

Applicability of Passive Samplers for Monitoring Hydrophilic Organic Micropollutants in Urban Stormwater

Applicabilité des échantillonneurs passifs pour la surveillance des micropolluants organiques hydrophiles dans les eaux pluviales urbaines

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RÉSUMÉ

Les eaux pluviales urbaines constituent une source majeure de contamination des eaux de surface, car elles transportent un mélange complexe de micropolluants organiques, notamment des substances persistantes, mobiles et toxiques (PMT) et les substances très persistantes et très mobiles (vPvM). La surveillance de la fraction dissoute de ces composés est difficile, l'échantillonnage étant souvent un facteur limitant majeur. Cette étude visait à évaluer l'applicabilité des échantillonneurs passifs pour certains contaminants organiques hydrophiles présents dans les eaux pluviales et à valider cette approche dans des conditions réelles. Deux phases de réception d'échantillonnage passif ont été comparées dans le cadre d'expériences en laboratoire dans des conditions contrôlées, notamment des concentrations variables de contaminants et des périodes de sécheresse intermittentes. Les résultats de laboratoire indiquent que les échantillonneurs passifs peuvent fournir des concentrations fiables, comparables à celles obtenues par échantillonnage automatisé, avec seulement une légère surestimation pour certaines substances. Une étude de validation sur le terrain est actuellement en cours au niveau d'un déversoir d'égout unitaire, où l'échantillonnage passif et automatisé sera comparé dans des conditions réelles d'eaux pluviales. Dans l'ensemble, les résultats suggèrent que les échantillonneurs passifs offrent une approche robuste et pratique pour surveiller les contaminants organiques hydrophiles dans les eaux pluviales urbaines.

ABSTRACT

Urban stormwater is a major source of surface water contamination, carrying a complex mixture of organic micropollutants, including persistent, mobile and toxic (PMT) and very persistent, very mobile (vPvM) substances. Monitoring the dissolved fraction of these compounds is challenging, with sampling often being a major limiting factor. This study aimed to evaluate the applicability of passive samplers for selected hydrophilic organic contaminants in stormwater and to validate the approach under field conditions. Two passive sampling receiving phases were compared in laboratory flume experiments under controlled conditions, including variable contaminant concentrations and intermittent dry periods. Laboratory results indicate that passive samplers can provide reliable concentrations comparable to automated sampling, with only slight overestimation for some substances. A field validation study at a combined sewer overflow is currently ongoing, where passive and automated sampling will be compared under real stormwater conditions. Overall, the findings suggest that passive samplers offer a robust and practical approach for monitoring hydrophilic organic contaminants in urban stormwater.

KEYWORDS

Hydrophilic organic micropollutants, passive sampling, stormwater monitoring

1 INTRODUCTION

Urban stormwater is a significant contributor to surface water pollution (Aryal et al., 2010; Björklund, n.d.; Gasperi et al., 2014). During rainfall events, a wide array of pollutants accumulated on roads, rooftops, and other surfaces are washed into nearby aquatic ecosystems. This runoff carries a complex mix of pollutants, including heavy metals, nutrients, pesticides, tyre-wear additives and industrial chemicals (Gasperi et al., 2012; LeFevre et al., 2015; Mutzner et al., 2023; Zgheib et al., 2012). Historically, scientific attention has focused on particle-bound pollutants in stormwater. However, recent studies have emphasized the critical role of dissolved organic micropollutants, many of which are biologically active and potentially more mobile in aquatic systems (Eriksson et al., 2007; LeFevre et al., 2015). Despite this recognition, environmental monitoring data for the dissolved fraction, particularly for emerging contaminant classes like tyre-wear additives and persistent, mobile and toxic (PMT) or very persistent, very mobile (vPvM) substances, remain scarce (Mutzner et al., 2023; Spahr et al., 2020). Thanks to recent advances in analytical chemistry, a wide range of tools is now available to identify and quantify emerging micropollutants (Hale et al., 2020).

Nevertheless, comprehensive data on the occurrence and hazard potential of many dissolved organic micropollutants in urban stormwater remain limited, largely because sampling is often the limiting factor. Conventional grab sampling, frequently carried out with automated samplers, is expensive, labor-intensive, requires electricity, and is therefore unsuitable for large-scale monitoring campaigns. In addition, the temporal resolution of such sampling is often insufficient to capture the true dynamics of pollutant concentrations. Passive sampling offers a promising alternative: by providing time-integrated detection of low-concentration pollutants (Mutzner et al., 2019), passive samplers can overcome many of these limitations and help fill critical knowledge gaps. In this study, we evaluate the applicability of passive samplers for a selected set of hydrophilic organic contaminants in stormwater and assess their performance in the field.

2 MATERIALS AND METHODS

2.1 Method Development in the Laboratory: Evaluation of Passive Samplers as a Sampling Technique

To assess the suitability of passive samplers for hydrophilic organic contaminants in urban stormwater, experiments were conducted in an experimental flume. Two sorbent phases (HLB and SDB-RPS, AttractSPE®) were mounted in stainless steel housings and exposed for up to 24 hours to rainwater spiked with a mixture of 40 hydrophilic organic compounds, including pesticides, biocides, industrial chemicals, and 16 PMT/vPvM substances. The accumulated pollutant mass and derived sampling rates were used to compare the performance of both materials.

In a first experiment, samplers were exposed under constant flow and contaminant concentrations to calculate the substance specific sampling rates (Ls^{-1}). A second experiment simulated a decreasing concentration profile to test sampler reliability under variable concentrations. In a third experiment, the impact of dry periods of 3 and 12 hours between exposures was examined to identify potential desorption effects or changes in accumulation between consecutive rainfall events. All samples were analyzed by liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS/MS) using isotope-labelled internal standards.

2.2 Field Validation: Evaluation of Passive Samplers Under Real-World Conditions

To assess the applicability of passive samplers for stormwater monitoring of organic contaminants, a field validation study was carried out at a combined sewer overflow between May and November 2025. The passive sampling approach developed in the laboratory was tested under real-world conditions and compared with established automated sampling. Both passive samplers and the automated sampler were installed in the overflow pipe (upstream of a planted horizontal wetland-sand filter). Continuous flow measurements in the sewer enabled the calculation of time-weighted average (TWA) concentrations from the passive samplers by combining the flow data with substance-specific sampling rates derived from laboratory experiments and the measured accumulated masses.

For the automated sampler, a sample was collected every two minutes and used to create event-based, time-weighted composite samples. TWA concentrations obtained from both approaches were then compared to evaluate whether passive and automated sampling produced comparable results. All samples were analyzed by

LC-HRMS/MS for the quantification of organic contaminants. Additionally, the field test was used to assess the added value of passive sampling, particularly regarding contaminant enrichment on the sorbents and sampling sensitivity.

3 RESULTS

3.1 Performance and Reliability of Passive Samplers for Stormwater Monitoring

Over the 24-hour exposure period, micropollutant uptake for most target compounds remained within the linear uptake phase, allowing substance-specific sampling rates to be derived and enabling the calculation of TWA concentrations using passive samplers. Experiments in the laboratory flume showed that the two sampler types accumulated largely comparable masses for many compounds (e.g., Diuron, Dimethachlor, MCPA; Fig. 1). However, for several micropollutants the HLB disks exhibited noticeably higher accumulation (e.g., 1,3-Di-o-tolylguanidine and 1,3-Diphenylguanidine; Fig. 1), suggesting superior suitability for these substances.

Dry periods between simulated rain events had no measurable effect on mass accumulation (Fig. 2). Samplers collected before flow interruption showed micropollutant masses similar to those retrieved after 3 and 12 hour dry phases, indicating that temporary flow cessation does not introduce significant bias.

Overall, the results demonstrate that passive samplers reliably accumulated most target compounds under simulated storm sewer conditions. While very polar substances showed only limited uptake and slight concentration overestimations were observed for a few compounds, calculated concentrations were generally consistent with those obtained from automated sampling. These findings support the suitability of passive samplers as a practical and robust approach for monitoring organic micropollutants in storm sewers.

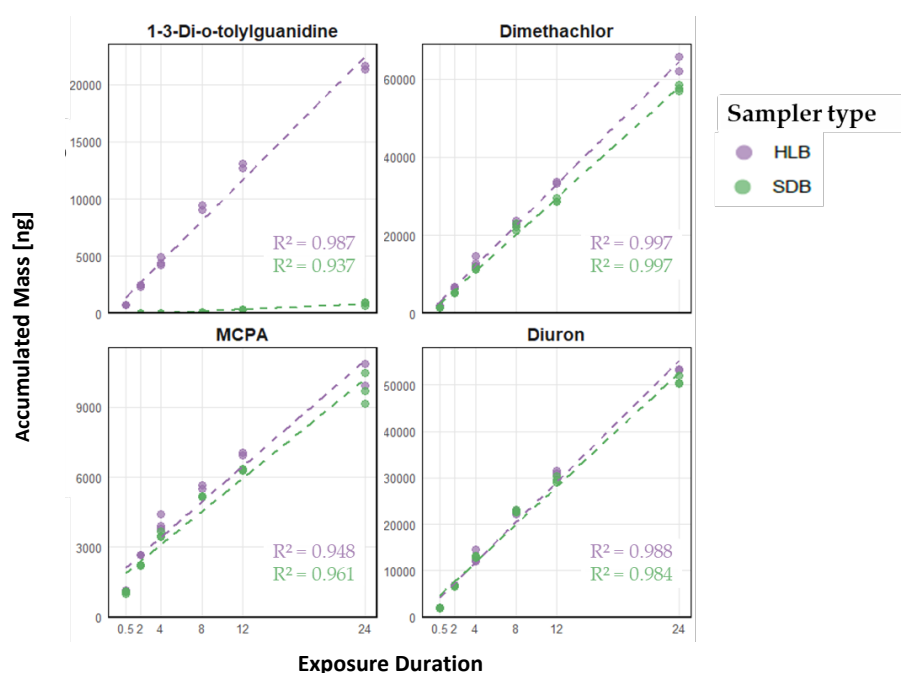


Fig. 1: Accumulated micropollutant mass as a function of exposure duration for four selected compounds. Shown are the measured values after 0.5, 2, 4, 8, 12, and 24 hours of exposure (points) and the corresponding fitted linear models (dashed lines).

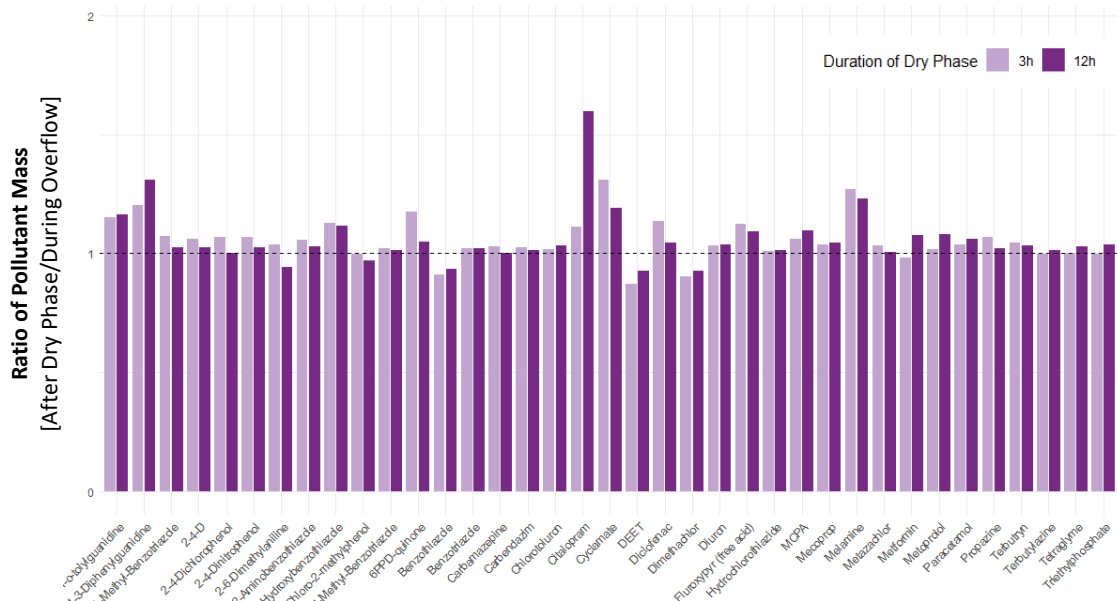


Fig. 2: Ratio of accumulated micropollutant mass after a dry phase to the mass accumulated during constant flow for selected compounds. Ratios were calculated for samplers retrieved after 3 h and 12 h dry periods. Values close to 1 indicate that interruptions in flow (dry phases) did not significantly affect contaminant accumulation, suggesting that dry periods do not introduce substantial error in the passive sampling results.

3.2 Field validation of the passive sampling approach

In the field validation study, concentrations derived from passive samplers will be compared with those measured directly by automated sampling to evaluate the applicability of passive sampling under real stormwater conditions. Due to the enrichment of analytes on the receiving phases, we expect passive samplers to detect the target compounds above the limit of quantification even at low ambient concentrations. Nevertheless, the complex stormwater matrix (contains 4–7% wastewater) may reduce analytical sensitivity and result in higher detection limits. Based on the laboratory findings, we anticipate that the TWA concentrations calculated from the passive samplers will fall within the range of concentrations obtained from automated sampling, with a slight overestimation possible for some compounds. Overall, the field results are expected to provide a realistic assessment of the robustness and practical applicability of passive samplers for monitoring organic micropollutants in storm sewer systems.

4 CONCLUSION

This study demonstrates the suitability of passive samplers as a monitoring technique for selected hydrophilic organic contaminants in stormwater. Both tested receiving phases effectively accumulated the target compounds, with HLB disks showing higher sensitivity and mass accumulation, making them better suited for the compounds investigated. Laboratory results indicate that the passive sampling approach is expected to provide reliable concentrations and results comparable to established sampling techniques, such as automated sampling, under realistic storm sewer conditions. Preliminary results from the field validation of this approach will be presented at the conference.

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