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Occurrence and Concentration of Pollutants from Stormwater Runoff in Receiving Water: A Case Study Fyrisån River

Occurrence et concentration des polluants provenant des eaux de ruissellement dans les eaux réceptrices : Une étude de cas Fyrisån

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RÉSUMÉ

Cette étude a examiné comment le ruissellement des eaux pluviales urbaines, connues pour contenir diverses substances chimiques, modifie les concentrations de polluants dans les masses d'eau réceptrices. Des échantillons ont été collectés dans des conditions de temps sec et humide dans 4 stations d'échantillonnage le long de la Fyrisån, une rivière qui passe le long de la ville d'Uppsala, en Suède. Les échantillons ont été analysés pour 80 substances organiques, 19 métaux (phase totale et dissoute), et des paramètres physico-chimiques conventionnels. 19 des 80 substances organiques ont été qualifiées au-dessus de la limite de quantification (LOQ) à au moins un des événements d'échantillonnage. La famille de substances la plus détectée était les substances polyfluoroalkyles (PFAS). Les concentrations des substances organiques et des métaux détectés ont augmenté par temps humide. Les concentrations de substances organiques et de métaux présentaient une variation spatiale similaire, les concentrations les plus élevées étant mesurées aux points d'échantillonnage proches des zones urbanisées.

ABSTRACT

This study investigated how urban stormwater runoff, known to contain various chemical substances, alters pollutant concentrations in the receiving water bodies. Samples were collected under dry and wet weather conditions at 4 sampling stations along the Fyrisån, a river that passes along the city of Uppsala, Sweden. Samples were analyzed for 80 organic substances, 19 metals (total and dissolved phase), and conventional physicochemical parameters. 19 of 80 organic substances were qualified above the limit of quantification (LOQ) in at least one sampling event. The most detected substance family was poly-fluoroalkyl substances (PFAS). The concentrations of detected organic substances and metals increased in wet weather conditions. Organic substance and metal concentrations showed similar spatial variation with higher concentrations measured at sampling locations close to urbanized areas.

KEYWORDS

(heavy metals, organic micropollutants, receiving water bodies, stormwater, surface water quality, urban runoff)

1 INTRODUCTION

To achieve good chemical status in water bodies, member countries oblige to meet environmental quality standards (EQS) for 45 priority substances, including polycyclic aromatic hydrocarbons (PAHs), alkylphenols, and several metals (*Directive 2013/39/EU*, 2013). Recently, new groups of chemicals containing poly-fluoroalkyl substances (PFAS) and bisphenol A have been proposed to be added to the list of priority substances in surface waters (Directorate-General for Environment, 2022). It is critical to know the pollutants' pathways to the receiving water bodies to implement necessary measurements, provide sufficient treatment, and meet guideline requirements. Stormwater runoff has been proved to be a pollution cocktail containing suspended solids (TSS), heavy metals, nutrients and organic pollutants from various anthropogenic sources to the receiving water bodies (Müller et al., 2020). While early studies focused on conventional pollutants such as TSS and metals (Brinkmann, 1985; Brown & Peake, 2006), the effort to monitor priority and emerging substances in stormwater runoff have increased recently (Launay et al., 2016; Zgheib et al., 2011). However, most of these efforts have been limited to the sampling campaigns at stormwater pipes, outlets, and/or runoff collected from various catchments to analyze pollutant composition in the stormwater runoff. Therefore, there is still a lack of knowledge regarding the expected concentrations of pollutants conveyed by stormwater, their spread, and transportation in the recipient after discharge. This study aims to contribute knowledge of heavy metals and organic micropollutants occurrence from stormwater to receiving water bodies and investigate how pollutant concentrations change along the water course through less urbanized to densely urbanized areas.

2 MATERIALS AND METHOD

Samples were collected from Fyrisån, a river that passes through Uppsala city, located in Southern Sweden. Uppsala is the fourth biggest city in Sweden with a population of approximately 238 000. The city has a separate sewer system. Wastewater is treated at the Kungsängsverket Wastewater Treatment Plant (WWTP) and discharged to Fyrisån river after treatment. Stormwater runoff collected during wet weather events is directly discharged to Fyrisån through several outlets, to large extent without any treatment.

ISCO autosamplers were installed at four sampling points along the river course: The first sampling point, UppA, is situated 3 km upstream the urbanized area, where Årna Air Force Base is located across the river. At the catchment upstream, the city consists mainly of agricultural land and few minor villages/towns. The second and third sampling points, UppB and UppC, are located directly downstream the urban catchment. UppB is 100 meters upstream, and UppC is 100 meters downstream of the wastewater discharge point of the WWTP. The last sampling point, UppD, is located 1,5 km downstream of the urbanized area.

A total of five sampling campaigns, two baseflow and three rainfalls, were conducted between June 2022 and October 2022. The autosamplers collected water samples from the river over 24 hrs with a 1-hour sampling interval during baseflow sampling campaigns. The objective of baseflow sampling is to represent pollution conditions in the river without any effect from stormwater runoff. Similarly, autosamplers were programmed to take samples during three rainfall events with the total measured precipitation of 6.1mm, 27.2 mm, and 39.6mm during each sampling campaign. The duration and sampling intervals of wet weather sampling campaigns varied from 6 hours to 18 hours and from 10 to 15 minutes, respectively, depending on the rain duration. In total, 7.2 L of water samples were collected from each sampling point per sampling campaign. The samples were transferred to an accredited laboratory (ALS Scandinavia AB) for analysis in cooled bags within 24 hours after sampling campaigns. Analyses included conventional physicochemical parameters, including pH, conductivity, turbidity, total suspended solids (TSS), total organic carbon (TOC), dissolved organic carbon (DOC), chloride, total phosphorus (TP), total nitrogen (TN), a total of 80 organic substances belonging to 6 groups of chemicals, 16 polycyclic aromatic hydrocarbons (PAHs), 32 Per- and polyfluoroalkyl substances (PFAS), 8 alkylphenols (AP), 13 phthalates, 10 organotin compounds (OTC), bisphenol A (BPA), as well as the total and dissolved fraction of 19 metals.

3 RESULTS AND DISCUSSION

TSS varied between 3.2 and 7.4 mg/L during baseflow events and between 5.3 and 26.0 mg/L during rainfall events. Similarly, TOC ranged from 10.8 to 15.3 mg/L for baseflow samples and 9.7 to 23.1 mg/L for rain event samples. The mean pH value during baseflow events was 7.9 and during rain events were

7.8. In general, TSS, conductivity, turbidity, TOC, DOC, and chloride values measured during rainfall events showed greater variation and higher mean and maximum values in comparison to baseflow samples.

Average TP and TN concentrations were greater in the samples collected during rain events (TP: 0.075 mg/L and TN: 3.28 mg/L) than in baseflow samples (TP: 0.058 mg/L and TN: 2.0 mg/L, respectively). Measured TP and TN concentrations were higher at UppC (downstream of WWTP) and UppD (the most downstream) in all baseflow and rainfall events, which might be the result of discharges from WWTP.

Among 19 analyzed metals, focus for this study were on Cd, Cr, Cu, Hg, Ni, Pb and Zn. Total (<0.02 µg/L) and dissolved Hg (<0.002 µg/L) concentrations were lower than LOQ in all sampling campaigns. Cd was not detected in the total phase (<0.05 µg/L) but quantified only in the dissolved phase in both baseflow and wet weather events (i.e. >0.005 µg/L). Metals associated with anthropogenic activities, particularly Cr, Cu, Ni, Pb, and Zn, showed similar spatial variation with higher concentrations measured at sampling locations in the urbanized area (UppB and UppC). Measured total concentrations of Cu, Ni, and Zn increased in all wet weather samples. Particularly, total Cr and Pb concentrations were lower than the limit of quantification (LOQ) for baseflow sampling events in almost all sampling locations whereas both metals were observed in samples collected during rain events (Fig. 1). These findings are in line with previous studies (Brown & Peake, 2006; Huber et al., 2016) suggesting stormwater is a major transportation path for metals in receiving water bodies.

Among 80 organic pollutants analyzed in this study, 19 substances were quantified above LOQ on at least one of the sampling occasions. 15 PAHs, 21 PFAs, 7 AP, 12 phthalates, 8 OTC were never above LOQ. The most frequently detected group of substances was PFAs. A total of 10 out of 32 targeted PFAs were quantified in more than one sampling event. The concentration of the sum of 20 PFAs compounds, defined by the European Commission (EU 2020/2184), ranged from 0.00455 µg/L to 0.01640 µg/L with the mean concentration of 0.00763 µg/l for baseflow sampling occasions and varied between 0.00412 µg/L and 0.03110 µg/L with a mean concentration of 0.01854 µg/L for rainfall sampling events (Fig. 1). These results imply that PFAs concentrations increase during rainfall events. The highest PFAs concentrations were measured at the closest locations to the city center (UppB and UppC). PFAs concentrations at the downstream of the WWTP (UppC) were slightly higher than concentration measured at upstream of WWTP (UppB) implying that, along with the stormwater runoff, WWTP discharge might be another way of transporting of PFAs to receiving water bodies.

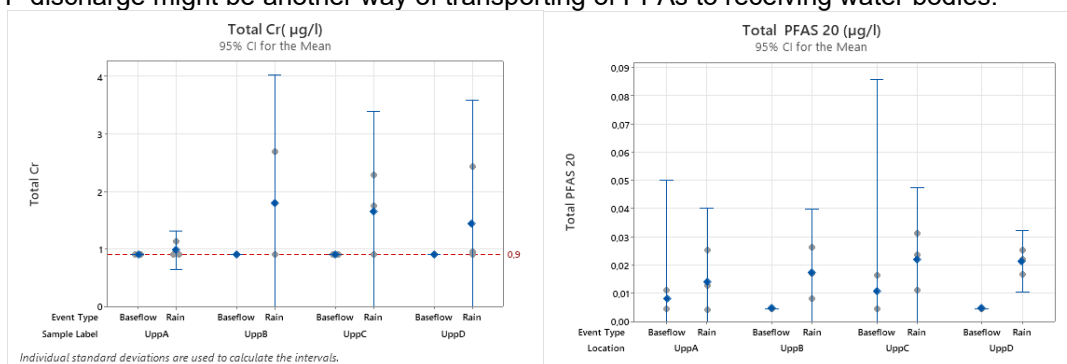


Figure 1. Measure concentrations (grey points) of Total Cr and Total PFAS 20 (µg/l) illustrated based on sampling location and event type with mean concentrations (blue points), confidence intervals (blue lines), and LOQ (red dashed line)

Monobutyltin (MBT), an organotin compound, was detected in all sampling occasions at all four sampling points (Fig. 2). Opposite to PFAs, MBT concentrations were higher in baseflow samples, with one exception (a rain event concentration at UppA). Decreased concentration of MBT during rain events suggests that MBT is an existing pollutant in Fyrisån and urban stormwater dilutes the pollutant concentration in the receiving water body.

For the alkylphenols group, 8 substances were analyzed. Only 4-nonylphenols exceeded the limit of quantification in 2 out of 5 sampling events, which were wet weather sampling campaigns. 4-nonylphenols concentrations were below LOQ in all the baseflow samples. Moreover, 4-nonylphenols were never detected in any samples collected under wet weather conditions at the most upstream point, UppA. It was only detected at the city center (UppB and UppC) and the most downstream (UppD) sampling points. This finding indicates that 4-nonylphenols, an anthropogenic substance, is conveyed to the receiving environment by urban runoff (Fig. 2).

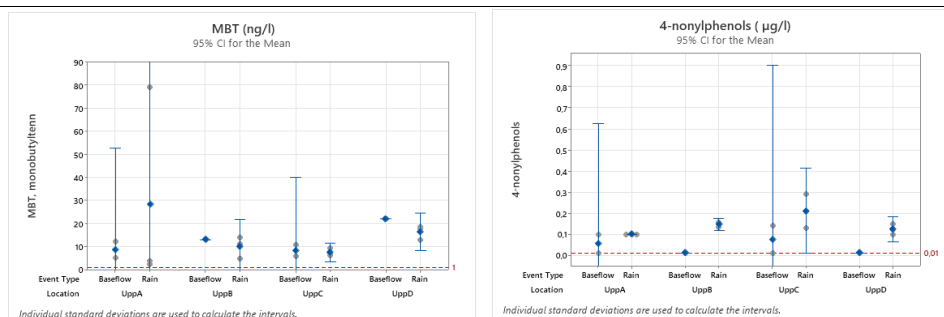


Figure 2. Measure concentrations (grey points) of MBT (ng/L) and 4-nonylphenols ($\mu\text{g/l}$) illustrated based on sampling location and event type with mean concentrations (blue points), confidence intervals (blue lines), and LOQ (red dashed line)

4 CONCLUSION

This study analyzed the effect of stormwater runoff on the receiving water bodies by measuring a wide range of pollutant concentrations in the recipient during dry and wet weather conditions. The most frequent organic substance group was PFAs. PAHs and Phthalates were almost never above LOQ in any of the samples. With one exception, MBT, almost all detected organic compound concentrations increased during the wet weather events and were slightly higher at the sampling locations located at the city center (UppB and UppC). Total metal concentrations of Cd, Cr, Cu, Hg, Ni, Pb and Zn showed a similar pattern to organic compounds with higher concentrations, both during wet weather events and sampling locations closer to the city center. Sampling in this study continues. More sampling campaigns, including rainfall and snowmelt events, will be organized during winter and spring 2022/2023. Further, all samples will be analyzed for microplastics. Thus, at the conference, results from more comprehensive data set will be presented.

5 ACKNOWLEDGEMENTS

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