

Spatial differences among micropollutants in sewer overflows: A multisite analysis using passive samplers

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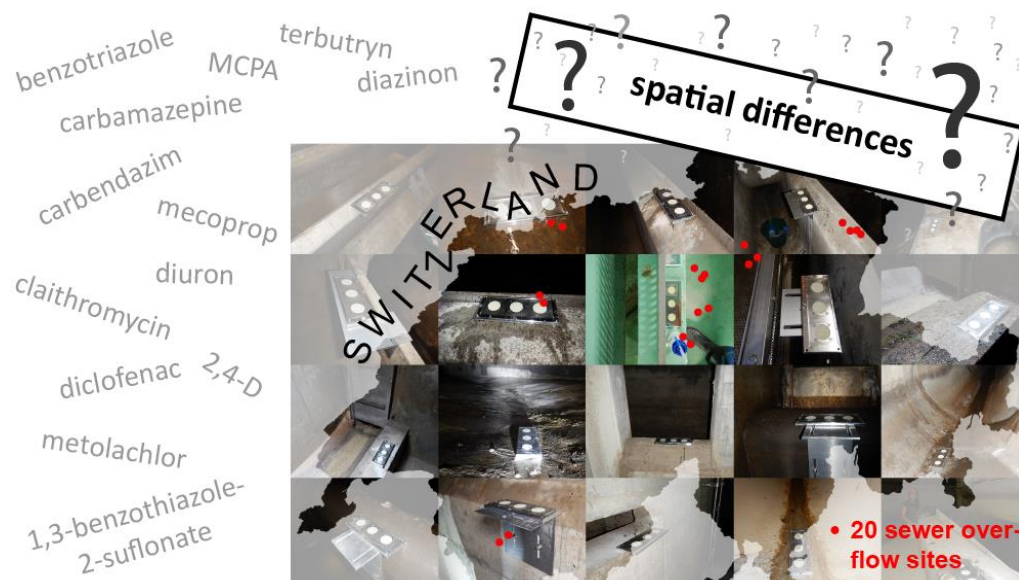
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KEYWORDS

wet-weather discharge, polar organic compound, monitoring, environmental quality standard, risk quotient

GRAPHICAL ABSTRACT



ABSTRACT

Untreated sewer overflows can contaminate receiving waters with micropollutants. Although concentrations of discharged micropollutants can be ecotoxicologically relevant, only limited data is available to assess occurrence and spatial differences among sewer overflow catchments. Therefore, we present an innovative type of data obtained with passive samplers at 20 combined sewer overflow sites (2–7 events per site; 95 events in total). The data sheds light on concentration ranges for 13 representative polar organic micropollutants and shows that micropollutants in both municipal wastewater and stormwater can be relevant sources of contaminants. We identify indicator micropollutants for further studies: benzotriazole (80% interquantile of time-weighted average concentration: 250–4,800 ng/L), carbamazepine (33–910 ng/L), diclofenac (78–1,000 ng/L), carbendazim (21–900 ng/L), diazinon (2.1–53 ng/L), diuron (22–1,100 ng/L), mecoprop (198–5,300 ng/L), metolachlor (6–230 ng/L), and terbutryn (29–810 ng/L). These concentration estimates are assumed to be on the safe side for comparison with environmental quality standards (EQS). A majority of sewer overflow sites (13 of 20) show discharge concentrations above acute EQS for at least one micropollutant and thus would have to rely on dilution by receiving waters to not exceed any EQS. The intersite variability among sewer overflows exceed the within-site variability. Hence, future monitoring studies should cover more sewer overflow sites. No correlation could be found with event durations, specific storage volume or land use data, thus showing the complexity of micropollutant occurrence and indicating that other factors led to the observed high spatial variability. In conclusion, our results clearly show the potential relevance of micropollutants in sewer overflows and the need to assess site-specific measures.

1 Introduction

Untreated sewer overflows can be important pathways of urban micropollutants to receiving waters ¹⁻⁵. Understanding the pollution of urban stormwater is needed to plan measures for stormwater treatment and reuse and so contribute to sustainable urban water systems. Thus, a model for estimating levels of micropollutant concentrations in stormwater and sewer overflows would help evaluate current systems and develop site-specific mitigation strategies. However, micropollutant water quality modeling is challenged by the lack of data to calibrate and verify such models, so the transferability of models to other catchments is limited ⁶⁻⁸. Hence, more data is needed to improve model predictions.

Monitoring sewer overflows with traditional sampling methods has limitations due to high temporal fluctuations in concentrations and large numbers of sewer overflow sites. Previously, we demonstrated the potential of passive samplers to monitor sewer overflows efficiently by (i) indicating that fluctuating stormwater concentrations can be sampled without leading to major deviations from true time-weighted average (TWA) concentrations ⁹, (ii) developing a model to describes the uptake mechanistics during short exposures ¹⁰, and (iii) comparing results of passive samplers with results from samples collected simultaneously with traditional autosamplers in a field study ¹⁰.

Moreover, studies indicate a high spatial variability of micropollutants at different sewer overflow sites ^{4, 11-14}. These studies covered a maximum of eight stormwater outlets ¹³, and most compared two to three sewer overflow sites ^{4, 11, 15, 16}. Therefore, we hypothesize that monitoring a large number of sites will allow the identification of typical micropollutant levels and, if possible, explanatory variables to better predict these micropollutant levels. The following questions are addressed in this study: i) Are there differences among sewer overflow sites? ii) Can land use explain spatial differences? iii) How do different events at a site, interevent variability, relate to differences among sites, intersite variability? iv) May concentrations in sewer overflows lead receiving waters to exceed acute environmental quality standards (EQS)?

2 Materials and methods

2.1 Micropollutants selection

Micropollutants were selected if they fulfilled five criteria: i) The micropollutant is representative of a specific urban source, such as municipal wastewater and, urban surface runoff, as well as an indicator for potential agricultural connections to the urban catchments. ii) The micropollutant is a polar organic contaminant with main transport in water phase (logKOW

< 4) and low sorption tendencies ($\log K_{OC} < 4$) to simplify the transport processes to be considered iii). It has previously been reported in stormwater or wastewater. iv) Its analytical detection is feasible with high selectivity and sensitivity. v) It persists in conventional treatment plant degradation processes, thus obviating consideration of in-sewer transformation processes. This resulted in a selection of 13 polar organic micropollutants (Table 1); it also includes substances that are ecotoxicologically relevant and substances that are suggested as substances to evaluate wastewater treatment plant performance in Switzerland upgraded for enhanced micropollutant removal ¹⁷.

Table 1. List of selected micropollutants with chemical properties, environmental quality standard (EQS) and source (Mun WW: Municipal Wastewater, Agr: Agriculture). The estimated main source is marked with a bold x.

Contaminant name	CAS Number	$\log K_{OW}^a / \log D_{OW}^b$	$\log K_{OC}^c$	Acute EQS ^d	Indic. MP removal WWTP ^e	Source		
		pH = 8		ng/L		Mun WW	Urban surface	Agr
2,4-D ^f	94-75-7	-1.0	1.5	4,000			x	x
1,3-BTH-2-S ^g	941-57-1	-0.4	1.9	-		x	x	
benzotriazole	95-14-7	1.2	3.0	158,000	x	x	x	
carbamazepine	298-46-4	2.8	3.6	2×10^6	x	x		
carbendazim	10605-21-7	1.8	2.2	700		x	x	x
clarithromycin	81103-11-9	2.7	-	190	x	x		
diazinon	333-41-5	4.2	3.1	20			x	
diclofenac	15307-86-5	0.9	2.9	50*	x	x		
diuron	330-54-1	2.5	2.1	250			x	x
MCPA ^h	94-74-6	-1.1	1.5	6,400			x	x
mecoprop	7085-19-0	-0.5	1.7	190,000			x	x
metolachlor	51218-45-2	3.5	2.5	3,300			x	x
terbutryn	886-50-0	2.9	2.8	340			x	

^a $\log K_{OW}$ were taken from JChem for Excel, Version 18.8.0.253 ¹⁸.

^b Distribution coefficients are normalized to the proportion of the neutral species at pH = 8 according to JChem.

^c EPISuite with PCKOCWIN v1.66 on www.chemspider.com (accessed: January 2019).

^d Acute environmental quality standard proposed for 24–96 h by the Swiss Centre for Applied Ecotoxicology ¹⁹.

^e Suggested as substance to assess performance of micropollutant removal in wastewater treatment plants (WWTP) ¹⁷.

^f 2,4-Dichlorophenoxyacetic acid

^g 1,3-Benzothiazole-2-sulfonate

^h 2-methyl-4-chlorophenoxyacetic acid

*Chronic environmental quality standard as no acute values are available ¹⁹

2.2 Urban catchment selection

All monitoring sites were located at combined sewer overflows (CSOs) capturing a mixture of stormwater and municipal wastewater. The main criterion for the selection of sewer overflow sites was that the corresponding urban drainage system had no upstream CSOs. This ensured that only surface runoff collected in the catchment was discharged at the monitored sewer overflow site. Otherwise, it would have been difficult to differentiate which proportion of runoff

of a particular surface had been discharged upstream and which had been forwarded to the CSO further downstream. In total, 20 CSO sites were selected in various regions of Switzerland (see graphical abstract and Figure SI 1). The surface areas of the catchments connected to the CSOs range from 14 to 467 ha and include pure residential zones (CSO ID 9) to pure industrial (CSO ID 20, Figure 1). The selection included a variety of systems: 16 catchments with storage volumes from 7 to 154 m³ per impervious hectare and four catchments without storage volume (Table SI 1). For 19 catchments, the area of four land-use categories (buildings, streets, other paved areas, urban green areas) was determined based on cadastral survey data ²⁰ using ArcGIS (Figure SI 5). No data on land use was available for CSO ID 17.

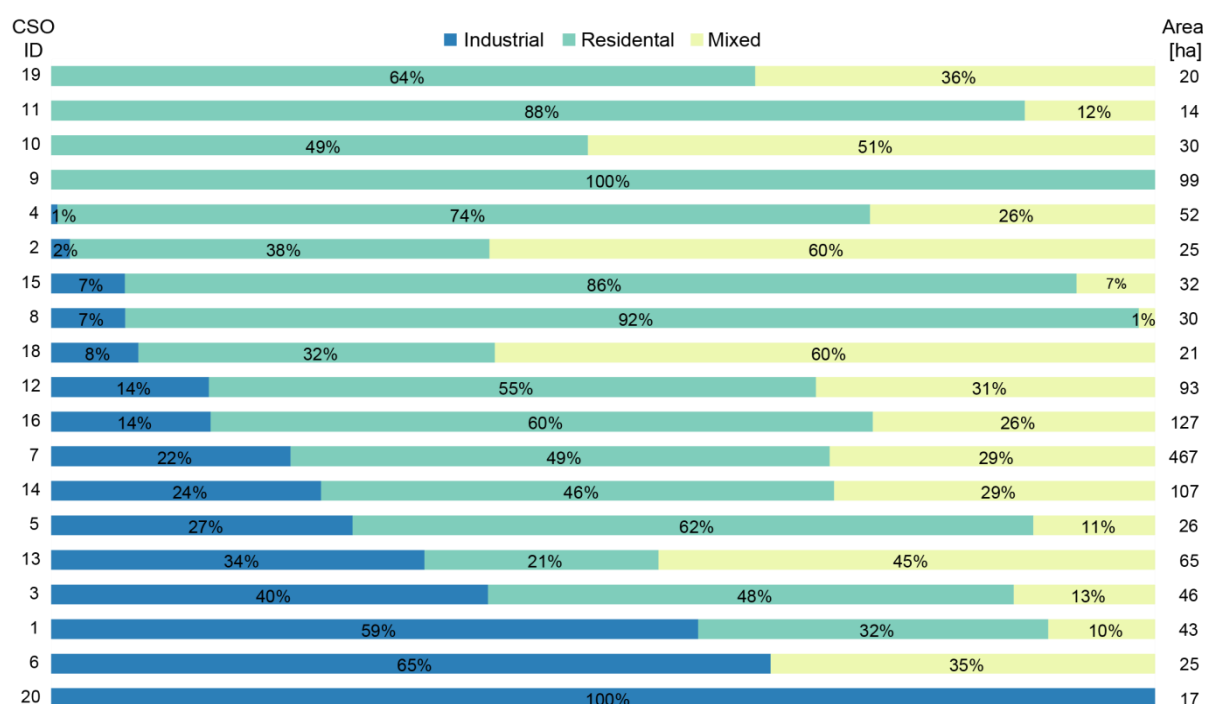


Figure 1. Zones of the monitored CSO sites (with unique CSO ID) by percentage of industrial area in ascending order. Total surface area of each CSO catchment in ha. No data was available for CSO ID 17.

2.3 Passive sampler installation at CSO sites

Passive samplers (Empore, styrenedivinylbenzene reverse-phase sulfonated – SDB-RPS – disks, 47 mm diameter, 0.5 mm thickness, total disk surface area 17.3 cm²) were preconditioned with methanol and nanopure water as detailed in Vermeirssen et al. ²¹ and stored in closed glass containers filled with nanopure water until exposure. At each site, three passive sampler disks, mounted on an aluminum alloy plate that we specifically designed for this purpose ¹⁰ with one side of each disk exposed ²¹ (area = 12.6 cm²), were deployed for each event. The mounting plates were installed horizontally on the weir crest at each of the 20 CSOs where combined sewage discharges to the receiving water (Figure SI 1). The passive samplers were removed after each discharge event. Wherever possible, water levels and discharge durations were

assessed with water level measurements available from the operators. In five cases where such measurements were not available, we installed an ultrasonic water-level measurement system (sensor: Maxbotix MB7369 HRXL at CSO ID 5, 6, 10, 11, 17).

2.4 Number and duration of sampled CSO events

The number of monitored events range from two to seven, resulting in 95 sampled events between March and August 2017 (Figure 2; CSO ID 20, one event was sampled in August 2016). The overflow durations range from as short as 2 min to 96 h (median: 43 min). The longest overflow event of 96 h occurred at CSO ID 4 due to snowmelt. The shortest events were observed at CSO ID 11 with durations between 2 to 4 min.

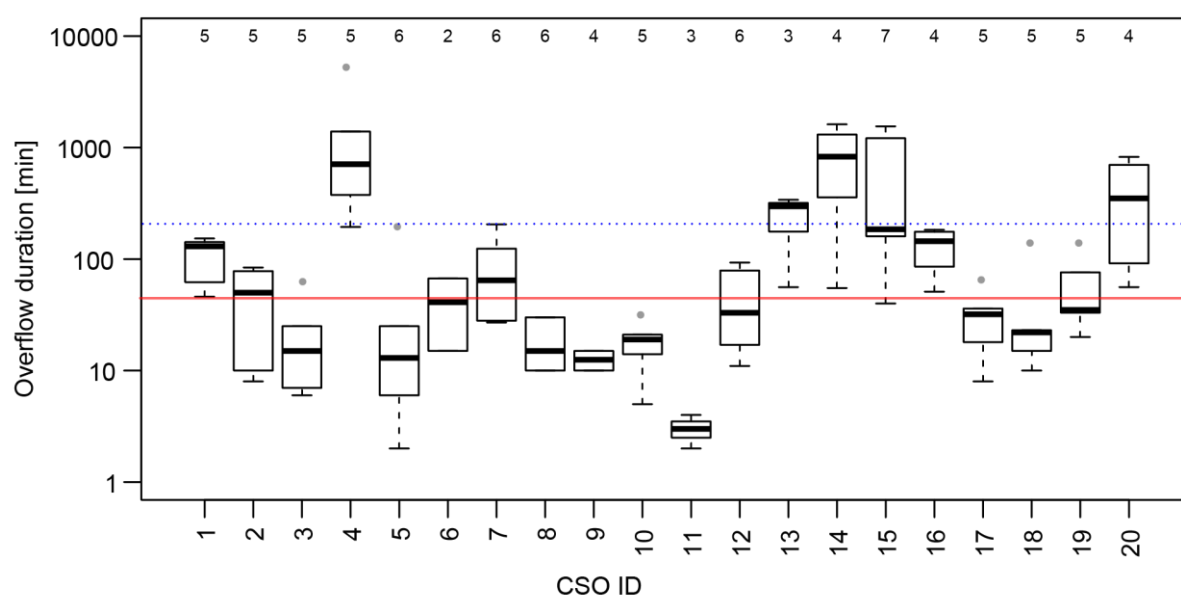


Figure 2. Overflow duration of the 20 CSOs and number of monitored events (on top of figure) for each CSO ID. The dotted, blue line shows the mean of 3.9 h and the red line the median of 43 min. Boxes represent the first and third quartile (Q1 and Q3), whiskers' lengths are max 1.5 x (Q3-Q1); see boxplot in R for details.

2.5 Sampler Extraction and chemical analysis

After exposure, the passive samplers were stored in acetone at -20 °C until analysis. In total, 284 samples were analyzed: 95 events with three passive sampler disks each, except in one case where only two disks were available. Directly before analysis, the disks were extracted as described previously^{10,21}. Briefly, the disks were stored in acetone after exposure and extracted with acetone and then methanol (LC/MS grade, 30min on rotary shaker for both). Structurally-identical isotope-labelled standards (>98% purity) were added before evaporation and filtration. The extracts were evaporated to ca. 0.05 mL and filled with nanopure water to 0.5 mL. The samples were analyzed with high-performance liquid chromatography coupled with tandem mass spectrometry systems (high resolution and triple quadrupole) using electrospray as ionization source. Quantification was performed via target screening using reference standards

for each contaminant and isotope-labeled internal standards (ISTD). One contaminant, 1,3-benzothiazole-2-sulfonate (1,3-BTH-2-S) was quantified with a structure non-identical ISTD (benzotriazole-d4) and corrected by relative recovery. Quality controls such as spiked samples for recoveries and field blind controls were analyzed for all measurement sequences. External reference standards were analyzed for one measurement sequence with relative recoveries within 80-120% (Table SI 11). Blind controls (field blind, filter blind) did not show detects for most contaminants. The limits of quantification (LOQ) were adjusted to at least three times the highest detected field blind concentration, if a compound was detected (benzotriazole, 1,3-BTH-2-S, clarithromycin). Intermediate sample preparation blind controls (for solvents/eluent and filtration) were performed to trace back the origin of a blind value. Additional information on chemical analyses can be found in SI section E (Tables SI 5-12).

2.6 TWA concentration estimates

The TWA concentration C_{TWA} was calculated based on the mass M_{PS} (ng) on the passive sampler disk according to a mixed-rate control model (Eq. 1). This mixed-rate model was found to be applicable for short-duration sewer overflows with intermediate cases between water boundary layer and sorbent-controlled uptake ¹⁰:

$$C_{TWA} = \frac{M_{PS}}{k \cdot m \cdot t^n} \quad \text{Eq. 1}$$

where k (L/kg/h^{*n*}) is the rate constant, n describes the rate controlling transport ^{22, 23} and m represents passive sampler mass (Empore, SDB-RPS; 332×10^{-6} kg). Parameter values (median) for k and n for each contaminant in Table 2 are based on flow channel calibration experiments ¹⁰. Based on these parameter values, the C_{TWA} concentration for each discharge event and location was calculated with Eq. 1 using the average of the triplicate M_{PS} . The resulting C_{TWA} was then corrected for systematic and contaminant-specific deviations. This deviation had been determined in a previous field study that compared passive sampling results with simultaneously collected water samples (3 locations, 10 events) ¹⁰, of which one location is also part of this study (CSO ID 20). Since we do not directly measure TWA concentrations in the water sample, we selected upper TW concentration estimates when comparing them with EQS to be on the conservative (safe) side, as for example recommended by Miège et al. ²⁴. To this end, the 10% quantile of the comparison between water sample and passive sample (correction factor) ¹⁰ was applied to obtain a $C_{TWA,corr}$ estimate with a 90% upper confidence limit. The resulting correction factors are based on only few field measurements, thus more field-based studies are recommended in the future to compare passive sampling with water

samples. We show the influence of the correction factor on estimated TWA concentrations in comparison to EQS in Table SI 4. The variability of replicates ranged from 19% to 63%; a higher replicate variability is assumed to be attributed to a higher analytical uncertainty for values close to LOQ or in case of very high concentrations (1,3-BTH-2-S). The percentage of events below LOQ are given in Table 2. We did not calculate C_{TWA} for values below LOQ, since replacing them with a fixed value such as zero or $0.5 \times \text{LOQ}$ can bias results depending on level of LOQ. Values below LOQ were not used for the calculated ranges of C_{TWA} . Consequently, we report concentration ranges but not mean TWA concentrations. As a result, it needs to be considered that low concentrations are underrepresented in our data set. Alternative results for C_{TWA} based on replacing values below LOQ are shown in SI section E. Values below LOQ were considered as censored values for the evaluation of intersite variability in section 2.7.

Table 2. Parameters used to calculate the TWA concentration C_{TWA} , as well as LOQ, occurrence expressed as a fraction of events below LOQ and variability of the event's replicates.

Contaminant	Mixed rate control model ¹⁰		correction factor	LOQ ^a	Events < LOQ	Median variability passive sampler replicates ^b
	k	n	$C_{TWA,corr}/C_{TWA}$			
	L/kg/h ⁿ	-	-	ng/disk	%	%
2,4-D	40	0.63	0.99	1.9–3.0	99	56
1,3-BTH-2-S ^c	50	0.52	1.73	0.7–1.0	1	39
benzotriazole	140	0.59	1.04	0.7–1.0	0	22
carbamazepine	110	0.88	1.71	0.2–0.3	40	26
carbendazim	220	0.60	9.20	0.1–0.3	64	63
clarithromycin	140	0.72	0.34	0.3–1.8	88	27
diazinon	450	0.63	1.60	0.2–0.3	58	19
diclofenac	120	0.72	1.52	0.3–0.7	35	31
diuron	240	0.70	1.37	0.4–0.6	13	22
MCPA	50	0.61	0.35	0.8	94	49
mecoprop	70	0.63	3.05	0.3–0.7	40	48
metolachlor	240	0.78	1.83	0.2–0.6	51	27
terbutryn	320	0.72	10.3	0.3–1.4	64	45

^aLOQ passive samples measured on two analytical devices; the range shows the different LOQs

^b(max-min)/median of passive sampler replicates per event for values > LOQ

2.7 Interevent and intersite variability

A linear regression that treated values below LOQ as left-censored was fitted to the TWA concentrations C_{TWA} using survreg from the R package survival²⁵. Based on this linear regression an analysis of variance (ANOVA) was performed to explore the significance of the

CSO site, testing if one or more sites differ significantly. A summary of the ANOVA output can be found in Table SI 3, MCPA and 2,4-D were not considered due to few data points.

Moreover, a multiple regression, including the censored TWA concentration values, was fitted with the explanatory variables event duration (Figure 2), specific storage volume (Table SI 1) and relative land use (Figure SI 5). In addition, the linear correlation of site-mean TWA concentrations with single relative land use areas was examined.

2.8 Risk quotient to predict required dilution by receiving water

To identify contaminants and CSO sites that could potentially be critical for the receiving water, a risk quotient (RQ) was estimated by dividing the TWA concentration C_{TWA} by the EQS (Table 1). Hence, RQ – quantified in the CSO, not the receiving water – is used as a simple measure to screen for high CSO concentrations. RQ gives an indication of the dilution that would be required to avoid the receiving water exceeding the EQS. However, the resulting dilution factor expressed as RQ does not account for background contamination in the receiving water. All calculations were performed in R, version 3.4.3 ²⁶.

3 Results and discussion

3.1 Micropollutant occurrences and TWA concentration ranges

The percentage of events with no detections ($< \text{LOQ}$) ranges from 0% for benzotriazole to 99% for 2,4-D (Table 2). Three micropollutants were almost never detected: 2,4-D, clarithromycin and MCPA (Figure SI 2-3). These micropollutants seem to be used only seldom or occur in very low concentrations in sewer overflows, at least in Switzerland. Therefore, they are unlikely to be good indicators for urban sources of micropollutants. In comparison, Launay et al. ² found MCPA in one CSO in Germany, 2,4-D and clarithromycin were not considered in their study. Wicke et al. ¹¹ report 2,4-D with a mean concentration of 10 ng/L in 5 of 95 stormwater outlet samples in Berlin, Germany, indicating low occurrence of 2,4-D in stormwater.

The monitoring results further show that both municipal wastewater and surface runoff are important contributors to the micropollutant concentrations found in CSOs, as discussed below (see Figures SI 2-3 for TWA concentration ranges also including replaced values below LOQ). The TWA concentration ranges that we report cover a wide array of potential concentration levels in CSOs. The reported upper TWA concentration estimates could be used for a first concentration evaluation in the receiving water to identify CSO sites where further steps such as monitoring may be required.

Municipal wastewater. Micropollutants with high detection rates in the 20 monitored CSOs, and thus good indicators for municipal wastewater in CSOs generally, are benzotriazole (80% interquartile: 250–4,800 ng/L, $< \text{LOQ}$: 0%), carbamazepine (33–910 ng/L, $< \text{LOQ}$: 40%), and diclofenac (78–1,000 ng/L, $< \text{LOQ}$: 35%). The concentration ranges expected in CSOs can be calculated from minimum and maximum raw wastewater concentrations in 14 primary clarifier effluents in Switzerland ²⁷. Assuming that 0.4–3.9% of the CSO volume is municipal wastewater ³, the expected concentration ranges in CSOs would be 70–4,700 ng/L for benzotriazole, 0.5–50 ng/L for carbamazepine, and 2–200 ng/L for diclofenac. All our measured municipal wastewater TWA concentrations are in a similar order of magnitude as these concentration estimates. However, higher upper values for carbamazepine and diclofenac were measured than had been estimated. Our finding indicates that the concentrations calculated from passive samplers with our evaluation approach might overestimate actual concentrations. We used the 90% upper concentration correction factor (Table 2) for passive samplers to be on the conservative (safe) side for environmental impact assessments.

Stormwater. Micropollutants expected to originate mainly from urban surfaces are 1,3-BTH-2-S (80% interquantile: 410–8,200 ng/L, < LOQ: 1%), carbendazim (21–900 ng/L, < LOQ: 64%), diazinon (2.1–53 ng/L, , < LOQ: 58%), diuron (22–1,100 ng/L, , < LOQ: 13%), mecoprop (198–5,300 ng/L, < LOQ: 40%), metolachlor (6–230 ng/L, , < LOQ: 51%), and terbutryn (29–810 ng/L, 64%). Comparison with the samples of one CSO in Switzerland by Hanke et al.²⁸ shows similar TWA concentrations for diazinon (mean: 49 ng/L) and mecoprop (730 ng/L). In contrast, our values are higher by a factor 10 or more for carbendazim (mean: 28 ng/L), diuron (97 ng/L), and terbutryn (3 ng/L). One reason for these higher TWA concentrations could be that we applied correction factors (see section 2.6). This leads to factor 10 higher concentrations for carbendazim and terbutryn than their uncorrected concentrations. Moreover, we did not consider values below LOQ, thus leading to overestimated lower concentration values. 1,3-BTH-2-S has only been monitored in very few studies so far; one shows that the concentration in a heavy traffic street runoff (15,000–55,000 ng/L) is a magnitude higher than in household wastewater (760–960 ng/L)²⁹; our reported concentrations for 1,3-BTH-2-S are in a similar range. Overall, we consider our estimated TWA concentrations from surface runoff to be on the “safe” side, i.e. rather overestimated.

3.2 Interevent and intersite variability

The ANOVA results show significant differences among CSO sites (intersite variability) for all considered micropollutants (p-value in SI Table 2). Hence, the variability in TWA concentrations among sites can be identified despite the variability among events. This finding indicates that several catchments should be covered for a comprehensive assessment of micropollutants in CSOs.

These substantial variability in CSO micropollutant concentrations among different sites could be explained by a variety of factors including event characteristics (e.g. duration, rainfall intensity), system (e.g. impervious area, storage volume) and catchment (e.g. substance application behavior, land use) specific factors. For stormwater, explanatory variables may include land use in the catchment and application patterns: application time, applied concentration, and product preferences¹³. Explanatory variables for municipal wastewater include usage rates and times of events, as municipal wastewater exhibits significant diurnal concentration variations (e.g.³⁰). Many of the above factors are *a priori* unknown (application behavior, diurnal variations, event durations, rainfall intensities), thus we focused our analysis on factors that could be available for predictions. An additional factor, that could influence the

observed differences between sites are site-specific environmental conditions, which influence uptake on passive samplers and corresponding correction factors.

Land use for predicting stormwater micropollutants. As the micropollutants in stormwater show distinct differences among CSOs, a potential explanatory variable could be differences in urban land use among the catchments. The model's prediction of micropollutant concentrations and loads in stormwater from land use would be very useful, as monitoring is cost- and time-intensive and a large number of CSO sites exist. Assessments using the Spearman rank correlation with relative land use areas of buildings, streets, urban green, and other impervious areas did not reveal significant correlations with land use for most of the studied micropollutants (Figure SI 6). Mecoprop shows a slight positive correlation with relative building area (Spearman correlation $R = 0.53$, correlation coefficient $p = 0.028$, Figure SI 6). Mecoprop is mainly used in bituminous roof sealing membranes to prevent root growth³¹. On the other hand, 1,3-BTH-2-S, which is expected to occur mainly in street runoff²⁹, does not show a correlation with relative street area in the catchment (Figure SI 6). Diuron and carbendazim have been reported in façade runoff^{32, 33}, so a correlation of the two micropollutants could indicate a correlation with façade area. The diuron and carbendazim concentrations measured in our study show a slight correlation (Spearman correlation $R = 0.46$, correlation coefficient $p = 0.013$, Figure SI 4).

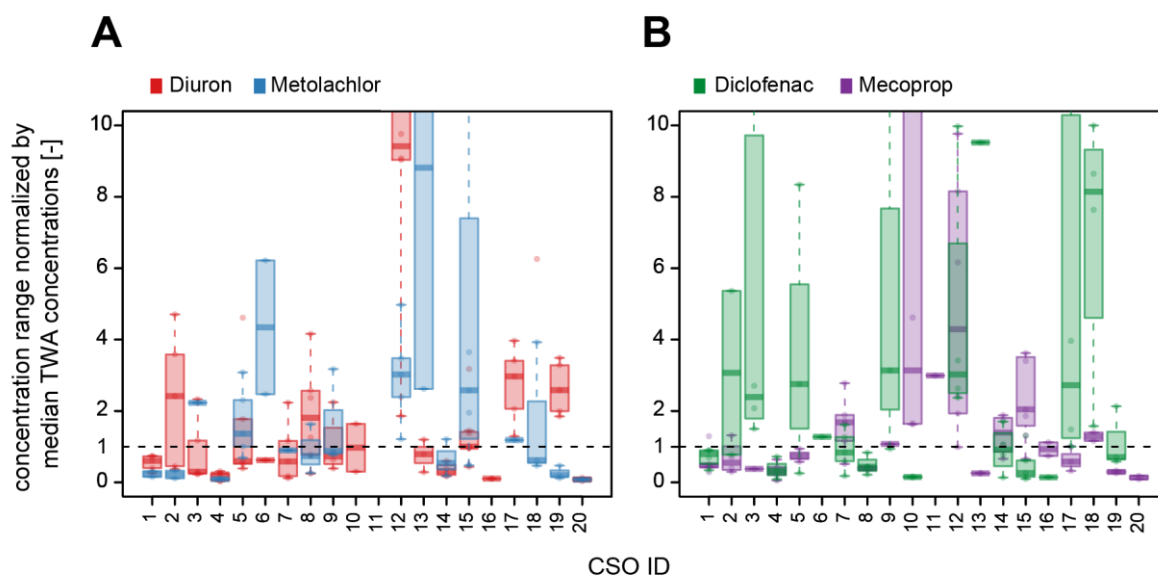


Figure 3. Comparison of concentration range normalized by median of corresponding TWA concentrations for all 20 catchments for **A.** stormwater micropollutants (diuron versus metolachlor) and **B.** wastewater (diclofenac) versus stormwater (mecoprop) micropollutants. Boxes represent the first and third quartile (Q1 and Q3), whiskers' lengths are max $1.5 \times (Q3-Q1)$; see boxplot in R for details.

Municipal wastewater. One factor apparently leading to spatial differences is the proportion of industry in the catchments (Figure 1). The catchments with the highest proportion of industry

and 0% pure residential area are CSO ID 6 (65% industry) and 20 (100% industry). These catchments show no occurrence of diclofenac (CSO ID 6) or lower TWA concentration than all other CSOs (CSO ID 20, Figure SI 3). In contrast, carbamazepine, also a pharmaceutical, is found in similar concentrations in these industrial catchments, as observed in some others (CSO ID 4, 5, 13, 15, 17, Figure SI 3). To generalize that the proportion of industry seems to have little influence on carbamazepine seems speculative based on these two catchments only. Rather it may emphasize that the presence or absence of a few individuals consuming the one or other pharmaceutical – in small catchments as the ones we investigated – is likely to impact levels of consumption. This in turn influences characteristics of (irregular) short-term and diurnal concentration variations and consequently also the observed spatial variability. The high occurrence rates of diclofenac and carbamazepine (together with benzotriazole) in the other 18 catchments still make these three compounds good indicators for municipal wastewater, despite the high spatial variability.

Multiple regression. The multiple regression based on event duration, specific storage volume and relative land use areas did not reveal any useful patterns for predictions, showing the complexity of micropollutant occurrences. The observed difference among sites entails the differences in event duration among sites (Figure 2). The analysis did not reveal significant effects for event durations (SI Table 3) although source limited micropollutants are likely to be diluted with longer event durations. This becomes also apparent in Figure 3 where the concentration ranges relative to the median TWA concentration for different micropollutants show no systematic pattern among CSO sites: e.g. the diuron and metolachlor concentrations – both surface runoff related micropollutants – are not systematically higher or lower at a specific site (Figure 3A). Hence, although we found significant variability among CSO sites, the considered factors do not explain the observed concentration differences. Thus, future studies to identify systematic correlations with explanatory variables may have to cover even more sites with more detailed land use data and monitor a larger number of substances or sums of substances in similar use categories.

Some previous studies have also indicated significant differences among CSOs ¹¹⁻¹³, but others have found no such differences ^{4, 14, 15, 34}. For example, Burant et al. ¹⁶ state that land use may be important in determining the composition and concentration of micropollutants in urban stormwater; however, they did not find significant differences between a residential stormwater outlet and a commercial one for pesticides. In contrast, Rippey et al. ¹³ found that stormwater pesticide composition varied significantly by catchment. Wicke et al. ¹¹ report positive correlations between relative façade area and concentrations of carbendazim and diuron in

stormwater outlets in Berlin, Germany. Moreover, their study showed a correlation between relative tiled roof area and terbutryn concentrations, as terbutryn is used for material protection. A potential correlation with façade area is also indicated by the observed slight correlation between diuron and carbendazim in our study (Figure SI 4). Overall, we conclude that either the land use categories available were insufficiently detailed (e.g. building type, roof type, and façade area not considered) or other factors such as application patterns are more influential.

3.3 Risk quotient to predict required dilution by receiving water

The division of the TWA concentrations by the EQS to provide the RQ indicates the dilution factor required for the CSO discharged into the receiving water. The measured TWA concentrations are higher than in previous studies, indicating that our assessment with passive samplers is on the conservative side. Meaning, if passive samplers identify a CSO site as noncritical with respect to EQS, it is likely that no further assessment and measures are required. Despite our conservative evaluation approach, the TWA concentrations of seven micropollutants were never quantified $> \text{EQS}$ (Figure 4): carbamazepine, clarithromycin, benzotriazole, 2,4-D, MCPA, mecoprop, and metolachlor. Therefore, the CSOs of these micropollutants evaluated at these sites seem to be unproblematic. In addition, the number and level of TWA concentrations $> \text{EQS}$ are very low for carbendazim.

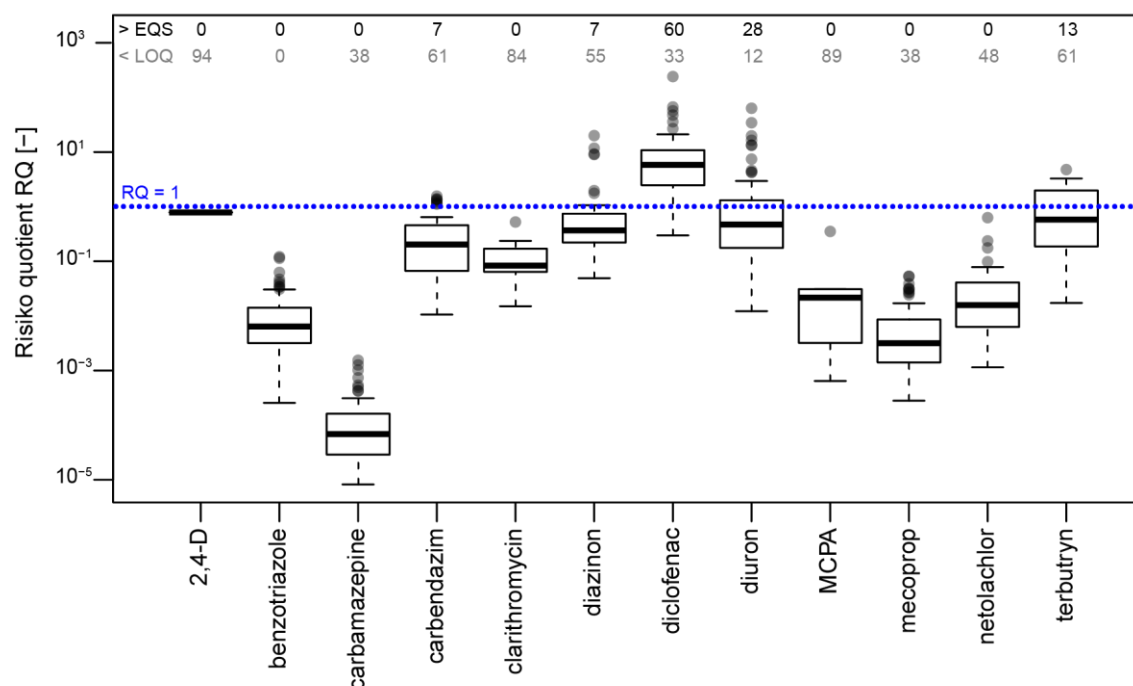


Figure 4. Risk quotient (RQ) based on TWA concentrations of all 20 CSOs divided by EQS. Only RQ values $> \text{LOQ}$ (limit of quantification) are shown, thus lower concentration ranges are overestimated. The black numbers at the top give the number of events $> \text{EQS}$ ($\text{RQ} > 1$) and the grey numbers the number of events $< \text{LOQ}$. The blue line shows $\text{RQ} = 1$. 1,3-BTH-2-S has no EQS value. Boxes represent the first and third quartile (Q1 and Q3), whiskers' lengths are $\max 1.5 \times (\text{Q3} - \text{Q1})$; see boxplot in R for details.

In contrast, RQ is > 1 for diazinon (80% interquantile: 0.11–2.7), diclofenac (1.6–21), diuron (0.087–4.3), and terbutryn (0.086–2.4) (Figure 4). Diclofenac shows the highest number of events $> \text{EQS}$ with the highest RQ values. In addition, 19 of the 20 CSO discharges show $\text{RQ} > 1$ for diclofenac for at least one event (Table 3). This is thought to be mainly attributed to the fact that the chronic EQS for diclofenac of 50 ng/L had to be used to calculate the RQ. In contrast, an acute EQS is available for all other micropollutants. In the case of a different EQS value for diclofenac, the number of CSO sites with $\text{RQ} > 1$ could potentially fall from 19 to 13. In addition, our estimation is based on upper limit 90% TWA concentration estimates and only values above LOQ. Thus, the number and magnitude of exceedances is likely to be lower than reported here. The influence of the correction factor on number of events with $\text{RQ} > 1$ is shown in Table SI 4; in short, terbutryn and carbendazim would have no events above EQS without correction factor.

Table 3. Assessment of the risk quotient RQ per catchment: Number of TWA concentrations $> \text{EQS}$ and assessment of the maximum RQ_{max} . The number in the boxes gives the number of events with TWA concentrations $> \text{EQS}$ ($\text{RQ} > 1$), the color indicates the maximum RQ (RQ_{max}) based on the maximum TWA concentration measured at the site divided by the EQS. 1,3-BTH-2-S has no EQS value. Concentrations $< \text{LOQ}$ were not considered. *Mecoprop is used in root protection agents.

Contaminant	Source	Registration	CSO ID																						
	Municipal wastewater Urban surface Agriculture	Pharmaceutical Plant protection Biocide																							
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20			
diclofenac	x	x	5	4	1	4	3		6	2	1	4	1	6	2	4	7	2	3	2	2	1			
carbamazepine	x	x																							
clarithromycin	x	x																							
benzotriazole	x	x																							
2,4-D		x																							
carbendazim	x	x																							
diazinon		x																							
diuron		x																							
MCPA		x																							
mecoprop		x																							
metolachlor		x																							
terbutryn		x																							
Number of sampled events			5	5	5	5	6	2	6	6	4	5	3	6	3	4	7	4	5	5	5	4			
Assessment RQ _{max}																									

The situation based on the maximum RQ_{max} is assessed as poor ($\text{RQ} > 10$) for diclofenac at six CSO sites, for diuron at three sites, and for diazinon at one site. Terbutryn shows $\text{RQ} > 1$ in seven CSO sites. However, the terbutryn concentration estimates via passive samplers might have led to very high values, as discussed in section 3.1. Most events with $\text{RQ} > 1$ are shorter than 9.7 h (90% quantile), with a mean duration of 7.5 h for all events with $\text{RQ} > 1$. However, no effect of the event duration on number of events with $\text{RQ} > 1$ was observed (Figure SI 7). These micropollutants with $\text{RQ} > 1$ require dilution so that concentrations in the receiving

waters do not exceed EQS. Thus, the individual risks posed by these micropollutant discharges depend on their concentrations in the CSOs, the flow in the receiving water, and the background levels of micropollutants from upstream. Additional measurements downstream of CSOs in small to medium rivers would be interesting to see actual concentrations.

3.4 Limitations of passive sampling CSOs

Event durations. In cases of very short event duration (<24 min for diclofenac, < 7min for diazinon, < 3min for diuron, <1min for all other micropollutants detected above EQS) and values below LOQ, it is possible that the TWA concentrations were higher than EQS but not detected with passive samplers¹⁰. In our study this is the case for one event for diazinon and none of the events for all other micropollutants. Moreover, the mixed-rate control model to estimate TWA concentrations was fitted for events <36 h (Eq. 1), thus for events >36 h the accumulation is overestimated and the TWA concentration is underestimated. This is the case for one event in our study (Figure 2). In general, in case of event durations >36, new parameter estimates for the mixed-rate model are needed. Another aspect is the volume of water – ca. 50 to max. 75 mL – remaining on the passive sampler after an event: if a peak concentration occurred at the end of a (short) event with a low concentration for the major part of the event, the TWA concentration might be overestimated. We anticipate that this effect is small, since the available mass for uptake is also very limited.

LOQ values. Additionally, there is a high number of values below LOQ, which we treated as censored values for regression analysis. Nevertheless, these values below LOQ could also have contributed to the fact that we did not detect correlations with catchment characteristics.

Number of micropollutants measured. Field or realistic laboratory studies are needed to estimate TWA concentrations with passive samplers, meaning that the number of analytes is limited to analytes with known model parameters. Hence, a limited number of carefully selected micropollutants was considered (section 2.1) and we did not find strong correlations of these micropollutants with available explanatory factors. Future studies could include a larger number of micropollutants or group of micropollutants (e.g. pesticides) to identify influences of catchment characteristics.

Site-specific conditions. The advantage of passive samplers is that the whole CSO event is sampled. As a result, the discharged short-term peak concentrations might have been substantially higher than the reported TWA concentration ranges. An important factor contributing to the uncertainty of passive sampling is that uptake depends on local

environmental conditions such as velocity, water matrix, and temperature^{35, 36}. Here, we applied model parameter estimates from a previous CSO field study to all CSO sites without correcting for local environmental conditions, which were not measured at the sites. Thus, the uncertainty of the TWA concentration estimates is increased; for example we found factor 1.9 higher uptake rates in wastewater-stormwater matrix at velocities of 0.8 m/s (see ref.¹⁰) than a previous study in river water at 0.14 m/s (see ref.²¹). However, the differences between these river water conditions and typical sewer conditions is assumed to be greater than the differences in environmental conditions among CSO sites. Moreover, site-specific environmental conditions could have contributed to the observed intersite variability but in view of Figure 3, they do not seem to be of systematic origin.

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Notes

Any additional relevant notes should be placed here.

ABBREVIATIONS

EQS	Environmental quality standard
LOQ	Limit of quantification
CSO	Combined sewer overflow
TWA	Time-weighted average
C_{TWA}	Time-weighted average concentration
RQ	Risk quotient
SDB-RPS	styrenedivinybenzene reverse phase sulfonated
1,3-BTH-2-S	1,3-Benzothiazole-2-sulfonate

Supporting Information. Passive sampler installation setup, Time-weighted average concentration estimates, Spatial variability (ANOVA, land use, multiple regression), Risk quotient, Chemical analysis.

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