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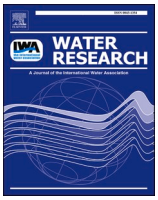

Realistic exposure scenarios in combined sewer overflows: how temporal resolution and selection of micropollutants impact risk assessment

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ABSTRACT

Organic micropollutants in combined sewer overflows (CSOs) pose a potential risk to aquatic ecosystems. Previous studies mainly reported event mean concentrations (EMCs) and often focused on a small number of substances. This study presents realistic exposure scenarios using high-temporal resolution (10-minute) data from 24 events at two CSO sites. We analyzed 49 dissolved organic micropollutants for all events and 198 for four events, including pharmaceuticals, pesticides, and road-related compounds, of which we detected 83 substances at least once. From these, we assessed the mixed chemical risk by applying acute quality criteria and evaluated how the risk assessment outcome changes for two aspects: temporal resolution and selection of substances. Our results reveal that total risk quotients (RQ_{tot}) can vary greatly within CSO events, with 10-minute data capturing peak concentrations that are missed with EMCs. Using EMCs underestimates the maximum RQ_{tot} of an event by a median factor of 4.9, up to a maximum factor of 6.9. When comparing a selection of 20 substances from the Swiss Waters Protection Ordinance to a broader list of 49 substances commonly detected at CSOs and a comprehensive list of 198 substances, the estimated RQ_{tot} increases between 1.1 to 2.3-fold. RQ_{tot} values exceed the threshold of 1 in 75 % of the events, requiring further dilution in the receiving water body. All three pollutant classes (pharma, pesticide, road) drive the total risk, and no specific phase during overflow events consistently poses higher risk than other phases, which challenges the design of effective mitigation measures. Furthermore, the exposure scenarios presented here offer essential input for future ecotoxicological research as they reveal high short-term fluctuations in RQ_{tot} whose ecological significance is still largely unknown.

1. Introduction

Organic micropollutants can adversely affect surface water quality and pose risk to the aquatic environment. Extensive monitoring of European rivers has shown that organic micropollutants exceed their acute or chronic ecotoxicological thresholds in 77 % of cases (Finckh et al., 2024), and over 200 bioactive anthropogenic contaminants, such as pesticides and pharmaceuticals, have been detected in US surface waters (Bradley et al., 2017). In urban areas, these anthropogenic pollutants primarily enter surface waters through effluents from wastewater treatment plants (WWTPs) and through untreated discharges from combined sewer overflows (CSOs) and stormwater outlets (SWOs). CSOs release a mixture of untreated raw wastewater and stormwater into open waters during storm events, posing potential risks to aquatic ecosystems (Andre et al., 2024; Gasperi et al., 2012; Petrie, 2021) and their frequency and duration will increase due to climate change (Rodriguez et al., 2024).CSOs contain a complex mixture of pollutants, such as nutrients, solids, heavy metals, and organic micropollutants. In particular, the ecotoxicological risk of dissolved organic micropollutants is still poorly estimated due to limited data availability (Perry et al., 2024).

Monitoring data over the past decade has shown that many micropollutants in CSOs exceed or approach their ecotoxicological thresholds

Abbreviations: AQC, acute quality criteria; CQC, chronic quality criteria; CSOs, combined sewer overflows; EMCs, event mean concentrations; LC-HRMS, liquid chromatography high-resolution mass spectrometry; LOQ, limit of quantification; MAC-EQS, maximal allowable concentration environmental quality standard; PPP, plant protection products; RQ, risk quotient (per substance); RQ_{tot}, total risk quotient; SWO, stormwater overflows; WFD, water framework directive; WPO, waters protection ordinance; WWTP, wastewater treatment plant.

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(Mutzner et al., 2022), and their combined effects might be even stronger than the estimates for single substances. Modelling chronic environmental risk indicates that CSOs are more important than WWTP effluent for certain substance classes (Ianes et al., 2023). CSOs discharge a mixture of raw wastewater and stormwater. Raw wastewater contains a wide range of ecotoxicologically relevant organic micropollutants such as pharmaceuticals, pesticides, plastic additives, surfactants, and other substances applied in urban areas (Finckh et al., 2022). In stormwater, the maximum reported concentrations of various pesticides exceed acute quality standards (Spahr et al., 2020), and high levels of insecticides from urban outdoor application and biocides from facade protection pose a strong potential threat to aquatic organisms (Beckers et al., 2018). A comprehensive literature review identified over 80 organic chemicals in stormwater at concentrations posing high ecological risk (Zhang et al., 2024). Another study found stormwater runoff from roads to be highly toxic to coho salmon (Tian et al., 2020). Furthermore, bioassay tests have shown that stormwater toxicity levels are comparable to those of secondary treated wastewater effluent (Tang et al., 2013).

Despite these indications of potential risk from organic micropollutants in CSOs, thorough risk assessments are hindered by the lack of concentration measurements at high temporal resolution, leading to potential underestimation of peak concentrations. Traditionally, organic micropollutants in CSOs are reported as event mean concentrations (EMCs), but concentrations can vary substantially within a single event (Furrer et al., 2023). Considering only low temporal resolution data may lead to a considerable underestimation of ecotoxicological risk, as shown by pesticide screening in a small stream (la Cecilia et al., 2021). Another typical limitation of chemical risk assessment is the narrow range of substances monitored. Comparing ecotoxicological effects with target substances often reveals a gap in accurately predicting observed toxicity (Neale et al., 2017), indicating that target lists often miss important toxic substances.

This study aims to provide more realistic exposure scenarios at high temporal resolution. We use 10-minute monitoring data from two CSO sites for 24 overflow events to investigate the influence of temporal resolution and substance selection on the chemical risk assessment of polar, dissolved organic micropollutants. Total risk quotients (RQ_{tot}) were calculated with acute quality criteria and the concentration addition concept. We compare peak RQ_{tot} values from data collected at 10-minute intervals with EMCs and evaluate the outcome for three substance lists: (1) 20 substances from the Swiss Waters Protection Ordinance (WPO), (2) 49 substances frequently monitored in CSO studies, and (3) 198 substances for which acute environmental quality criteria (AQC) are available and that are suitable for quantification (chemical standard available, good analytical performance). The results provide insights into the temporal dynamics of RQ_{tot}, reveal risk driving substances, and quantify the impact of temporal resolution and substance selection on risk assessment outcomes.

2. Material and methods

2.1. Data acquisition

Two CSO sites in Switzerland were investigated. The first CSO site, CSO A, 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. An effective hydraulic area of 17 ha_{red} and 2700 people are connected to the combined sewer system. A retention basin with 230 m^3 stores the initial discharge of an overflow event. The second CSO site, CSO B, lies in a much larger catchment (368 ha_{red}, 159,000 people) that also consists primarily of residential areas, roads, agriculture, and a small amount of industry. A retention basin with storage capacity of 3000 m^3 is available.

An automated sampler (MAXX TP5C) collected grab samples at 2-minute intervals (150 mL each), pooling five consecutive samples to 10-minute composite sample (750 mL). Samples were collected at the inflow channel of the CSO structure, upstream of the side weir and retention basins (SI1, Fig. 1 & 2). The sampler was automatically triggered by the increasing water level once it exceeded the maximum dry weather flow. Consequently, samples were already taken before overflow occurred, thus capturing micropollutant dynamics during the beginning of a rain event when the retention volume started to be filled. We collected 16 overflow events at CSO A, and 8 at CSO B. The samples were analyzed for organic micropollutants with liquid chromatography (water–methanol gradient) followed by high-resolution mass spectrometry (Q-Exactive, Thermo Fischer) (LC—HRMS) with electrospray ionization in two separate runs for positive and negative mode. 198 target compounds were quantified by using reference standards and 138 identical or similar isotopic-labelled standards as internal standards. More detailed information on the study sites, sampling and analytical procedure, and additional measurements can be found in our previous study (Furrer et al., 2023).

2.2. Risk assessment

2.2.1. Environmental quality criteria

To assess the ecotoxicological relevance of the substances detected, we applied the AQC, also known as the maximum allowable concentration EQS (MAC-EQS), because CSO events typically last only several hours. AQCs are based on results from short-term bioassays with an exposure duration of 48–96 h, whereas chronic quality criteria (CQC) are based on ecotoxicity data from chronic exposures, for which 2-week averages are more representative (Ashauer et al., 2020). We used the AQC values from the Swiss Ecotox Centre, which provides values for a total of 359 substances (Ecotox Centre Switzerland, 2024). The AQC were derived according to the guidance for deriving environmental quality standards (EQS) under the EU Water Framework Directive (WFD) (European Commission, 2018). These AQC values are classified into three robustness levels: (1) high robustness criteria from the Swiss Ecotox Centre, (2) high robustness criteria from European authorities, and (3) ad hoc values from either the Ecotox Centre or European authorities for orientation of possible risk. In addition, we used the ad hoc AQC value for 1–3-diphenylguanidine of 14 µg/L, which is not included in the Swiss Ecotox Centre's list, to rate a road runoff compound (ANSES, 2020).

2.2.2. Risk quotient

To determine the risk of a substance at a given time, we divide its concentration by its AQC value (Eq. (1)). If the resulting risk quotient (RQ_i) lies above 1, toxic effects are to be expected; if it is below 1, toxic effects from this substance are not expected. However, CSOs contain a complex mixture of at least several hundred substances. Therefore, we also calculate the RQ of the mixture (RQ_{tot}) (Eq. (2)) by summing the individual RQ_i of all substances at a given time point following the concept of concentration addition (Loewe and Muischnek, 1926). This approach aggregates the risks of individual substances regardless of their modes of action, providing a conservative risk estimate that tends to overestimate the risk. If only a few substances drive the overall risk aggregation, this overestimation remains within acceptable limits (Price and Han, 2011). A refinement of the risk estimation is possible in a later stage (Backhaus and Faust, 2012; Spycher et al., 2018).

$$RQ_i(t) = \frac{c_i(t)}{AQC_i} \quad (1)$$

$$RQ_{tot}(t) = \sum RQ_i \quad (2)$$

2.2.3. Discharge

A CSO occurs when the discharge exceeds the capacity of the sewer pipes and/or the WWTP. Figure 3 in SI1 shows a typical overflow event. During wet-weather, discharge in the sewer increases above dry weather

flow due to additional stormwater. Combined sewer system and WWTP have typically a higher capacity than the maximum dry weather flow (often 2–3 x dry weather). Once the inflow to the CSO structure exceeds this capacity, excess water is released into nearby water bodies. If a retention basin is available, part of the overflow can be temporarily stored. Overflow continues until the inflow drops below the capacity limit. The content of the retention basin is transported to the WWTP once dry weather conditions are reached.

In this study, we started to sample the overflow events once the inflow exceeded the maximum dry weather flow. For the following analysis, we used the micropollutant data collected during periods when the potential overflow exceeded 0 L/s, making the results independent of the actual retention basin size at the sites. However, for the dilution calculations, we considered the real overflow.

2.2.4. Dilution

A risk quotient above 1 in the CSO does not necessarily indicate a risk to the receiving water body because the CSO discharge is diluted by the river's flow. The final risk quotient is determined by this dilution and the background concentration of the receiving water body (Eq. (3)).

$$RQ_{river}(t) = \frac{RQ_{CSO}(t) * Q_{CSO}(t) + RQ_{river}(t) * Q_{river}(t)}{Q_{CSO}(t) + Q_{river}(t)} \quad (3)$$

To assess the risk in the receiving water body, we calculate the dilution using both the discharge of the real water body at the monitoring sites and a general approach with three typical size categories (small, medium, large) of Swiss rivers (SI1 Fig. 5). In both cases, we neglect the background micropollutant concentration in the rivers from upstream pollution. An overview of the discharges at the CSO overflow and the real receiving waterbodies, including the corresponding dilution factors, can be found in SI1 Fig. 4. For the three size categories, we used the Swiss river network divided into stream orders, with medium annual discharge data available for each stream order (FOEN, 2024). For each size category, we used the mean discharge from the stream orders (SI1 Tab. 4).

2.3. Temporal resolution

2.3.1. Duration of RQ_{tot} exceeding 1

For each event, we calculated the duration during which the RQ_{tot} exceeded 1. This calculation includes both the absolute duration for which $RQ_{tot} > 1$as well as the percentage of the total overflow duration during which RQ_{tot} was larger 1.

2.3.2. Influence of temporal resolution on maximum RQ_{tot}

To assess the influence of the temporal resolution, we compare the estimation of the maximum RQ_{tot} of each event using (1) 10-minute resolution data and (2) EMC values. The maximum RQ_{tot} refers to the highest RQ_{tot} value within an event: for 10-minute resolution data, this corresponds to the highest 10-minute RQ_{tot} value, while for the EMC scenario, it is the RQ_{tot} based on EMC values. The EMC was calculated from the 10-minute data using Eq. (4). It represents the flow-proportional mean concentration over the entire event and is commonly used in studies investigating organic substance concentrations during CSOs to reduce analytical efforts.

$$EMC = \sum (c_n * V_n) \Big/ \sum V_n \quad (4)$$

c_n: measured concentration of sample number 'n', V_n: measured volume of stormwater of sample 'n'

2.4. Substance selection

Three sets of substances were used to test the influence of the substance selection on the estimated RQ_{tot}. All substances were quantified through target analysis (see Section 2.1).

2.4.1. Swiss waters protection ordinance

The first substance list consists of legal thresholds for surface water quality in Switzerland. The Swiss WPO regulates 21 organic chemicals with AQC values, which are also included in the Swiss Ecotox Centre's list (see 'Swiss_WPO' in SI2). The WPO values are comparable to EQSs under the EU WFD and were consulted during the revision of the priority substance list. The AQC should never be exceeded at any time in any Swiss open water body. Our analytical method enabled us to measure all of the substances on the WPO list except cypermethrin. Thus, our final list contains 20 substances: 2 pharmaceuticals and 18 pesticides. We screened for substances on this list for all events at both sites.

2.4.2. Typical CSO substances

This target list consists of the 20 compounds from the Swiss WPO plus 29 organic compounds that are often found in CSOs, stormwater, or raw wastewater and for which an AQC is available from the Swiss Ecotox Centre. These substances originate from various sources and include 19 pharmaceuticals, 27 pesticides, 1 from road runoff, and 2 others (see 'Typical_CSO' in SI2). All events at both sites were analyzed for these 49 compounds.

2.4.3. Comprehensive list

The comprehensive target list includes 198 substances with available AQC values and a good analytical performance (available chemical standard, sufficient sensitivity). The list comprises 159 pesticides, 29 pharmaceuticals, 1 road-related compound, and 9 others (see 'Comprehensive_list' in SI2). These substances were analyzed only for selected events due to the high effort of evaluation: three shorter events at CSO A and one long event at CSO B (SI1 Tab. 1). Due to matrix interferences, the concentration of carbendazim and diazinon could not be determined in CSO B.

The distribution of AQC values per robustness class can be found in SI1 Table 3. The comprehensive list contains 72 of the total 91 AQC values with robustness class 1.

2.4.4. Influence of substance selection

To test the influence of the three substance lists on the estimated RQ_{tot}, we evaluated various metrics. First, we depicted the boxplot of all RQ values for each substance over all events per site, ordered by decreasing median RQ. To calculate the median, we excluded all values lower than the limit of quantification (LOQ), to not underestimate the relevance of substances that are applied only temporarily, such as pesticides. From these, we displayed the top 20 substances distributed across the three substance lists and indicating the substance source. Then, we calculated the number of substances detected above LOQ and the RQ_{tot} values in each sample for the three lists.

2.5. Temporal resolution vs. substance selection

To compare the influence of the temporal resolution directly with the substance selection, we calculated the maximum RQ_{tot} of each event for the three substance lists and two temporal resolutions (10-min vs. EMCs). Because the comprehensive list was not evaluated for all events, we computed the maximum event RQ for the WPO and CSO list for two cases: (1) for all events and (2) for only the events for which the comprehensive list was assessed. We then calculated the ratios of the median and maximum values between the scenarios:

1. **Temporal resolution:** We compared the 10-minute and EMCs results for each substance list separately. With the WPO and CSO lists, the comparison was based on all events, whereas in the case of the comprehensive list, the comparison was based on the limited number of events (3 events at CSO A, 1 event at CSO B).
2. **Substance selection:** We compared the substance lists with each other for the 10-minute resolution scenario. Specifically, we compared the WPO with the CSO list based on all events and both the

WPO and CSO lists were compared with the comprehensive list based on the limited number of events.

3. Results and discussion

In the following sections, we investigate the influence of the temporal resolution and the substance selection on the estimated chemical risk of dissolved organic micropollutants in the effluent of CSOs.

3.1. Temporal resolution

The dynamics of the total risk from dissolved organic micropollutants of different CSO events are highly diverse. Fig. 1 shows the dynamics of the RQ_{tot} based on individual RQ values within a single event for both sites (all events see SI1 Fig. 6 & 7). Substances from the categories *pharmaceutical, pesticide*, and *road-related compound* (categorization of each substance can be found in SI2) contribute to the RQ_{tot}. The figures include all substances evaluated for the corresponding events (49 substances for all except 4 events, 198 for the remaining 4 events (SI1 Tab. 1)). In our previous study (Furrer et al., in prep.), which analyzes source-specific dynamics of micropollutants at the same CSO sites, we found consistent concentration dynamics for road-derived substances in both catchments and indoor substances in the larger catchment (CSO B). However, indoor substances in the small catchment (CSO A) were too random due to the small number of point sources (consumers of pharmaceuticals), and plant protection products (PPPs) in both catchments show single peaks at different points in time, which indicates source-limited dynamics. As the risk from micropollutants is driven by both indoor and outdoor substances, these complex dynamics overlap, presenting challenges for the prediction of risk dynamics. Notably, no first-flush effect is observed for dissolved organic micropollutants, and elevated risk persists even after several hours of overflow. Nor is there any specific point in an event that is consistently more toxic, so partial overflow retention cannot fully protect receiving water bodies. Additionally, although more stormwater increases the dilution of indoor substances, stormwater itself can be a significant source of toxic substances. Therefore, higher discharge does not necessarily lower the risk, and future research should compare risk assessments between combined and separate sewer systems. To capture the start of a rain event, we collected samples in the influent to the CSO structure once the dry weather discharge was exceeded, which for some periods might be without actual overflow. When overflow occurs, the effluent concentrations correspond to the influent concentrations. In addition, the potential overflow indicates the emission if no retention basin would be available. Therefore, the risk presented here reflects a conservative estimate, which could potentially be decreased through partial retention.

The high temporal resolution data allows the estimation of the duration during which the RQ_{tot} exceeds 1 in the CSO effluent in each event (SI1 Fig. 8). The median absolute duration per event is 10 mins at CSO A, with a maximum of 220 mins, while at CSO B, the median duration is 130 mins, with a maximum of 330 mins. When the RQ_{tot} does exceed 1, it is not just for a single sample but for several consecutive ones. This is also reflected in the relative duration per event: for half of the events in CSO A and 75 % of the events in CSO B, the RQ_{tot} exceeds 1 for >50 % of the total event duration. If an event is deemed critical ($RQ_{tot} > 1$), it tends to be so for the majority of the overflow duration. However, this duration is still significantly shorter than the standard laboratory tests used to determine the risk of a substance, which typically last between 48 and 96 h for AQC. Future research is necessary to determine whether exposures of a few hours produce the same effects as those observed in acute toxicity tests. This outcome is highly dependent on the uptake characteristics and mode of action of the individual substances. Applying Haber's rule (effect = concentration × time), it can be assumed that the effects will be smaller and the risks lower.

3.2. Relevant substances

When examining the substances contributing to the total risk, only a few show substantially elevated RQ values. Fig. 2 shows the 20 substances with the highest median RQ_i from all events for both CSO sites (for all substances, see SI1 Fig. 9 & 10). Of the 198 substances, we found 83 at least once above LOQ. However, only 17 substances in CSO A and 22 in CSO B have at least one RQ value higher than 0.1. Notably, not all the top 20 substances are included in the Swiss WPO or the initial target list. For CSO A, three of five pharmaceuticals and six of thirteen pesticides are not covered by the Swiss WPO (CSO B: six of eight pharmaceuticals, seven of eleven pesticides). Given the limited number of substances contributing to the total ecotoxicological effect, the overestimation of the RQ_{tot} due to concentration addition without considering the mode of action is small. Of the top 20 list, 14 substances appear at both CSO sites, indicating that most substances are not site-specific. The top substances comprise pesticides, pharmaceuticals, and one road-related compound.

3.2.1. Pharmaceuticals

Among the pharmaceuticals, all except paracetamol, atorvastatin,

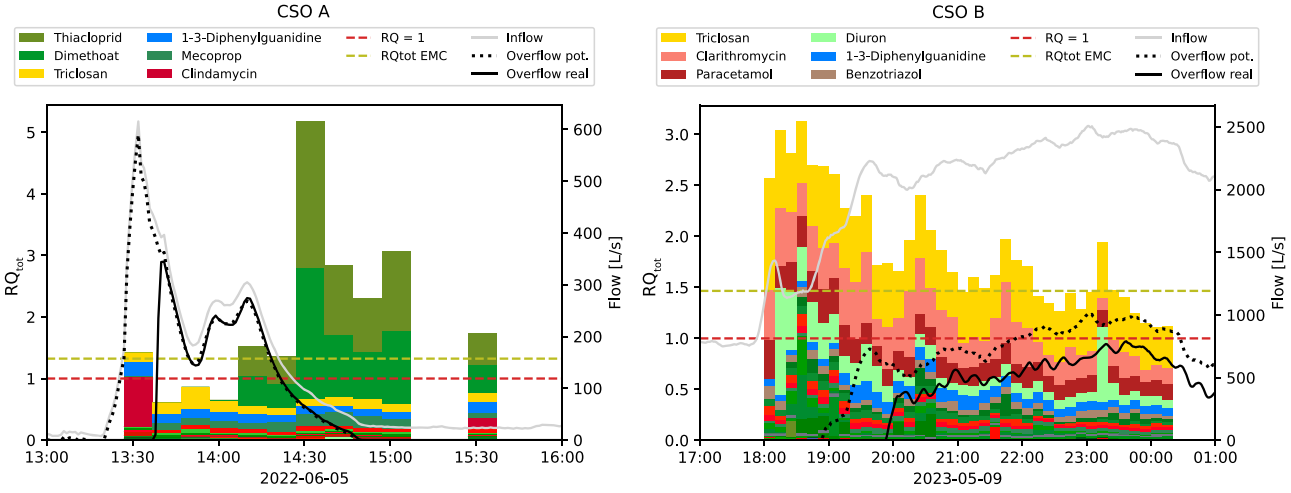

Fig. 1. RQ_{tot} over time at two CSO influents. **Left:** CSO A event 5.6.2022, **right:** CSO B event 9.5.2023. **Colors:** Red: pharmaceuticals, yellow: indoor biocides, green: pesticides, blue: road, grey: other; names of top six compounds in legend. **Horizontal lines:** Mean RQ_{tot} (dashed olive) and threshold of 1 (dashed red). **Flow:** Inflow to CSO (grey), potential overflow if no retention basin (dotted black), real overflow with actual retention basin (solid black).

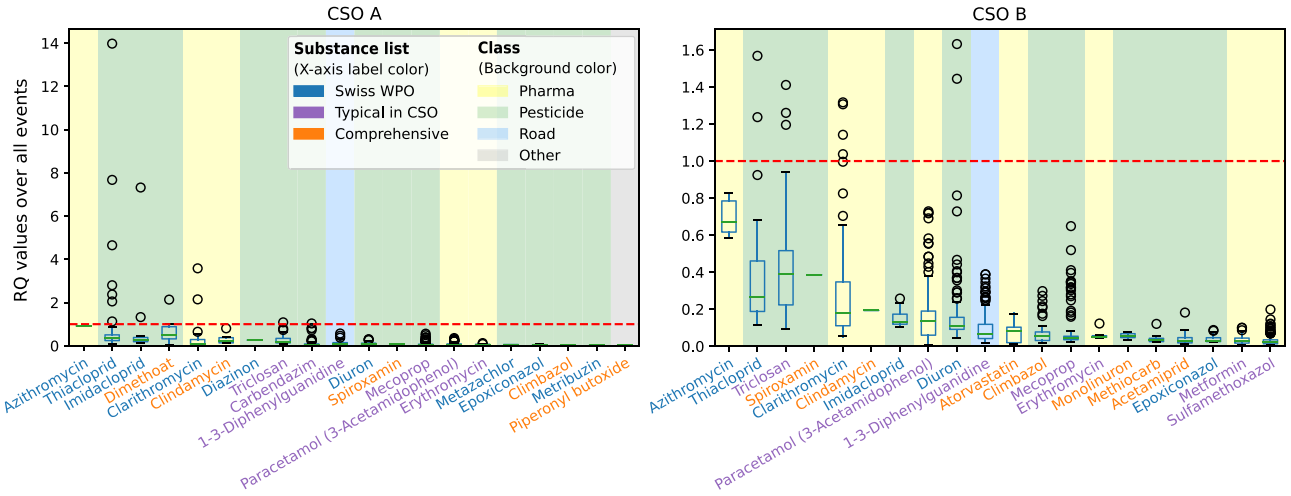

Fig. 2. Boxplot with RQ values assessed from all events in the CSO discharge of the top 20 substances sorted by median RQ. X-axis label color corresponds with the three substance lists: Swiss WPO (20 substances), typical substances in CSO (49 substances), and comprehensive list (198 substances). Background color corresponds with substance class: pharmaceutical, pesticide, road-related substance, and other. Left: CSO A, right: CSO B.

and metformin (Glucophage) are antibiotics (SI1 Tab. 5). This can be explained by the high prevalence of antibiotics in domestic wastewater (Wang et al., 2020) combined with their low AQC values. The release of antibiotics into the environment is also problematic due to the potential increase in antibiotic resistance (Wang et al., 2020). Far fewer AQC values are available for pharmaceuticals (31 values of our target list) than for pesticides (167 values). Notably, of the 29 pharmaceuticals with AQC and good analytical quality, we detected 28, compared to 48 out of 159 pesticides. Hence, we probably underestimate the risk posed by pharmaceuticals and developing more AQC values is crucial, including for nonantibiotic medications.

Diclofenac (no AQC, CQC: 50 ng/L) and ibuprofen (AQC: 1700 µg/L, CQC: 11 ng/L) show large discrepancies between their AQC and CQC values due to a very high acute to chronic ratio; hence, even though they do not appear problematic acutely, they could be a concern for longer exposures. Although CSOs typically last only a few hours, prolonged wet weather phases, such as in summer 2024 in Switzerland, can extend their impact, potentially contributing to chronic effects. However, WWTPs without advanced treatment remain the primary source of these indoor-applied compounds.

3.2.2. *Pesticides*

Among the top pesticides, four are only applied as biocides, three are exclusively used as PPP, mecoprop and acetamiprid are applied as both, and seven are not permitted for either use (SI1 Tab. 6). Of the banned substances, climbazole and triclosan are still allowed in other primarily indoor-use products (cosmetics, disinfectants), and thiacloprid, epoxiconazole, and dimethoate were only recently banned. We assume the illegal usage of remaining stock as a main reason for these detections and not leaching from soils, because they show short peaks indicating wash-off after usage (SI1 Fig. 11). Thiacloprid and epoxiconazole are both listed in the Swiss WPO, highlighting the need to regularly update the Swiss WPO to account for banned substances and their substitutes. Overall, biocides pose slightly higher risks than PPPs. This could be because biocides are applied throughout the year, whereas PPPs are used only seasonally, or because biocides are often applied in large deposits in wall paint or bitumenous flat-roof layers, which leach over longer periods.

3.2.3. *Road-related compounds*

Of the road-related compounds in our target list, only 1–3-diphenylguanidine has an AQC value and is among the top 20 substances in both catchments. With tire wear containing over 200 organic compounds (Muller et al., 2022), the toxic effects of these leachates may be underestimated with the currently available AQC values. The example of 6PPD-quinone highlights this concern, as it is toxic to coco salmons at very low levels. Although no AQC is available for 6PPD-quinone, its LC50 for different species ranges from 95 ng/L (Tian et al., 2022) to 1000 ng/L, and some species do not show a lethal effect at all (Brinkmann et al., 2022). The concentrations we measured of 50 to 100 ng/L fall within the range of possible lethal effects, indicating potentially problematic levels from CSOs. Detailed investigation of the ecotoxicity of tire wear leachates and the development of AQC values are crucial for their inclusion in future risk assessments.

3.2.4. *Comparison with literature*

Comparing the top 20 substances from our study with literature reveals that many have been reported in CSOs at similar risk levels. In a review by Mutzner et al. (2022), which compiled a decade of CSO micropollutant data based on EMCs, several of our top compounds were also detected: Diuron with an RQ greater than 1, triclosan, mecoprop, and carbendazim with RQs between 0.1 and 1 (detected at over 75 % of sites), and clarithromycin with RQs close to 1 (found at <50 % of sites). Finckh et al. (2022) screened 52 European WWTP effluents for 499 organic chemicals, identifying 32 substances of high concern. Our target list includes 19 of the 21 substances of high concern with available experimental AQC, 11 of which we detected with RQs of at least 0.1. Notably, our top 20 list contains seven pesticides and six pharmaceuticals not listed as of high concern by Finckh et al. (2022). This could be because pesticides primarily enter the sewer system through stormwater, making them less prevalent in elevated concentrations in WWTP effluents, and because biodegradable substances are degraded in WWTPs but are still present in CSOs. Recent monitoring campaigns in Swiss rivers have revealed that pyrethroids such as cypermethrin, lambda-cyhalothrin, and deltamethrin pose high risks to aquatic ecosystems (VSA, 2024). Unfortunately, our analytical method cannot detect these substances. Hence, even with our comprehensive list of 198 compounds, some relevant substances may be missed, potentially leading to an underestimation of the actual risk. This underscores the need to complement chemical risk assessment with effect-based screening methods such as bioassays.

3.2.5. *Influence of substance selection on number of detections*

The different lists result in varying numbers of substances detected (SI1 Fig. 12). As expected, screening for more substances generally increases the number of substances detected. However, the increase is not

proportional to the number of substances on the lists. For CSO A, expanding from the WPO (20 substances) to the CSO list (49 substances) leads to a 5.3-fold increase in the number of substances detected (CSO B: 4.5-fold), but further expanding to the comprehensive list (198 substances) results in only a 1.5-fold increase (CSO B: 1.9-fold). Similarly, Moschet et al. (2014) conducted a comparison of pesticides in small rivers and found that moving from a target list with 36 substances to a comprehensive list with 249 substances resulted in only a two-fold increase in substances detected and associated risk.

3.3. Temporal resolution vs. substance selection

Fig. 3 presents the maximum RQ_{tot} values of each event at CSO A and compares the three substance lists at both 10-minute resolution and EMCs (for CSO B, see SI1 Fig. 13). The two boxplots per substance list represent all events (left) and only the events for which the comprehensive list was assessed (right). The ratios between the median and maximum values across these scenarios for both sites are listed in Table 1.

To evaluate the influence of **substance selection** on the maximum event RQ_{tot}, the 10-minute resolution data are considered. With more substances investigated, the median increases, with the largest rise (2.3-fold) observed at CSO A from the WPO list to the CSO list. The maximum RQ_{tot} is identical across all three substance lists for CSO A, because imidacloprid and thiacloprid, which are responsible for these high risks, are included in the Swiss WPO. The number of events with an RQ_{tot} exceeding 1 increases from four for the WPO list to twelve for the CSO list at CSO A and from five for the WPO list to eight for the CSO list at CSO B.

Comparing the influence of **temporal resolution** on the maximum event RQ_{tot}, we observe that the values are consistently lower for EMCs than for 10-minute resolution data, with differences ranging from a factor of 2 to 4.9. This trend was expected, because with EMCs, concentrations are averaged over the event duration, which reduces peak values. The number of events exceeding an RQ_{tot} of 1 also decreases substantially for EMCs. Given that the AQC in the Swiss WPO should be maintained at any given timepoint, this underscores the fact that achieving high accuracy in risk assessment requires very high temporal resolution.

Overall, both, substance selection and temporal resolution affect the estimated maximum RQ_{tot} of an event, with temporal resolution having a stronger influence. Notably, some RQ_{tot} values may be derived from a single 10-minute sample. The ecological significance of these underestimations remains uncertain as the ecotoxicological impacts of very short-duration peaks are not fully understood. Furthermore, the impact of the substance selection may be more pronounced if additional substances, such as e.g. pyrethroids, are included in the analysis.

3.4. Dilution in receiving water bodies

CSOs discharge into open water bodies, often rivers, where pollutants are diluted before aquatic organisms are exposed to them. To assess the environmental risk, RQ_{tot} values in the receiving water bodies were calculated in four dilution scenarios: typical small, medium, and large Swiss rivers, and the actual conditions at the measurement sites. For the analysis, 10-minute data for all substances evaluated for the corresponding events are considered (49 substances for all except 4 events, 198 for the remaining 4 events (SI1 Tab. 1)). Fig. 4 shows boxplots of RQ_{tot} values across all events of each scenario per site.

For CSO A, the median RQ_{tot} lies well below 1 in the real scenario (0.07), as well as in all other scenarios. However, a few outliers exceed the threshold of 1, due to a single event in spring (5.5.2022), when the pesticide thiacloprid showed high concentrations. This highlights the importance of the sampling period, in this case the application of PPP, and the need to monitor the appropriate substances, as this exceedance was driven by a single compound.

For CSO B, the RQ_{tot} values are below 1 in the real as well as the medium and large river scenarios. In the small river scenario, the median, 0.8, is close to the threshold of 1, with a maximum of 2.4. Hence, the dilution in a small river is not sufficient to reduce the risk from a CSO connected to such a large catchment.

Because the median annual discharge was used for the calculation of the three Swiss river size scenarios while CSOs are only active during wet-weather periods, the dilutions of the RQ_{tot} values displayed here are a conservative estimate.

These scenarios illustrate that dilution in the receiving water is mostly sufficient to reduce RQ_{tot} values to below 1 for the CSO sites investigated and substances selected, and assuming no background concentration from upstream. However, at CSO A, a few RQ_{tot} values exceed 1 in the real river, indicating that the sampling period and

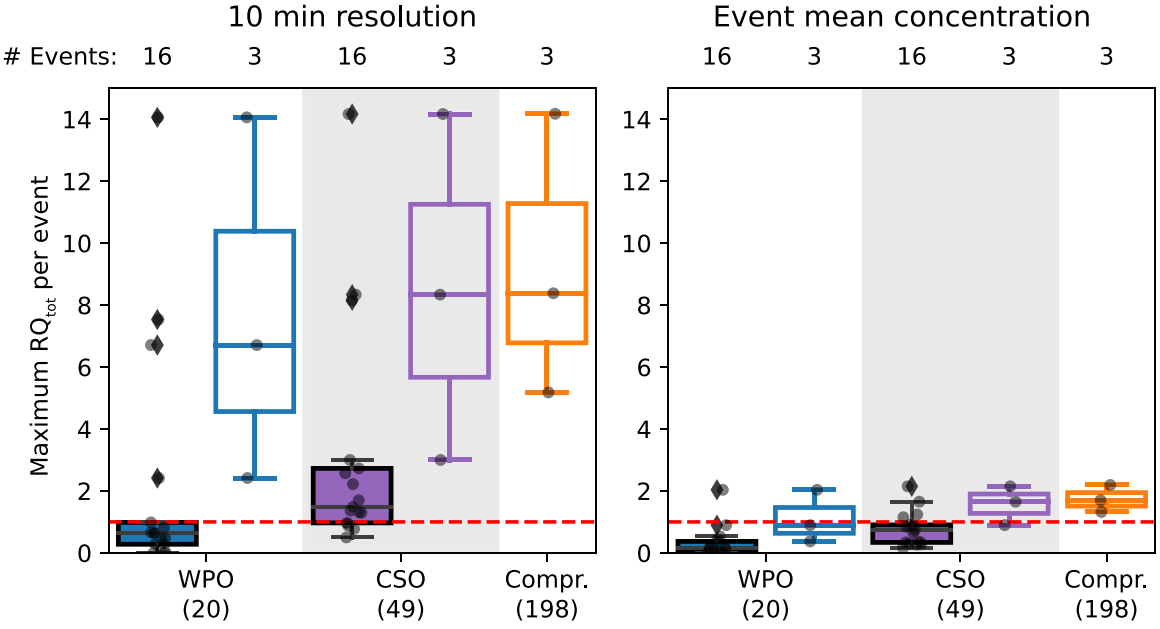

Fig. 3. Maximum RQ_{tot} per event calculated from the target list Swiss WPO (20 substances), typical substances in CSO (49 substances), and the comprehensive list (198 substances) and for different temporal resolutions: 10 min vs. event mean concentration for site CSO A (site CSO B see SI Fig. 13).

Table 1
Comparing ratios of median and max of maximum RQ_{tot} per event for the different substance lists and temporal resolutions for CSO A and B.

	Substance list	Temporal resolution	# Events	Ratio CSO A		Ratio CSO B	
				Median	Max	Median	Max
Substance list	WPO vs. CSO	10 min	16	2.3	1	1.7	1.7
	CSO vs. Compr.	10 min	3	1.0	1	1.9	
	WPO vs. Compr.	10 min	3	1.2	1	1.1	
Temporal resolution	WPO	10 min vs. EMC	16	4.3	6.9	4.6	3.1
	CSO	10 min vs. EMC	16	2	6.6	2.9	2.1
	Comprehensive	10 min vs. EMC	3	4.9	6.5	2.1	

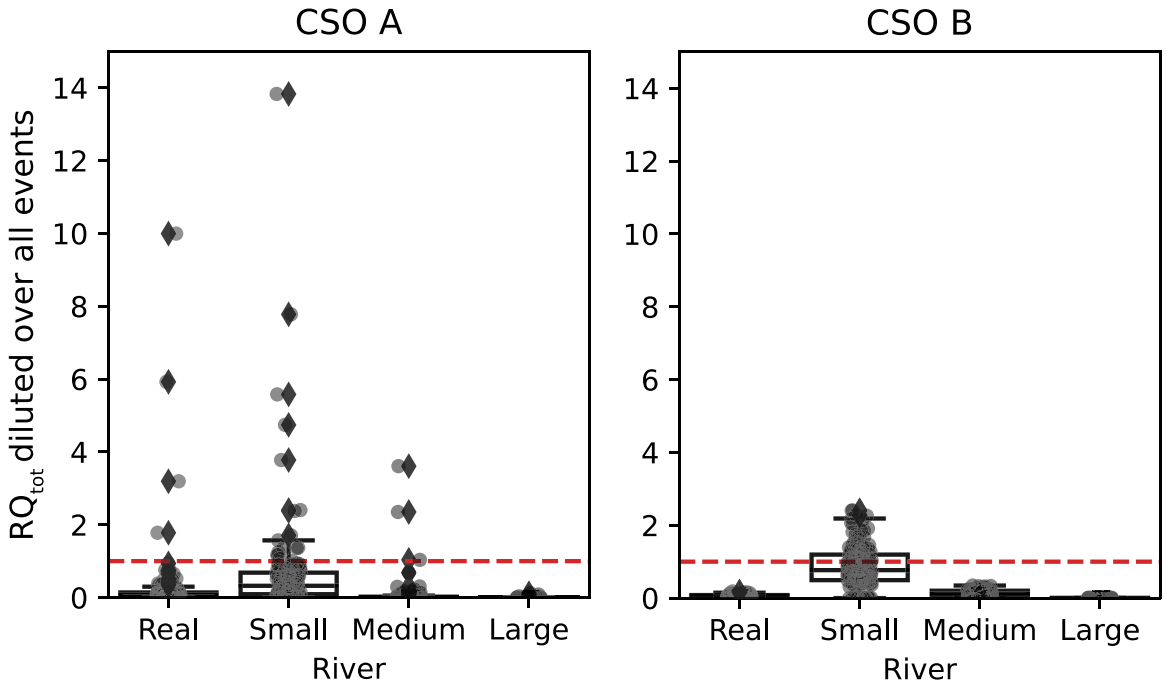

Fig. 4. Boxplot of RQ_{tot} over all events (10-minute resolution) diluted in the receiving water body for the four scenarios: real river at measurement site and small, medium, and large Swiss rivers. Red line: threshold of 1 for RQ_{tot} above which negative ecotoxicological impacts are likely, grey circles: individual data points.

substance selection can influence strongly the risk assessment outcome. The exceedance due to a single substance also underscores that further investigations using bioanalysis and suspect or nontarget screening are necessary to more accurately assess the chemical risk in the receiving water.

The results also indicate the importance that a CSO discharges into a river of adequate size, which might not be feasible in all urban areas. Similar findings were reported by Goore Bi et al. (2015) when conducting bioassays in CSOs, where no toxicity was observed with a sufficient dilution but would be expected when discharging into a smaller river. Therefore, considering flow conditions of the receiving river is crucial when planning CSO sites. The size of the connected urban area and receiving river can help prioritize further investigations. In addition, rivers often receive discharges from several CSOs as well as WWTPs and direct runoff from agricultural fields, leading to increase of micropollutant concentrations along a stretch of river; these must be considered, for instance by modelling approaches.

4. Conclusion

The real exposure scenarios of dissolved organic compounds in CSOs from high-temporal resolution data revealed the following:

- Temporal resolution and substance selection both influence the chemical risk assessment outcomes. The median underestimation of the maximal RQ_{tot} when considering only EMCs compared to 10-minute resolution is a factor of 2 to 4.9 (depending on numbers of substances contained in the respective list), with a maximum factor of 6.9. The acute toxicity is driven by only a few substances. However, of the 20 substances presenting the highest risk, <50 % are included in the Swiss WPO. Yet, the maximum RQ_{tot} of each event was only underestimated by a median factor of 1.2 when considering the Swiss WPO (20 substances) compared to the comprehensive list (198 substances).
- Substances from all three classes pharmaceuticals, pesticides, and road-related compounds are among the 20 compounds with highest RQ values; hence, raw wastewater and stormwater are both important sources of toxic compounds in CSOs.
- The RQ_{tot} exhibits high temporal variation during CSO events, with no specific time period consistently posing higher risk than others. Often the RQ_{tot} exceeds 1 throughout the entire event. This suggests that focusing on retaining the first flush or discharge from any other specific time window is insufficient to reduce acute toxicity from dissolved organic micropollutants. Moreover, because the risk is primarily driven by a small number of substances, implementing measures at the source might be a more efficient strategy for managing this risk. Dilution in the receiving water body is necessary to reduce the total risk below 1, which seems to be sufficient for the CSOs and substances investigated.
- In certain events, especially in the smaller catchment, short RQ_{tot} peaks are observed, down to 10 mins. Many overflow events also last only a few hours, which is much shorter than the temporal scale for

which AQC values are typically developed. Future research should investigate the ecotoxicological relevance of such short-term exposures and establish appropriate assessment tools; these are crucial for developing effective mitigation measures in urban water management.

- This assessment relies solely on target chemical analysis. To assess the actual risk of CSOs, future research should incorporate bioassays to identify risk-driving but yet unknown chemicals. Furthermore, there is a significant gap in toxicity data for pharmaceuticals and road-related compounds, which needs to be filled to assess their impact. Because a multitude of other pollutants (solids, nutrients, heavy metals, etc.) are potentially present in CSOs, the findings of our paper should be combined with existing knowledge of these pollutants for a holistic risk assessment. Furthermore, open water bodies are often contaminated by multiple CSOs, WWTP effluents, and surface runoff from agricultural fields. To gain a comprehensive understanding of river pollution, it is crucial to use modelling approaches that account for these factors.

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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 – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Marion Junghans:** Writing – review & editing, Methodology. **Heinz Singer:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. **Christoph Ort:** Writing – review & editing, Supervision, 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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Data availability

All data is available through Eawag's Research Data Institutional Collection (ERIC-open) at 10.25678/000DMX.

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