water to 1 mL. The extracts from the field site were evaporated to 0.05 mL and filled with nanopure water to 0.5 mL.

All samples were stored at -20° C until analysis. Water samples from Experiment II and the field study were measured on an online-SPE-LC-HRMS/MS system (QExactive by Thermo Fisher Scientific Corporation) with the method from Huntscha et al. (2012). Due to the elevated concentrations, SDB disc extracts and water samples from Experiment II were measured via direct injection (100 µL) without enrichment, but with the same chromatography and data acquisition on the MS than in the method mentioned above. Quantification was done by using the internal standard method. For twelve of the 13 investigated substances structure-identical isotope labelled standards were available.

**Parameter estimation for uptake on samplers**

An exponential function is used to describe the uptake of micropollutant mass \( M_s \) on the PS (Eq. 1), where \( C_w \) is the concentration in the water phase, \( V_s \) the PS volume (344 µL) and \( t \) the exposure duration. Two main uptake phases can be distinguished: i) a first, almost linear phase, where uptake is mainly controlled by the uptake rate \( R_s \) and ii) an equilibrium phase described by the sampler-water partition coefficient \( K_{sw} \) (e.g. Greenwood et al. 2007).

\[
\frac{dM_s}{dt} = R_s \left( C_w - \frac{M_s}{V_s \cdot K_{sw}} \right)
\]

The water concentration profiles in the experimental channel were considered by integrating Eq. 1. Parameter estimation \((R_s, K_{sw})\) was done for both flow channel experiments simultaneously using Bayesian Inference assuming independent Gaussian errors with uniform priors. The TWA concentration via PS was back-calculated from the estimated model parameters based on the integrated Eq. 1 above.

We investigated the influence of typical concentration patterns expected to occur in sewer overflows on the final mass on the PS disk. The PS mass was calculated according to Eq. 1 for 216,052 realistic, variable concentration patterns (modelled sewer overflow Mecoprop concentration patterns as described in Mutzner et al. (2016)). Based on the estimated PS mass, the TWA concentration in the water is back-calculated (Eq. 1) and compared to the true TWA water concentration.
Results and Discussion

Environmentally relevant concentrations can be measured after very short exposure

The water concentrations were relatively constant over time in both channel experiments for most substances with coefficients of variations (CV) below 10%. Both experiments show increasing PS mass with longer exposure time. The resulting model parameters range between 0.09 L/d and 1.47 L/d for Rs and between 340 and 7,360 for KSW (Tab. 1).

Tab. 1. Properties and estimated model parameters: sampling rate Rs, sampler-water partition coefficient KSW. aChemspider & EPI Suite, bBased on Otto et al. (2014)

<table>
<thead>
<tr>
<th>Substance</th>
<th>logKow</th>
<th>Biological Degradation</th>
<th>Rs [median] (L/d)</th>
<th>KSW [median] (L/d)</th>
<th>Standard deviation of error term (ng/disk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diclofenac</td>
<td>4.51</td>
<td>medium</td>
<td>0.64</td>
<td>1,750</td>
<td>70</td>
</tr>
<tr>
<td>Clarithromycin</td>
<td>3.16</td>
<td>medium</td>
<td>0.58</td>
<td>3,490</td>
<td>25</td>
</tr>
<tr>
<td>Carbamazein</td>
<td>2.45</td>
<td>persistent</td>
<td>0.80</td>
<td>4,870</td>
<td>161</td>
</tr>
<tr>
<td>Benzotriazol</td>
<td>1.44</td>
<td>medium</td>
<td>0.63</td>
<td>1,070</td>
<td>92</td>
</tr>
<tr>
<td>1,3-Benzothiazole-2-sulfonate</td>
<td>-0.99</td>
<td>unknown</td>
<td>0.18</td>
<td>340</td>
<td>34</td>
</tr>
<tr>
<td>Carbofuran</td>
<td>1.52</td>
<td>persistent</td>
<td>1.07</td>
<td>1,720</td>
<td>64</td>
</tr>
<tr>
<td>Mecoprop</td>
<td>3.20</td>
<td>persistent</td>
<td>0.35</td>
<td>750</td>
<td>81</td>
</tr>
<tr>
<td>Terbutryn</td>
<td>3.74</td>
<td>persistent</td>
<td>1.47</td>
<td>6,460</td>
<td>66</td>
</tr>
<tr>
<td>Diuron</td>
<td>2.68</td>
<td>persistent</td>
<td>1.24</td>
<td>3,610</td>
<td>68</td>
</tr>
<tr>
<td>Diazinon</td>
<td>3.81</td>
<td>persistent</td>
<td>1.45</td>
<td>7,000</td>
<td>42</td>
</tr>
<tr>
<td>MCPA</td>
<td>3.25</td>
<td>high</td>
<td>0.09</td>
<td>7,360</td>
<td>46</td>
</tr>
<tr>
<td>2,4-D</td>
<td>2.81</td>
<td>medium</td>
<td>0.20</td>
<td>450</td>
<td>26</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>2.90</td>
<td>persistent</td>
<td>1.28</td>
<td>5,890</td>
<td>81</td>
</tr>
</tbody>
</table>

However, for all substances a fast initial uptake was observed that cannot be sufficiently represented by the exponential model. This fast initial uptake allowed to measure the PS mass already after 5 min exposure for all substances. A similar fast initial uptake was observed in previous studies for the exposures of hours to days for polar substances for POCIS (Mazzella et al. 2007; Fauvelle et al. 2014) and for naked EmporeTMSDB disks (Vermeirssen et al. 2013). A suggested explanation for this phenomena is a two-stage process with an initial fast superficial adsorption phase and a slower adsorption and absorption phase.

Fig. 1. Measured mass from duplicate PS disks (points) and predicted uptake behaviour (lines). Dark shading: 80%-confidence intervals, light shading: 80%-prediction intervals.

We find an exponential, integrative uptake behaviour on PS for up to 36 hours for almost all substances in Experiment II. Typical sewer overflow durations of 1.7 hours (median, 80%}-
interquantile 0.3h-6.7 hours, Mutzner et al. (2016)) imply that most discharge events can be sampled in an integrative mode with PS. Compared to a previous studies with naked SDB disks by Vermeirssen et al. (2013) (flow velocities 0.08 – 0.14 m/s), we find on average a factor 3.1 higher Rs (for nine comparable substances). Higher flow velocities can lead to substantially higher Rs (Vermeirssen et al. 2008) and, thus the higher Rs are attributed to the higher flow velocity in the flow channel (0.8 – 0.9 m/s), which we choose to appropriately represent typical sewer system conditions. The high sampling facilitates uptake and measurement of the substances on PS.

Passive sampling in sewer application overestimates true water concentration

In total five events were monitored with duplicate PS (event 2 with triplicate PS) and TWA water sampling. The five events covered a proceeding dry time range of 30 hours to 6 days and an event duration of 2.9 hours to 17.8 hours.

All substances except Carbamazepine were found at least in two TWA water samples. For PS all substances were detected at least in one event except Carbamazepine, which was not found in any of the PS (see number of detections in PS in Fig. 2B). Five substances were detected equally with PS and TWA water samples (Ben佐triazol, 1.3-Be佐thiazol-2-sulfonate, Diclofenac, Diuron, Mecoprop). Overall, more substances were detected in TWA water samples than PS (2.4D: 4 events, Terbutryn: 2 events, Carbendazim: 2 events, Clarithromycin: 1 event, MCPA: 1 event).

None of the monitored events results in systematic deviations of the duplicates/triplicates for all substances, showing that the sampler disks were subject to the same environmental conditions at the installation point.

The estimated TWA concentration via PS is higher by a factor 2.7 over all detections (n=84) as shown in Fig. 2A. Possible explanations for this observed overestimation are: i) The fast initial uptake is not considered in the exponential model for the rather short event durations (maximum 17.8 hours), thus leading to an overestimation of the TWA concentration, ii) the flow velocity in the sewer systems (1.0 – 1.4 m/s) are higher than in the channel experiments (0.8 – 0.9 m/s).

![Graph A](image1.png)

![Graph B](image2.png)

**Fig. 2.** A TWA concentration back-calculated from PS (duplicates) vs. TWA water concentration. Black, solid line: linear regression based on data points. Grey area: 80%-confidence interval. Dashed-blue lines: 10% and 90% quantiles of the data points. B TWA concentration via PS relative to TWA water sample concentration for individual substances. Number of detections are given above the individual boxplots (n).
Especially wastewater-derived substances (Benzotriazol, Clarithromycin, Diclofenac) are overestimated (Fig. 2B). This can be explained by the setup in the sewer system, where the PS might have been exposed in dry-weather conditions in case of high water levels. In addition, four substances are close to the limit of quantification in the PS (2,4D, Carbendazim, MCPA, Terbutryn) resulting in a high uncertainty of the TWA concentration estimates.

In comparison, Moschet et al. (2015) and Petrie et al. (2016) found for in-situ calibration of SDB-disks/Atlantic HLB disks, covered with PES membranes, an agreement within a factor 2 for 90% of all detections. Birch et al. (2013) reported an overestimation for heavy metals monitored with flow-through PS.

**Impact of variable concentration patterns on TWA concentration estimates is higher for longer events**

With higher sampling rates Rs, the modelled deviation from the true TWA concentration increases as the sampler equilibrium is reached faster (Fig. 3). The deviation from the true TWA concentration highly depends on the concentration pattern (e.g. peak in the beginning/end). A peak in the beginning leads to slow desorption and an underestimation of the TWA concentration, while a peak in the end leads to an overestimation.

The longer the event duration the higher the deviation from the true TWA concentration (Fig. 3). Especially an underestimation of the true TWA concentration is to be expected for typical sewer overflows, as indicated by the 10% quantiles lines. This can be explained by the dependence of the equilibrium on the current water concentration and thus desorption during times of flows with low concentration. For example a sampling rate Rs of 0.1 L/h (and KSW of 3000) leads to a deviation from the true TWA concentration of 0.98 to 1.01 for an event of 5 hours duration and of 0.72 to 1.11 (both 80%-interquantile range) for an event of 50 hours duration. Similarly, Shaw and Mueller (2009) compared experimental uptake for peak exposures over a period of three days with model predictions. They found a maximum deviation between the predicted and measured concentration of a factor two.

![Fig. 3. Impact of variable concentration patterns on modelled TWA concentration calculated via PS mass (PS Conc) relative to true TWA concentration (Water Conc). Lines: 10% and 90% quantiles of the concentration patterns. KSW fixed at 3000.](image-url)
Our estimated experimental, analytical and parameter estimation uncertainty from the flow channel experiment indicates a similar uncertainty range for constant water concentrations as influenced by variable concentration patterns for the Rs parameter ranges of the investigated substances (Tab. 1).

Conclusions

Our results show that PS are suitable to monitor events with short durations of minutes to hours in a semi-quantitative manner. We find an overestimation of the TWA concentration via PS in the field application.

The estimated influence of highly variable concentration patterns during rain events is in a similar range as the predicted measurement and analytical error in the flow channel experiments (where concentrations were constant). Variable concentration patterns tend to lead to an underestimation of the TWA concentration for longer event durations. However, for the monitored events with durations <20hours, the expected deviation from the TWA concentration is small for the investigated substance and corresponding parameter ranges. More influential might be site-specific environmental conditions.

Our results indicate that more locations could be sampled in a cost and time-effective way with PS. PS are especially suitable to identify locations with potentially critical concentrations, for which semi-quantitative information is sufficient.

References


