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# A data-driven analysis of trace contaminants in wet-weather discharges

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## Highlights

- Trace contaminants from 5 different chemical classes with potential risk for receiving waters
- 32 trace contaminants require dilution to comply with environmental quality standards
- High variability and censoring stresses the importance to redesign future monitoring campaigns

## Introduction

Urban wet-weather discharges (combined sewer overflows, CSO and stormwater outlets from separate sewers, SWO) contain various trace contaminants which can pose a threat to receiving waters (Launay et al., 2016; Mutzner et al., 2020; Wicke et al., 2021). Hence, there is a need to identify critical contaminants and to quantify pollutant concentrations in wet-weather discharges to assess effective control strategies. Efforts have been made in the last decade to increase our understanding of the presence, magnitude, and diversity of contaminants in wet-weather discharges (e.g. Gasperi et al., 2014; Launay et al., 2016; Masoner et al., 2019; Mutzner et al., 2020; Rippy et al., 2017). Despite these efforts, the information gained with these monitoring campaigns is still limited, as most contain small, local datasets both in terms of sampled discharge events and spatial coverage. In this study, we use a data-driven statistical analysis of existing measurements collected at more than 60 wet-weather discharge sites to gain insight on the frequency of detection and relative abundance of trace contaminants. This information can be used to inform future monitoring efforts as utilities and regulators work towards building effective management strategies.

## Methodology

### Data on trace contaminants in urban wet-weather discharges

**Table 1.** List of datasets with location, number of sites, events, medium type, sampling strategy and reference for campaign details.

#	Country	# sites	# events/site <sup>a</sup>	Type <sup>b</sup>	Sampling	Reference
1	Germany	5	18 to 41	SWO	Vol-prop. C-WS	(Wicke et al., 2021)
2	US	21	1 to 4	SWO	Flow-prop C-WS	(Masoner et al., 2019)
3	Switzerland	22	1 to 7	CSO	Time-prop PS & C-WS	(Mutzner et al., 2020)
4	US	2	11 & 13	SWO	Vol-prop C-WS	(Burant et al., 2018)
5	France	2	19 & 22	SWO	Flow-prop C-WS & time-prop manual WS	(Gasperi et al., 2014)
6	France	1	11	SWO	Flow-prop C-WS	(Garnier, 2020; Gasperi et al., 2014; S�������� et al., 2015)
7	Australia	9	5 to 21	SWO	Flow-prop C-WS	(Rippy et al., 2017)
8	Denmark	2	27 & 28	CSO, SWO	C-WS	Danish EPA (Milj������������, 2017, 2006)

<sup>a</sup>Total number of events sampled per site, single substances were often analysed for fewer events, <sup>b</sup>SWO: stormwater outlets, CSO: combined sewer overflows, <sup>c</sup>C-WS: Composite water sampling with automated sampler, PS: Passive sampling

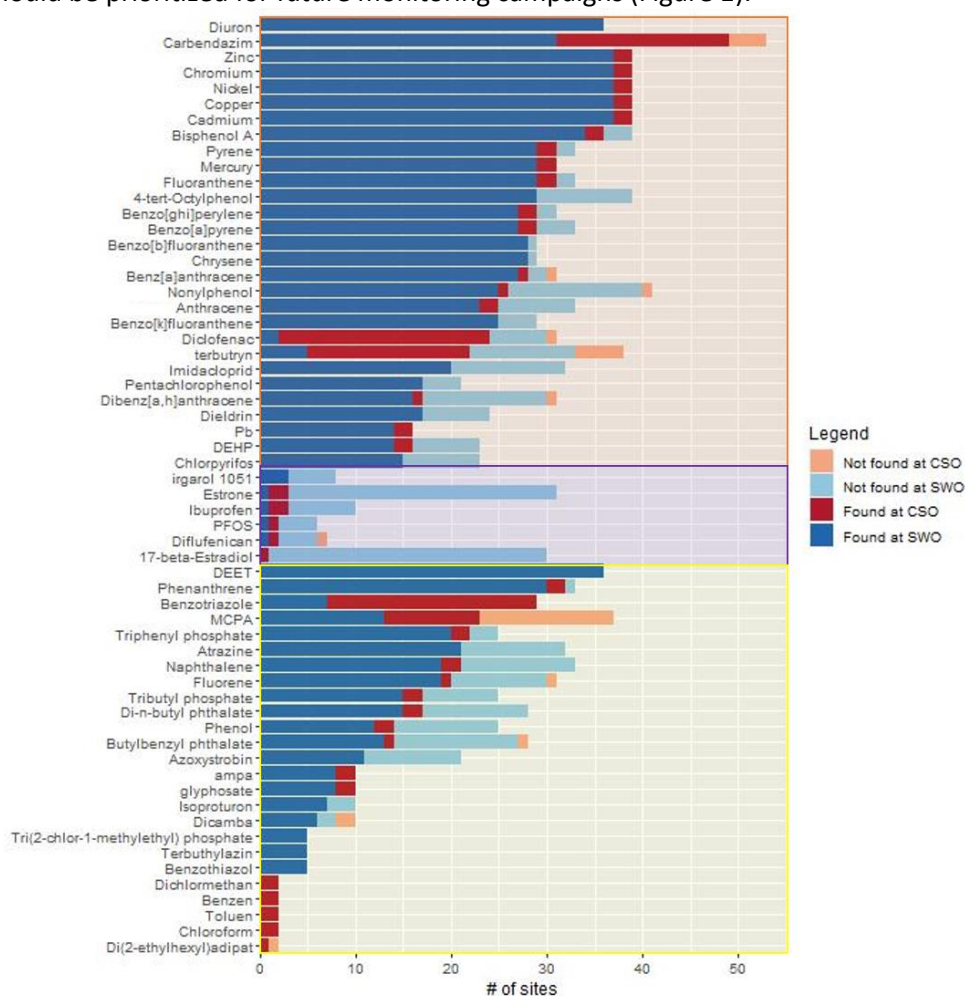
We selected data sets of urban wet-weather discharges (CSO and SWO) fulfilling the criteria that sampling was done by composite sampling, meaning the collection of several samples per event, resulting in an event mean concentration (EMC). The authors were contacted for the raw data resulting in 63 sites, 506 monitored events and more than 42'000 observations (Table 1). Details on sampling, chemical analysis and sample preparation are explained in the publications corresponding to the data.

### Contaminants occurrence and required dilution factor

The data was transformed to consider the different limit of quantifications (LOQ) or detection (LOD) in the data sets. Contaminant concentrations <LOQ were treated as censored values and estimated using regression on order statistics (ROS). All calculations were done in R (R Core Team, 2020). ROS was done if there were more than 3 observations per site and less than 80% left-censored data (<LOQ). We then assessed which contaminants i) are often found if looked for (occurrence: at least once >LOQ at site) and ii) are found in concentration above environmental water quality limits, calculated as a required dilution factor (DF). DF was assessed by using the 90%-percentile EMC concentration of all sites divided by the environmental chronic water quality standard (CQS). The higher DF the more problematic a contaminant is expected to be for aquatic organisms. Water quality standards for surface waters were found for 125 contaminants by the Swiss Ecotox Center, EU and Danish regulations.

## Results and discussion

The majority of the analysed observations are <LOQ, or less than 3 observations per site are available. Thus around 30% (13'800 out of >42'000 observations) are used for the assessment of site mean concentrations (SMC). Comparing contaminant occurrence with DF highlights contaminants with global relevance, which should be prioritized for future monitoring campaigns (Figure 1).



**Figure 1.** Top-60 list selection of trace contaminants based on occurrence and required DF at number of CSO and SWO sites. Orange group (n=29): occurrence >=50% (CSO & SWO combined) and required DF >= 1; Purple group (n=6): occurrence <50% (CSO & SWO combined) and required DF >= 1; Yellow group (n=25): occurrence > 50% (CSO & SWO combined) and required DF <1.

Twenty-nine contaminants have a high occurrence (>50%) and  $DF \geq 1$  (orange zone, Figure 1). These contaminants cover different chemical classes (pesticide, household, industrial, PAHs, heavy metals) showing that various urban sources contribute to potential environmental impacts. Six contaminants have a low occurrence but are found in concentrations above the CQS (purple zone, Figure 2). Moreover, if the focus of a monitoring campaign lies in finding urban sources, the above top-list could be extended with contaminants that have a high occurrence (twenty-nine contaminants, yellow zone, Figure 1). The sampled contaminant's concentrations are highly variable, with the coefficient of variation (CV) of the EMC ranging from 0.2 to 1.2 (80%-interquantile range, median: 0.6). These high CV are associated with the inherent variability due to use patterns, sources and urban land use. Previous studies on TSS and other traditional pollutants indicate that the number of events that need to be sampled is related to the coefficient of variation (Bertrand-Krajewski et al., 2002; Burton and Pitt, 2001; McCarthy et al., 2018). Thus, we anticipate in a next step to show the overall number of events and sites that should be sampled.

## Conclusions and future work

- The results highlight 35 contaminants that should be prioritized in regulatory and research monitoring campaigns, thus ensuring that efforts and resources are optimized. The proposed contaminants need to be carefully assessed as country-specific regulations and habits might lead to changes in prioritization.
- Efforts need to go towards an analysis of different compound classes as one class might not cover much of the toxicity spectrum.
- The observed high variability and censoring in the collected data leads to high uncertainty for decision making and stresses the importance to redesign future wet-weather monitoring programs.

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