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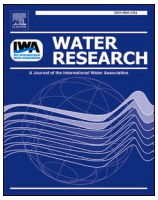

Source-specific dynamics of organic micropollutants in combined sewer overflows

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ABSTRACT

Combined sewer overflows (CSOs) discharge organic micropollutants (MPs) into open water bodies, posing potential environmental threats. Knowledge of the numbers, sources, and dynamics of MPs during CSOs is scarce but crucial for assessing their impact and developing mitigation strategies. To shed light on the dynamics of dissolved organic MPs in CSOs, we conducted high-temporal-resolution sampling (10 min composite samples) followed by liquid chromatography high-resolution mass spectrometry analysis, both target (60 substances) and nontarget, at two CSO sites in a small [17 hectares reduced (ha_{red})] and a large (368 ha_{red}) catchment for over 10 events each. We observe similar patterns among indoor substances in the large catchment and among tire-associated compounds in both catchments, indicating source-specific behavior. Due to high and diverse concentration variability, no temporal correlations were found among indoor substances in the small catchment or among pesticides in either catchment. A random forest classifier was applied to assign nontarget time series to indoor and road sources in the large catchment. The results indicate that CSOs discharge several thousand substances from indoor sources, followed by a few hundred from outdoor sources with continuous leaching. These high numbers substantially surpass the scope of traditional target lists and underscore the importance of broad-spectrum screening methods when assessing MP contamination.

1. Introduction

A large number of synthetic chemicals reach the aquatic environment, and organic micropollutants (MPs) are prevalent in rivers, lakes, and oceans (Bradley et al., 2017; Lara-Martin et al., 2020). From urban areas, organic MPs enter open water bodies mainly through wastewater treatment plant (WWTP) and during rain events through combined sewer overflows (CSOs) or stormwater outlets (SWOs). While WWTPs have been extensively studied and can now reduce organic MPs through enhanced treatment, CSO discharges remain a less understood source. CSOs release a mixture of poorly or not treated raw waste- and stormwater into the environment and they are not designed to remove dissolved compounds at all. In Europe, about 75 % of sewer systems are combined, with a rough estimate of 650,000 CSO sites (EurEau, 2020). With increasing urbanization and climate change, the frequency and volume of CSOs is expected to increase in the near future, with predictions of up to a 256 % increase in annual CSO discharge volume by the end of this century (Abdellatif et al., 2015; Cavadini et al., 2024; Rodriguez et al., 2024). Therefore, CSOs are an increasingly important pathway for organic MPs, potentially causing adverse effects on the ecosystem and human health (Mutzner et al., 2022; Phillips et al., 2012).

CSOs contain a large variety of organic MPs originating from various urban sources (Launay et al., 2016). Raw wastewater carries various indoor-applied chemicals, such as pharmaceuticals, artificial sweeteners, and biocides (mainly in cosmetics and detergents) (Eggen et al., 2014; Michael et al., 2013; Patel et al., 2019). Additionally, stormwater washes off organic MPs from urban areas, including biocides from construction material, pesticides from urban greens and agriculture, and tire wear leachates (Burkhardt et al., 2012; Chibwe et al., 2022; Spahr et al., 2020). Among this broad range of substances, some may be

Abbreviations: CD, Compound Discoverer; CSO, combined sewer overflow; DOC, dissolved organic carbon; EMC, event mean concentration; FP, false positive; ha_{red}, hectares reduced; HMMM, hexa(methoxymethyl)melamine; ILS, isotopic-labelled standard; LC-HRMS, liquid chromatography high-resolution mass spectrometry; LOQ, limit of quantification; MAPE, mean average percentage error; MPs, micropollutants; M(V) curve, mass-volume curves; NH4-N, ammonium; PPP, plant protection products; TP, true positive; TRWP, tire and road wear particles; WWTP, wastewater treatment plant.

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harmful to aquatic environments, as was illustrated recently with the compound 6PPD-quinone, which causes acute mortality among salmon populations during storm events (Tian et al., 2020). To mitigate the risks that organic MPs pose to ecological and human health, an improved understanding of their temporal dynamics throughout CSO events is crucial. Knowledge on concentration dynamics would enable: (1) modelling MP concentrations not only on the spatial but also temporal scale, (2) developing real-time control for effective pollution reduction, (3) evaluating effective in-sewer measures, such as retention basins or onsite treatments (e.g. filtration), or catchment-wide strategies, such as the integrated management of sewer system and WWTP. However, high-temporal-resolution data of organic MP in CSOs is currently lacking because most studies only report event mean concentrations.

To address this gap, we collected high-temporal resolution data on dissolved organic micropollutants at two sites over several CSO events to explore the dynamics of substance from different sources. In order to further enlarge our dataset, we incorporate a nontarget analysis, where we leverage temporal information of targets coupled with classification algorithm to allocate nontarget MPs to target time series (Hollender et al., 2017). This approach has gained traction in various fields, such as source allocation of nontargets in streams (Carpenter et al., 2018), historical accumulation of organic MPs in lake sediments (Chiaia-Hernandez et al., 2017), and persistence of organic MPs in natural drinking water sources (Albergamo et al., 2019). In our study, we use this approach to quantify the number of nontarget substances per source and uncover dynamics that are not captured by target time series but can be crucial for improving management of CSOs.

In order to achieve those goals, we conduct a two-step process:

(1) **Dynamics of target MPs:** First, we use the 10 min interval time series of 60 target compounds from 10 CSO events at each of the two sites (2700 and 159,000 people) to characterize the temporal patterns of MPs from three sources, i.e. *indoors, roads*, and *pesticides*. Also, we look for further parameters, such as discharge, ammonium, and dissolved organic carbon (DOC), to identify proxies that are easier to measure.
(2) **Source allocation of nontarget MPs:** In the second step, we conduct a nontarget analysis on two CSO events and assign nontarget time series to sources based on the temporal dynamics with a random forest classifier that was trained with targets from Step 1. This allows quantifying the number of unknown substances per source and to uncover further temporal patterns.

2. Material and methods

2.1. Data acquisition

Site and events. Two CSO sites in Switzerland were investigated (see catchment scheme in SI Figs. 1 and 3). The first CSO site is situated in a small rural village characterized by predominantly residential areas and roads, with agriculture on the outskirts of the urban area and little industry. In its sub-catchment, 2700 permanent residents (in this study referred to as "people") are connected to the sewer system. The second CSO site lies in a much larger catchment, with 159,000 people connected, that also consists primarily of residential areas, roads, agriculture, and a small amount of industry. Table 1 provides an overview of the key characteristics of the two sampling sites and the overflow events sampled. The overflow events are also depicted in SI Fig. 5. More detailed information on the study sites, sampling method, analytical procedure, and additional measurements can be found in our previous study (Furrer et al., 2023).

Sampling. A detailed description of the sample storage, preparation and analysis procedure can be found in our previous study (Chapter 4.4) (Furrer et al., 2023). In brief, we collected 10 min composite samples (750mL) consisting of five 2 min grab samples (150mL) using an automated sampler (MAXX TP5C) with integrated cooling system and 24 glass bottles. Two samplers in series enabled us to sample up to 8 h. Samples were collected at the inflow channel a few meters upstream of the CSO, to be able to start measuring at the beginning of the storm event and independently of the CSO characteristics (retention basin, weir height) (see CSO schemes in SI Fig. 2 and 4). The sampler started automatically once the water level reached a certain threshold above dry-weather flow (CSO small catchment: $>$ 80 L/s, CSO large catchment: $>$ 1′500 L/s), which is the discharge of raw wastewater in the sewer during periods with no precipitation. Sampling the MP concentration transition from dry to wet weather proved infeasible due to clogging of the suction hose within a few minutes. Therefore, we sampled two events in the large catchment after the WWTP screen (20 m and 40 s downstream the original sampling point), which facilitated capturing 1 h dry-weather periods prior to the overflow events and a 24 h dry-weather pattern.

Table 1
Key characteristics of the two sampling sites and the overflow events sampled.

Parameter	Small catchment	Large catchment
Effective hydraulic area [ha_{red}]	17	368
People connected	2700	159,000
Volume retention basin [m^3]	280	3000
Max. dry-weather flow [L/s]	20	600
Sampling period	Sep 2021–Jun 2022	Aug 2022–Jun 2023
# of events	14	10
# of samples	320	240
Overflow duration [h/event]*	2.8 (17.9)	6.8 (23.5)
Overflow volume [m^3/event]*	996 (8684)	15,316 (47,004)
Rain intensity [mm/h] *	2.6 (45)	3.2 (52)
*mean (max)		

Analytics. A detailed description of the sample storage, preparation and analysis procedure can be found in our previous study (Chapter 4.4) (Furrer et al., 2023). Briefly, the samples were analyzed for organic MP with liquid chromatography (water–methanol gradient) followed by high-resolution mass spectrometry (Q-Exactive, Thermo Fischer) with electrospray ionization in two separate runs for positive and negative mode. Full-scan MS1 spectra at a resolution ® of 140,000 (at m/z 200) were acquired over the mass range m/z 100–1000 followed by five data-dependent MS2 scans (R = 17,500 at m/z 200; triggered by target analyte masses) (also see SI Section 3.3). In total, we screened for 60 target substances, of which we found 57 substances (list in SI Table 1) above the level of quantification (LOQ) at least once (concentration ranges in SI Fig. 7). In total, we spiked 159 isotopic-labelled standards (ILS). For a precise quantification of the 60 target compounds, 61 structural identical ILS and 2 structural similar ILS with similar retention time from the 159 spikes ILS were used as internal standards (see SI Table 1). In brief, the relative recoveries for the 57 targets are 103 ± 15 % (median ± std), the precision 4 ± 6 %, and the LOQ ranges from 5 to 250 ng/L (see details in SI Table 1, 2 & 3). Lab and field blank samples were used to check that no substance carryover during sampling and in the laboratory was present. In each sample, we also analyzed ammonium (NH_4^+-N) using either ion chromatography (930 Compact IC Flex, Methrom), photometry (Lachat QC8500), or Dr. Lange LCK304/05), depending on the expected concentration levels and numbers of samples to be analyzed at a time. All ammonium measurements were cross-validated before use. Additionally, we measured DOC using a total organic carbon analyzer (Shimadzu TOC-L). There is a data gap for DOC from August to December 2022 due to technical issues with the measuring instrument. Furthermore, we have data on precipitation, inflow, and overflow discharge of both CSO sites.

2.2. Dynamics of target substances

We calculated the Pearson correlations between the concentrations of the substances from the same source over all events in each catchment to assess their suitability for source allocation. A source is considered

suitable for source allocation when the median correlation of all compounds of this source exceeds 0.6, indicating strong linear correlation. Furthermore, we analyzed the Pearson correlation between the MPs of each substance class, defined as substances from the same source, with the parameters discharge, ammonium, and DOC. For better comparison of the dynamics independent of absolute concentration levels, we normalized each time series by the mean value of the corresponding substance over the entire event. For each source, we also conducted additional analyses:

Indoors. Due to the high correlation of indoor MPs with discharge and ammonium in the large catchment (see Fig. 1B and Section 3.1.1), we explored the potential to estimate concentrations of MP from indoor sources during rain events using measured dry-weather concentrations and dry-to-wet discharge ratios (SI Eq. 1). We further tested whether we could derive the daily dry-weather pattern for MP from the mean dry MP concentrations and the daily ammonium pattern (SI Eq. 2). Then, we calculated the mean average percentage error (MAPE) to compare the estimated MP concentrations with the measured MP concentrations during overflow events.

$$\text{MAPE} = mean\left(\frac{\left| c_{true} - c_{pred} \right|}{c_{true}}\right)$$

MAPE: Mean absolute percentage error

c_{true}: Measured MP concentration during overflow event

c_{pred}: Predicted MP concentration during overflow event

Roads. The three substances originating from tire wear leachates, 6PPD-quinone, 1,3-diphenylguanidine and hexa(methoxymethyl)melamine (HMMM), were investigated in their relationship with antecedent dry-weather days and discharge within events. The antecedent dry-weather days were defined as number of days before the event where the discharge did not exceed a maximum flow of 70 L/s for the small and 1000 L/s for the large catchment. To test whether the tire-associated compounds show a first flush, the mass vs. volume [M(V)] curves were derived for each substance and event with which the cumulative mass of an MP is depicted over the cumulative discharged volume of an overflow event (Bertrand-Krajewski et al., 1998).

Pesticides. We categorized pesticides into plant protection products (PPPs) and biocides (SI Tab. 4) and analyzed their seasonal trends and first-flush dynamics. The seasonality was evaluated by calculating the ratio of maximum monthly concentrations to the overall maximum concentration. The first-flush dynamics were investigated as tire wear leachates with M(V) curves.

2.3. Nontarget analysis

Nontarget analysis was conducted with Compound Discoverer (CD) version 3.3 software from ThermoFisher. The CD workflow can be found in SI Fig. 22. A first evaluation of both positive and negative mode revealed that over 70 % of the nontarget compounds were detected in positive mode. Therefore, we present here only the results of the positive mode. Two events in the large catchment, from 09.05.2023 and 22.06.2023, were selected due to their large number of samples per event and distinctive source-specific dynamics (Fig. 2). Each event was analyzed separately in CD. The results, consisting of mass, retention time, and peak area intensity in each sample, were exported from CD and further processed with the Python coding language. To ensure high quality time series, the initial datasets were reduced with two filter criteria: (1) only keep time series with at least four samples with peak area $> 10^6$ and 10 times larger than the maximal blank area, and (2) the retention time must fall within the range of 2.8 to 22 min. After filtration, only a minority of the nontarget time series remained, although these still number several thousands.

A comprehensive overview of the filtered nontarget time series was obtained through three prioritization steps: (1) comparing the cumulative intensity over all samples of a compound to the total cumulative intensity over all samples and compounds, (2) ordering the maximal intensity of each compound among all samples by magnitude, and (3) calculating the percentage of samples for a compound exceeding the area intensity threshold 10^6.

We validated the CD software's peak-picking process by estimating the recall (True Positive (TP) / (TP + False Negative (FN))) as the portion of spiked ILS and detected targets which were identified by the CD software compared to the total amount of spiked ILS and detected targets. The recall was assessed for 159 ILS and 29 quantified targets in the 1000 ng/L calibration point and all wastewater samples. Recall values for ILS and targets lie above 85 % for the calibration point and above 79 % for the wastewater samples (SI Fig. 24). The filtration process efficiently reduces the total number of time series in the wastewater samples by 55 % without impacting the recall values. As False Positives (FP) per se cannot be derived from the spiked substances in wastewater samples, we assessed the precision (TP / (TP + FP)) by manually inspecting the chromatographic shape of 300 randomly selected peaks and distinguished between peaks with good (gaussian) shape (TP) and poor (noisy) shape (FP). This analysis revealed 83 % TPs and 17 % FPs independent of intensity levels, leading to a precision of 0.83.

A comparison of the results from CD with those from Tracefinder demonstrated strong correspondence in targets' areas (SI Fig. 25). To assess the impact of the matrix effect on the relative dynamics of the nontarget time series, we examined the peak area variation of 60 ILS, which we also used for target analysis. All ILS displayed a maximum variation of ± 20 % within the time series (SI Fig. 26). These uncertainties lie within the range of analytical precision, and therefore the matrix effect is negligible when calculating the relative dynamics of the nontargets.

2.4. Machine learning analysis

The filtered nontarget time series were allocated to a source based on their temporal behaviors. For this, we evaluated three classifiers commonly used for time series classification: random forest, nearest neighbor, and Gaussian. We trained the classifiers with the time series of targets exhibiting source-specific dynamics. As evident from the results in Section 3, only targets from the indoor and road sources display high correlation (> 0.6) with each other; thus, we solely consider these for source allocation. The random forest classifier was chosen as it yielded the best performance metrics and is known as a robust algorithm (Fernandez-Delago et al., 2014; Genuer et al., 2008).

The classification was performed with three Python packages: SciPy, scikit-learn, and tslearn. The training set consisted of the normalized time series (see Section 2.2) of two classes: indoors with 30 target time series and roads with 3. From each class, the entire time series of 70 % of the substances were used for training and 30 % for validating the classifier by applying a stratified splitter. The trained classifier reached an accuracy of 1, which might be surprising but can be attributed to the very distinct patterns exhibited by the two classes in the training set. To better assess the goodness of classification for individual compounds by the trained classifier, we calculated the probability of each nontarget time series being assigned to its class. Thereby, a higher probability indicates a better match of the time series with the target substances. We decided to only display and proceed with those having at least 50 % probability. Detailed description of the classification analysis can be found in SI Chapter 6.

Subsequently, nontarget time series that could not be assigned to either source, were clustered to identify further patterns beyond these two target classes. This was conducted with a hierarchical cluster analysis using the Ward's method, which performed better than KMeans and DBSCAN. The Ward's method is often used to cluster environmental data (Carpenter and Helbling, 2018; Chiaia-Hernandez et al., 2017; Yun et al., 2023). For this clustering, we considered only the top 2000 prioritized nontarget time series (described in Section 2.3) to obtain distinct clusters. We chose a cluster number of 20, as this resulted in a

variety of temporal patterns while grouping similar time series together. Detailed description of the clustering analysis can be found in SI Chapter 7.

An overview of the method workflow can be found in the SI (Fig. 9).

3. Results and discussion

3.1. Dynamics of target substances

The per-event normalized MP concentrations are displayed for each substance class in three events per catchment in Fig. 1 (for all events see SI Fig. 10–14). The substances were divided according to expert knowledge into two main sources: indoors and outdoors, each comprising distinct substance classes. Indoor sources contain the substance classes pharmaceuticals, nutrition, and indoor biocides. Outdoor sources comprise road-runoff related compounds and pesticides (encompassing PPPs and biocides). The substances from indoors enter the sewer system mainly via toilet flushes, with a few exceptions of substances from other uses such as dishwashers, washing machines and showers, whereas the road-related substances and pesticides are washed off from urban surfaces and transported to the sewer network by stormwater. In the subsequent analysis, indoor substance classes are evaluated jointly, given their uniform entry into the sewer system. Conversely, the outdoor classes roads and pesticides are considered separately due to their different application and wash-off behaviors.

For each substance class (indoors, roads, pesticides), we assessed the Pearson correlation between the substances within each class to determine their potential usefulness in allocating nontarget time series to target substances (wherever median correlation > 0.6). Then, we examined correlations with additional parameters that could be used to explain and ultimately predict the observed concentration dynamics.

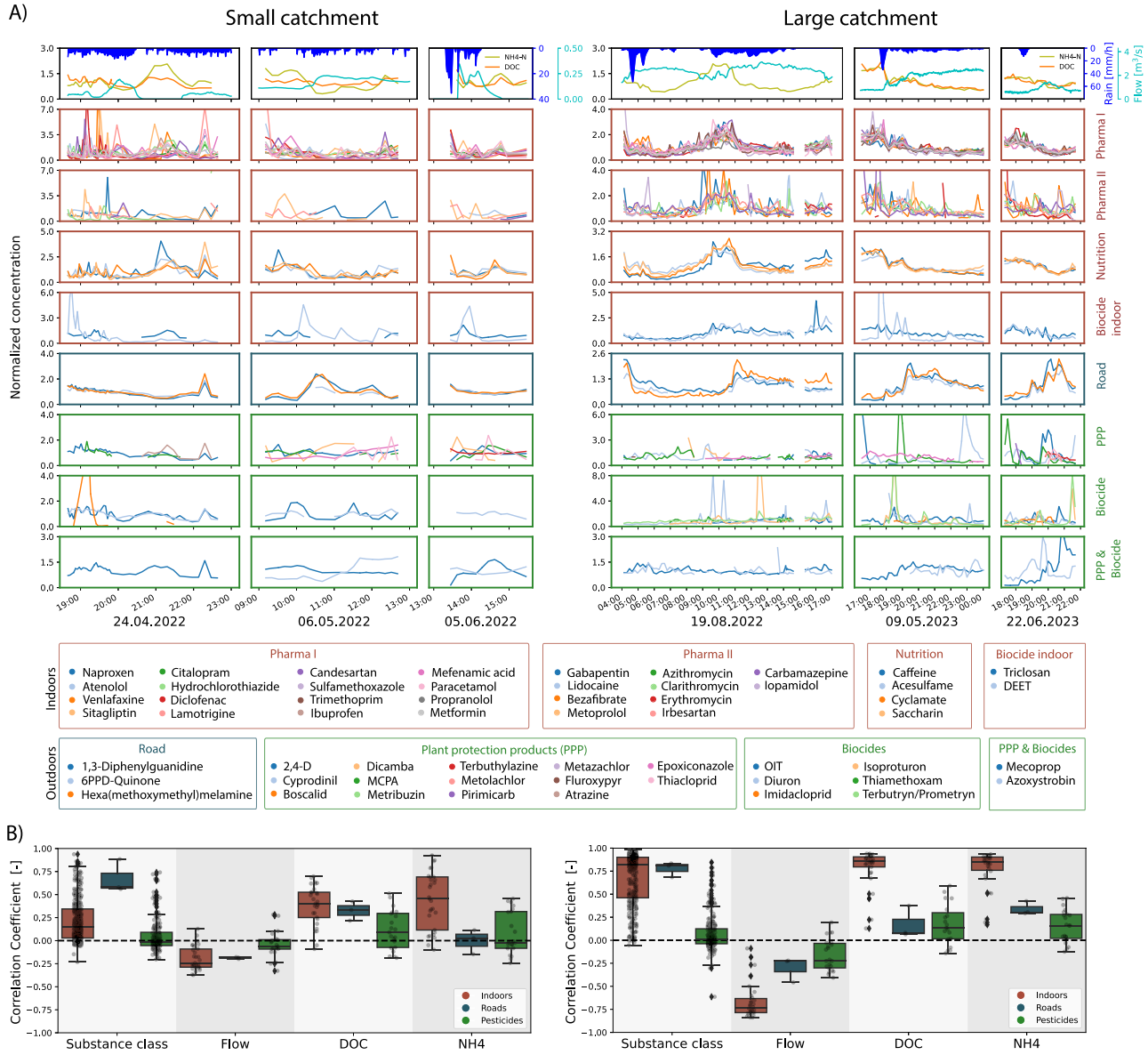

Fig. 1. A) Precipitation, inflow to CSOs, ammonium, and DOC (first panel) and MP concentrations normalized by the mean of each substance per event and grouped by sources (PPP = plant protection products), for the small and large catchment. B) Boxplots of Pearson correlation coefficients of the substances within each substance class (indoors, roads, pesticides) and between the substances of each class and the parameters flow, ammonium, and DOC for all events in the small and large catchment. Dates format: DD.MM.YYYY.

3.1.1. Indoors

The substances from indoor sources can be divided into pharmaceuticals with many consumers, *Pharma I*; pharmaceuticals with few consumers, *Pharma II*; nutrition, such as artificial sweeteners and caffeine; and indoor-applied biocides.

Source selectivity. For the indoor substances, substantial differences can be observed between the Pearson correlation coefficients for the small and large catchments (Fig. 1B). In the small catchment, no correlation can be observed among the indoor substances, but the indoor substances in the large catchment are strongly correlated with each other. In the large catchment, a few substances, such as clarithromycin, erythromycin, and iopamidol, show lower correlations. This may be because they are consumed by fewer people. Clarithromycin and erythromycin, antibiotics for respiratory infections, are likely less common during the study period which excludes winter season, while iopamidol, an X-ray contrast agent, is excreted in high concentrations and by only a small number of individuals. The substance DEET also shows a lower correlation with ammonium in some events, which can be explained by the fact that the substance has many different applications and can therefore originate from different sources. Hence, allocating the sources of indoor substances for nontarget time series is possible for the large catchment but not for the small catchment.

The weak correlation among indoor MPs in the small catchment can be attributed to the catchment's small population size (2700 people), resulting in higher concentration fluctuations during dry and consequently wet weather periods. An example comparing 15 pharmaceuticals in the small and large catchments during an overflow event, illustrates this disparity (SI Fig. 15). Despite stronger dilution (max. 17×) in the small catchment than in the large one (max. 5×), concentration variations relative to the event mean concentration are much higher and more random in the small catchment. This indicates that concentration variations of indoor substances during wet weather are not solely driven by dilution but also by the inherent fluctuations in the raw wastewater, which is particularly more pronounced in smaller catchments. Although our sampling campaigns were conducted during a period impacted by the COVID-19 pandemic, we expect this to have minimal impact on the results, as our focus is mainly on relative variations.

Additional parameters. Indoor MPs in the large catchment exhibit strong positive correlations with ammonium and DOC, and strong negative correlation with discharge (Fig. 1B). This negative correlation facilitates the estimation of wet-weather concentrations using dry-weather concentrations and discharge measurements. This is illustrated with the example of cyclamate, where wet-weather concentrations can be predicted fairly accurately (SI Fig. 16). The mean absolute percentage error (MAPE) for all indoor substances is generally low (< 40 %) across events (SI Fig. 18). However, accurate predictions require a high-resolution daily pattern for the dry-weather concentrations, as using daily mean concentrations leads to higher errors. Hence, wet-weather concentrations of indoor substances not only depend on dilution but also on the time of day. Previous research has shown similar strong daily variations in the inflow to a WWTP during dry weather (Koke et al., 2022). The high correlation (median corr. coeff.: 0.61) of ammonium with indoor MP also during dry weather (SI Fig. 17) suggests that the daily pattern of ammonium can serve as a proxy for daily MP variation. Calculating wet-weather concentrations based on the daily ammonium pattern and the daily mean MP concentration only slightly increases the MAPE. The strong correlation between indoor substances and ammonium primarily applies to substances, such as pharmaceuticals, excreted by humans. This correlation may be weaker for substances originating from other indoor sources, such as washing machines, dishwashers, or showers.

Two events included a one-hour dry-weather period prior to the event, which slightly increased correlation of indoor MP with discharge, as dilution effects are more pronounced. However, as sampling dry-weather discharge is challenging due to clogging and the correlation did not improve significantly, it is recommended to start sampling during the first stormwater discharge.

3.1.2. Outdoors

3.1.2.1. Road substances. **Source selectivity.** The substances leaching from tire and road wear particles (TRWPs), 6PPD-quinone, 1,3-diphenylguanidine and HMMM, exhibit strong correlations with each other across all the events and in both catchments (Fig. 1B). The high correlation allows us to assign nontarget time series with similar patterns to this source.

Additional parameters. There is no correlation of road substances with ammonium, DOC, or discharge (Fig. 1B). The lack of correlation with ammonium and DOC is expected, because these parameters represent raw wastewater, whereas road substances are transported with stormwater. Although stormwater does contain DOC, its concentrations are much lower (4 – 16 mg/L from (Kalev and Toor, 2020; Lin et al., 2022; McElmurry et al., 2014)) compared to raw wastewater (40 mg/L, see SI Fig. 8). Therefore, DOC correlates well with indoor substances but not with road substances. The relationship between discharge and concentration shows a complex picture: initial concentrations increase at low discharge levels, then decrease at higher discharges due to stronger dilution effects (SI Fig. 19). Therefore, a minimum discharge is required to mobilize these tire-associated compounds, and above a certain discharge, dilution effects become more pronounced. Interestingly, concentration ranges and median concentrations of each compound are similar for both catchments (SI Fig. 7), suggesting independence from catchment size.

Analysis of mass vs. volume distribution [M(V)] curves in Fig. 2 reveals constant wash-off of tire-associated compounds during storm events without following a first-flush pattern, defined as 80 % of the cumulative mass transported in the first 30 % of discharge (Bertrand-Krajewski et al., 1998). Furthermore, concentrations remain consistently above the LOQ. Thus, the wash-off process appears to be transport-limited rather than source-limited. Similar patterns have been observed in urban streams, where concentrations of tire-associated compounds remained elevated throughout and even after rain events (Johannessen et al., 2022; Peter et al., 2020; Rauert et al., 2022). Moreover, no clear correlation emerges between maximum event concentration and the number of antecedent dry-weather days (SI Fig. 20), which aligns with previous studies (Challis et al., 2021). These findings imply a substantial deposit of TRWPs in the catchments which is not depleted during single rain events. However, the origins of these sources, whether from roads, gully pots, or road embankments, remain unclear. Lab-scale experiments in a former study demonstrated that over 80 % of the leachable compounds in tires are not completely leached out after 28 days of contact with water (Muller et al., 2022). This underscores the necessity of not merely retaining TRWPs, as in a filtration system, but regularly removing them from the catchment and treatment system to prevent continual organic MP release. However, the lack of correlation between concentration and dry days may also stem from uncertainties over the minimum rain intensity and duration required for mobilization as well as the large variability in maximum discharge for the different events.

Although some knowledge is available on TRWP accumulation and wash-off processes (Unice et al., 2019), further investigation is needed into the leaching mechanisms of polar organic compounds from these particles and their transport by stormwater (Wagner et al., 2018). Moreover, identifying the primary sources of TRWPs in the catchment is crucial for designing effective mitigation measures.

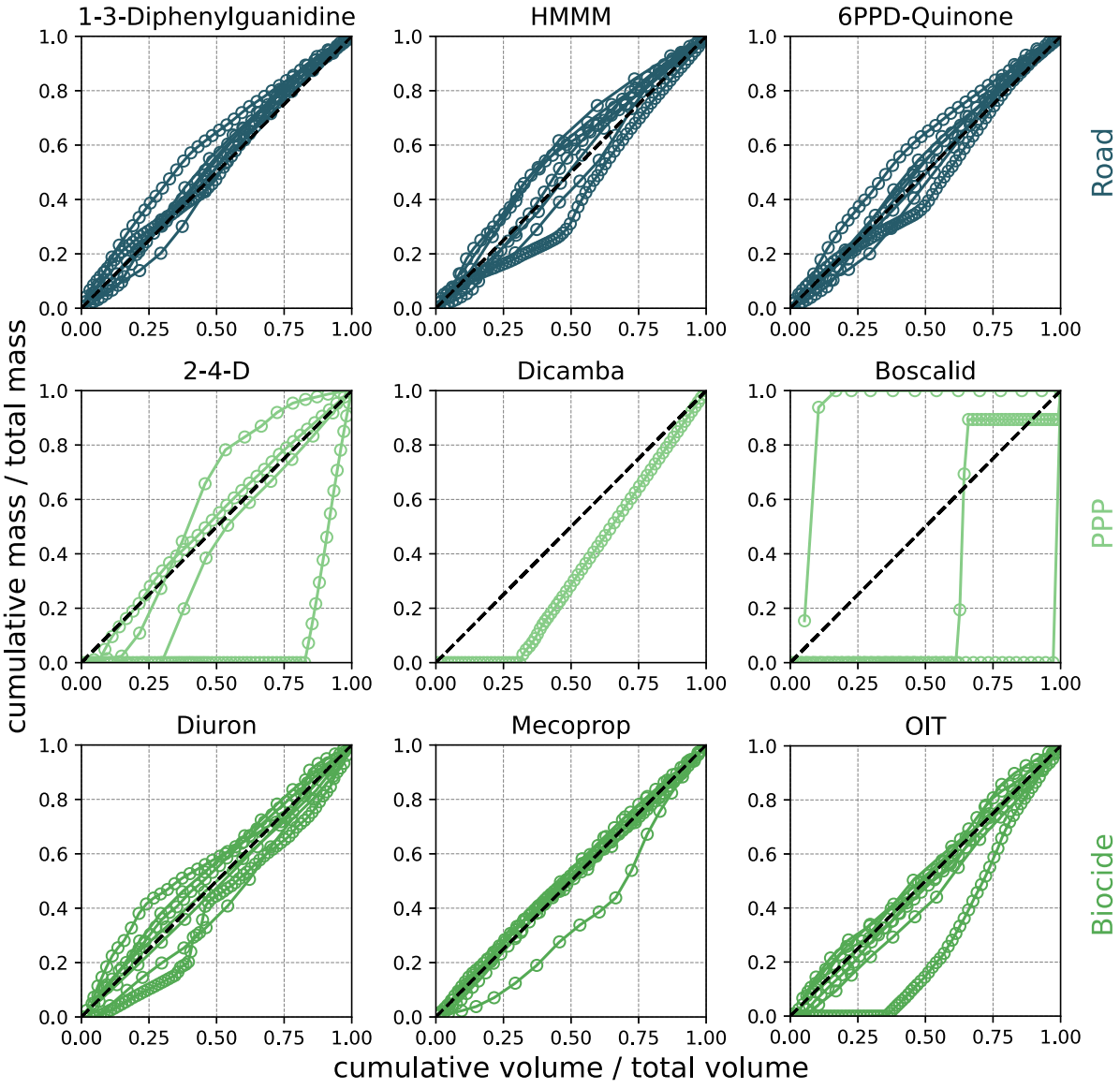

Fig. 2. Mass vs. volume [M(V)] curves of tire-associated compounds, plant protection products, and biocides, each for all events in the large catchment. Mecoprop is categorized as 'biocide', as suspected main use in material protection.

3.1.2.2. Pesticides. In this substance class, we distinguish between PPPs and biocides; some substances can fall into both categories (SI Tab. 4). The PPPs are applied in agriculture, urban green areas, and private gardens to control plant growth. Biocides can have various applications. Material protection agents, for example, are incorporated in facades and roofs to minimize fouling.

Source selectivity. Pesticides do not correlate with each other or with ammonium, flow, or DOC (Fig. 1B). There are a few exceptions, such as 2,4-D with MCPA and terbuthylazine in the small catchment and terbutryn/prometryn with isoproturon in the large catchment. This could be due to shared products or co-application. Overall, the diverse dynamics make pesticides unsuitable for source allocation of nontarget compounds.

This lack of correlation is evident in the relative concentrations of pesticides (Fig. 1A), which exhibit either isolated peaks at different time points or sustained elevated levels. This variability can be attributed to the distinct application modes of PPPs and biocides.

PPPs, when applied temporarily, undergo a source-limited wash-off process, leading to short, isolated peaks with varying timings that challenge the notion of a first-flush pattern (Fig. 2). Similar findings have been reported in agriculturally influenced small creeks, revealing varied temporal patterns (la Cecilia et al., 2021) and different wash-off times (Stravs et al., 2021), and in runoff from agricultural fields, showing no first flush of PPPs (Lefrancq et al., 2017). Possible explanations for these delayed occurrences include different traveling times within a catchment depending on distance, slope, inhomogeneous rain patterns, and different wash-off processes. In contrast, biocides, mainly from construction materials, constitute continuous sources and result in elevated concentrations throughout events, represented by linear M(V) curves. Studies have also found no first flush pattern for biocides from construction materials (Burkhardt et al., 2011). Exceptions such as diuron and isoproturon, both of which exhibit short, high peaks in August and May events, may be due to illegal continued use, because these were banned only recently, or encapsulation in paint, where only the top layer of chemicals is washed out by stormwater.

Mecoprop, used as both PPP and material protection product, shows 10 times higher concentrations in June, indicating additional PPP application. Interestingly, this is reflected in the concentration dynamics, resulting in a nonlinear M(V) curve (Fig. 2). This illustrates that high temporal resolution data can help in identifying the application of a

pesticide, especially with multiple authorized uses.

Additional parameters. Concentrations of the pesticides (SI Fig. 21) tend to be high in the months between March and June and very low from September to November. Six substances show high concentrations in only one month, indicating single rather short application periods. This indicates that the season in which samples are taken matters strongly when investigating pesticides. Similar findings were reported in a prior study which demonstrated that understanding seasonal occurrence and mobilization during rainfall can aid in determining whether a substance originates from agricultural or urban sources; agricultural sources typically exhibit pronounced seasonal variation, and urban sources remain relatively constant throughout the year (Wittmer et al., 2010).

3.2. Dynamics of nontargets

3.2.1. Source allocation of nontargets

As shown in the previous Chapter 3.1, only indoor substances in the large catchment and road substances in both catchments show source-specific dynamics and can therefore be used for source allocation of nontarget time series.

In total, 21,473 nontarget time series were derived for Event 1 (09.05.2023) and 25,372 for Event 2 (22.06.2023). The prioritization steps for the nontarget time series (SI Fig. 27) reveal that the 20 % of time series with the highest intensities comprise 80 % of the total summed intensities with 82 (0.4 %) time series showing maximum concentrations exceeding 1E+09 for Event 1 and 77 (0.3 %) for Event 2. The filtered nontarget time series were classified, which resulted in the allocation of several thousand time series to one of two classes, indoors and roads (Fig. 3).

Indoors. Several thousand nontarget time series (Event 1: 3469, Event 2: 4778) show similar dynamics as the indoors target MPs; high concentrations in dry-weather samples and decreasing concentrations with increasing stormwater discharge indicate indoors as the most likely source. In a previous study, an extensive screening of raw wastewater for organic MPs revealed a substantial number of 398 detections from 2316 targets, supporting our findings that raw wastewater can contain a large number of organic MPs (Gago-Ferrero et al., 2020). Another study conducting nontarget analysis in WWTP effluent found only 4 out of the 30 most intensive peaks were targets, despite over 100 quantified targets (Schymanski et al., 2014). Hence, the large number of over 1000 nontarget MPs from the indoor source in our study seems plausible.

Roads. This class with tire-associated substances contains a few hundred nontarget compounds (event 1: 154, event 2: 488). This underscores the importance of TRWPs as a substantial organic MP source in urban areas, and they should be considered when investigating stormwater contamination. Prior studies have already emphasized the role of traffic, particularly tire wear, as a source of organic MP and other contaminants (Awonaike et al., 2022). Lab-scale leachate tests revealed that tires can leach a substantial number (145) of organic MPs, with a majority being sufficiently polar to be mobile in aquatic systems (Muller et al., 2022). Previous nontarget analysis of roadway runoff detected between 443 and 1061 nontarget compounds per site (Peter et al., 2019). Moreover, the relevance of tire wear leachates is amplified by their bioaccessability (Masset et al., 2022) and ecotoxicity (Chibwe et al., 2022; Tian et al., 2020). Hence, identifying the most critical tire wear compounds and expanding the target lists for stormwater contamination becomes crucial and should be part of future research. The high number of nontarget MPs from stormwater aligns with previous findings, where thousands of nontarget compounds were detected in stormwater in several watersheds (Peter et al., 2022). It is possible that not all nontarget MPs within this class originate from tire wear leachates, as substances applied in other domains with a large source, such as biocides in material protection, can exhibit similar transport-limited behavior. Nonetheless, we assume that the number of biocides applied in material protection is likely small compared to the diverse array of organic MPs present in tire wear.

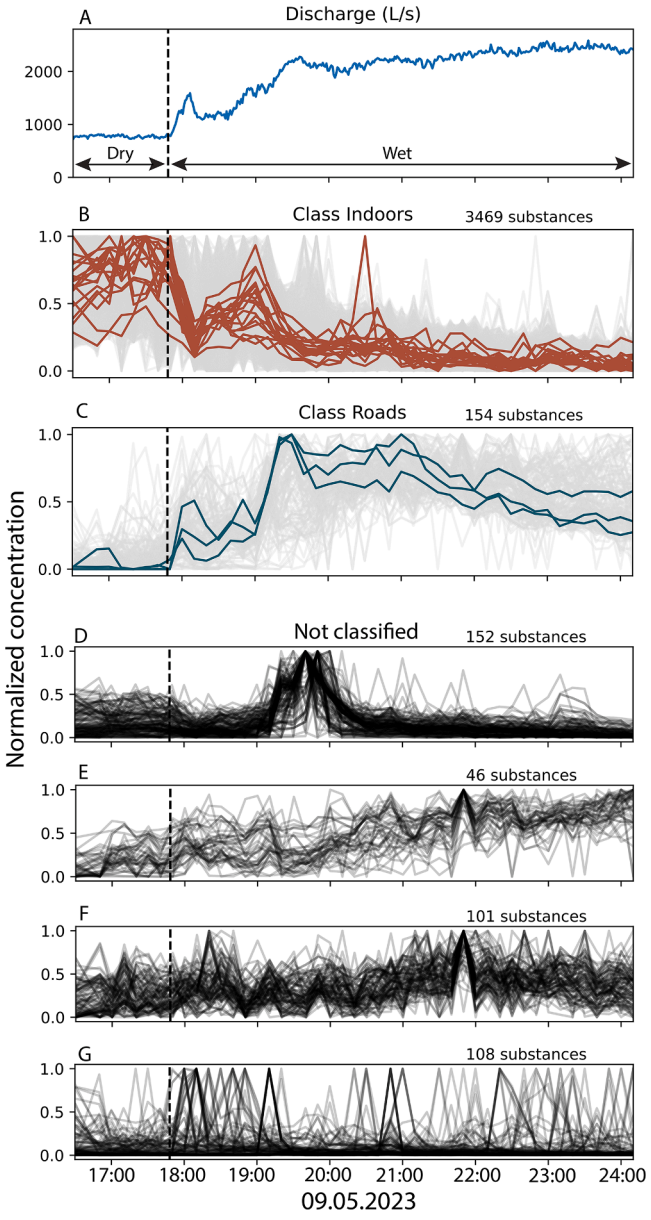

Fig. 3. Event from 9.5.2023 in the large catchment. A) Discharge at inflow CSO with 1h dry weather followed by 7h wet weather, with dashed line indicating start of stormwater discharge. B) – C) Classification results of normalized (by mean intensity) nontarget time series (grey) with similar dynamics as the target substances for indoor (red) and road (blue) substances. D) – G) Clustering results of 2000 top priority nontarget time series (normalized by mean intensity) which were not classified as indoors or roads. Dates format: DD.MM.YYYY.

Both events show similar numbers of nontarget MPs per class, supporting the effectiveness of the nontarget workflow (second event see SI Fig. 29). The fact that the indoors class has roughly ten times more nontarget time series than the roads class indicates that raw wastewater contains much more diverse organic MPs than road runoff. It should be noted that our current analysis focuses solely on the numerical count of nontarget MPs within each class. Future research requires identification of the individual compounds, followed by the determination of their concentration and ecotoxicological significance. This is crucial for gaining a comprehensive understanding of the importance to attribute to each pollution source.

The nontarget analysis workflow is subject to uncertainty, arising from such processes as peak picking, time series construction, filtration,

and the impracticality of manually verifying all derived time series for true and false positives. Especially filtering based on intensity results in substances with poor ionization or low intensities not being considered. Additional uncertainties arise from the small set of road substances as input to the classification and the consideration of only the positive mode. Thus, the absolute number of allocated nontarget time series per source should be treated with caution, but it provides a first insight into the estimation of relative importance of various sources and the extent to which we underestimate the organic pollution situation with existing target lists.

3.2.2. Further dynamics

The unassigned time series from Section 3.2 were prioritized by their maximal intensities, because higher intensities typically correspond to higher concentrations. We then clustered the top 2000 time series to uncover additional temporal patterns beyond those represented by the target substances. In Fig. 3 (D–G), four clusters are displayed (all clusters see SI Fig. 30 and second event see SI Fig. 31). Cluster D shows a single peak occurring two hours after the start of storm event, suggesting a source-limited wash-off process, which could be a PPP. Clusters E and F exhibit higher concentrations during wet weather compared to dry weather, with cluster E showing slightly higher concentrations during the first 2 h of increased flow and cluster F showing elevated concentrations throughout the storm event. Cluster G displays single peaks that could stem either from indoor substances with few consumers or from PPPs. Overall, clustering the remaining nontarget time series reveals further dynamics not necessarily represented by target substances. Hence, this approach provides a more holistic overview of potential MP dynamics in CSO. Even though the specific sources and identity of the substances remain unknown, the approach aids CSO management by revealing that organic MPs exhibit various patterns beyond a distinct first flush.

4. Conclusions

- Dissolved organic MPs show diverse temporal patterns during CSOs, influenced by source and catchment size. Indoor MPs dilute with increasing stormwater, while outdoor-applied MPs like tire wear leachates and pesticides exhibit elevated concentrations during wet weather, with either source- or transport-limited wash-off. Tire-associated substances exhibit transport-limited wash-off behavior, indicating large reservoirs within the catchments, which might be problematic due to long-lasting leaching effects. Consequently, traditional first-flush retention strategies may be insufficient to effectively protect water bodies, especially as concentrations of numerous substances persist above their LOQ throughout CSO events. Further research is needed to compare these concentrations with ecotoxicological data for optimal management strategies.
- Consistent source-specific dynamics were observed for indoor substances in the large catchment and tire-associated compounds in both catchments. In the large catchment, indoor MP concentrations during CSOs correlate with discharge and ammonia, and could be predicted based on dry weather concentrations and dilution.
- No consistent source-specific dynamics emerged for indoor sources in the small catchment or for pesticides in either catchment. This complicates monitoring, as it becomes difficult to identify suitable proxy signals, as well as modelling and optimizing mitigation measures, as a wide range of potential dynamics must be considered. This complexity is particularly true for small catchments, where we only observed source-specific dynamics for tire wear leachates. Hence, for CSO catchments of similar or smaller size, assessing and predicting MP dynamics is challenging.
- Nontarget analysis reveals thousands of organic compounds in CSOs, underscoring their significance as pathway of a wide range of organic MPs entering open water bodies. Source allocation of nontargets detected several thousand indoor substances, emphasizing the importance of raw wastewater as an MP source, even when diluted. Around 150 substances with transport-limited wash-off behavior, likely from road runoff, were detected, indicating that road runoff is an underestimated pollution source. Our current target list vastly underestimates the numbers of present MPs, emphasizing the need for broad screening methods and nontarget analysis. Future research should also investigate the ecotoxicological relevance of nontarget compounds, as their impact cannot be determined by their numbers alone.
- Exploring the dynamics of nontarget time series unveils temporal patterns beyond those of target time series, increasing the variety of possible MP dynamics that need to be considered in CSO management. Even without identifying these substances, clustering nontarget time series offers valuable insights for future studies by providing a more holistic view of pollution dynamics. It also helps to prioritize identification efforts towards clusters that are not represented by targets, contain large numbers of nontargets, or show patterns that cannot be explained with the current knowledge of systems and processes.

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Data availability

All data is available through Eawag's Research Data Institutional Collection (ERIC-open) at https://doi.org/10.25678/000DNY.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the authors used ChatGPT in order to improve language. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

CRediT authorship contribution statement

Viviane Furrer: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Andreas Froemelt:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Heinz Singer:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Christoph Ort:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Viviane Furrer reports financial support was provided by Federal Office for the Environment. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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