Micropollutant Emissions from Combined Sewer Overflows

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Abstract

Anthropogenic substance inputs impair the chemical and ecological status of water bodies. An increasing number and variety of micropollutants – occurring in low concentrations in the range of nano- to micrograms per litre – causes concern over significant ecotoxicological risks and represents a major challenge for water protection.

Combined sewer overflows (CSOs) from sewer systems during storm events are an important input pathway for pollutant emissions to water bodies. As a result of advances in wastewater treatment and water protection requirements, this pathway is becoming increasingly relevant. At the same time, the availability of data on the quantity and quality of CSOs is comparatively low. In order to develop effective measures to reduce water pollution from combined sewer systems, improved monitoring of wet weather discharges and an assessment of the emissions from both wastewater and stormwater treatment are required.

This work contributes to the expansion and updating of knowledge on chemical pollution from combined sewer systems. The overarching aim of this work was to improve the assessment of CSO emissions for substance emission modelling at river basin level. For this purpose, new data on CSO quality were collected in an extensive monitoring programme. In addition, a water balance approach was developed, which allows to estimate the annual CSO volume in catchments of wastewater treatment plants (WWTPs) as well as its dry weather flow content (wastewater and infiltration water) using few input data.

The monitoring comprised the collection of volume-proportional composite samples of overflow events at selected CSOs in southern Germany over periods of at least one year. This strategy aimed to quantify representative average concentrations. The comparability of the sampling systems used – large volume samplers with a capacity of up to 1,000 l – to conventional autosamplers was investigated. Specific advantages of the large volume samplers became apparent, including the flexibility in sampling highly variable overflow events, the efficient generation of volume-proportional event composite samples, as well as the possibility of carrying out detailed analyses of the collected solids, e.g. particle size distribution and particulate pollutant loading, in addition to the analysis of the total sample.

The concentrations of more than 40 individual substances from different substance groups were analysed in the samples, including metals, polycyclic aromatic hydrocarbons (PAHs), biocides and pesticides, benzotriazoles, pharmaceuticals, the sweetener acesulfame and the plasticiser di(2-ethylhexyl)phthalate. To a lesser extent, perfluorinated alkyl substances, phenols, and additional biocides were analysed. The majority of the substances could be detected and reliably quantified. The variability of the concentrations was high. The impact of catchment characteristics, hydraulic conditions, and seasonal trends on concentrations was investigated. However, it could be demonstrated that no simple relationships exist that would be suitable for predicting concentrations at non-monitored sites. Due to the large number of possible influences, it is questionable whether such relationships could be derived even with larger datasets. Consequently, a high and unpredictable variability must be taken into account when assessing chemical pollution from CSOs, e.g. by using stochastic approaches based on value distributions.

The CSO data were merged with the data of a total of 49 WWTPs and two stormwater outfalls from separate sewer systems. The data were collected according to strictly harmonised sampling and analytical methods, summarised consistently, and can be used as representative input data for modelling substance emissions from urban areas, if no site-specific data are available. From an overall perspective, the relation of concentrations between WWTPs, CSOs, and stormwater outfalls could be explained primarily by the main areas of origin and the environmental behaviour (i.e. removal in WWTPs due to adsorption or biodegradation) of individual substances. It could be demonstrated that CSOs can be an important input pathway especially for substances that are transported into sewer systems with surface runoff and/or have a high removal rate in wastewater treatment. These include some heavy metals and PAHs, which often cause failure to achieve a good chemical status of surface waters.

The urban water balance approach allows to estimate annual CSO volume in individual WWTP catchments based on area, precipitation, and WWTP inflow data. With the adjustments made, it is also possible to estimate the volume-based emission target values recently proposed for regulating emissions from combined sewer systems (e.g. the proportion of wastewater discharged via CSOs). The approach was successfully verified in a test catchment using measurement data from water level sensors at CSO facilities. However, the sensitivity and area-wide transferability of the approach should be investigated in additional test catchments. The further installation of measurement equipment at CSOs will contribute essentially to improving the general knowledge on CSO activity as well as the basis for modelling substance emissions.

Based on the water balance and the new concentration data, emissions were exemplarily estimated for the test catchment. The uncertainties resulting from the use of representative data were indicated to account for the high concentration variability and allow an informed assessment. Against the background of the limited availability of quantitative data on CSOs, the approach combined with the new concentration data provides a valuable instrument to prioritise catchments for further detailed assessment and support the strategic planning of measures.

Kurzfassung

Anthropogene Stoffeinträge beeinträchtigen den chemischen und ökologischen Zustand von Gewässern. Eine beständig zunehmende Anzahl und Vielfalt von Mikroschadstoffen – die in niedrigen Konzentrationen im Bereich von Nano- bis Mikrogramm pro Liter auftreten – gibt Grund zur Besorgnis erheblicher ökotoxikologischer Risiken und stellt den Gewässerschutz vor große Herausforderungen.

Mischwasserüberläufe aus Kanalisationssystemen bei Regenereignissen sind ein wichtiger Eintragspfad für Stoffeinträge aus Siedlungsgebieten. Infolge von Fortschritten bei der Abwasserbehandlung und zunehmenden Anforderungen des Gewässerschutzes gewinnt dieser Eintragspfad weiter an Bedeutung. Gleichzeitig sind vergleichsweise wenige Daten zur Quantität und Qualität von Mischwasserüberläufen verfügbar. Um effektive Maßnahmen zur Reduzierung der Einträge entwickeln zu können, ist eine verbesserte Überwachung von Regenwetterabflüssen und eine Gesamtbetrachtung der Beiträge aus Abwasser- und Regenwasserbehandlung erforderlich.

Diese Arbeit trägt dazu bei, den Kenntnisstand über stoffliche Belastungen aus Mischsystemen zu erweitern und zu aktualisieren. Das übergeordnete Ziel war es, die Grundlagen für die Modellierung der Stoffeinträge aus Mischwasserüberläufen auf Flussgebietsebene zu verbessern. Dazu wurden in einem umfangreichen Monitoring-Programm neue Daten zur Qualität der Überläufe erhoben. Weiterhin wurde ein Wasserbilanzansatz weiterentwickelt, der eine Abschätzung des jährlichen Überlaufvolumens in Kläranlageneinzugsgebieten sowie des darin enthaltenen Trockenwetterabflussanteils (Schmutzwasser und Fremdwasser) auf Basis weniger Eingangsdaten ermöglicht.

Das Monitoring umfasste die Sammlung volumenproportionaler Mischproben von Überlaufereignissen an ausgewählten Mischwasserüberläufen im süddeutschen Raum über Zeiträume von mindestens einem Jahr. Mit diesem Ansatz sollten möglichst repräsentative, mittlere Stoffkonzentrationen erfasst werden. Das eingesetzte Probenahmesystem – bis zu 1.000 l fassende Feststoffsammler – wurde hinsichtlich der Vergleichbarkeit mit konventionellen automatischen Probenehmern untersucht. Dabei wurden spezifische Vorteile deutlich, insbesondere die Flexibilität bei der Beprobung hochvariabler Überlaufereignisse, die effiziente Erzeugung volumenproportionaler Ereignis-Mischproben, sowie die Möglichkeit, zusätzlich zur Analyse der Gesamtprobe, detaillierte Analysen der gesammelten Feststoffe durchzuführen, z.B. Korngrößenverteilung und partikuläre Schadstoffbeladung.

In den Proben wurden die Konzentrationen von mehr als 40 Einzelsubstanzen verschiedener Stoffgruppen analysiert, darunter Metalle, polyzyklische aromatische Kohlenwasserstoffe (PAK), Biozide und Pestizide, Benzotriazole, pharmazeutische Wirkstoffe, der Süßstoff Acesulfam und der Weich-macher Di(2-ethylhexyl)phthalat. In geringerem Umfang wurden perfluorierte Alkylsubstanzen, Phenole und weitere Biozide analysiert. Die Mehrzahl der Stoffe konnte nachgewiesen und sicher quantifiziert werden. Die Variabilität der Konzentrationen war erwartungsgemäß hoch. Der Einfluss von Einzugsgebietsmerkmalen, hydraulischen Bedingungen und saisonalen Trends auf die Konzentrationen wurde geprüft. Es konnte gezeigt werden, dass keine einfachen Zusammenhänge existieren, die sich für die Vorhersage von Konzentrationen an nicht untersuchten Standorten eignen. Aufgrund der Vielzahl möglicher Einflüsse ist fraglich, ob solche Zusammenhänge selbst mit größerem Datenumfang abgeleitet werden könnten. Daher ist bei der Bewertung stofflicher Belastungen aus Mischwasserüberläufen stets eine hohe, zufallsgeprägte Variabilität zu berücksichtigen, etwa durch die Verwendung stochastischer Ansätze auf Basis von Werteverteilungen.

Die Konzentrationsdaten der Mischwasserüberläufe wurden mit den Daten von insgesamt 49 Kläranlagen und einzelnen Regenwassereinleitungen aus Trennsystemen zusammengeführt. Die mit harmonisierten Probenahme- und Analyseverfahren erhobenen und einheitlich zusammengefassten Daten können als repräsentative Eingangsdaten für die Modellierung der Stoffeinträge aus Siedlungsgebieten genutzt werden, wenn keine gebietsspezifischen Daten verfügbar sind. Insgesamt betrachtet, lies sich das Verhältnis der Konzentrationen zwischen Kläranlagen, Mischwasserüberläufen und Regenwassereinleitungen hauptsächlich durch die Herkunftsbereiche und das Umweltverhalten (im Speziellen der Rückhalt in Kläranlagen durch Adsorption oder biologischen Abbau) der einzelnen Stoffe erklären. Es konnte gezeigt werden, dass Mischwasserüberläufe vor allem ein wichtiger Eintragspfad für Stoffe sein können, welche überwiegend mit dem Oberflächenabfluss in Abwassersysteme eingetragen werden und/oder einen hohen Rückhalt in Kläranlagen aufweisen. Dazu zählen einige Schwermetalle und PAK, die häufig ursächlich dafür sind, dass ein guter chemischer Zustand von Oberflächengewässern nicht erreicht wird.

Der Wasserbilanzansatz ermöglicht eine Abschätzung des jährlichen Überlaufvolumens in Kläranlageneinzugsgebieten auf Basis von Flächeninformationen, Niederschlags- und Kläranlagenzuflussdaten. Mit den vorgenommenen Anpassungen können zudem die aktuell für die Regulierung der Emissionen aus Mischsystemen vorgeschlagenen, volumenbasierten Emissionszielwerte abgeschätzt werden (z.B. Anteil des jährlichen Trockenwetterabflusses in Mischwasserüberläufen). Der Ansatz konnte anhand von Messdaten, die mit Wasserstandssonden an Überläufen ermittelt wurden, erfolgreich für ein Testgebiet verifiziert werden. Die Sensitivität und flächenhafte Übertragbarkeit des Ansatzes sollten jedoch anhand weiterer Gebiete untersucht werden. Der weitere Ausbau von Messtechnik an Mischwasserüberläufen wird wesentlich dazu beitragen, den allgemeinen Kenntnisstand zu deren Aktivität sowie die Grundlagen für die Modellierung der Stoffeinträge zu verbessern.

Auf Grundlage der Wasserbilanz und den neuen Stoffdaten wurden exemplarisch Stoffeinträge für das Testgebiet ermittelt. Die aus der Verwendung repräsentativer Daten resultierenden Unsicherheiten wurden dargestellt, um der hohen Konzentrationsvariabilität Rechnung zu tragen und eine möglichst informierte Bewertung zu ermöglichen. Vor dem Hintergrund der begrenzten Verfügbarkeit quantitativer Daten zu Mischwasserüberläufen bildet der Ansatz gemeinsam mit den neuen Stoffdaten ein geeignetes Instrument, um Einzugsgebiete für eine weitere detaillierte Bewertung zu priorisieren und damit die strategische Planung von Maßnahmen zu unterstützen.

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List of Acronyms

1,2,4TZL	1,2,4-Triazole
2AB	2-Aminobenzimidazole
4iNP	4-iso-Nonylphenol
4MBT	4-Methylbenzotriazole
4tOP	4-tert.-Octylphenol
5MBT	5-Methylbenzotriazole
AA	Annual Average
ACE	Acesulfame
ACF	Aclonifen
ACN	Acenaphthene
ACY	Acenaphthylene
ANT	Anthracene
ATR	Atrazin
BaA	Benzo(a)anthracene
BaP	Benzo(a)pyrene
BbF	Benzo(b)fluoranthene
BDF	Brodifacoum
BFX	Bifenox
BghiP	Benzo(ghi)perylene
Bi	Bismuth
BIT	1,2-Benzisothiazolin-3(2H)-on
BkF	Benzo(k)fluoranthene
BTR	Benzotriazole
CBT	Cybutryne
CBZ	Carbamazepine
Cd	Cadmium
cHCE	cis-Heptachlor epoxide
Chr	Chrysene
COD	Chemical Oxygen Demand
COD_{sol}	Dissolved Chemical Oxygen Demand
Cr	Chrome
CSO	Combined Sewer Overflow
Cu	Copper
CV	Coefficient of Variation
CYM	Cypermethrin
CZIM	Carbendazim
DahA	Dibenz(ah)anthracene
DCF	Diclofenac
DCS	Diclosan
DCV	Dichlorvos
DEET	Diethyltoluamide
DEHP	Di-(2-ethylhexyl)phthalate
DFTL	Difethialon
DIF	Dicofol
DIU	Diuron
DWF	Dry Weather Flow
EQS	Environmental Quality Standard
EU	European Union
Fe	Iron
FL	Fluorene
Fluo	Fluoranthene
H4PFOS	1H,1H,2H,2H-Perfluoroctansulfonic acid
HBCDD	Hexabromocyclododecanes
HC	Heptachlor
Hg	Mercury
IMI	Imidacloprid
IP	Indeno(1,2,3-cd)pyrene
ISO	Isoproturon
IZL	Imazalil
$K_{a4.3}$	Acid capacity
LOQ	Limit of Quantification
LVS	Large Volume Sampler

MAC	Maximum Acceptable Concentration
MCPP	Mecoprop
MDCS	Methyl-Diclosan
MET	Metolachlor
MIT	2-Methyl-3-isothiazolinon
Mo	Molybdenum
MoRE	Modeling of Regionalised Emissions
MPL	Metoprolol
MTCS	Methyl-Triclosan
NAP	Naphtalene
NH_4-N	Ammonia Nitrogen
Ni	Nickel
NO_2-N	Nitrite Nitrogen
NO_3-N	Nitrate Nitrogen
OIT	2-Octyl-3-isothiazolinon
PAH	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PCZ	Propiconazole
PD	Population Density
PE	Population Equivalents
PFAS	Per- and polyfluorinated Alkyl Substances
PFBA	Perfluorobutyric acid
PFBS	Perfluorobutanesulfonic acid
PFDA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFDS	Perfluorodecane sulfonic acid
PFHpA	Perfluoro-n-heptanoic acid
PFHpS	Pentadecafluoro-1-heptanesulfonic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexanesulfonic acid
PFNA	Perfluoro-n-nonanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFPA	Perfluoropentanoic acid
PFPeS	Perfluoropentane-1-sulfonic acid
PFUnA	Perfluoro-n-undecanoic acid
PHE	Phenanthrene
PLN	Prallethrin
PMN	Permethrin
PMNS	Permethric acid
PO_4-P	Phosphate phosphorous
Pyr	Pyrene
QNX	Quinoxyfen
Sb	Antimony
SMC	Site Mean Concentration
Sn	Tin
SSO	Separate Stormwater Outfall
TBA	Terbuthylazine
TBY	Terbutryn
TBYD	Terbutryn-desethyl
TBYS	Terbutryn-sulfoxide
TCS	Triclosan
TCZ	Tebuconazol
tHCE	trans-Heptachlor epoxide
THIA	Thiabendazol
TNb	Total Nitrogen Bound
TP	Total Phosphorus
TSS	Total Suspended Solids
TSS63	Total Suspended Solids <63 µm
UWB	Urban Water Balance
UWS	Urban Wastewater System
UWWTD	Urban Waste Water Treatment Directive
WFD	Water Framework Directive
WWTP	Wastewater Treatment Plant
Zn	Zinc

1 Introduction

1.1 Micropollutants in the Aquatic Environment

The majority of freshwater bodies on earth is altered by human activities. These alterations result from the use of their water, energy, ecosystem services, or the area in their catchment and include morphological, physical, chemical, and ecological changes to the natural state (Vitousek *et al.* 1997; Wohl and Merritts 2007; Khatri and Tyagi 2015). The disposal of wastewater into surface waters is among the most impactful of various stressors on ecosystem multifunctionality (Brauns *et al.* 2022). While chemical pollution by anthropogenic pollutants and micropollutants occurring in the range of ng/l to µg/l may be one of the least visible alterations, it raises significant concern regarding the potential impact on aquatic ecosystems as well as human health (Schwarzenbach *et al.* 2006). It can be considered one of the major challenges in water management for several reasons: a) there is a large and rapidly increasing number and variety of chemical substances to be considered, b) the ecotoxicological risks of their presence in environmental compartments are not sufficiently understood (e.g. long-term effects of persistent substances, mixture toxicity), and c) the low concentrations of the substances "*represent a challenge for both detection and elimination strategies*" (Gerbersdorf *et al.* 2015).

Persson *et al.* (2022) recently concluded that the increasing production and emission of "*novel entities*", i.e. global chemical and plastic pollution, "*outstrips our efforts at safety assessment and monitoring"* and transgresses the *"planetary boundaries*" (Persson *et al.* 2022). In the EU, more than 23,000 chemicals are currently registered under REACH regulation (ECHA 2021a), more than 900 biocidal active substance are registered under the biocidal products regulation (ECHA 2021b), and approximately 1,500 active substances, safeners and synergists are registered in the EU Pesticides Database (European Commission 2021). Various other categories of chemical substances are used in medicinal products, personal care products, or cleaning products. More than 30,000 substances have been considered relevant for aquatic systems (Fatta-Kassinos *et al.* 2016). These substances may reach water bodies via various pathways, accumulate in water or sediments and pose long-term risks to ecosystems and drinking water supplies. There are numerous reports of widespread occurrence of various micropollutants in wastewater treatment plant effluents, surface and ground waters (Luo *et al.* 2014; Gavrilescu *et al.* 2015; Sousa *et al.* 2018). Several groups of substances show ubiquitous environmental occurrence, such as polycyclic aromatic hydrocarbons (PAH) or per- and polyfluorinated alkyl substances (PFAS)[1]. And most critical, certain persistent, mobile, and toxic substances might become increasingly challenging for water supplies (Rüdel *et al.* 2020)[1]. There is also growing public concern regarding the presence of residues of pharmaceuticals (Wenzel 2022) or pesticides (Ruhwedel 2022) in surface waters. A relatively short list of priority substances is used to assess the chemical status of water bodies under EU legislation (European Commission 2000, 2008, 2013). According to the 2018 EEA status report, 46 % of European water bodies have not yet

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[1] Sentence adopted from: Nickel, J. P., Sacher, F. and Fuchs, S. 2021 Up-to-date monitoring data of wastewater and stormwater quality in Germany. *Water Research*, 202, 117452. https://doi.org/10.1016/j.watres.2021.117452.

achieved a good chemical status (Kristensen *et al.* 2018)[2]. And ecotoxicological risks might be underestimated. Brack *et al.* (2019) suggest that a more comprehensive assessment is needed that considers the risks of chemical pollution from more than just a few priority substances.

The main strategy to achieve improvements in water quality is precautionary management, i.e. reduction of emissions, because the treatment of contaminated water resources is technically difficult or sometimes infeasible (Schwarzenbach *et al.* 2006; Gerbersdorf *et al.* 2015). This strategy requires precise knowledge of the sources, the release dynamics, and the environmental behaviour of substances. Inventories of the input pathways of substances are a central tool to this strategy. In the EU, Article 5 of Directive 2008/105/EC (European Commission 2008) specifies environmental quality standards and requires the member states to establish an inventory of emissions, discharges, and losses of priority substances and other pollutants at the level of river basin districts. Based on these inventories, measures can be planned and prioritised to reduce emissions and achieve a good chemical and ecological status.

1.2 Emission Pathways from Urban Wastewater Systems (UWS)

One important input pathway of micropollutants is the discharge of wastewater to receiving waters. Therefore, the current approaches of many EU states to reduce micropollutant emissions from UWS are mainly aimed at expanding selected wastewater treatment plants with advanced micropollutant treatment (Brander 2021; Cimbritz 2021; Pistocchi 2021; Tettenborn 2021; Uijterlinde 2021).

Wastewater treatment in the EU has improved during the last decades. The implementation of the Urban Waste Water Treatment Directive (UWWTD) (European Commission 1991), which is currently undergoing a re-evaluation, has led to significant reductions of emissions of organic matter, nutrients, and coliforms from wastewater treatment plants (WWTPs) (Pistocchi *et al.* 2019). While full compliance with the UWWTD is still to be achieved, 95% of urban wastewater in the EU were collected in 2016 and more than 85% were treated by biological or more stringent treatment (European Commission 2020). Conventional WWTPs are highly effective in removing suspended solids, biodegradable organic matter, and nutrients[3]. The removal of micropollutants in such WWTPs depends on their environmental behaviour, i.e. susceptibility to sorption to sewage sludge, biodegradation, or volatilisation (Luo *et al.* 2014; Margot *et al.* 2015). Hydrophilic and poorly biodegradable substances are not sufficiently removed during wastewater treatment, including for example pharmaceuticals or pesticides. Therefore, advanced treatment processes for the elimination of micropollutants (e.g. adsorption or oxidation) are being developed and successively implemented in WWTPs (Eggen *et al.* 2014; Luo *et al.* 2014)[3].

During storm events, the flow volumes transported through urban wastewater systems (UWS) periodically exceed the capacity of sewers, storage tanks, and, in combined sewer systems, wastewater treatment. This leads to additional non-continuous emissions from urban areas, including stormwater outfalls in separate sewer systems (SSOs) and combined sewer overflows (CSOs) in combined sewer systems (Figure 1.1).

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[2] Sentence adopted from: Nickel, J. P. and Fuchs, S. 2019 Micropollutant emissions from combined sewer overflows. *Water Science and Technology*, 80(11), 2179–2190. https://doi.org/10.2166/wst.2020.035

[3] Sentence adopted from: Nickel, J. P., Sacher, F. and Fuchs, S. 2021 Up-to-date monitoring data of wastewater and stormwater quality in Germany. *Water Research*, 202, 117452. https://doi.org/10.1016/j.watres.2021.117452.

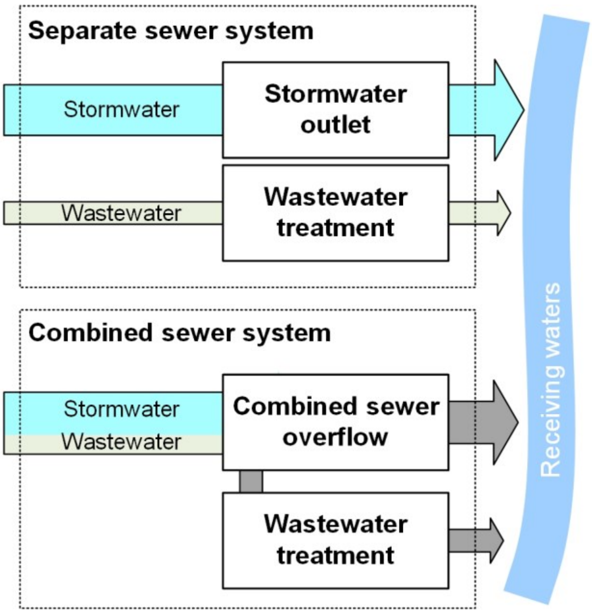

Figure 1.1: Emission pathways to receiving waters in separate and combined sewer systems.

Stormwater runoff is recognised as a relevant source of pollution (Brombach *et al.* 2005; Zgheib *et al.* 2012; Wicke *et al.* 2021), but is usually discharged through SSOs into receiving waters without any treatment in separate sewer systems. In combined sewer systems, it is mixed with dry weather flow (DWF)[4]. CSOs consequently contain constituents from both matrices and are an input pathway for various water pollutants, such as suspended solids, oxygen-consuming substances, microbial contaminants, nutrients, heavy metals, and organic substances (Brombach *et al.* 2005; Aarts *et al.* 2013; Jalliffier-Verne 2015; Madoux-Humery *et al.* 2015)[5]. From the data compiled in Table 1.1, it can be seen that SSOs and CSOs can contribute significantly to total emissions from UWS depending on the pollutant considered[6]. The estimates for individual substances show similar trends but differ due to the different types of systems, local specifics, and the approaches used for estimation.

With the continuing improvement of wastewater treatment, the relative contribution of sewer system discharges will further increase (Pistocchi *et al.* 2019; Pistocchi 2020). In urban areas, SSOs and CSOs could become major pressures on receiving water body quality. Consequently, a holistic assessment of the emissions from both wastewater and stormwater treatment is needed to manage surface water pollution effectively[6]. In addition, several studies suggest that increasing extreme precipitation intensities due to climate change might increase urban runoff and CSOs (Semadeni-Davies *et al.* 2008; Abdellatif *et al.* 2015; Tavakol-Davani *et al.* 2016; Salerno *et al.* 2018; Roseboro *et al.* 2021).

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[4] The term dry weather flow (DWF) is used to describe the sum of the flow components wastewater (including domestic, commercial, and industrial wastewater) and infiltration water in the sewer system.

[5] Sentence adopted from: Nickel, J. P. and Fuchs, S. 2019 Micropollutant emissions from combined sewer overflows. *Water Science and Technology*, 80(11), 2179–2190. https://doi.org/10.2166/wst.2020.035

[6] Sentence partly adopted from: Nickel, J. P., Sacher, F. and Fuchs, S. 2021 Up-to-date monitoring data of wastewater and stormwater quality in Germany. *Water Research*, 202, 117452. https://doi.org/10.1016/j.watres.2021.117452.

Table 1.1: Estimated contribution of combined sewer overflows (CSOs), stormwater outfalls (SSOs), and wastewater treatment plants (WWTPs) to emitted loads from urban wastewater systems reported in literature.

Substance	**Contribution to emitted loads (%)**			**Spatial reference**	**Reference**
	CSO	**SSO**	**WWTP**		
Metals					
Zinc	28	42	28	Germany (ca. 55% combined sewer systems)	(Fuchs and Toshovski 2016)
	~10	~75	~15	Berlin (ca. 20% combined sewer system)	(Wicke *et al.* 2015)
Polycylic aromatic hydrocarbons (PAH)					
Benzo(a)pyrene	~11	~64	~25	Berlin (ca. 20% combined sewer system)	(Wicke *et al.* 2015)
	92	- [a]	8	Möhringen (3,500 ha, 65,000 inhabitants)	(Launay 2017)
PAH16	30	56	12	Germany (ca. 55% combined sewer systems)	(Fuchs and Toshovski 2016)
	~10	~58	~32	Berlin (ca. 20% combined sewer system)	(Wicke *et al.* 2015)
	30	- [a]	70	Hypothetical catchment (187 ha, 9,900 inhabitants)	(Welker 2007)
Plasticisers					
Bisphenol A	27	- [a]	73	Möhringen (3,500 ha, 65,000 inhabitants)	(Launay 2017)
	14	- [a]	86	Leipzig subcatchment (537 ha)	(Musolff *et al.* 2010)
	8	- [a]	92	Burlington, Vermont, USA (30,000 inhabitants)	(Phillips *et al.* 2012)
DEHP	~8	~59	~33	Berlin (ca. 20% combined sewer system)	(Wicke *et al.* 2015)
	57	- [a]	43	Möhringen (3,500 ha, 65,000 inhabitants)	(Launay 2017)
	18	- [a]	82	Hypothetical catchment (187 ha, 9,900 inhabitants)	(Welker 2007)
Biocides					
Terbutryn	13	17	69	Germany (ca. 55% combined sewer systems)	(Fuchs and Toshovski 2016)
	19	- [a]	81	Möhringen (3,500 ha, 65,000 inhabitants)	(Launay 2017)
	~10	~75	~15	Berlin (ca. 20% combined sewer system)	(Wicke *et al.* 2015)
Triclosan	28	- [a]	72	Möhringen (3,500 ha, 65,000 inhabitants)	(Launay 2017)
	16	- [a]	84	Burlington, Vermont, USA (30,000 inhabitants)	(Phillips *et al.* 2012)
Pharmaceuticals					
Carbamazepine	3	- [a]	97	Möhringen (3,500 ha, 65,000 inhabitants)	(Launay 2017)
	0.4	- [a]	99	Leipzig subcatchment (537 ha)	(Musolff *et al.* 2010)
	0	0	100	Berlin (ca. 20% combined sewer system)	(Wicke *et al.* 2015)
Diclofenac	3	0	95	Germany (ca. 55% combined sewer systems)	(Fuchs and Toshovski 2016)
	1	- [a]	99	Möhringen (3,500 ha, 65,000 inhabitants)	(Launay 2017)
Ethinylestradiol	3	- [a]	97	Hypothetical catchment (187 ha, 9,900 inhabitants)	(Welker 2007)
Caffeine					
Caffeine	90	- [a]	10	Leipzig subcatchment (537 ha)	(Musolff *et al.* 2010)
	78	- [a]	22	Burlington, Vermont, USA (30,000 inhabitants)	(Phillips *et al.* 2012)
	91	- [a]	9	Möhringen (3,500 ha, 65,000 inhabitants)	(Launay 2017)

[a] Combined sewer system only, no contribution from stormwater outfalls reported.

~ Value read off graph.

Approximately 70% of the sewer systems in Europe are built as combined sewer systems (Botturi *et al.* 2020). The European Federation of National Associations of Water Services (EurEau) estimates that there are approximately 650,000 CSO facilities (EurEau 2016). While CSOs are recognised as a threat to water quality, harmonised standards for the regulation of CSOs are still lacking (Woods-Ballard and Cherrier 2019). The UWWTD leaves it to the member states to "*decide on measures to limit pollution from storm water overflows. Such measures could be based on dilution rates or capacity in relation to dry weather flow, or could specify a certain acceptable number of overflows per year*" (European Commission 1991). National CSO policies of member states use common approaches based on these recommendations, e.g. using a maximum number of overflow events or days with overflow per year, minimum dilution of dry weather flow, or maximum overflow volume (Moreira *et al.* 2016; Botturi *et al.* 2020).

The extensive study by Moreira *et al.* (2016) showed that the availability of quantitative data on CSOs is very limited in most states. There is a "*significant lack of data on the occurrence and impact of CSOs*" (Woods-Ballard and Cherrier 2019). In contrast to WWTPs, whose effluent volumes and emitted loads (nutrients and oxygen-demand) are available due to monitoring and reporting requirements, there is no standard monitoring of CSOs. Low-cost methods are available (Botturi *et al.* 2020) but measurement equipment is not installed by standard at overflow structures in most states. Water level sensors are increasingly used for the detection of overflow frequencies, durations or, in the best case, quantities. In Germany, the federal states of Baden-Württemberg, North Rhine-Westphalia, and Bavaria have equipped a part of their CSO structures with water level sensors during the last years, which, with careful set-up and data evaluation, in many cases can be used for hydraulic discharge determination. However, it is currently still not possible to determine the occurrence of CSOs at the state or EU level in a measurement-based way (Moreira *et al.* 2016). The existing measurements may come with significant uncertainties and need to be expanded to more CSOs to become useful for determining emissions in a way comparable to WWTP data. Until then, modelling approaches are needed to estimate emissions from CSOs. These must be implementable area-wide and cannot be data-intensive, since also "*substantial data gaps exist in parameters that could be used to calculate storm water overflows*" (Moreira *et al.* 2016). Nevertheless, they should aim to provide a preliminary assessment of the emissions, their relative contribution compared to other input pathways, and an identification of priority areas for detailed assessments.

1.3 Modelling Emissions from Combined Sewer Overflows (CSOs)

A model-based determination of CSO emissions is challenging since UWS are complex and highly dynamic systems. Wet weather flows in UWS depend on precipitation intensities, the imperviousness and topography of the catchment, and the flow and storage capacities of sewers and retention facilities amongst other factors. Thus, models have been developed for different applications on different spatial and temporal scales.

Urban drainage modelling has reached a high level of sophistication at the local scale. There are various urban-hydrological and hydrodynamic models available that simulate the flow conditions in UWS on a physical basis and with high temporal resolution, e.g. SWMM[7] (Rossmann 2015), or HYSTEM-EXTRAN (ITWH 2022). These kinds of models require detailed local input data (e.g. Krebs *et al.* 2014; Muschalla *et*

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[7] StormWater Management Model

al. 2015) and need to be thoroughly calibrated to provide meaningful results (Tscheikner-Gratl *et al.* 2016). This applies all the more to the quality modelling approaches used in urban drainage modelling. Most stormwater quality models rely on equations describing the pollutant accumulation on surfaces with time (build-up) and their mobilisation by stormwater runoff (wash-off). These models can be calibrated and successfully applied to small-scale settings and individual storm events, but they may lack physical meaning (Bonhomme and Petrucci 2017), are hardly transferable (Rietveld *et al.* 2021), and show poor performance when applied to real UWS at the catchment scale (Bonhomme and Petrucci 2017; Jia *et al.* 2021). The underlying pollutant transport processes in urban catchments are insufficiently understood and characterised by stochastic variability (Leutnant *et al.* 2018). The data needed to run these kinds of urban drainage models are typically not available at river basin level. And the results obtained from existing locally validated models are not collected and aggregated, e.g. by authorities. On the other hand, for eco-hydrological models which are used on a higher spatial scale to model large urbanised catchments, a "*detailed description of sewers and drainage networks appears unfeasible*" (Salvadore *et al.* 2015). Consequently, an area-wide process-based modelling of CSO quantities and qualities at river basin level does not seem possible at present.

Thus, models conceptualised to model substance sources and emission pathways in river basins such as MONERIS[8] (Behrendt *et al.* 1999; Venohr *et al.* 2011), MoRE[9] (Fuchs *et al.* 2017a), or STOFFBILANZ (Gebel *et al.* 2010), usually use empirical approaches or mass balance methods. These models work with larger spatial units, have a moderate data-demand and operate at a lower, e.g. annual, temporal resolution. The emission pathways from UWS are often described by their mean total flow volume and a pathway-specific emission factor (e.g. mean total population-specific or area-specific load of a pollutant) or mean concentration. Consequently, the quantitative determination of the flow volumes in UWS is the basis for estimating pollutant emissions discharged from CSOs. Different approaches have been proposed.

The methods described by Fuchs and Hahn (1999), Nafo and Geiger (2004) and LUBW (2019a) use precipitation and WWTP inflow data to set up an urban water balance of a WWTP catchment (defined by the area connected to one individual WWTP). They apply a simple rainfall-runoff-calculation to estimate annual stormwater runoff in the combined sewer system (Equation 1.1).

$$Q_{\mathrm{R,CSS}} = A_{\mathrm{imp,CSS}} \cdot P \cdot \Psi_{\mathrm{m}} \tag{1.1}$$

$Q_{\mathrm{R,CSS}}$ = Annual stormwater runoff in the combined sewer system (m³/year)
$A_{\mathrm{imp,CSS}}$ = Impervious area in the combined sewer system (ha)
P = Annual precipitation (mm/year)
Ψ_{m} = Mean annual runoff coefficient (-)

Impervious area is either estimated from land cover based on empirical relations (Nafo and Geiger 2004) or available from a federal sewer system survey (LUBW 2019a). From WWTP data on total inflow and dry weather flow, the volume of stormwater runoff treated in the WWTP is calculated (Equation 1.2).

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[8] MOdelling of Nutrient Emissions in RIver Systems

[9] Modelling of Regionalised Emissions

$$Q_{R,WWTP} = Q_{TOTAL,WWTP} - Q_{DWF,WWTP} \tag{1.2}$$

$Q_{R,WWTP}$ = Stormwater runoff treated in the WWTP (m^3/year)
$Q_{TOTAL,WWTP}$ = Total inflow to the WWTP (m^3/year)
$Q_{DWF,WWTP}$ = Dry weather flow to the WWTP (m^3/year)

Then, annual CSO volume (Q_{CSO}) is calculated according to Equation 1.3.

$$Q_{CSO} = Q_{R,CSS} - Q_{R,WWTP} \tag{1.3}$$

This robust method benefits from existing measured data, i.e. standard WWTP monitoring data. However, the DWF content in CSOs is not considered. The method lacks an approach to quantify the proportion of DWF or wastewater discharged via CSOs past wastewater treatment. The proportion of wastewater discharged via CSOs was recently proposed as an emission target value for regulating the discharge of wastewater-borne substances from combined sewer systems (DWA 2021; Schmitt 2021).

MONERIS uses a different approach based on empirical equations resulting from former German design standards for CSOs (ATV-A 128E 1992) to determine the overflow rate during CSO events (Equation 1.4) in a hydrological subcatchment (analytical unit) (Venohr *et al.* 2011).

$$e = \left[\left(\frac{\frac{4000 + 25 \cdot q_R}{0.551 + q_R}}{\frac{CSV}{100} \cdot 23.3 + \frac{36.8 + 13.5 \cdot q_R}{0.5 + q_R}}\right) - 6 + \frac{P - 800}{40}\right] \tag{1.4}$$

e = Overflow rate (%)
q_R = Stormwater runoff rate (l/(s·ha)), assumed to be 1 l/(s·ha) for all analytical units
CSV = Storage capacity of combined sewer system (%), with 100% corresponding to a storage capacity of 23.3 m^3/ha
P = Annual precipitation (mm/year)

The overflow rate represents the ratio of stormwater runoff discharged by CSOs and total stormwater runoff. Stormwater runoff in the combined sewer system is calculated like above (Equation 1.1) using runoff coefficients based on empirical relations between population density, the percentage of impervious urban area, and runoff coefficient (see Venohr *et al.* 2011). The overflow rate is then applied to both, annual stormwater runoff in the combined sewer system and the wastewater generated from inhabitants and commercial areas during an "*effective number of days of heavy rainfall events*" (Venohr *et al.* 2011) to estimate annual CSO volume (Equation 1.5).

$$Q_{CSO} = ((Q_{Inh} + Q_{Com}) \cdot DHR_{eff} + Q_{R,CSS}) \cdot e/100 \tag{1.5}$$

Q_{CSO} = Total combined sewer overflow volume (m^3/year)
Q_{Inh} = Wastewater from households (inhabitants) (m^3/d), assuming a population-specific wastewater production of 130 l/(inhabitant·d)
Q_{Com} = Wastewater from commercial areas (m^3/d), assuming 1 l(s·ha) for 10 hours after heavy rainfall events from 0.8% of the total urban area
DHR_{eff} = Effective number of days of heavy rainfall events (d/year) (Equation 1.7)
$Q_{R,CSS}$ = Stormwater runoff in the combined sewer system (m^3/year)
e = Overflow rate (%) according to Equation 1.4

The effective number of days of heavy rainfall events is meant to describe the number of heavy rainfall days that cause a CSO event. For this purpose, Venohr *et al.* (2011) estimate the number of heavy rainfall days (*DHR*) according to Equation 1.6 and adjust it according to Equation 1.7, to reflect that in sewer systems with high storage capacity, "*heavy rainfall events less often cause an overflow event*" (Venohr *et al.* 2011).

$$DHR = P^{2,5} \cdot 0.0000012 \tag{1.6}$$

$$DHR_{\mathrm{eff}} = DHR \cdot (e \;/\; e_{\mathrm{CSV=0}}) \tag{1.7}$$

DHR = Number of days of heavy rainfall events (d/year)
P = Annual precipitation (mm/year)
DHR_{eff} = Effective number of days of heavy rainfall events (d/year)
e = Overflow rate (%) according to Equation 1.4
$e_{\mathrm{CSV=0}}$ = Overflow rate (%) according to Equation 1.4 considering 0% storage capacity

With this approach, the proportion of wastewater discharged via CSOs could theoretically be determined separately, by applying the overflow rate to the wastewater generated during the heavy rainfall days. However, the empirical equations used to calculate the CSO overflow rate are non-transparent, do represent the planning situation only, and cannot be adapted to an improving data situation.

Pistocchi *et al.* (2019) state to "*attempt a first-ever modelling of CSO volumes at the large scale (whole EU)*". They use a global precipitation dataset (Beck *et al.* 2019) to estimate surface runoff on impervious areas in approximately 700 functional urban areas (FUA) across Europe with a 3-hourly time step. The total flow volumes in the system (sum of runoff and dry weather flow) exceeding a design dilution rate, i.e. a multiple of dry weather flow, are considered to be CSO discharges (Equation 1.8).

$$Q_{\mathrm{CSO}} = \max(0, f \cdot A_{\mathrm{U}} \cdot R + (1 - \mathrm{d}) \cdot p \cdot P) \tag{1.8}$$

Q_{CSO} = Total combined sewer overflow volume
f = Runoff coefficient, percentage of rainfall on urban area turning into runoff
A_{U} = Urban area served by combined sewer system
R = Rainfall
d = Design dilution rate
p = Population-specific dry weather flow rate
P = Total population

The authors acknowledge that this model represents an acceptable approximation only and can be considered a worst-case scenario because the runoff coefficient for impervious area is set to 1 and available storage volume in UWS is not considered (Pistocchi *et al.* 2019). The model has been developed further to consider surface and sewer system storage and verified using case studies (Quaranta *et al.* 2022a). The DWF content in CSO is computed as an indicator for pollution with wastewater-borne substances (Quaranta *et al.* 2022a). Although relying on default values and assumptions, it can be considered a valuable instrument for comparing policy scenarios at the EU scale.

In summary, detailed process-based urban-hydrological models are not applicable for area-wide estimation of CSO emissions in river basins due to lacking data. As long as these models are not calibrated with measured data, they offer no advantage over simple estimates. Approaches used in river basin emission models should make the most of existing monitoring data (e.g. WWTP data) and use transparent and adaptable calculation steps since in the future, data will increasingly become available that can validate or replace estimates. Therefore, despite its simplicity, the urban water balance approach applied by Nafo and Geiger (2004) and LUBW (2019a) seems promising. However, it needs to be adapted to consider the proportion of wastewater discharged via CSOs. The data required for the urban water balance approach is available or could be collected at river basin level with reasonable effort. Mean concentrations or emission factors applied to the total flow volumes need to be derived from monitoring data that are as substantiated and representative as possible. Consequently, although the approaches are less detailed, there is still a need for a reliable data basis, especially regarding micropollutant concentrations.

1.4 Sources and Fate of Micropollutants in UWS

The components that contribute to the total flow in UWS are wastewater (consisting of domestic, commercial, and industrial wastewaters), infiltration water, and stormwater runoff. While the volume contributed by infiltration water may be significant, its pollutant loads are expected to be comparatively low under regular conditions. Therefore, wastewater and stormwater are considered here as the main sources of pollutant loads to UWS.

Wastewater contains a variety of chemical constituents used or generated in households, businesses and industries. This includes pharmaceuticals, steroid hormones, and substances found in food or drinks, e.g. artificial sweeteners and caffeine from human excretion. Further, substances used in personal care products or other household chemicals used for bathing, laundry, dishwashing, and cleaning (e.g. disinfectants, surfactants, anticorrosives). The washing of specific textiles may release nonylphenols or PFAS. Improper disposal of expired pharmaceuticals and household products, or improper cleaning of biocide containers or spraying tools contribute to wastewater pollution. Other constituents are substances leaching out of various materials (e.g. heavy metals and plasticisers) (Thornton *et al.* 2001; Bester *et al.* 2008; Luo *et al.* 2014).

Stormwater mobilises pollutants from surfaces in the urban catchment that are exposed to rainfall and runoff (Figure 1.2). These may be fresh input sources or temporary sinks of accumulated pollutants. The pollution’s origins are various, but can be categorised into atmospheric deposition, urban materials, and anthropogenic activities (Müller *et al.* 2020).

Figure 1.2: Stormwater mobilises pollutants from surfaces in the urban catchment.

Atmospheric pollutants are introduced into catchments by dry or wet deposition. Wet deposition occurs either through rain-out of liquids that were formed by condensation and diffusion processes during cloud formation, or through wash-out of aerosols or gases by rain and snow, while dry deposition describes the settling of particles and gases (Brinkmann 1985). These processes may introduce significant pollution, e.g. metals, PAH, PFAS, pesticides, anticorrosives, or flame retardants (Müller et al., 2020; Murakami et al., 2009; Spahr et al., 2020). Original sources of anthropogenic atmospheric pollutants are likely power plants, heating systems, industries, traffic, and agriculture (Brinkmann 1985; Spahr *et al.* 2020).

Urban surfaces exposed to rain, including streets and parking lots, roofs and facades of buildings and other structures comprise a variety of materials and affect the quality of stormwater runoff. Pollutants are released by corrosion or leaching processes from materials like bitumen, asphalt, concrete, metal and plastic coverings, paints and coatings to name a few (Bester *et al.* 2008; Müller *et al.* 2020). Significant release from urban materials was reported for various substances including heavy metals, biocides, plasticisers, flame retardants, and anticorrosives (Burkhardt *et al.* 2007; Müller *et al.* 2020; Spahr *et al.* 2020).

Anthropogenic activities that cause pollution of stormwater runoff include traffic, construction, wrecking, industrial activities, leakages, spills, littering, and the use and maintenance of urban green spaces. Mineral oil hydrocarbons, PAH, and metals are released with exhausts, leakages, tire and brake wear of vehicular traffic (Brown and Peake 2006; Bester *et al.* 2008; Müller *et al.* 2020). Street runoff has been reported to contain PFAS (Murakami *et al.* 2009), plasticisers, nonylphenols (Björklund 2010), de-icing fluids, and anticorrosives (Müller *et al.* 2020). Runoff pollution by commercial or industrial activities highly depends on the type of activity, but may be due to transport or materials used in manufacturing processes (Müller *et al.* 2020). In urban green spaces, applications of pesticides and biocides contribute to runoff pollution (Wittmer *et al.* 2010).

Table 1.2: Sources of pollutants to urban wastewater systems compiled from Thornton *et al.* 2001; Bester *et al.* 2008; Björklund 2010; Wittmer *et al.* 2010; Luo *et al.* 2014; Wieck *et al.* 2018; Müller *et al.* 2020; Spahr *et al.* 2020.

Sources		**Pollutants**
Stormwater	Atmospheric deposition	Metals, PAH, PFAS, anticorrosives, and flame retardants originally emitted from power plants, heating systems, industries, or traffic Agricultural pesticides
	Urban materials	Metals, e.g. zinc and copper (metal roofs) PAH (bitumen, asphalt) Biocides (facades) Plasticisers, flame retardants
	Anthropogenic activities	Mineral oil hydrocarbons, PAH, metals (traffic exhausts, leakages, vehicle wear) De-icing fluids and anticorrosives (traffic) Pesticides and biocides (green spaces) Plasticisers (traffic, littering)
Wastewater	Domestic wastewater	Pharmaceuticals, steroid hormones, artificial sweeteners (human excretion) Personal care products (bathing) Surfactants, disinfectants, anticorrosives (laundry, dishwashing, cleaning) PFAS and nonylphenols (textiles) Plasticisers, biocides (leaching of materials)
	Industrial wastewater	Industrial chemicals, by-products

There is an increasing number and variety of substances and transformation products to be considered. Some micropollutants are easily attributed to specific sources, e.g. substances from human excretion to domestic wastewater (Table 1.2). Therefore, artificial sweeteners like acesulfame or pharmaceuticals like carbamazepine are often used as markers for wastewater (Buerge *et al.* 2009; Scheurer *et al.* 2011; Pongmala *et al.* 2015). Other substances are more difficult to trace back due to ubiquitous occurrence and multiple sources (e.g. PFAS (Murakami *et al.* 2009)), or complex emission patterns (e.g. biocides with periodic applications or rain-driven release (Götz *et al.* 2010)).

The environmental fate of chemicals is defined by their primary sources and the interdependent processes of phase partitioning between air, aqueous, and solid phases, biological and chemical transformation, transport, and retention in temporary or permanent sinks. The fate processes in UWS are visualised in Figure 1.3: in the sewer system, chemicals are transferred between the water phase, suspended particles, sewer sediments, biofilms, moisture layers on sewer walls, and a sewer headspace (Hvitved-Jacobsen *et al.* 2013). In each component, abiotic or biotic transformation processes may occur. In standard WWTPs, sedimentation and biotransformation processes are specifically used and optimised to eliminate suspended solids, biodegradable organic matter, and nutrients. Pollutants are removed from the water phase which will reach the receiving water by one or more of the following processes: adsorption followed by sedimentation or filtration, biodegradation, or to a minor degree by volatilisation or photolysis (Margot 2015). Suspended solids as a standard analysis parameter therefore play a key role for the transport of many pollutants.

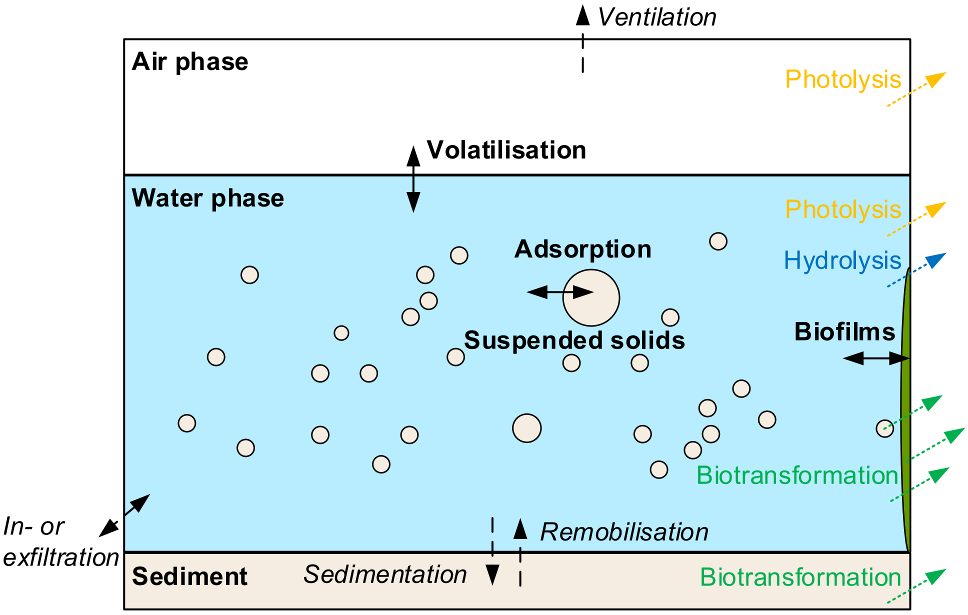

Figure 1.3: Fate of micropollutants in urban wastewater systems: Partitioning (solid arrows) and transformation (dotted) processes, temporary and permanent sinks (dashed).

Chemicals can be attributed to different profiles of environmental behaviour based on intrinsic physico-chemical properties, e.g. their water solubility, vapour pressure, partition coefficients between air, water, and octanol, and susceptibility to degradation or transformation (Mackay *et al.* 2006). Multi-media fate models use these properties to model the distribution and fate of chemicals in the environment (Mackay *et al.* 1996; Harrad 2001; Suciu *et al.* 2013). There are models to assess fate of chemicals in WWTP with typical activated sludge processes (Seth *et al.* 2008) and fate models have also been combined with integrated urban water system models to assess mass fluxes of organic pollutants (Keyser *et al.* 2010; Vezzaro *et al.* 2014). Basic physico-chemical data are also frequently used in schemes for suspect screening, for prioritisation or ranking of pollutants, or for the selection of substances for monitoring. Baun *et al.* (2006) used filter definitions based on physico-chemical properties and data on bioaccumulation, biodegradation, and ecotoxicity to identify and rank xenobiotic organic compounds of environmental concern in stormwater. Parameters selected as being particularly important in determining the fate of chemicals were volatility from aqueous solution, affinity to suspended solids, and resistance to biodegradation. Eriksson *et al.* (2007) identified relevant stormwater priority pollutants using a five step assessment tool, including source characterisation and hazard and problem identification. Lundy *et al.* (2012) proposed a risk prioritisation methodology for stormwater pollutants originating from differing land uses. The likelihood of occurrence was assessed either using published field data or by theoretical consideration of the physico-chemical characteristics, i.e. partition modelling. Götz *et al.* (2010) presented a methodology to select compounds for monitoring programmes and water quality guidance adapted to the Swiss situation, using three filters to consider the distribution behaviour between environmental media, degradability, and input dynamics. Gerbersdorf *et al.* (2015) proposed four groups to classify micropollutants into in order to identify suitable indicator substances for monitoring: (a) water-soluble, effectively biodegradable, (b) particle-bound, effective elimination by solids removal, (c) particle-bound, effectively biodegradable and (d) water-soluble, non-biodegradable.

In summary, the sources (i.e. initial release to either wastewater or stormwater) and the environmental behaviour of substances (i.e. susceptibility to removal processes, especially in WWTPs) are main factors defining their transport and fate in UWS and consequently their emission pathways to receiving waters. Information about the origin or uses/applications of substances, their predominant transport form (particle-bound or dissolved) and their biodegradability should be considered to structure the large number of micropollutants to deal with.

1.5 Water Quality Monitoring in UWS

Water quality monitoring of discharges in UWS has become increasingly important. Reliable data are needed both to improve and validate process-based quality modelling, and to derive valid mean concentrations or emission factors for use in river basin models in order to develop effective strategies for mitigating pollutant emissions.

In order to collect representative data in UWS, monitoring strategies need to take into account the spatial and temporal concentration dynamics of the target pollutants. These dynamics are influenced by the sources of a pollutant, its release patterns (e.g. continuous, periodic, or complex) and environmental behaviour, the presence and size of temporary sinks (e.g. deposits), and the variable flow conditions in the system. Concentrations can be subject to significant fluctuations both in short time intervals (minutes, storm events) and in the long-term (daily and weekly fluctuations, seasonal patterns). Due to the concentration variability, single discrete samples typically do not provide meaningful results (Lee *et al.* 2007). Regular or continuous sampling over sufficiently long periods of time is required to record concentrations in a representative manner (Leecaster *et al.* 2002). Two basic sampling strategies can be distinguished: (a) high temporal resolution sampling and analysis aims to record the short-term concentration variability as detailed as possible, (b) long-term composite sampling aims to determine mean concentrations representative of specific time periods while saving analytical costs. The sampling strategy must always be adapted to the monitoring objectives, technical requirements and financial constraints. However, when aiming at quantifying average concentrations or loads, long-term composite sampling can be considered a suitable and cost-efficient strategy (McCarthy and Harmel 2014).

For monitoring sewer system discharges such as CSOs and SSOs, an event-based analysis has become common practice. Event-based sampling has the advantage of a short-term control of the sampling process and a short time until the samples are analysed. Both the pollutograph produced from single samples collected throughout a storm event and a composite sample can be used to quantify the event mean concentrations (EMC) (Ma *et al.* 2009; McCarthy *et al.* 2018)[10]. Generally, ideal representative EMC require volume-proportionally distributed subsamples from as large a part of the event as possible, with a temporal resolution adapted to concentration dynamics[10]. The EMCs of individual sampling sites can again be aggregated to derive site mean concentrations (SMC) (Mourad *et al.* 2005; McCarthy *et al.* 2018). Volume-weighted SMCs are considered to be the most appropriate quantity for the calculation of long-term loads (Mourad *et al.* 2005; May and Sivakumar 2013)[11].

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[10] Sentence adopted from: Nickel, J. P. and Fuchs, S. 2021 Large-Volume Samplers for Efficient Composite Sampling and Particle Characterization in Sewer Systems. *Water*, 13(20), 2831. https://doi.org/10.3390/w13202831.

[11] Sentence adopted from: Nickel, J. P., Sacher, F. and Fuchs, S. 2021 Up-to-date monitoring data of wastewater and stormwater quality in Germany. *Water Research*, 202, 117452. https://doi.org/10.1016/j.watres.2021.117452.

Similar to the lack of data on the occurrence and quantities of CSOs, area-wide data on the quality of these discharges is not available. Existing data pools based on research-oriented studies are outdated and do not take into account the comparability of data derived from different areas or methodologically different studies (Brombach *et al.* 2005). In addition, historical data is limited to standard water quality parameters (e.g. suspended solids, nutrients, heavy metals). In the last decade, several studies have collected the first data on micropollutants in CSOs (e.g. Gasperi *et al.* 2012; Clara *et al.* 2014; Kemper *et al.* 2015; Launay *et al.* 2016b; Becouze-Lareure *et al.* 2019; Gruber *et al.* 2020; Mutzner *et al.* 2020; Paijens *et al.* 2021). Table 1.3 shows a selection of results for frequently analysed substances. Due to spatial, strategical and/or methodological differences, the comparability of the studies is not always clear and their applicability for an area-wide assessment of micropollutant emissions is limited.

There is a need for research to expand the data available to date, to investigate the comparability of studies, and improve the understanding of concentration variability. In order to generate representative data for calculating emissions from CSOs, event-based and volume-proportional composite sampling is considered a suitable strategy to be further applied and explored.

Table 1.3: Concentrations of selected micropollutants in combined sewer overflows (CSOs) reported in literature.

Substance	**CSO concentration (µg/l)**		**Sampling details**	**Country**	**Reference**
	Central value[a]	**Range[b]**			
Metals					
Zinc	110	28–510*	48 grab samples from 11 CSOs	Germany	(Engelmann *et al.* 2016)
	110*	42–300	7 composite samples from 2 CSOs	Austria	(Clara *et al.* 2014)
	108*	SD 33.7	12 composite samples from 1 CSO	France	(Becouze-Lareure *et al.* 2019)
Polycylic aromatic hydrocarbons (PAH)					
Benzo(a)-pyrene	0.08	0.03–0.21	7 composite samples from 1 CSO	Germany	(Launay *et al.* 2016b)
	<0.003/<0.01	<0.003/<0.01	50 grab samples from 12 CSOs	Germany	(Engelmann *et al.* 2016)
	0.125*[c]	0.057–0.203[c]	4 composite samples from 1 CSO	France	(Gasperi *et al.* 2012)
Benzo(ghi)-perylene	0.073	0.059–0.18	7 composite samples from 1 CSO	Germany	(Launay *et al.* 2016b)
	<0.008/<0.01	<0.008/<0.01	50 grab samples from 12 CSOs	Germany	(Engelmann *et al.* 2016)
	0.0017*	<LOD–0.0035	5 composite samples from 2 CSOs	Austria	(Clara *et al.* 2014)
	0.0251*	SD 0.019	12 composite samples from 1 CSO	France	(Becouze-Lareure *et al.* 2019)
	0.142*[c]	0.06–0.259[c]	4 composite samples from 1 CSO	France	(Gasperi *et al.* 2012)
Plasticisers					
DEHP	2.1	0.7–5.4	7 composite samples from 1 CSO	Germany	(Launay *et al.* 2016b)
	0.54	<0.01–1.2*	48 grab samples from 11 CSOs	Germany	(Engelmann *et al.* 2016)
	1.7*	<0.35–5.1	7 composite samples from 2 CSOs	Austria	(Clara *et al.* 2014)
Biocides					
Carbendazim	0.034	0.015–0.042	7 composite samples from 1 CSO	Germany	(Launay *et al.* 2016b)
	0.072*	<LOD–0.18	6 composite samples from 2 CSOs	Austria	(Clara *et al.* 2014)
	-	0.021–0.9*	95 time-weighted average concentrations (passive samplers) from 20 CSOs	Switzerland	(Mutzner *et al.* 2020)
	0.079	0.024–0.25	8 composite samples from 1 CSO	France	(Paijens *et al.* 2021)

Substance	**CSO concentration (µg/l)**		**Sampling details**	**Country**	**Reference**
	Central value[a]	**Range**[b]			
Diuron	0.26	0.068–0.68	7 composite samples from 1 CSO	Germany	(Launay *et al.* 2016b)
	-	Max. 2.68	33 composite samples from 1 CSO	Germany	(Christoffels *et al.* 2016)
	<0.01/<0.07	<0.01/<0.07	48 grab samples from 11 CSOs	Germany	(Engelmann *et al.* 2016)
	0.12*	<0.05–0.22	6 composite samples from 2 CSOs	Austria	(Clara *et al.* 2014)
	-	0.022–1.1*	95 time-weighted average concentrations (passive samplers) from 20 CSOs	Switzerland	(Mutzner *et al.* 2020)
	0.072	SD 0.09	12 composite samples from 1 CSO	France	(Becouze-Lareure *et al.* 2019)
	0.1	0.047–0.2	8 composite samples from 1 CSO	France	(Paijens *et al.* 2021)
Mecoprop	0.14	0.10–0.378	7 composite samples from 1 CSO	Germany	(Launay *et al.* 2016b)
	-	Max. 0.44	33 composite samples from 1 CSO	Germany	(Christoffels *et al.* 2016)
	<0.03/3	<0.03–0.18*	48 grab samples from 11 CSOs	Germany	(Engelmann *et al.* 2016)
	-	0.098–5.3*	95 time-weighted average concentrations (passive samplers) from 20 CSOs	Switzerland	(Mutzner *et al.* 2020)
	0.13	0.086–0.29	8 composite samples from 1 CSO	France	(Paijens *et al.* 2021)
Terbutryn	0.083	0.055–0.122	7 composite samples from 1 CSO	Germany	(Launay *et al.* 2016b)
	<0.01	<0.01–0.19*	48 grab samples from 11 CSOs	Germany	(Engelmann *et al.* 2016)
	-	0.029–0.81*	95 time-weighted average concentrations (passive samplers) from 20 CSOs	Switzerland	(Mutzner *et al.* 2020)
	0.044	0.029–0.064	8 composite samples from 1 CSO	France	(Paijens *et al.* 2021)
Pharmaceuticals					
Carbamazepine	0.08	0.03–0.154	7 composite samples from 1 CSO	Germany	(Launay *et al.* 2016b)
	-	Max. 0.65	33 composite samples from 1 CSO	Germany	(Christoffels *et al.* 2016)
	<0.2	<0.2–0.3*	48 grab samples from 11 CSOs	Germany	(Engelmann *et al.* 2016)
	-	0.033–0.91*	95 time-weighted average concentrations (passive samplers) from 20 CSOs	Switzerland	(Mutzner *et al.* 2020)
Diclofenac	0.15	0.062–0.276	7 composite samples from 1 CSO	Germany	(Launay *et al.* 2016b)
	-	Max. 1.18	33 composite samples from 1 CSO	Germany	(Christoffels *et al.* 2016)
	0.06	<0.03–1.04*	48 grab samples from 11 CSOs	Germany	(Engelmann *et al.* 2016)
	-	0.078–1.0*	95 time-weighted average concentrations (passive samplers) from 20 CSOs	Switzerland	(Mutzner *et al.* 2020)
	0.203*	Max. 1.805	14 grab samples from 4 CSOs	U.K.	(Kay *et al.* 2017)
Anticorrosives					
Benzotriazole	0.727	0.358–1.79	7 composite samples from 1 CSO	Germany	(Launay *et al.* 2016b)
	-	0.25–4.8*	95 time-weighted average concentrations (passive samplers) from 20 CSOs	Switzerland	(Mutzner *et al.* 2020)

[a] Median, except for arithmetic mean values marked with *.

[b] Min–Max, except for 10th–90th percentile ranges marked with *, or standard deviation indicated with "SD".

[c] Particulate concentration.

LOD = limit of detection.

1.6 Research Objectives and Structure of this Thesis

Emissions from sewer systems discharges come increasingly into focus in the context of the management of micropollutants. Against the background outlined in the chapters 1.1–1.5, this thesis focuses on micropollutant emissions from CSOs and has the overarching goal to improve the assessment of this emission pathway at river basin level using new monitoring data.

The main part of the thesis is based on three peer-reviewed scientific publications (chapters 2–4) and puts a focus on water quality of CSOs. As a central element, a comprehensive monitoring programme was conducted using automated large-volume samplers (LVS). In addition, in chapter 5, an urban water balance approach for estimating CSO flow volumes is adapted and tested on a first catchment for verification. This approach is then used in combination with the water quality data to estimate substance emissions from CSOs. Both new original data and an instrument for assessing of CSO emissions in larger planning areas are developed.

The work presented followed five research objectives:

1. **Explore the characteristics, suitability and comparability of methods used for sampling in UWS.**

   Substance concentrations in UWS are characterised by high and stochastic variability. Monitoring strategies need to either record or integrate this variability. Event-based composite sampling is considered a suitable strategy to generate representative data for calculating emissions. The comparability of studies using different strategies and methods (e.g. equipment) needs to be evaluated. Thus, in chapter 2, the strategy, the samplers and the methods used for CSO sampling in this study are characterised in detail. Results obtained from LVS sampling are compared to more widely used conventional autosamplers which were installed at the same sampling sites to investigate the comparability these methods. This is done by comparing total suspended solids (TSS) concentrations as a standard water quality parameter measured in most urban stormwater quality studies. This is important because of the key role of suspended solids as a transport matrix for adsorptive substances and because representative sampling of the particulate phase can generally be considered more critical than representative sampling of the water phase. As LVSs were first developed as a method for improving the quality of particle analyses by collecting high solids masses, further insight is given to the effect of subsampling and analytical methods on particle size analyses in CSO samples and the resulting concentrations of TSS < 63 µm (TSS63). Chapters 3 and 4 provide additional verification of the CSO sampling regarding the representative coverage of events and the successful analytical quantification of micropollutants.

2. **Improve the knowledge of substance concentrations in CSOs by contributing new original data on micropollutants.**

   Existing quality models are hardly transferable and not applicable to UWS at the catchment scale. Representative monitoring data is needed instead to improve the knowledge of substance concentrations in CSOs. In chapters 3 and 4, a new dataset obtained from the monitoring programme on concentrations of both, standard water quality parameters and micropollutant substances, is documented and subjected to thorough statistical analyses. Chapter 3 was based on a preliminary dataset and is completed by the evaluations in chapter 4.

3. **Improve the understanding of concentration variability in CSOs.**

   To improve the understanding of concentration variability in CSOs, the observed variability between events and sites is analysed to identify patterns considering information about the sources and environmental behaviour of the substances. Additionally, correlation analysis is used to verify similar behaviour of substance groups representing different expressions of these characteristics. Accompanying data is used to test explanatory approaches based on catchment properties and hydraulic conditions.

4. **Assess the importance of CSOs to receiving water quality regarding both substance concentrations and emitted loads.**

   To manage surface water pollution from UWS effectively, a holistic assessment of the emissions from both wastewater and stormwater treatment is needed[12]. Consequently, chapter 4 puts the final CSO dataset into context by merging it into an up-to-date dataset covering also extensive investigations of WWTPs and SSOs. All sampling and analytical methods used in these investigations were strategically adapted and strictly harmonised to generate comparable data that allowed straightforward statistical analyses and summarisation. The evaluations aim to analyse the relation of concentrations and loads between the different emission pathways from UWS. Finally, the concentration data are aggregated in a harmonised way to derive representative data suitable for estimating emissions at river basin level.

5. **Adapt an urban water balance approach as a basis for modelling CSOs at river basin level.**

   The quantitative determination of the flow volumes in UWS is the basis for estimating emissions from CSOs. Since detailed process-based urban-hydrological models are not applicable for area-wide estimation of CSO emissions in river basins, simple solution-oriented tools are needed to provide a preliminary emission assessment as a basis for identifying priority areas for detailed investigation. Chapter 5 describes an adapted urban water balance approach using data available in many catchments today. The approach is tested on a catchment for verification and used in combination with the quality data to estimate substance emissions from UWS.

Finally, a synoptic discussion of the findings is presented in chapter 6.

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[12] Sentence adopted from: Nickel, J. P., Sacher, F. and Fuchs, S. 2021 Up-to-date monitoring data of wastewater and stormwater quality in Germany. *Water Research*, 202, 117452. https://doi.org/10.1016/j.watres.2021.117452.

2 Large-Volume Samplers for Efficient Composite Sampling and Particle Characterisation in Sewer Systems

This chapter has been published as an article in Water:

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Abstract: The assessment of pollution from sewer discharges requires flexible and reliable sampling methods. The characteristics of the sampling system must be known to allow comparison with other studies. Large volume samplers (LVS) are increasingly used for monitoring in sewer systems and surface waters. This article provides a comprehensive description of this widely applicable sampling system, gives insight into its comparability to standard methods, and provides recommendations for researchers and practitioners involved in water quality monitoring and urban water management. Two methods for subsampling from LVS are presented, i.e., collection of homogenized or sedimented samples. Results from a sampling campaign at combined sewer overflows (CSOs) were used to investigate the comparability of both subsampling methods and conventional autosamplers (AS). Event mean concentrations (EMC) of total suspended solids (TSS) derived from homogenized LVS samples and AS pollutographs were comparable. TSS-EMC of homogenized and sedimented LVS samples were also comparable. However, differences were found for particle size distribution and organic matter content. Consequently, sedimented LVS samples, which contained solids masses in the range of 3–70 g, are recommended to be used for particle characterization. The differences between homogenized and sedimented LVS samples, e.g., the quality of homogenization and the stability of samples during sedimentation in LVS, should be further investigated. Based on LVS results, average TSS concentrations of 50–60 mg/L were found for CSOs from centralized treatment facilities in Bavaria. With a median share of 84%, particles < 63 µm were the dominant fraction.

2.1 Introduction

Discharges from sewer systems contribute significantly to the total pollutant load to receiving water bodies (Fuchs *et al.* 2010b; Launay *et al.* 2016b; Becouze-Lareure *et al.* 2019; Paijens *et al.* 2021; Wicke *et al.* 2021). The monitoring of stormwater runoff and combined sewer overflows (CSOs) has become increasingly important for better quantifying these contributions and for developing effective strategies to reduce pollutant emissions.

Solids play a key role for water quality management. They impact the physical, chemical, and biological properties of water bodies and represent a transport matrix for adsorbed pollutants (Bilotta and Brazier 2008). Consequently, total suspended solids (TSS) are among the most frequently measured parameters in stormwater monitoring (Pitt *et al.* 2017) and are often used as a proxy for overall water quality in urban drainage modeling (Todeschini *et al.* 2018). The environmental fate of suspended solids and the magnitude of their effects in aquatic ecosystems depend on their properties, e.g., particle size distribution (PSD) and chemical composition (Bilotta and Brazier 2008). Knowledge of these properties is necessary for assessing the origin, the significance to water quality, and the treatability of suspended solids for effective modeling and for designing effective stormwater management measures (Kim and Sansalone 2008; Fuchs *et al.* 2010a; Selbig *et al.* 2016; Pitt *et al.* 2017; Todeschini *et al.* 2018).

Due to highly variable flow conditions and fluctuating concentrations, the sampling time in a storm event is decisive for representative quality assessment (Lee *et al.* 2007). Two main strategies for sampling storm events are to collect either discrete single samples distributed across an event (Lee *et al.* 2002; Barco *et al.* 2008; Wittmer *et al.* 2010; Madoux-Humery *et al.* 2013) or one composite sample representative of the entire discharge period (Paijens *et al.* 2021; Wicke *et al.* 2021). Both the pollutograph produced from single samples and a composite sample can be used to quantify the event mean concentrations (EMC) (Ma *et al.* 2009; McCarthy *et al.* 2018). Generally, events should be sampled as completely as possible to avoid over- or underestimation of EMC. Composite sampling lacks time-resolved information but is advantageous in sampling entire event durations while reducing analytical costs (McCarthy and Harmel 2014).

Large-volume samplers (LVS) are composite samplers with increased capacity of up to 1000 L. The high volume gives flexibility in capturing long-duration and high-volume events while maintaining a sufficiently representative subsample volume of several liters. Particularly, the amount of solids collected in the sampler enables further particle analyses to be carried out (Fuchs *et al.* 2014).

LVSs were first developed in the late 2000s as a method for improving the quality of particle analyses by collecting high solids masses. They have since been used for monitoring street runoff (Grotehusmann *et al.* 2014), stormwater discharges in separate sewer systems (Eyckmanns-Wolters *et al.* 2013; Baum *et al.* 2021), combined sewer overflows (Fuchs *et al.* 2014; Kemper *et al.* 2015; Nickel and Fuchs 2019), and surface waters (Wagner; Fuchs *et al.* 2018; Fuchs *et al.* 2019a). However, the comparability with other sampling methods has not been investigated so far.

The objectives of this article are (1) to provide a comprehensive description of LVS and two methods for subsampling from LVS composite samples (i.e., collection of homogenized samples and sedimented samples) and (2) to evaluate the results of a CSO sampling campaign (Nickel and Fuchs 2020) with simultaneous use of LVS and conventional autosamplers (AS). The comparability of the TSS-EMC derived from both sampling systems was investigated. Furthermore, both LVS subsampling methods were applied to the same original samples to investigate the influence of subsampling on the quantification of TSS and the concentration of total suspended solids < 63 µm (TSS63). TSS63 were recently introduced as a new regulatory parameter for stormwater treatment in Germany (DWA-A 102-2/BWK-A 3-2 2020). The clay and silt-sized solids have been identified as the dominant particle size fraction in stormwater runoff following wash-off from impervious surfaces due to hydraulic sorting (Droppo *et al.* 2002). Larger particles have a lower wash-off mobility and are more likely to be retained on surfaces (Zhao *et al.* 2018). In addition, larger particles are preferentially deposited during transport in the sewer system depending on flow conditions (Pitt *et al.* 2017; Fuchs *et al.* 2019b). With TSS63, which are not biased by larger particles, a better comparability of the results of different sites is achieved. Furthermore, fine particles are associated with high pollutant loading (Sansalone and Buchberger 1997; Vaze and Chiew 2004; Gunawardana *et al.* 2014; Baum *et al.* 2021) and represent the most critical fraction to physical separation processes common in stormwater treatment, i.e., sedimentation or filtration (Boogaard *et al.* 2016; Fuchs *et al.* 2019b). Our analyses are considered important to better understand the comparability of monitoring results produced with LVS. In addition, the results provide new data on the concentrations, organic matter content, and pollutant loading of solids in CSOs.

2.2 Materials and Methods

2.2.1 Large-Volume Samplers

LVS were designed to collect long-term or event-based volume-proportional composite samples and to collect sufficient solids masses to allow reliable quantification and particle characterization, e.g., PSD and chemical composition. For this purpose, large collecting tanks of up to 1000 L, powerful pumps with capacities ≥ 1000 L/h, and tubings with diameters of 19–25 mm are used. The general setup is shown in Figure 2.1. A control unit processes water level or flow measurement signals to integrate the discharge volume at the sampling site. The sampling pump is activated at defined volume intervals. The specific duration of one pumping action defines the subsample volume. Different setups of LVS have been used and adapted to specific research objectives, e.g., glass-fiber reinforced plastic tanks were replaced by stainless steel tanks to provide a sampling container with minimized ad- or desorption effects suitable for the quantification of micropollutants (Nickel and Fuchs 2019). In another study, a three-way valve was installed before the tank inlet to realize a flushing of the tubing system prior to sampling (Fuchs *et al.* 2019a). Assuming a TSS concentration range of 10–1000 mg/L and a LVS sample volume of 100–1000 L, the total dry mass in the tank may range from 1 to 1000 g.

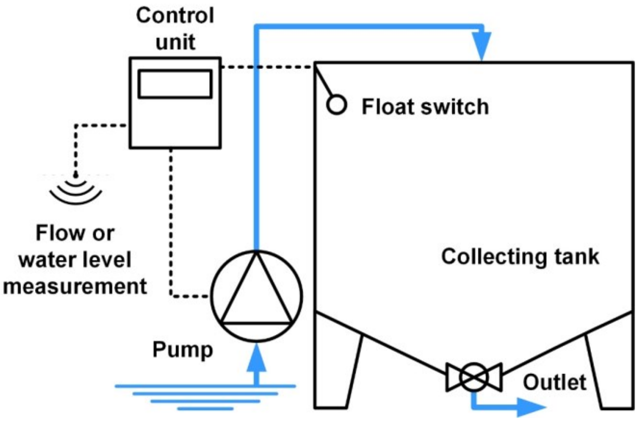


Figure 2.1: General setup of the large-volume sampler.

2.2.2 Subsampling Methods

On completion of a sampling period, there are two methods for subsampling the large-volume composite samples from the collecting tank (Figure 2.2).

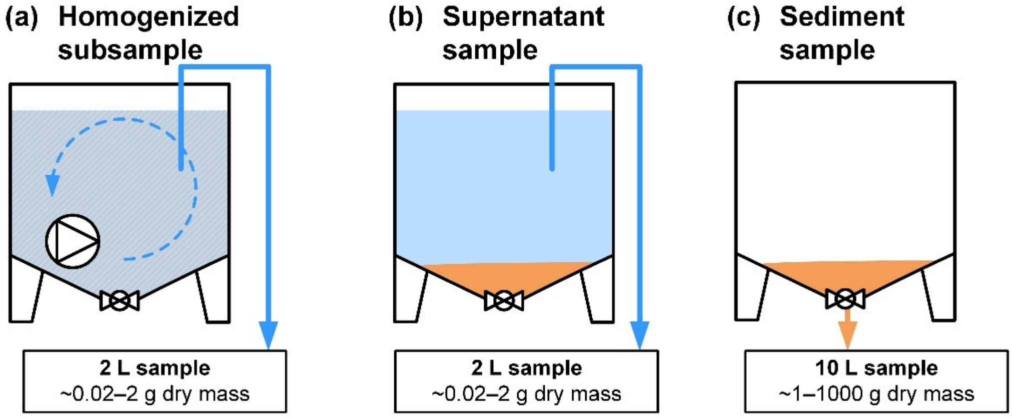


Figure 2.2: Methods for subsampling from large-volume composite samples.

2.2.2.1 Homogenized Sample

Homogenized subsamples of the total composite sample are used to quantify total concentrations of pollutants (Nickel and Fuchs 2019). After the sampling period, sediments and suspended solids in the container are homogenized by using a submersible pump to agitate the sample (Figure 2.2a). After several minutes, 2 L subsamples are collected. From the total dry mass calculated above, approximately 0.02–2 g are sampled for analysis. This method is fast and easy to carry out.

2.2.2.2 Sedimented Sample with Supernatant Sample

Sedimented samples are used for particle analyses and for quantifying loads based on high solids masses (Eyckmanns-Wolters *et al.* 2013; Kemper *et al.* 2015). For this purpose, composite samples are left to settle for 1–2 days until settling is completed, according to visual inspection. Considering particle settling velocity distributions of combined sewage reported in the literature (e.g. Michelbach and Wöhrle 1994; Fugate and Chant 2006), all settleable solids should settle in the tank within one day. Grab samples from the supernatant water are collected (Figure 2.2b) to quantify the remaining suspended solids concentration, or to analyze dissolved substances. From a bottom valve, the first flush of sediments is collected into a 10 L sampling container before the supernatant water is drained at low speed to avoid flushing of sediments. Afterwards, all remaining sediments are mobilized using supernatant water and quantitatively collected in a 10 L sampling container (Figure 2.2c). In this way, the complete dry mass is sampled for analysis.

2.2.3 Sampling Campaign

In a study on CSO quality in Bavaria, ten CSO facilities were investigated with regard to different objectives (Nickel and Fuchs 2020). To assess EMC, homogenized LVS samples were collected at all sites. Autosamplers were used to assess concentration dynamics at selected CSOs (SED02, SED05, SES02). At two CSOs from sedimentation facilities, additional LVS samples were taken from the inlet to estimate sedimentation efficiency (SED02, SED06). For a robust quantification of the TSS load and for conducting particle analyses, sedimented LVS samples were used at these two sites and one additional CSO (FFR02). For the present evaluation, those datasets were selected in which different sampling techniques were used simultaneously (Table 2.1). The five CSOs considered were all CSOs from centralized stormwater tanks with storage volumes of 10–30 m^3/ha. Samples were collected either directly at the inlet or overflow weir, or in the sewer connecting CSO and receiving water (Figure A2.1–Figure A2.5).

Each sampling was intended to capture one discrete event, which was defined as the overflow occurring during the period from filling to emptying of the storage volume. In few cases, multiple consecutive events were combined into one composite sample because the sample containers could not be emptied in time. AS were programmed to collect 18 min composite samples in each of the 12 bottles at the sites SED02 and SED05, and 15 min composite samples in 24 bottles at SES02. The maximum sampling duration was 3.6 and 6 h, respectively. LVS sampling intervals were adjusted so that high-volume events could also be sampled before the collecting tank was filled (Table 2.1). Figure 2.3 shows the LVS setup used in the study.

Table 2.1: Properties of the samplers used in the sampling campaign.

Property	**Large-Volume Sampler**	**Autosampler**
Sampling strategy	Volume-proportional	Time-proportional
Sampling interval	40–350 m³	3 min
Subsample volume	8–10 L	150–200 mL
Sample containers	Stainless steel, 1000 L	PE, 12–24 × 1 L
Samples per container	10–100	5–6
Pumping system	Peristaltic	Vacuum
Pump capacity	1090 L/h	No data available
Pumping speed	~0.62 m/s	>0.5 m/s
Suction height	Max. 8 m	Max. 8 m
Max. particle size	5 mm	No data available
Suction hose	PVC, Ø 25 mm	PVC, Ø 12–16 mm
Active cooling	No	Yes

Figure 2.3: Photographs of the large-volume samplers and subsampling procedures used in this study.

2.2.4 Analytical Methods

2.2.4.1 Standard Water Quality Parameters

AS samples and homogenized LVS samples were analyzed for pH, conductivity, and concentrations of TSS, chemical oxygen demand (COD), total nitrogen bound (TNb), and total phosphorus (TP) using standard methods (Table A2.1). Additionally, homogenized LVS samples were analyzed for phosphate-phosphorus (PO_4-P).

2.2.4.2 Particle Size Fractionation and Loss on Ignition

For both homogenized and sedimented LVS samples, wet sieving was used to separate TSS63 and TSS 63–2000 µm. Since sample volume and solids content differed significantly between the sample types, different analytical methods were required.

For the analysis of TSS in homogenized water samples by means of filtration (Figure 2.4a), further subsampling was needed to yield an appropriate filtered mass in the range of 5–50 mg (DIN EN 872 2005). To ensure representative subsampling, homogenization was required. This was done by manual shaking. Subsequently, wet sieving was conducted at mesh sizes of 2 mm and 63 µm. Solids > 2 mm were separated to avoid bias from coarse solids that are not reliably sampled by most sampling devices (Baum *et al.* 2018). For filtration, glass-fiber filters (Macherey-Nagel MN 85/70) with an average pore size of 0.6 µm were used. The boundary to the dissolved fraction was defined at 0.45 µm by using membrane filters for filtration. However, in practice, glass-fiber filters are prevalently used because they are resistant to clogging, even if samples have a high organic content. Differences are considered negligible (Sprenger *et al.* 2016). The filters were dried for at least 1–2 h at 105 °C until constant weight. The loss on ignition (LOI) was determined after heating the filters at 550 °C until constant weight.

Contrastingly, the sedimented samples of approximately 10 L (Figure 2.4c) contained all solids from the respective composite sample, e.g., around 1–100 g in CSO. The total sample was subjected to wet sieving. Afterwards, the individual particle size fractions were dried at 105 °C. A dry mass of at least 0.1 g of a fraction is required for reliable quantification. The fine fraction < 63 µm was thickened to a maximum of 1–1.5 L before drying by decanting the supernatant after sedimentation. To derive the concentration in the original composite sample, the dry mass was related to the total composite sample volume in the collecting tank (derived from water level and tank geometry). Supernatant samples from the large-volume composite sample (Figure 2.4b) were processed following the same procedure as for homogenized samples (Figure 2.4a).

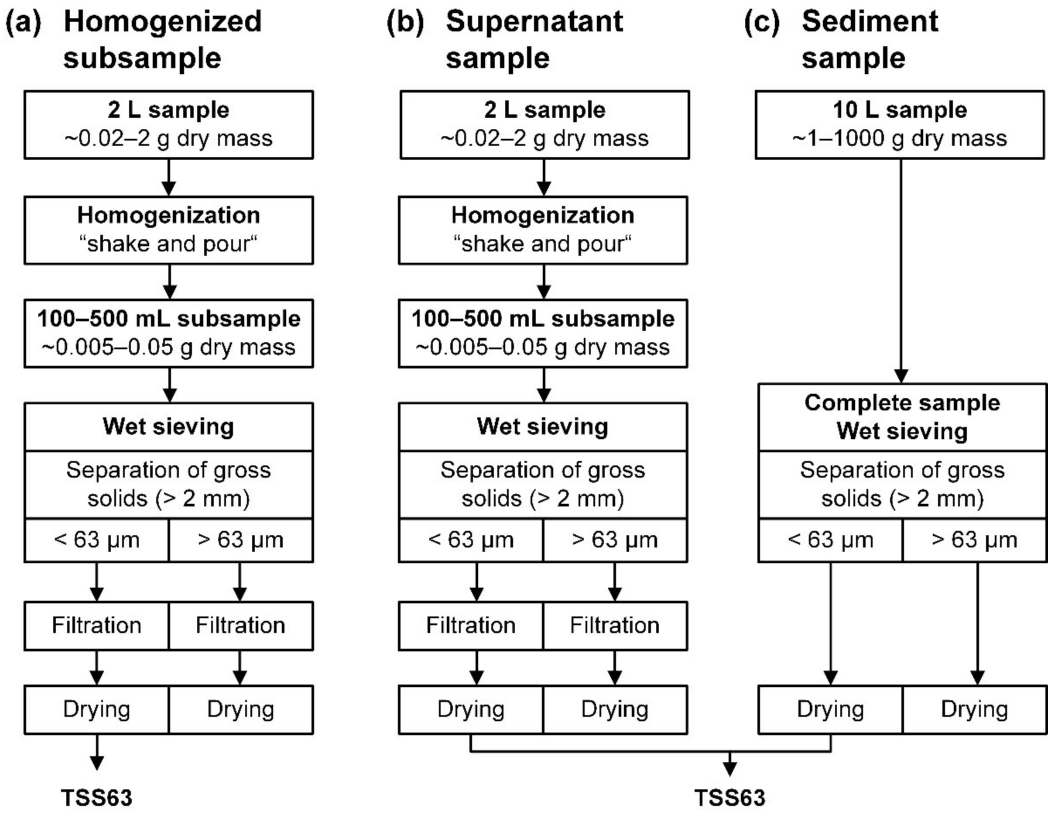


Figure 2.4: Analytical steps for measuring the concentration of total suspended solids < 63 µm (TSS63).

2.2.4.3 Particle-Bound Phosphorus and Metals

The dried particle size fractions from LVS sediments were analyzed for TP and the metals lead (Pb), copper (Cu), and zinc (Zn) (Table A2.2).

2.2.5 Quality Assurance

The LVS control units recorded flow data and status information of the sampling pump (times of subsampling) and float switch (time of tank filling) with a 1 min time step. This information was used to assess the course of sampling during an event. The expected number of subsamples was calculated from the event volume and the sampling interval. The expected sample volume was calculated from the expected number of subsamples and the expected subsample volume, i.e., 8–10 L, depending on the suction height at each site. Maximum 25% deviation of the actual from the expected sample volume was accepted for the composite samples to qualify as volume-proportional. Other samples were excluded from this analysis.

2.2.6 Data Analysis

2.2.6.1 Calculation of Event Mean Concentrations from Sedimented LVS Samples

EMC_{LVS} from sedimented samples were calculated according to Equation 2.1, with M_{Sed} being the dry mass determined from drying the sedimented sample, V_{LVS} being the total volume of the composite sample in the LVS, and $C_{Supernatant}$ being the concentration determined in the supernatant sample:

$$EMC_{LVS} = (M_{Sed} / V_{LVS}) + C_{Supernatant} \tag{2.1}$$

EMC_{AS} were calculated as the volume-weighted mean concentration according to Equation 2.2, with C_i being the concentration of the individual samples, and V_i being the flow volume discharged during the sampling period of the individual samples:

$$EMC_{AS} = (\sum C_i \times V_i) / (\sum V_i) \tag{2.2}$$

2.3 Results and Discussion

2.3.1 Sampled Events

From September 2018 to October 2019, a total of 29 samplings were carried out at five CSOs using different sampling techniques simultaneously. Applying the quality criterion, eight of the datasets were excluded from the analysis, as LVS samples did not qualify as volume-proportional. Consequently, data from 21 samplings were used to investigate the influence of different sampling techniques on suspended solids concentrations and particle size separation (Table 2.2). In four cases, multiple consecutive events were combined into one composite sample. However, for simplicity, all sampling periods are referred to as events in the following. The number of samples from each CSO differed due to different CSO frequencies as well as operational reasons. Inlet concentrations were analyzed for selected events only.

The LVS successfully captured ≥ 80% of the total volume in 88% of the overflow or inlet samplings. In the other cases, the container was full before the end of the event. Quite differently, AS pollutographs captured ≥ 80% of the total volume in only 23% of the samplings even though relatively long time intervals were used (Table 2.1). This was due to long event durations. The LVS proved to be flexible when long or high-volume periods needed to be captured. This is considered to be important to derive representative EMC.

Table 2.2: Events sampled with large-volume samplers (LVS) or autosamplers (AS) at the inlet or overflow of combined sewer overflow (CSO) facilities.

CSO facility	Date	Total Overflow Duration (h)	Total Overflow Volume (m^3)	Share of Total Volume Represented in the Composite Sample or Pollutograph (%) *			
				LVS Overflow	LVS Inlet	AS Overflow	AS Inlet
SED06	09-04-2018	1.5	4504	100 [I,II]	-	-	-
SED06	09-23-2018	2.6	7215	100 [I,II]	100 [I,II]	-	-
SED06	05-20-2019	24.2	43,880	-	100 [I,II]	-	-
SED06	06-22-2019	4.1	10,167	100 [I,II]	-	-	-
SED06	07-01-2019	1.4	6282	100 [I,II]	-	-	-
SED06	07-28-2019	6.3	15,173	100 [I,II]	-	-	-
SED02	12-02-2018	8.8	2807	100 [I,II]	100 [I,II]	-	-
SED02	05-11-2019	5.1	1657	100 [I,II]	100 [I,II]	76	82
SED02	10-01-2019	8.9	2721	100 [I,II]	100 [I,II]	46	53
SED05	10-09-2019	7.5	2481	100 [I]	-	33	-
FFR02	09-23-2018	4.8	8474	99 [I,II]	-	-	-
FFR02	12-02-2018	4.7	4306	100 [I,II]	-	-	-
FFR02	10-05-2019	1.7	2054	100 [I,II]	-	-	-
SES02	05-20-2019	46.0	71,054	11 [I]	-	7	-
SES02	05-28-2019	12.4	9353	81 [I]	-	51	-
SES02	07-01-2019	5.2	5827	100 [I]	-	100	-
SES02	07-27-2019	12.8	20,777	36 [I]	-	40	-
SES02	08-02-2019	4.1	6227	100 [I]	-	100	-
SES02	08-20-2019	11.8	9890	77 [I]	-	43	-
SES02	10-04-2019	11.8	9015	86 [I]	-	40	-
SES02	10-30-2019	12.7	8255	94 [I]	-	53	-

* Refers to CSO volume for overflow samples and to the sum of storage and CSO volume for inlet samples. [I] Homogenized sample collected. [II] Sedimented sample collected. - Not sampled.

2.3.2 Comparability of LVS and Autosamplers

To investigate the comparability of LVS and AS results, 2 inlet and 11 overflow samplings were available (Table 2.2, Table A2.3 and Table A2.6). Figure 2.5 shows the hydrograph and pollutograph for a CSO event sampled with both AS and LVS. In this case, both sampling techniques captured the complete 5.2 h event duration. The AS collected 22 bottles containing 15 min composite samples composed of five subsamples each, except for the last one (one subsample). This resulted in a total of 106 subsamples. The LVS collected a total of 73 subsamples each 80 m^3, meaning that the resolution of LVS subsampling was slightly lower. LVS subsamples were more concentrated in the high flow periods due to the volume-proportional sampling regime. Despite these differences, the EMC derived from both sampling methods were close. The EMC$_{AS}$ (calculated from AS pollutograph) are plotted for discrete time steps in Figure 2.5, assuming that sampling was terminated after the respective sample. It can be seen how the evolution of the EMC$_{AS}$ approach the EMC$_{LVS,hom}$ (homogenized LVS sample) toward the end of the event. The final EMC$_{AS}$ and the EMC$_{LVS,hom}$ were 82 mg/L and 77 mg/L, respectively. Figure 2.5 clearly shows the possible effect of incomplete sampling of CSO events.

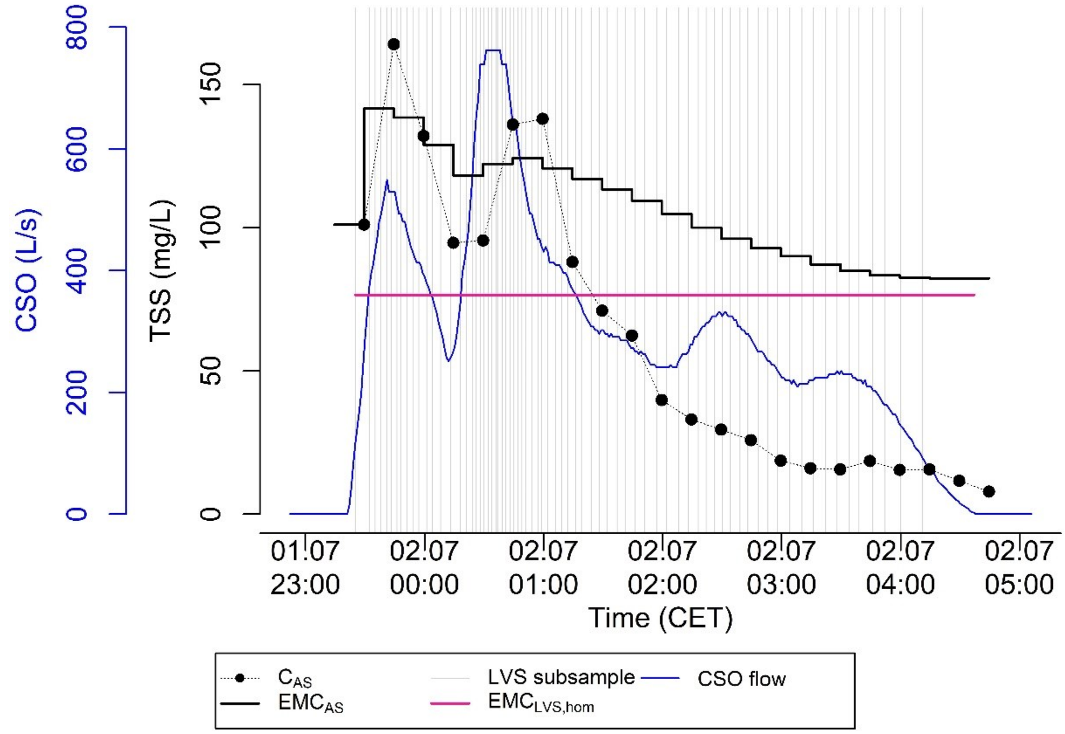


Figure 2.5: Evolution of the TSS event mean concentrations (EMC_{AS}) derived from the autosamplers pollutograph (C_{AS}) during a combined sewer overflow (CSO) event compared to the EMC derived from the large-volume samplers ($EMC_{LVS,hom}$).

Additionally, for other events, good agreement between both sampling techniques was found (Figure 2.6). Most EMC_{AS} were higher than the corresponding $EMC_{LVS,hom}$, but the deviation of EMC_{AS} from $EMC_{LVS,hom}$ was within a range of ±20% for most samples, even though the sampling was not harmonized, e.g., by using synchronized volume-proportional subsampling or synchronized termination of sampling. Moreover, for several events, the share of total event volume represented in the composite samples or pollutographs was different (Table 2.2). For three events, a deviation > 20% was found. On 20 August 2019 at SES02, the LVS sampled a significantly higher share of the overflow volume, while the concentration level was particularly low (<30 mg/L). On 4 October 2019 at SES02, the LVS sampled an additional overflow peak on the following day. However, on 27 July 2019 at SES02, similar periods were covered by both AS and LVS. The differences in EMC may be due to different discrete subsampling times, lower representativeness of small volume AS subsamples (150–200 mL) compared with LVS subsamples (8–10 L), or other uncertainties in sampling and laboratory methods. Due to these influences, it cannot be conclusively determined whether the differences between EMC_{AS} and $EMC_{LVS,hom}$ were systematic.

Generally, ideal representative EMC require volume-proportionally distributed subsamples from as large a part of the event as possible, with a temporal resolution adapted to concentration dynamics. Uncertainties in flow measurement may affect sampling intervals (in case of volume-proportional sampling) and the calculation of the EMC (in case of time-proportional sampling), especially if flow is derived from a function based on water level measurements. The representativeness of the EMC may be evaluated if reliable continuous TSS surrogate measurements are available, e.g., turbidity or UV-VIS online measurements (Sandoval *et al.* 2018). However, due to fluctuations of particle composition, the relationship of TSS and surrogate measurements can rarely be assumed to be constant throughout an event. In this study, the accordance of both methods indicates that an acceptable quantification was achieved. Good agreement was also found for conductivity, COD, TP, and TNb (Figure A2.6).

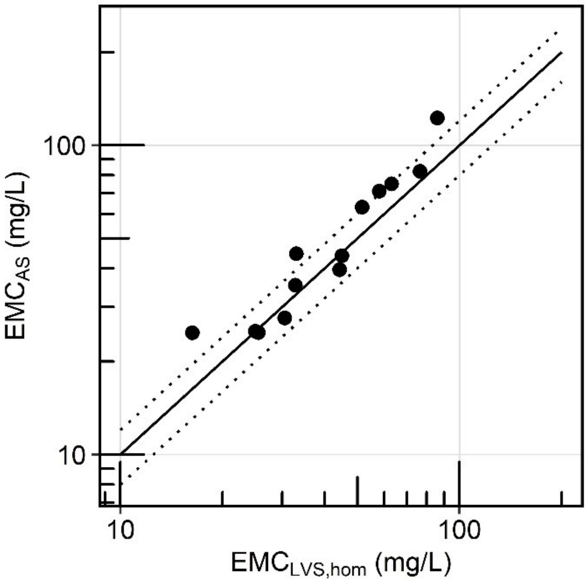


Figure 2.6: Scatterplot of TSS event mean concentrations derived from homogenized large-volume samplers samples ($EMC_{LVS,hom}$) and autosamplers pollutographs (EMC_{AS}). Dotted lines show 20% deviation.

2.3.3 Differences between Homogenized and Sedimented LVS Samples

LVS subsampling methods were compared for 5 inlet and 11 overflow samples (Table 2.2, Table A2.3 and Table A2.4). EMC_{LVS} from homogenized and sedimented samples showed acceptable agreement, but more variable differences for individual samples (Figure 2.7). Possible reasons for these differences are discussed in the following subsections.

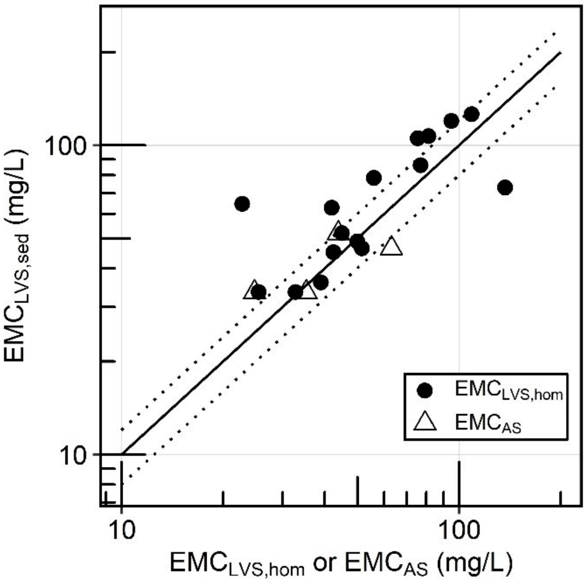


Figure 2.7: Scatterplot of TSS event mean concentrations derived from homogenized (EMC$_{LVS,hom}$) and sedimented (EMC$_{LVS,sed}$) large-volume samplers samples. Triangles show the EMC derived from autosamplers (EMC$_{AS}$) pollutographs of the same events compared with sedimented samples. Dotted lines show 20% deviation.

2.3.3.1 Subsampling Bias

On average, EMC$_{LVS,sed}$ tended to be slightly higher than EMC$_{LVS,hom}$, notably for concentrations > 50 mg/L. This could indicate that LVS homogenization and subsampling was not sufficiently representative. The potential bias introduced by improper subsampling is known from comparisons of TSS and suspended sediment concentrations (SSC) results (Gray *et al.* 2000; Galloway *et al.* 2005; Clark and Siu 2008; Selbig and Bannerman 2011). According to American standard methods, TSS are determined by filtration of a subsample, while SSC are determined from the entire sample volume (Pitt *et al.* 2017). If the PSD of a sample includes sand-sized particles, subsampling will likely be less representative and tend to underestimate the solids concentration (Gray *et al.* 2000; Selbig and Bannerman 2011). The SSC method was demonstrated to representatively quantify EMC compared with whole-storm samples from parking lot runoff collected in a 15,000 L sample basin (Roseen *et al.* 2011). In this context, sedimented LVS samples might be more comparable with SSC analytical procedures. Given that the results from homogenized samples were generally confirmed by AS, this would mean that both AS and homogenized LVS could possibly underestimate TSS-EMC.

2.3.3.2 Size Fractionation at 63 µm

The results of the size fractionation to quantify TSS63 do not necessarily indicate bias from sand-sized particles. Instead, the percentage of TSS63 was higher in sedimented samples (Figure 2.8). On average, TSS63 amounted to 81% and 84% in sedimented inlet and overflow samples, respectively. In homogenized samples, TSS63 were only 63% and 68%, and showed higher variability than in sedimented samples. In order to correctly evaluate these differences, it is important to consider the mass of the solids analyzed in each method. Results from sedimented LVS samples were based on a median dry mass of 17.3 g (3.3–71.1 g). This is a factor 10^3 higher than the median mass analyzed in homogenized LVS samples. Only 12.2 mg (5.0–20.6 mg) was quantified after filtration of 200 mL (100–500 mL). Similar values can be obtained for the analyses of individual AS samples by filtration, i.e., 12.0 mg (1.1–35.3 mg). Therefore, if reliable size fractionation is required, sedimented samples should be preferred. These are also suitable for complete sieving analyses, as conducted by Kemper *et al.* (2015) or Baum *et al.* (2021).

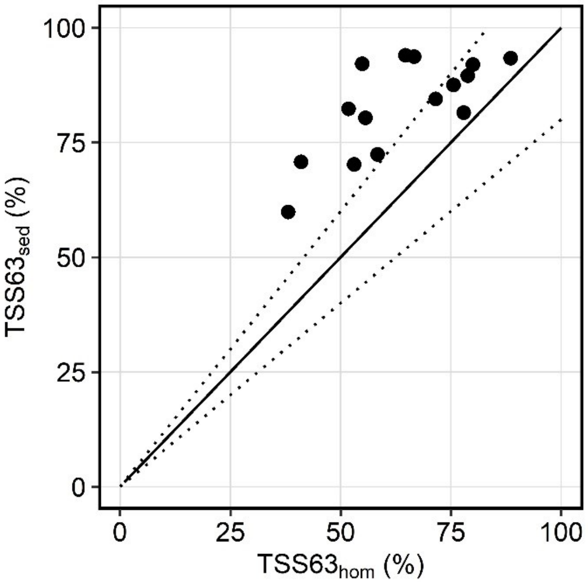
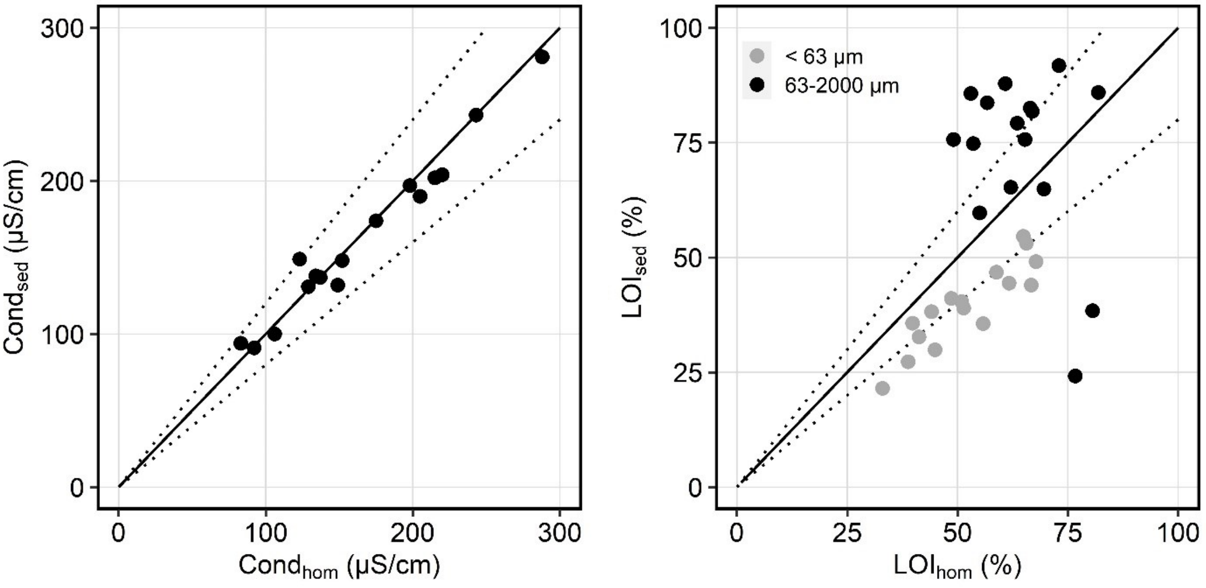


Figure 2.8: Scatterplot of the percentage of TSS < 63 µm measured in homogenized ($TSS63_{hom}$) and sedimented ($TSS63_{sed}$) large-volume samplers samples. Dotted lines show 20% deviation.

2.3.3.3 Differences in Sample Processing

Differences between the results obtained for homogenized and sedimented samples are also likely affected by the sampling procedures. Both agitation during homogenization and settling before collection of the sedimented samples will alter the original in situ PSD of a sample by agglomeration of particles or disintegration of agglomerates (Phillips and Walling 1995). These are effects that must be taken into account in any sampling system but could have different impacts in the two approaches. Li *et al.* (2005) reported particle size in highway runoff samples to increase with storage time due to naturally occurring coagulation or flocculation. Contrarily, in this study, the sedimented samples taken 1–3 days after the homogenized sample showed systematically higher content of particles < 63 µm. Therefore, the difference must be mainly due to other reasons, e.g., more representative sample mass and differences in analytics. This finding needs to be further explored in future research.

Another factor that could alter the sample during settling is mineralization of organic matter. Grotehusmann *et al.* (2014) conducted 30-day stability tests of LVS samples of street runoff at 20 °C. They found a significant increase in dissolved organic carbon concentrations and conductivity in the supernatant water, indicating hydrolysis of organic matter into faster degradable dissolved organic substrates but no measurable effect on the LOI. In this study, conductivity was not affected by the settling period, but the LOI differed between homogenized and sedimented samples (Figure 2.9). Sedimented samples contained clay and silt particles < 63 µm with systematically lower LOI and sand particles (63–2000 µm) with higher LOI than homogenized samples. This is likely not an effect of the settling period but bias introduced by limited homogenization of the water column in the tank.



(**a**) (**b**)

Figure 2.9: Scatterplots of conductivity (Cond) (**a**) and loss on ignition (LOI) (**b**) measured in homogenized (hom) and sedimented (sed) large-volume samplers samples. Dotted lines show 20% deviation.

2.3.3.4 Differences in Analytics

In addition to sampling, laboratory procedures may affect the results (Figure 2.4). Subsampling of homogenized samples for filtration was conducted by the shake-and-pour method. Regarding total concentrations, the laboratory homogenization was verified by comparing the sum of TSS63 and TSS > 63 µm with the total TSS analyzed in a second subsample. The latter was within 82–116% (mean 100%) of the former, confirming successful homogenization. The sedimented samples were completely subjected to sieving facilitated by flushing with tap water. These two procedures may result in different levels of agglomerate disintegration. Welker *et al.* (2019) propose to use mechanical dispersion by stirrers or blenders to obtain reproducible disintegration, while accepting potential alteration of PSD. This approach was applied by Baum *et al.* (2021) on LVS-sedimented samples. However, it remains questionable whether it is possible to reproduce the original PSD from the moment of sample collection (Phillips and Walling 1995). Moreover, it may be more important to establish reproducible methods with as few processing steps as possible. The method-related inaccuracies may be acceptable in practice.

After sieving, homogenized samples were filtered (0.6 µm), while sedimented samples were decanted and dried. Therefore, the latter also include particles < 0.6 µm, colloids, and salts dissolved in the remaining 1–1.5 L of water after decanting. Based on the conductivity measurements, the dissolved solids of each sedimented sample were estimated assuming 1 µS/cm to correspond to 0.65 mg/L. This ratio was selected from a range commonly used for natural water (Rusydi 2018), as no data were available for CSOs. Since the relationship of dissolved solids to conductivity is influenced by wastewater composition, this should only be considered a rough estimate. The amount of dissolved solids determined in this way accounted for only a small part of the solids concentration, i.e., 0.2–5.6% (mean 1.6%).

2.3.4 Characterization of Solids in CSOs

2.3.4.1 Concentration Levels Lower than Previously Reported

Regarding sedimented LVS samples as the most representative basis, median TSS-EMC measured at the overflow of CSO facilities were 62.8 mg/L (33.5–126 mg/L). This concentration level was confirmed by 168 homogenized LVS samples collected from 12 CSOs (including the CSOs in this evaluation), with a median of 53 mg/L (chapter 4) (Nickel *et al.* 2021b), and by other recent studies (Clara *et al.* 2014; Kemper *et al.* 2015). However, it is considerably lower than the median of 175 mg/L in Central European CSOs reported by Brombach *et al.* (2005) based on studies from the 1970s to the 1990s. Similar TSS reductions were reported for stormwater runoff in the United States (Smullen *et al.* 1999) and Southeastern Australia (Francey *et al.* 2010) when compared with previously reported studies. Francey *et al.* (2010) suggested reduced atmospheric pollution and refined monitoring procedures as potential reasons. Our results show that a reduced concentration level must be considered for CSOs in Bavaria too.

2.3.4.2 Particle Size and Organic Matter Content

The solids found in CSO were dominantly clay and silt-sized particles. The median TSS63 content of LVS sediments was 84%. This corresponded well to results from other CSO in Germany (Fuchs *et al.* 2014; Kemper *et al.* 2015). A similar share of clay and silt-sized particles was also reported from detailed PSD analyses by laser diffraction of CSO in Italy, with d_{50} values of 22 to 35 µm (Piro *et al.* 2010).

While the TSS63 were mainly mineral particles, the fraction > 63 µm had a high organic matter content with a median LOI of 75%. The average LOI of the total samples was 45% (27–66%), indicating the potential of CSO to impact dissolved oxygen concentrations in receiving waters.

2.3.4.3 Pollutant Loading

The loading of the solids with total phosphorus (TP), copper, lead, and zinc is shown in Figure 2.10. The results were very close to the findings by Kemper *et al.* (2015). Metal loading in both fractions was slightly higher than total particulate metal concentrations reported for CSO in France (Becouze-Lareure *et al.* 2019). The magnitude of metal loading was also comparable with results of a 1997 highway runoff study (Sansalone and Buchberger 1997), except for reduced lead concentrations due to the phase-out of leaded gasoline (Huber *et al.* 2016) and to a recent study of treated stormwater runoff (Baum *et al.* 2021).

There was a tendency to higher pollutant loading of TSS63 when compared with solids > 63 µm, which can be attributed to the higher specific surface area of the smaller particles. However, the difference between both fractions was significant for TP only (Mann–Whitney U Test, $p < 0.001$). In addition to the specific surface area, there are other parameters influencing metal adsorption, such as organic carbon content, effective cation exchange capacity, and clay-forming minerals content (Gunawardana *et al.* 2014). Kemper *et al.* (2015) suggest that the pronounced difference for TP is due to higher content of iron oxides in the fine fractions that have a high sorption potential.

To compare the results with selected homogenized samples that were analyzed for the total metal content, particle-bound metal concentrations in the total sample were calculated (Figure A2.7). These concentrations are not directly comparable. Lead is mainly transported in particulate form, but zinc and copper also have relevant dissolved fractions (Huber *et al.* 2016; Baum *et al.* 2021). Still, good agreement was found for most samples.

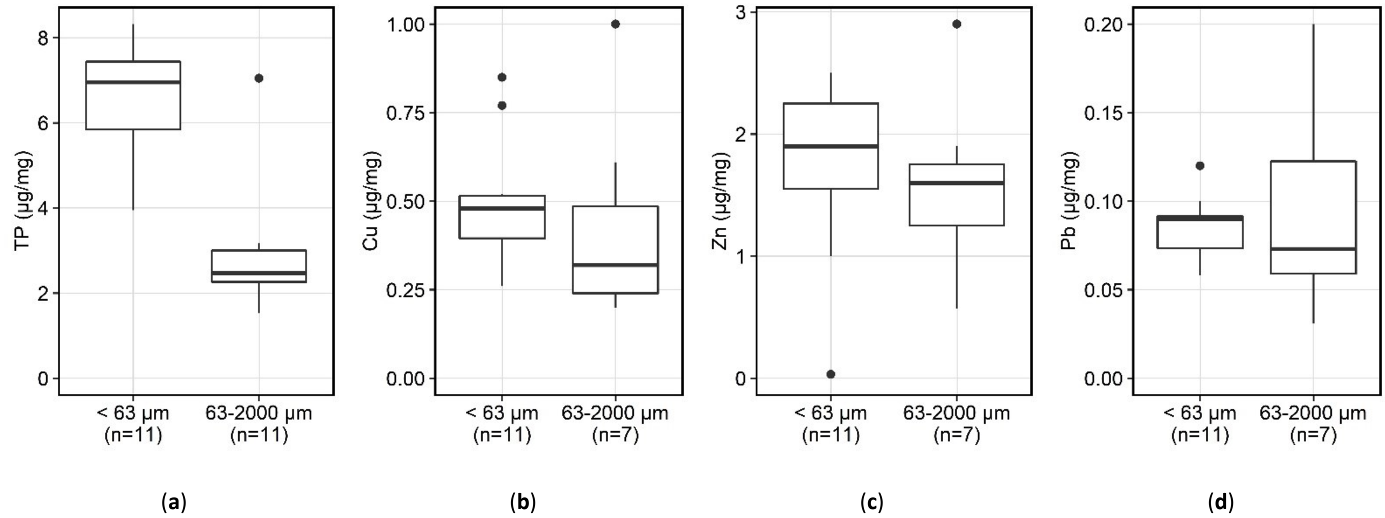


Figure 2.10: Pollutant loading of sedimented LVS samples collected from combined sewer overflows: (**a**) Total phosphorus (TP), (**b**) Copper (Cu), (**c**) Zinc (Zn), (**d**) Lead (Pb).

2.4 Conclusions

Generally, representative sampling in sewer systems requires a temporal resolution adapted to the concentration dynamics and the flexibility to sample widely varying event volumes and durations as completely as possible. In this regard, LVS are an efficient composite sampling technique. They come with specific advantages compared with conventional autosamplers. Whenever the research objective does not require pollutograph data but representative mean concentrations, the LVS methodology is strategically superior to standard AS due to its flexibility in capturing varying event volumes and due to lower analytical costs.

EMC derived from homogenized LVS samples and AS pollutographs of the same events were comparable even though the sampling was not synchronized. Considering the high inherent variability of the investigated sewer systems, the influence of the sampling technique can be considered negligible. TSS-EMC derived from homogenized and sedimented samples of the same LVS were also comparable. However, differing TSS63 content and loss on ignition suggested that results were impacted by the method of subsampling from LVS or laboratory procedures. Sedimented LVS samples may contain solids masses in the range of 1–1000 g, depending on the media sampled, and are therefore considered to improve the robustness and quality of particle analyses compared with conventional filtration approaches.

In general, the required sample amounts (in terms of volume or mass) and the sampling strategy are closely linked to the particular research question. The use of sedimented LVS samples is recommended for a reliable quantification of TSS loads, e.g., for the assessment of removal efficiencies of stormwater treatment facilities and for particle analyses, e.g., particle size distribution, organic matter content, or pollutant loading. Homogenized LVS samples are suitable for the quantification of pollutant EMC, long-term average concentrations, or for general screenings.

LVS are increasingly used for the monitoring of sewer systems and surface waters and are continuously being further developed. Our findings are considered important to the comparison of monitoring results of different sampling systems. Further development of LVS should also include further investigation of the observed differences between homogenized and sedimented LVS samples, e.g., regarding the quality of homogenization and the stability of samples during sedimentation in LVS.

The results obtained from LVS monitoring indicate that a lower average TSS concentration level than previously reported must be considered for CSOs in Bavaria. TSS63 were confirmed as the dominant size fraction at the inlet and overflow of centralized CSO facilities.

2.5 Funding

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2.6 Acknowledgments

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3 Micropollutant Emissions from Combined Sewer Overflows

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Abstract: In an extensive monitoring program, event mean concentrations of 12 heavy metals, 16 PAH, 9 pesticides/biocides, 3 pharmaceuticals, 3 benzotriazoles, acesulfame, and DEHP were measured at 10 combined sewer overflow (CSO) facilities throughout Bavaria, Germany, for more than 110 overflow events. A harmonised approach with large volume samplers was used to produce volume-proportional event composite samples. A wide range of event durations and volumes was covered successfully. All substances analysed were detected in CSO samples and the majority were quantified in more than 80 % of the samples. Our results confirm that CSOs need to be considered in the debate on micropollutant emissions and solidify knowledge regarding their concentrations at a regional level. Distinct substance-specific patterns can be observed in the variability between events and sites as well as in a correlation analysis of substance concentrations. These trends underline the need for differentiation of the substances by their predominant sources, pathways, and transport behaviours. Compared to WWTP, CSOs are an important pollution source especially for ubiquitous, primarily stormwater-transported pollutants, including substances causing failure to achieve good chemical status of surface waters, such as uPBT substances Hg and PAH.

3.1 Introduction

Micropollutants or trace contaminants are terms for a large group of substances from various anthropogenic sources that can be measured in environmental compartments. They usually occur at low concentrations and can be of ecotoxicological concern (Schwarzenbach *et al.* 2006; Gavrilescu *et al.* 2015). It remains one of the major challenges in water management to reduce the pollution of water bodies with these substances (Gerbersdorf *et al.* 2015; Hillenbrand *et al.* 2016). General objectives are the protection of water resources, the mitigation of risks for aquatic ecosystems and, in the sense of the precautionary principle, the reduction of overall emitted loads accumulating in natural sinks. In addition to all ecotoxicological concerns, the acceptability of the occurrence of micropollutants in water bodies must be discussed.

The number and variety of substances are high and further increasing through the development of new products and applications. This largely complicates the identification, assessment, and management of micropollutants. Therefore, it is essential to characterise substances according to their usage or sources, physico-chemical properties, environmental behaviour, and transport pathways (Gerbersdorf *et al.* 2015).

For European water bodies to achieve a good ecological and chemical status, a list of priority substances was introduced with the EU Water Framework Directive (WFD) and later directives (European Commission

2000, 2008, 2013). Environmental quality standards and monitoring requirements were defined and the phasing out of particularly hazardous substances was agreed upon. After almost two decades, implementation of this progressive and highly ambitious environmental legislation remains challenging (Voulvoulis *et al.* 2017). This also applies to the chemical status of European waters. According to the 2018 EEA status report, 46 % of European water bodies have not yet achieved a good chemical status (Kristensen *et al.* 2018).

Among the main sources of micropollutant emissions are urban areas (Hillenbrand *et al.* 2005; Fuchs and Toshovski 2016). Urbanisation increases areas impervious to water and intensive anthropogenic land use, resulting in increased runoff and water pollution. This may have a significant impact on receiving waters (Fletcher *et al.* 2013; Liu *et al.* 2015). The main entry pathways of micropollutants from urban areas into surface waters include wastewater treatment plant effluents and overflows from combined sewer systems and storm sewer outlets (Hillenbrand *et al.* 2005; Musolff *et al.* 2010; Launay *et al.* 2016a). The latter regularly occur during storm events when transported volumes exceed the capacity of sewer systems and storage tanks. According to German regulations and standards, stormwater with a discharge rate of up to 15 l/(s·ha) impervious area has to be treated in stormwater treatment facilities (ATV-A 128E 1992). This usually corresponds to > 90 % of the annual precipitation runoff volume (DWA-A 102-2/BWK-A 3-2 2020). Treatment options include storage of the first flush with subsequent routing to wastewater treatment plants or a combination of storage and sedimentation, and in less frequent cases filtration. In combined sewer systems both treated discharges from overflows with storage as well as untreated excess discharges from overflows without storage are referred to as combined sewer overflow (CSO).

CSOs are well-recognised sources of water pollutants, such as suspended solids, oxygen-consuming substances, microbial contaminants, nutrients, heavy metals, and organic substances (Brombach *et al.* 2005; Aarts *et al.* 2013; Jalliffier-Verne 2015; Madoux-Humery *et al.* 2015). With regard to micropollutants, CSOs might be particularly relevant to substances with outdoor applications, significant atmospheric deposition (BMUB 2017), and/or high elimination rates in wastewater treatment plants (Musolff *et al.* 2010). Several studies of micropollutants in CSOs were carried out (e.g. Gasperi *et al.* 2012; Clara *et al.* 2014; Launay *et al.* 2016b; Becouze-Lareure *et al.* 2019). However, usability of the data available for deriving representative average micropollutant concentrations or for the estimation of emissions on larger scales is still limited. Reasons impeding the comparability of results are major differences of monitoring programs, study areas, sampling techniques, and analytical methods (Hillenbrand *et al.* 2016). Moreover, sample numbers are usually low due to the difficulties associated with event-based sampling in a harsh and highly dynamic environment like sewer systems. Consequently, further research is needed for an adequate assessment of CSO micropollutant emissions and subsequent decision making (BMUB 2017).

To improve the data basis of micropollutant concentrations in CSO, an extensive monitoring program was launched on behalf of the Bavarian Environment Agency. Samples from 10 different sites were collected and analysed for a large set of substances in a harmonised approach. To generate data that could be used for load calculations, event composite samples were collected using large volume samplers (LVS). This article presents the methods applied and first data evaluations. Final concentration values will be published in 2020.

3.2 Methods

3.2.1 Sampling Sites

Bavaria is the largest federal state of Germany stretching from the Swabian-Franconian cuesta landscape in middle Germany to the Alps and the borders to Switzerland, Austria, and Czech Republic. Two major rivers, the Main and the Danube drain the region. The climate is continental with a distinct gradient of annual precipitation increasing from the North to the South. More than 60 % of the population is connected to combined sewer systems. There are approximately 6,800 CSO tanks with a total storage volume of 3.3 million m³ and an additional 4,000 direct CSO facilities without storage across the state (DESTATIS 2018b).

Ten CSO facilities with storage were selected for sampling. An attempt was made to make a selection that corresponded to the state of technology and was as representative of Bavaria as possible. Each CSO facility was to comply with current German design guidelines (ATV-A 128E 1992) and have preinstalled discharge measuring equipment and favourable practical aspects (e.g. accessibility and the willingness of plant operators to cooperate). Based on these criteria, a preselection was made. For preselected sites, specifications from a federal database were assessed to select CSO facilities with typical overflow frequencies. In Germany, typical overflow frequencies range from 16 – 27 days per year. Typical durations range from 42 – 140 h per year depending on the CSO type (Baumann *et al.* 2017). The final selection included a range of specific storage volumes (Table 3.1) and three types of CSO facilities, i.e. sedimentation tanks (SED), first flush retention tanks (FFR), and sewers with extended storage capacity (SES). The sites were spatially distributed across Bavaria (Figure 3.1) and included catchments with different sizes and characteristics (Table 3.1).

Table 3.1: Characteristics of CSO sampling sites.

CSO type	Specific volume in m³/ha *	Catchment character	Directly connected area in ha	Imperviousness in %	Population density in inhab./ha	Annual precipitation in mm
FFR1	15.5	Urban	73.1	40	34	662
FFR2	53.1	Rural	77.7	27	35	1,459
SED1	22.7	Rural	44.2	17	17	729
SED2	29.9	Rural	39.3	51	30	705
SED3	13.3	Urban	129.9	48	69	1,238
SED4	89.1	Urban	108.2	39	59	1,078
SED5	16.6	Urban	345.7	23	48	1,010
SED6	20.8	Urban	1,845.0	15	35	838
SES1	9.9	Urban	221.3	66	61	1,672
SES2	56.5	Urban	153.0	47	71	709

* Specific volumes are based on the directly connected impervious area. CSO tanks with specific volumes > 20 – 30 m³/ha have substantial amounts of indirectly connected areas via upstream overflow structures.

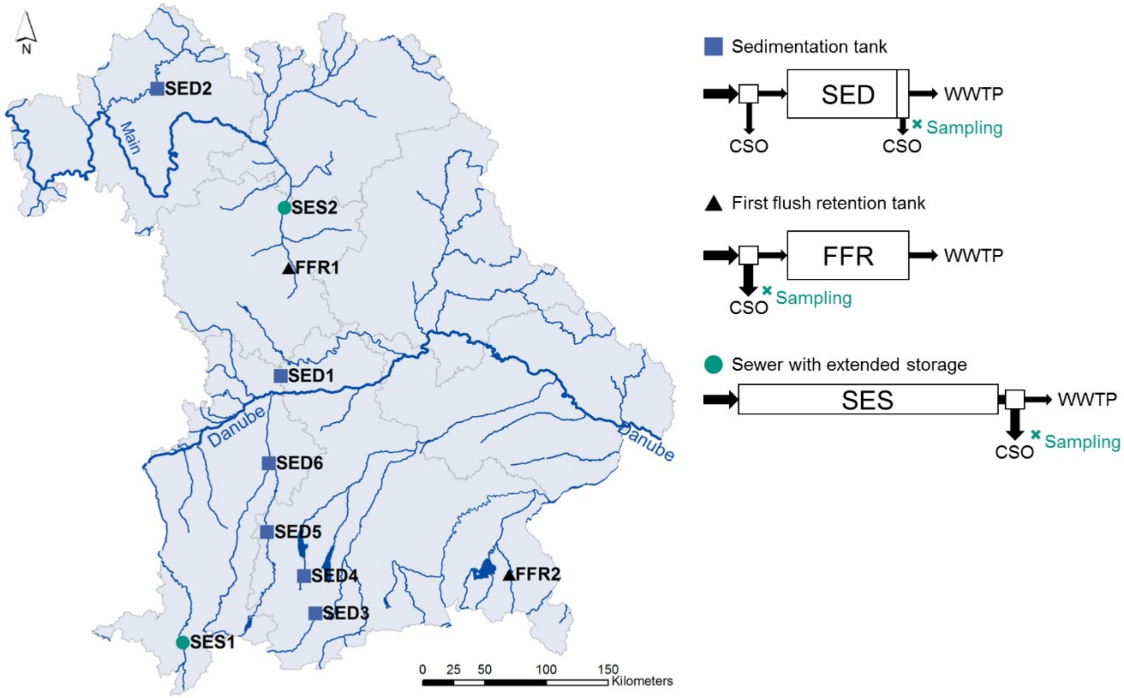

Figure 3.1: Distribution of sampling sites across Bavaria and schematic depiction of treatment types.

3.2.2 Monitoring Strategy and Set-up

With the main objectives of evaluating average CSO quality and generating data for the estimation of emissions on larger time scales, the chosen strategy was to generate volume-proportional composite samples of CSO events (Ort and Gujer 2006; Lee *et al.* 2007). Measured concentrations therefore represent event mean concentrations (EMC) and do not reflect concentration dynamics during the event. The samples of CSO events were collected using automated large volume samplers (LVS) as developed in previous studies (Fuchs *et al.* 2014; Kemper *et al.* 2015).

The LVS set-up consisted of a tank with a volume of 1 m^3, a powerful 220 V peristaltic pump with a capacity of 1 m^3/h, and a control unit. The control unit processed analogue signals from water level measurement devices to activate the pump based on overflow thresholds and adjustable volume intervals. The measurement devices were ultrasonic probes or pressure sensors using Poleni or manufacturer formulas to calculate the flow over weirs or through dam shields. Sensors that not been newly installed or inspected during the year before monitoring were tested by simulating a series of water levels in-situ. In accordance with Bavarian guidelines, the measurements were required to be within ± 2 cm of simulated values. If necessary, measurement devices were replaced or recalibrated.

The sampling intervals ranged from 20 to 400 m^3 and were set site-specifically with the aim of covering high volume events (e.g. 80 %-quantile of historical event volumes, if available) to their full extent. The interval was adjusted during monitoring, if historical data could not be used. The time needed for taking one subsample of 10 l was approximately 30 s depending on pumping head. During maximum flow, this defined a lower limit for the interval. In practice, depending on the variation of flow rates, several hours of overflow events could be sampled in one composite sample. Hydraulic data and subsampling times were logged with a 1 min time step. Steel spiral enforced 25 mm PVC suction hoses were used for sampling. A float switch prevented overflowing of the tank. Stainless steel tanks were used, as they have proven to minimise ad- or desorption effects. The tanks were kept at ambient temperature and the whole set-up was enclosed in wooden huts for protection from direct sunlight.

LVS allow for the complete coverage of long event durations and produce sufficient sample volumes for a variety of analyses. They reduce limitations associated with the use of regular automatic samplers, e.g. limited sampling duration during a storm event (Lee *et al.* 2007) or unreliable sampling of solids (Clark *et al.* 2009). Since substantial quantities of solids are collected in the tank, sedimented solids and supernatant water can also be subjected to separate analyses after a sedimentation period of two days. This is particularly interesting when particle-bound pollutants are not detectable in homogenised subsamples or for further characterisation of solids.

In the present study, the composite sample was homogenised using a submersible pump before subsamples were filled into suitable containers: i.e. 2 l PE bottles for the analysis of pH, conductivity, suspended solids, nutrients, and chemical oxygen demand; 2 l amber bottles for the analysis of organic pollutants; 0.25 l LDPE bottles for the analysis of heavy metals (stabilised with 2.5 ml of dilute concentrated nitric acid); 0.1 l glass bottles for mercury analysis (stabilised with 2 ml of dilute concentrated nitric acid and 1 ml potassium dichromate solution). Stability of the samples was ensured by bottling the samples as soon as possible after an event and keeping them dark and refrigerated. The bottling was done within 1 – 2 days after an event depending on the day of the week and the time of day. The transport of the samples from the sites to the laboratory in insulated transport boxes equipped with freezer packs took another 1 – 2 days.

3.2.3 Micropollutant Analysis

Samples were analysed for the total content (particulate + water phase) of 45 micropollutants which can be grouped by their characteristic sources and predominant transport pathways and forms. Heavy metals and polycyclic aromatic hydrocarbons (PAH) are pollutants with ubiquitous occurrence and predominantly transported to CSO facilities by stormwater runoff. For most of these substances, a particle-bound transport can be assumed (Manzetti 2013). The same applies to the plasticiser di-(2-ethylhexyl)phthalate (DEHP) (Welker 2007). Both agricultural pesticides (e.g. terbuthylazine) and biocides with urban applications (e.g. terbutryn, mecoprop) were included in the parameter set. Their occurrence is linked to specific sources and their transport can be assumed to occur predominantly in dissolved form (Wittmer *et al.* 2010). The sweetener acesulfame, the anticonvulsant carbamazepine, and the anticorrosive benzotriazole are regarded as typical wastewater tracers (Giger *et al.* 2006; Scheurer *et al.* 2011). Further substances predominantly transported to CSO facilities via wastewater are the biocide triclosan which is used as an antiseptic in health care and personal care products and the analgesic diclofenac. Analytical methods were optimised to yield low limits of quantification (Table 3.2). Furthermore, conventional wastewater quality parameters, i.e. total suspended solids (TSS), chemical oxygen demand (COD), total bound nitrogen (TNb) and phosphorus (TP) were analysed.

Table 3.2: Measured pollutants, abbreviations, analytical methods, and limits of quantification (LOQ).

Group	Parameter	LOQ in µg/l	Sample preparation	Analytical methods
Heavy metals (n=12)	Fe, Zn	5	Digestion	ICP-MS
	Cu	1		
	Ni*, Pb*, Cr, Sb, Sn	0.1		
	Bi, Mo	0.01		
	Cd*#	0.002		
	Hg*#	0.001	Digestion	AFS
PAH (n=16)	Naphtalene* (NAP)	0.01	LLE	GC-MS/MS
	Acenaphthene (ACN), Acenaphthylene (ACY), Fluorene (FL), Anthracene*# (ANT), Phenanthrene (PHE), Pyrene (Pyr), Fluoranthene* (Fluo), Benzo(a)anthracene (BaA), Benzo(b)fluoranthene*# (BbF), Chrysene (Chr), Benzo(k)fluoranthene*# (BkF), Dibenz(ah)anthracene (DahA)	0.001		
	Benzo(a)pyrene*# (BaP), Benzo(ghi)perylene*# (BghiP), Indeno(1,2,3-cd)pyrene*# (IP)	0.0005		
Pesticides / biocides (n=9)	Carbendazim (CZIM), Atrazin* (ATR), Diuron* (DIU), Isoproturon* (ISO), Metolachlor (MET), Mecoprop (MCPP), Terbuthylazine (TBA), Terbutryn* (TBY), Triclosan (TCS)	0.01	Online-SPE	LC-MS/MS
Pharmaceuticals (n=3)	Metoprolol (MPL), Carbamazepine (CBZ), Diclofenac (DCF)	0.01	Online-SPE	LC-MS/MS
Benzotriazoles (n=3)	Benzotriazole (BTR), 4-Methylbenzotriazole (4MBT), 5-Methylbenzotriazole (5MBT)	0.01	Online-SPE	LC-MS/MS
Sweetener	Acesulfame (ACE)	0.1	SPE	LC-MS/MS
Phthalates	Di-(2-ethylhexyl)phthalate*# (DEHP)	0.1	LLE	GC-MS/MS

LLE = Liquid-liquid extraction, SPE = Solid-phase extraction, ICP-MS = Inductively coupled plasma with mass spectrometry, AFS = Atomic fluorescence spectrometry, GC-MS/MS = Gas chromatography with tandem mass spectrometry, LC-MS/MS = Liquid chromatography with tandem mass spectrometry

* Priority substances according to (European Commission 2008, 2013) $^{\#}$ Priority hazardous substances.

3.2.4 Statistical Methods

Relative standard deviation (RSD) was calculated as the standard deviation divided by the arithmetic mean. Correlation analysis was conducted using Spearman's rank correlations. Shapiro-Wilk and Anderson-Darling tests were used to check the normal distribution of the data. Differences in central tendency between groups of normally distributed values were tested by t-test for two groups or by single factor variance analysis and post hoc test (Tukey Honest Significant Differences) for more than two groups. For non-normally distributed values, the Mann-Whitney U test was used for two groups and the Kruskal-Wallis rank sum test with subsequent pairwise Wilcoxon rank sum tests for more than two groups.

3.3 Results and Discussion

3.3.1 Sampling Campaign

Monitoring started in autumn 2016 and continued for more than two years in order to cover seasonal variability. The dataset covers pollutant concentrations for more than 110 CSO events collected at 10 sites. A variety of overflow events with a wide range of event durations and volumes was sampled (Table 3.3). The average number of subsamples per event was 49, corresponding to a composite sample volume of 484 l. In 80 % of the samples the respective events could be covered to their full extent. Therefore, the results can be regarded as a sound representation of the event mean concentration. For quality assurance, the course of sampling was evaluated for each event. Few samples had to be excluded from subsequent analyses due to irregularities. In total, the results of 99 samples are discussed in the following sections.

Table 3.3: Event and sampling details (n=99).

	25 %	Median	Mean	75 %
Event duration in h	3.0	4.7	6.9	8.4
Overflow volume in m³	1,622	2,920	5,028	6,449
Share of event volume represented in sample	1.0	1.0	0.92	1.0
Number of subsamples	21	47	49	76
Composite sample volume in l	195	455	484	791

3.3.2 Wastewater Quality Parameters

Conventional wastewater quality parameters allow for a general plausibility check of the results. Conductivity and pH ranged between typical values for wastewater and stormwater. The approach of Passerat *et al.* (2011) was used to estimate based on the conductivity the proportions of sewage and stormwater in the samples. Values of 1,250 µS/cm and 75 µS/cm were assumed for dry weather wastewater and stormwater runoff, respectively. This resulted in a median stormwater share of 91 %, corresponding to a mixing ratio of 10. A similar median mixing ratio could be calculated using the wastewater tracer acesulfame and assuming concentrations of 27 µg/l and 0 µg/l for dry weather wastewater and stormwater, respectively (Launay *et al.* 2016b). The mixing ratio based on acesulfame is less sensitive to other constituents of the sewage, e.g. de-icing salts, which is reflected by the narrower distribution of the values (Table 3.4). Both estimates result in a range (≥ 7) that is targeted by dimensioning according to German guidelines.

Table 3.4: Distribution of mixing ratios (n=99).

Mixing ratio	25 %	Median	Mean	75 %
based on conductivity	5.5	10	20	19
based on acesulfame	7.6	11	13	16

The average concentrations of COD and nutrients were lower by a factor of 7 – 8 than wastewater treatment plant influent concentrations in Bavaria (DWA 2018), which is a plausible range for CSO. However, these concentrations are considerably below values published formerly for CSOs in central Europe (Brombach *et al.* 2005; Aarts *et al.* 2013). Apart from the mixing ratio which might be higher on average than in some other studies (e.g. Gasperi *et al.* 2012; Launay *et al.* 2016b), the differences can be explained by methodological reasons. In the context of this project, composite samples of events with median durations > 4 h were obtained (Table 3.3). For the majority of events, their entire course was covered. This included long-lasting rains with low concentration levels. In contrast, studies with autosamplers in the 1980 – 1990s often aimed at reaching a high temporal resolution. This implied short sampling intervals and limited the maximum sampling duration to the early part of storm events. This may have led to an overestimation of event mean concentrations (Lee *et al.* 2007). Additionally, it must be taken into account that we only investigated CSO facilities with a storage volume and predominantly sedimentation facilities. This is in contrast to existing data pools, which do not always distinguish between CSO facilities with or without storage.

3.3.3 Micropollutant Occurrence and Concentrations

All substances analysed were detected in CSO samples and the majority were quantified in more than 80 % of the samples (Figure 3.2). Since all particle-bound pollutants could be quantified reliably in homogenised samples, no separate sampling of the particulate phase from the LVS was conducted.

Pesticides and biocides were less frequently quantified, especially pesticides with agricultural applications, i.e. metolachlor (MET) and terbuthylazine (TBA). Atrazine (ATR), the use of which has been prohibited since 1991, was quantified in one sample only.

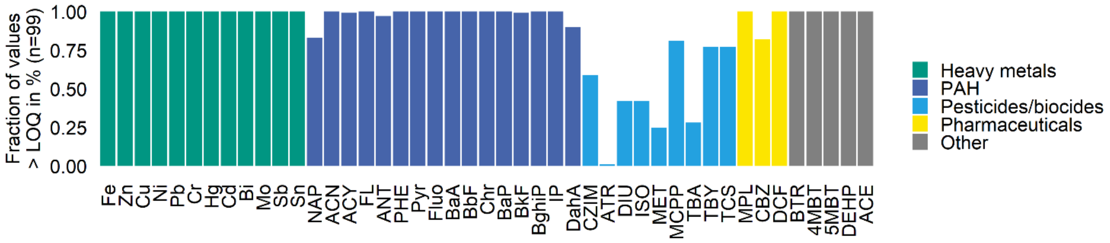

Figure 3.2: Fraction of values > LOQ micropollutants in CSO event composite samples (n=99). Abbreviations are explained in Table 3.2.

Concentration data across all substances are right-skewed (median < arithmetic mean) and approach a log-normal distribution in most cases. The variability is high in the range of 1 – 2 orders of magnitude and measured ranges are generally comparable to literature results where available (e.g. Gasperi *et al.* 2012; Clara *et al.* 2014; Christoffels *et al.* 2016; Launay *et al.* 2016b; Kay *et al.* 2017).

3.3.4 Variability between Events and Sites

Comparing the mean of relative standard deviations (RSD) of each site to the RSD of site median concentrations reveals that both variability between events and variability between sites are substantial, with one predominating the other depending on the substance considered (Figure 3.3). There is a clear pattern of heavy metals and PAH varying more between events than between sites, which indicates a basic potential with an event-dependent mobilisation and confirms their ubiquitous occurrence. Event-related variability is caused, for example, by rainfall volume, duration, intensity, and antecedent dry days. On the contrary, pesticides and pharmaceuticals, with the exception of MCPP and diclofenac, show more of a site-specific occurrence.

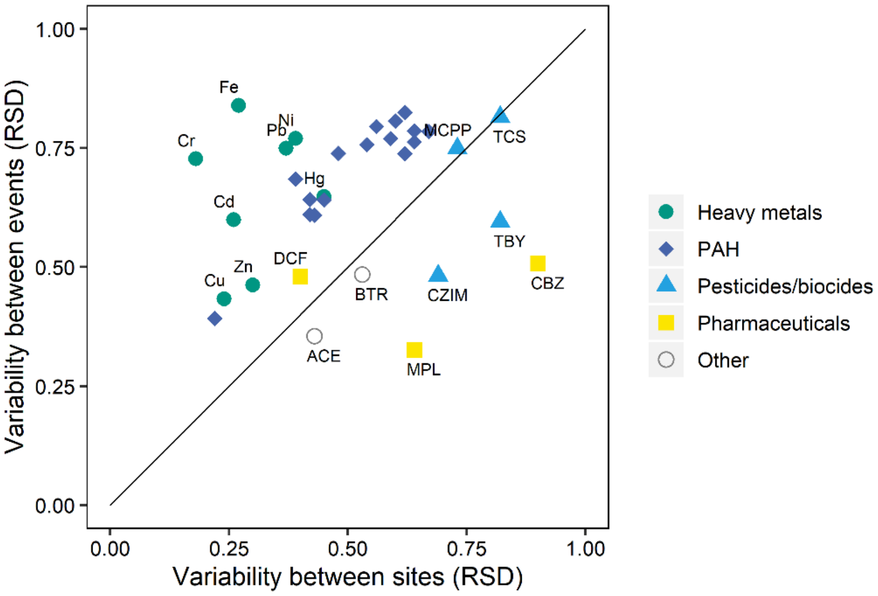

Figure 3.3: Scatterplot of relative standard deviation (RSD) of site median concentrations (variability between sites) and the mean of RSDs of each site (variability between events). Abbreviations are explained in Table 3.2. Substances with > 50 % of values < LOQ were excluded from this analysis.

3.3.5 Transport Pathways

The correlation analysis in Figure 3.4 underlines the importance of considering sources, transport behaviour, and pathways of the micropollutants. Concentrations of substances with the same main source (wastewater/stormwater) and predominant transport form (particulate/dissolved) are significantly correlated and can be categorised accordingly. The particle-transported metals, PAH, and DEHP form one large group. Another group consists of substances that mainly originate from the wastewater pathway. The mixing ratio in the overflow remains an important factor for expectable quality. Low mixing ratios based on acesulfame (ACE) are linked to higher concentrations of other wastewater-transported substances. Especially in larger urban catchments, indirectly connected areas (through upstream overflow structures) and wastewater inflows from separate sewer systems may shift this ratio and be relevant influences for such substances. However, both, varying mixing ratios and varying concentrations in the original components (wastewater/stormwater), contribute to concentration variability. For substances with multiple sources and complex emission patterns, the mixing ratio is less meaningful to explain the variability.

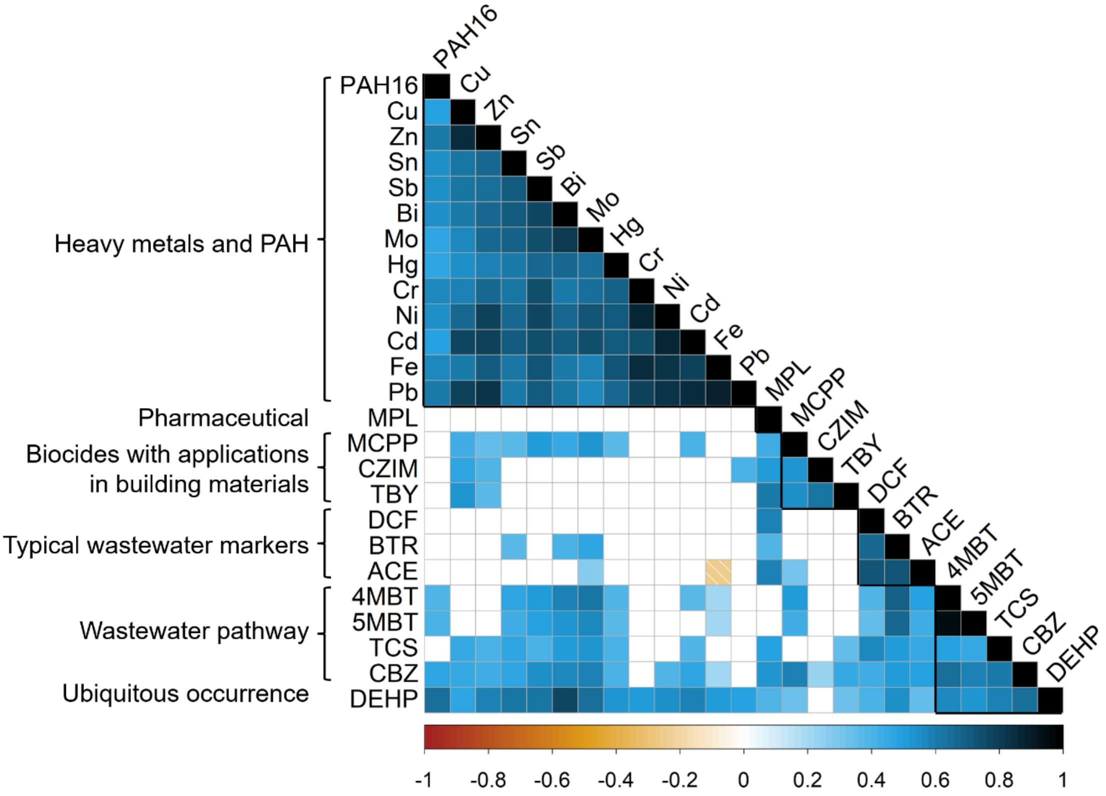

Figure 3.4: Correlation matrix of micropollutant concentrations sorted by hierarchical clustering. Colour indicates Spearman's rank correlation coefficients. Only significant correlations are displayed ($p < 0.05$). Negative correlations are shown with shading. Substances with > 50 % of values < LOQ were excluded from this analysis.

3.3.6 Differentiation of Emissions from Rural and Urban Catchments

Catchments were qualitatively categorised into urban and rural catchments based on the results of on-site visits (Table 3.1). Factors taken into consideration were the intensity of urban land use in the form of housing, businesses and traffic, population density as well as the size and complexity of catchments, e.g. indirectly connected areas and wastewater inflows from areas with separate sewer systems (e.g. newly developed areas). Catchment urbanisation proves to be a factor relevant to CSO micropollutant concentrations regardless of their main pathways and transport behaviour. Significantly higher concentrations of the pharmaceuticals diclofenac and carbamazepine, the sweetener acesulfame, the disinfectant triclosan, the benzotriazoles, DEHP, several biocides (mecoprop, terbutryn, diuron), heavy metals (Zn, Bi, Mo, Sn, Sb, Cu), and 11 out of 16 PAH were found in CSOs from urban catchments (Mann-Whitney U test, $p < 0.05$). Figure 3.5 shows the comparison for DEHP and diclofenac. No substance had significantly higher concentrations in CSOs from rural catchments.

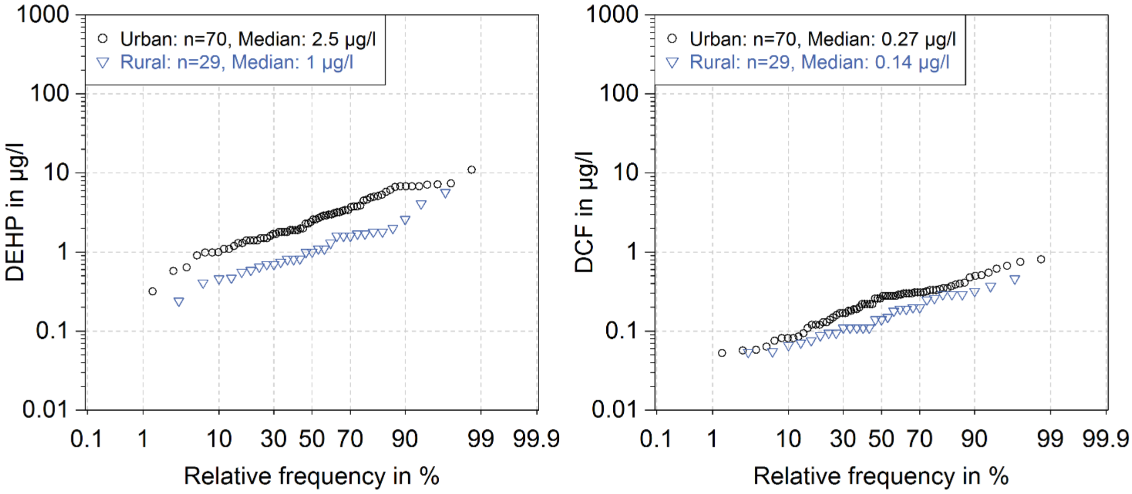

Figure 3.5: Distribution of measured concentrations of DEHP and diclofenac in CSOs from urban and rural catchments.

3.3.7 Relevance of CSO Emissions in Relation to WWTP

To assess the relevance of micropollutant emissions from CSO facilities in relation to those of wastewater treatment plants (WWTP), concentrations were compared to results from 7-day composite samples collected under dry and wet weather conditions at 49 WWTP and made available from a Germany-wide monitoring project (Fuchs *et al.* 2020c). Figure 3.6 illustrates the concentration differences for median effluent concentrations. Median CSO concentrations of ubiquitous, primarily particle-bound and stormwater-transported pollutants, i.e. all 16 PAH, Pb, Cd, and Hg, are significantly higher than both dry- and wet-weather effluent concentrations from WWTP (Pairwise Wilcoxon test, $p < 0.001$). The concentration difference is considerable, e.g. factors of 6, 11, and 27 for Hg, Cd, and Pb, respectively. In case of PAH, concentrations in WWTP effluents were often < LOQ, which is why CSO concentrations can be > 90 times higher, e.g. for priority hazardous substances BaP and BghiP. For some pesticides/biocides, CSO concentrations are significantly lower than in WWTP effluent. However, the difference is less distinct and could be impaired by values < LOQ in both datasets. In addition, WWTP monitoring was aimed at completely capturing concentrations throughout one year, while rain-dependent CSO sampling might have missed application periods of pesticides/biocides.

A rough estimate of annual loads in Germany using median concentrations was calculated based on a balance of the total wastewater load of surface waters (Table 3.5). 55 % of the resulting annual wastewater load originate from WWTP, 28 % from CSOs, and 16 % from stormwater outfalls (SSO) in separate sewer systems. To close the balance for SSOs, additional concentration data were obtained from Fuchs *et al.* (2020c). Median concentrations based on 20 events sampled with LVS at two SSOs were used. From each substance group for which comparative data were available (Figure 3.6), one substance was selected to estimate loads, i.e. the heavy metal Hg, the PAH benzo(a)pyrene (BaP), and the biocide terbutryn (TBY).

In case of TBY, emissions from CSOs amount to 10 % of the total. However, in case of Hg and BaP, resulting annual loads from CSOs may be 1.8 – 27 times higher than from WWTP. For BaP, it has to be noted that 66 % of values in WWTP effluent were < LOQ and substituted by LOQ/2 for this calculation.

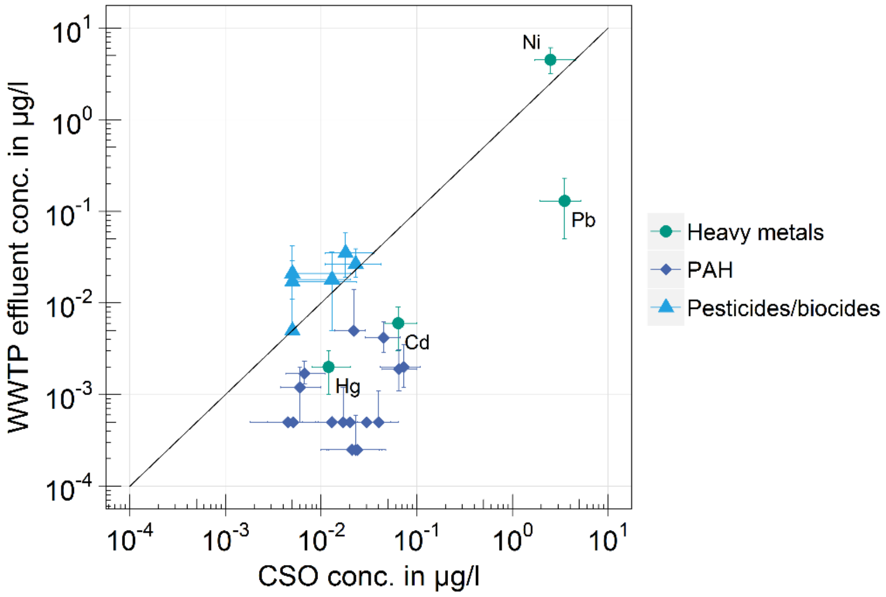

Figure 3.6: Comparison of median micropollutant concentrations in combined sewer overflows (n=99) and wastewater treatment plant effluents (n=709). Error bars show the 25 % and 75 % quantiles.

These proportions confirm general trends observed in regional estimations (Launay *et al.* 2016a; Becouze-Lareure *et al.* 2019) as well as results from nation-wide emission budgets (Fuchs and Toshovski 2016) and underline the importance of CSOs as an emission pathway for micropollutants. In conclusion, emissions from both SSOs and CSOs prove to be especially relevant to substances causing failure to achieve good chemical status of surface waters, such as uPBT substances Hg, BaP, BghiP, IP, BbF, and BkF (Kristensen *et al.* 2018).

Table 3.5: Balance of the total wastewater load of surface waters in Germany and annual emissions of mercury (Hg), benzo(a)pyrene (BaP), and terbutryn (TBY).

Wastewater loads	**Formulas and assumptions**	**Annual volume in 10^9 m³**	**Annual load in kg**		
			Hg	**BaP**	**TBY**
Wastewater treatment plants	$Q_{WWTP} = Q_{dw} + x \cdot (1-e) \cdot Q_r$	10.06	20.1	2.5	352.2
Stormwater outfalls	$Q_{SSO} = (1-x) \cdot Q_r$	5.14	64.2	254.3	138.7
Combined sewer overflows	$Q_{CSO} = x \cdot e \cdot Q_r$	2.96	35.5	68.0	53.2
Total wastewater load of surface waters	$Q_{WWTP} + Q_{SSO} + Q_{CSO}$	18.16	119.8	324.9	544.2

Q_{dw} = dry weather flow: sum of annual sewage and infiltration according to DESTATIS (2018b)
x = share of combined sewer systems: 54 % (DESTATIS 2018b)
e = share of stormwater discharged via CSOs in combined systems: 50 % (assumption)
Q_r = stormwater: settlement area 32,898 km² (DESTATIS 2018a) · 60 % imperviousness · 800 mm per year · 0.7 runoff coefficient (assumptions)

3.4 Conclusions

This monitoring program was aimed at improving the database of CSO micropollutant concentrations using a harmonised methodology for several catchments. Automatic sampling with stainless steel LVS was used to produce volume-proportional event composite samples. A wide range of event durations and overflow volumes was covered successfully. The typical wastewater quality parameters show plausible concentrations ranges and ratios. However, median concentrations of COD and nutrients are considerably below values published formerly for CSOs in central Europe. The differences might be partly due to site-specific characteristics, but can more likely be explained by methodological reasons. For better comparability of CSO monitoring results, it is concluded that studies should document whether CSO facilities with or without storage were studied and up to which duration or volume fraction events were sampled.

All of the micropollutants analysed were detected in CSO samples and most of them were quantified in more than 80 % of the samples. Our results confirm that CSOs need to be considered in the debate on micropollutant emissions and complement our knowledge of their concentrations on a regional level. Although the methodology is harmonised, concentration data vary widely and no simple and generally transferable relationships between concentrations and catchment characteristics can be identified. This confirms the need for comprehensive monitoring. Distinct substance-specific patterns can be observed in both variability between events and sites as well as in a correlation analysis of substance concentrations. These underline the need for differentiation of the substances by their predominant sources, pathways, and transport behaviours. Heavy metals and PAH show ubiquitous occurrence with high event-dependent variability. A site-specific assessment of their concentrations is considered less relevant than for biocides terbutryn and carbendazim and pharmaceuticals metoprolol and carbamazepine, which exhibit high site-dependent variability. Catchment urbanisation is a factor relevant to CSO micropollutant concentrations regardless of their main pathways and transport behaviours. Further research is needed to improve knowledge on transport and retention of micropollutants in catchments and sewer systems.

In relation to micropollutant emissions from WWTP, CSOs are an important pollution source especially for ubiquitous, primarily stormwater-transported pollutants, including substances causing failure to achieve good chemical status of surface waters, such as uPBT substances Hg, and PAH. Fortunately, one practicable measure for reduction of particle-transported pollutants would be the optimisation of available solid retention treatment processes.

3.5 Acknowledgement

We would like to thank the Bavarian State Ministry of the Environment and Consumer Protection for financing the project. Our thanks also go to the operating personnel of the plants involved, the Bavarian Environment Agency, and our partners DVGW Technologiezentrum Wasser (TZW), Umwelt- und Fluid-Technik GmbH, and Bioplan Landeskulturgesellschaft for their good cooperation.

4 Up-To-Date Monitoring Data of Wastewater and Stormwater Quality in Germany

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Abstract: A comprehensive dataset of pollutant concentrations in German urban wastewater systems is available from recently completed monitoring projects. It contains up to 1,000 concentration values for each of 79 substances in wastewater treatment plant (WWTP) effluents from 49 sites, and up to 157 values for each of 95 substances in combined sewer overflows (CSOs) from 12 sites. WWTP influents and stormwater outfalls were sampled to a lesser extent. All sampling methods were harmonised and aimed at collecting event or multi-day composite samples over periods of ≥1 year. Among the substances analysed were biocides and pesticides, polycyclic aromatic hydrocarbons, perfluorinated alkyl substances, metals, pharmaceuticals, benzotriazoles, phenols, acesulfame, di-(2-ethylhexyl)phthalate, and hexabromocyclododecanes. Occurrence, concentration ranges, and removal rates of selected WWTPs are presented. CSOs can be confirmed as an important pathway of metals and PAH to receiving waters when compared to WWTPs on the basis of annual per capita loads. The derived volume-weighted site mean concentrations are qualified to be used as representative input data for estimation of average substance emissions in large areas, e.g. on river basin scale, if no site-specific data are available. As such, they will contribute to the development of strategies to reduce substance emissions, taking into account not only WWTPs but also stormwater-related discharges.

4.1 Introduction

State-of-the-art wastewater treatment plants (WWTPs) are highly effective in removing suspended solids, biodegradable organic matter, and nutrients. Still, wastewater discharges from urban areas are among the main pressures on surface water quality (Kristensen *et al.* 2018). In addition to continuous emissions from WWTPs, increased attention needs to be paid to non-continuous, stormwater-related emissions from urban wastewater systems (UWS). These are stormwater outfalls (SSOs) in separate sewer systems and combined sewer overflows (CSOs) in combined sewer systems. SSOs and CSOs may contribute significant shares to the total emission from UWS depending on the pollutant considered (Fuchs and Toshovski 2016). Consequently, a holistic assessment of the emissions from both wastewater and stormwater treatment is needed to manage surface water pollution effectively.

The increasing contamination of surface water bodies with micropollutants is one of the major challenges for water management (Schwarzenbach *et al.* 2006). New chemicals are developed, produced, and brought to application at a rapid pace. At the same time, the uncertainties regarding ecotoxicological risks connected to the emission of these substances are high (Schwarzenbach *et al.* 2006). Several groups of substances show ubiquitous environmental occurrence, such as polycyclic aromatic hydrocarbons (PAH) or per- and polyfluorinated alkyl substances (PFAS). Only 38% of the surface water bodies in the EU are in a good chemical status according to environmental quality standards (EQS) (Kristensen *et al.* 2018). Certain persistent, mobile, and toxic substances might become increasingly challenging for water supplies (Rüdel *et al.* 2020). While advanced treatment processes for the elimination of micropollutants (e.g. adsorption or oxidation) are being developed and implemented in WWTPs (Eggen *et al.* 2014; Luo *et al.* 2014), emissions from SSOs and CSOs are so far rarely considered.

Information on the quality of wastewater and stormwater is used for treatment design and management planning and therefore needs regular updating. However, operational quality monitoring is typically limited to WWTPs and to standard water quality parameters such as oxygen demand and nutrient concentrations. Available compilations of urban runoff quality data from research-oriented studies are outdated (Smullen *et al.* 1999; Brombach *et al.* 2005). Data on micropollutants are often insufficient to reliably estimate emissions on larger spatial scales (Hillenbrand *et al.* 2016). This is due to the growing number of substances to be considered, the large sampling effort, and the costs of analysis. In addition, extensive accompanying data are required for the proper interpretation of the results. The informative value of data compiled from different studies is often limited by differing sampling procedures, insufficiently sensitive analytical methods, or non-comparable boundary conditions. In addition, the reported substance concentrations often exhibit stochastic variability, which impedes the development of transferable quality models.

Recently completed studies on behalf of the German Environment Agency (Fuchs *et al.* 2020b; Fuchs *et al.* 2020c) and the Bavarian Environment Agency (Nickel and Fuchs 2020) therefore addressed two main data needs: up-to-date data on urban runoff quality, and reliable data for the quantification of micropollutant emissions from UWS on river basin level as required under EU legislation. Therefore, the main focus was on regulated priority substances (European Commission 2013). Here, the analytical results of these studies were combined to provide a high-quality comprehensive dataset, which allows an up-to-date assessment of urban wastewater and stormwater quality that is representative of the situation in Germany.

4.2 Methods

4.2.1 Monitoring Strategy and Sampling Locations

From 2016 to 2019, sampling campaigns were conducted to collect new data on the pollution of wastewater and stormwater in Germany (Fuchs *et al.* 2020b; Fuchs *et al.* 2020c; Nickel and Fuchs 2020). One mutual objective of the studies was to improve the database for the nation-wide calculation of substance emissions into surface waters with the model MoRE (Fuchs *et al.* 2017b; Fuchs *et al.* 2017a). Therefore, all campaigns aimed to collect data as representative as possible of the main emission pathways from urban areas into surface water bodies, i.e. WWTPs, CSOs, and SSOs (Figure 4.1). Spatial variability was taken into account by selecting multiple sampling locations with different characteristics. Temporal variability was accounted for by using long-term composite samples and sampling periods of more than 1 year. All sampling procedures and analytical methods were carried out following strictly harmonised protocols.

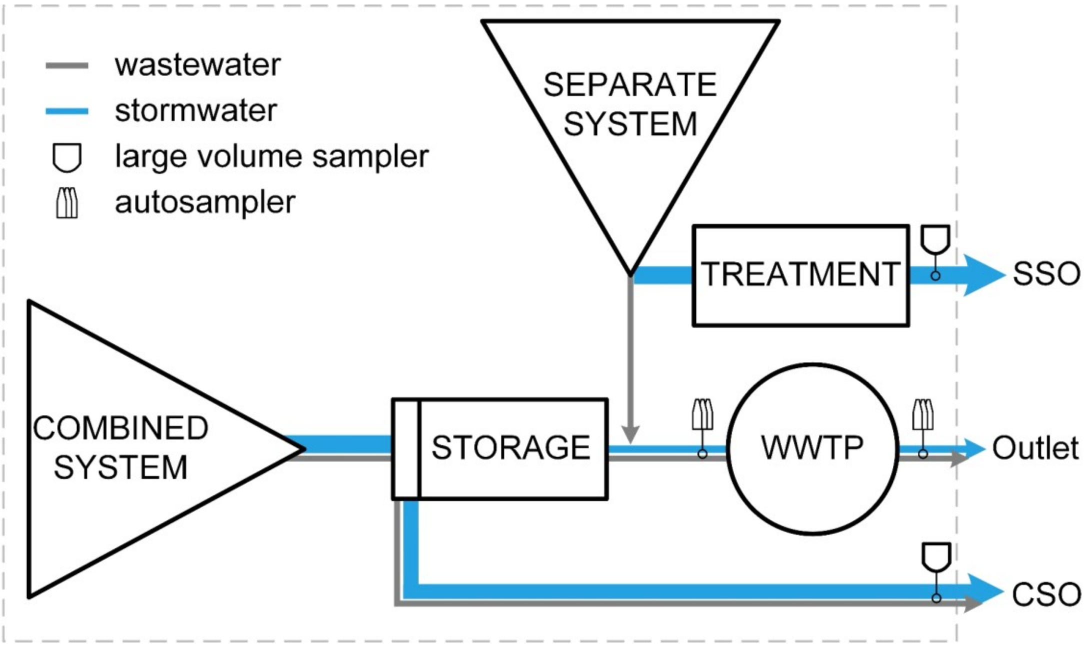

Figure 4.1: Schematic overview of a generalised urban wastewater system with sampling points: WWTP = wastewater treatment plant, CSO = combined sewer overflow, SSO = (separate) stormwater outfall.

For investigation of the WWTP effluent quality, 49 WWTPs of various sizes equipped with different process technologies were selected. The capacities of the selected WWTPs ranged from 1,500 to 1,600,000 population equivalents (PE) (Table A4.1). The fraction of catchment area drained by a combined sewer system ranged from 0 to 100% with a median of 60%. Treatment steps common to all selected WWTPs were primary sedimentation, conventional activated sludge treatment with chemical precipitation of phosphorus, and secondary clarification. None of the WWTPs had advanced treatment processes for micropollutant removal in operation. The WWTPs were spatially distributed across Germany (Figure A4.1). Five WWTPs were selected for additional detailed investigations. At these sites, samples were also collected from the influent.

Ten of the 12 CSOs were sampled on behalf of the Bavarian Environment Agency and were located in Bavaria (Figure A4.1). Two SSOs were selected. All CSOs were facilities with storage volume. Eight of these facilities were sedimentation tanks, and samples were collected from the tank overflow. Also, both SSOs were overflows from sedimentation tanks. Catchment sizes ranged from 44 to 3,850 ha (Table A4.2). The median specific volume of 22 m³/ha impervious catchment area of the selected sites (min. 10 – max. 89 m³/ha) was typical of the average storage volume targeted by combined sewage treatment design in Germany. In separate systems, the provision of treatment capacity for stormwater is less common. Despite the fact that 46% of the population in Germany is connected to separate systems, there are only 2.8 million m³ of treatment capacity available in separate systems as opposed to 16 million m³ in combined systems (Dettmar and Brombach 2019).

4.2.2 Sampling of Wastewater Treatment Plant In- and Effluents

WWTPs were sampled monthly for a period of 1 to 1.5 years. Effluent samples were collected from the secondary clarifier outlet except for three sites where effluent samples were collected after a final filtration step, and seven sites where effluent samples were collected at the outlet of tertiary treatment ponds. Influent samples were always collected from the inlet of the primary sedimentation tank. 7-day composite samples were collected using preinstalled autosamplers of the WWTPs. Since the same autosamplers were also used for routine operational monitoring of the WWTPs, the sampling regimes varied according to local preferences. The sampling was flow-proportional at about half of the WWTPs, and time-proportional at the other half. Each day a 24-hour composite sample of 1 l was collected. Dry and wet weather days were distinguished based on a site-specific daily inflow threshold (ranging between 1.2 and 2.6 multiples of dry weather flow). The 24-hour sample was then filled into one of two 10 l stainless steel vessels for dry and wet weather composite samples and kept deep-frozen at -18 °C until the completion of one 7-day period.

4.2.3 Sampling of Combined Sewer Overflows and Stormwater Outfalls

All CSOs located in Bavaria were sampled for a total period of 2 to 3 years, CSOs outside Bavaria for 1.5 years. The event-dependent sampling was conducted with large-volume samplers (LVS) which were triggered by flow measurements based on water level sensors. Volume-proportional composite samples of up to 1,000 l were collected in stainless steel tanks. This allowed to capture even large events for their full duration. The samples were homogenised using a submersible pump to collect subsamples of 0.1 to 2 l as required for different analyses. The method has been described in detail in chapters 2 and 3 (Nickel and Fuchs 2019, 2021). The sampling of SSOs was conducted with the same method as described for CSOs. At one of the two sites, an autosampler was used instead of a LVS to collect the composite samples.

4.2.4 Selection of Substances

One main objective of the sampling campaigns was to address data requirements for regulated priority substances. A selection of almost 100 different substances was considered, including mainly priority substances according to Directive 2013/39/EU (European Commission 2013), substances with national EQS according to the German ordinance on the protection of surface waters (OGewV 2016), biocides proposed for monitoring in a previous prioritisation study (Rüdel *et al.* 2017), and few others. Among the substances were 40 biocides and pesticides, 16 PAH, 16 PFAS, 12 metals, 8 pharmaceuticals, 3 benzotriazoles, 2 phenols, acesulfame (ACE), di-(2-ethylhexyl)phthalate (DEHP), and hexabromocyclododecanes (HBCDD). However, the lists of substances analysed at each sampling point differed slightly, and several substances were analysed in samples from selected WWTPs or CSOs only. This resulted in differing numbers of sites and samples for individual substances, which are reported with the results. A full list of substances is found in Table A4.3.

4.2.5 Analytical Methods

WWTP samples were defrosted at room temperature for 1 to 2 days. Following homogenisation by repeated manual shaking, aliquots were filled into amber bottles for the analysis of organic pollutants, and polyethylene bottles for the analysis of metals. The subsamples for metal analysis were stabilised with

1 volume-% of concentrated nitric acid. CSO and SSO samples were already bottled, stabilised, and cooled on site (Nickel and Fuchs 2019). All samples were stored at 4 °C until analysis.

The analytical methods were adapted to the respective matrices and optimised to ensure low limits of quantification (LOQ) which were below or at least in the range of EQS for most substances. Methods were also adjusted to ensure that all concentrations refer to the total content of a substance in the samples, i.e. the sum of particulate and dissolved fractions. LOQ are reported in Table A4.3. A list of the analytical methods used is provided in Table A4.4.

Standard water quality parameters, including total suspended solids (TSS), chemical oxygen demand (COD), total nitrogen bound (TNb), and total phosphorus (TP), were analysed in all samples from CSOs, SSOs, and five WWTPs selected for detailed investigations.

4.2.6 Data Analysis

4.2.6.1 Statistics

For the evaluation of the data, median values and 80% interquantile ranges (10th-90th percentile) were calculated replacing values <LOQ by LOQ/2. The frequency of values >LOQ was reported to indicate the quality of the statistics. If medians or quantiles resulted in values <LOQ, they were not reported.

4.2.6.2 Removal Rates

WWTP influent concentrations (C_{in}) and effluent concentrations (C_{out}) from the same sampling period were paired to calculate the removal rate (RR) according to Equation 4.1. If influent concentrations were <LOQ, removal rates were not calculated.

$$RR = (C_{\text{in}} - C_{\text{out}}) / C_{\text{in}} \tag{4.1}$$

4.2.6.3 Mixing Ratios in Combined Sewer Overflow

Mixing ratios of stormwater and wastewater in the CSO samples were estimated using the artificial sweetener ACE as a wastewater marker. Site-specific dry weather wastewater concentrations were not available and were therefore assumed to range from 20 to 60 µg/l based on WWTP influent concentrations reported in the literature (Scheurer *et al.* 2009; Scheurer *et al.* 2011; Sacher and Thoma 2014; Launay *et al.* 2016b). The mixing ratio was then calculated using wastewater concentrations randomly sampled from a uniform distribution within these boundaries. Stormwater concentrations of ACE were assumed to be zero.

4.2.6.4 Volume-weighted Site Mean Concentrations

Site mean concentrations ($SMCs$) were calculated by weighting the single concentration measurements (C_{i}) at each site with the volume (V_{i}) represented by the sample according to Equation 4.2. For WWTPs, the sum of the daily inflow of all days in the multi-day composite sample was used. For CSOs and SSOs, the fraction of event volume that had been sampled was used. Only events that had been sampled to at least 50% were considered. SMCs of substances with >50% of samples <LOQ at the site were reported as LOQ/2.

$$SMC = \sum (C_{\text{i}} \times V_{\text{i}}) / \sum V_{\text{i}} \tag{4.2}$$

4.2.6.5 Per Capita Loads

To compare emissions from CSO and WWTP, annual per capita loads (*PCL*) were calculated for each site using volume-weighted *SMC*, annual discharge volume (*AV*), and population equivalents (*PE*) as shown in Equation 4.3.

$$PCL = SMC \times AV / PE \tag{4.3}$$

For WWTPs, per capita loads were calculated based on the annual discharge volume measured in 2016 and the connected PE. For CSOs, per capita loads were calculated based on the average annual CSO volume measured during the monitoring campaign and the number of inhabitants in the directly connected catchment area. SSO per capita loads were not calculated because population data were not available and because connected area is considered a more appropriate basis for comparing loads from separate system outlets.

4.3 Results and Discussion

4.3.1 Scope and Quality of the Datasets

The data compiled from the sampling campaigns comprises analytical results for standard water quality parameters and 79 substances in WWTP influents and effluents, 95 substances in CSOs, and 77 substances in SSOs. The number of sites and the number of samples vary for the individual substances (Table A4.5–Table A4.8). The largest datasets are available for WWTP effluent (up to 1,000 multi-day composite samples) and CSO concentrations (up to 157 event composite samples). Since only five WWTPs were selected for detailed investigations including influent sampling, the influent dataset covers less spatial variability. SSO data is available from 20 events at two sites.

The WWTP composite sampling integrated concentration fluctuations over 7 days in approximately 70% of the samples. The other part of the samples included <7 days due to variable weather conditions. Therefore, the samples are referred to as multi-day composite samples. There were no systematic concentration differences between flow-proportional and time-proportional samples (Fuchs *et al.* 2020c). All samples were considered equally in the evaluations.

The samples collected from CSOs and SSOs covered a wide range of event characteristics that reflect the rainfall variability during the sampling periods. The 80% interquantiles of event durations and volumes were 2 – 20 h and 850 – 12,000 m³, respectively. For ten CSOs, a complete record of events during the sampling period was available. This allowed to confirm that the sampled events were representative of all events in the sampling period, but with a tendency towards events with higher volume, duration, and intensity (Nickel and Fuchs 2020). By using LVS for sampling of CSOs and SSOs, the majority of events (72%) could be covered to their full extent, and 90% of the composite samples represented at least 60% of the event volume. Therefore, the results represent reliable estimates of event mean concentrations. Ten events were excluded from these statistics, because volume and duration could not be determined due to technical problems or measurement error.

For 32 of the substances analysed in WWTP effluents and 30 of the substances analysed in WWTP influents, more than 50% of concentrations were >LOQ. The concentration ranges (total content) found for these substances in are shown in Figure 4.2. The frequency of values >LOQ affects the usability of the datasets for calculating emissions (Fuchs *et al.* 2010b) and is considered an important quality criterion reflecting the sensitivity of analytical methods. In WWTP effluents, high frequencies of values >LOQ were found for metals (≥68%), the plasticiser DEHP (100%), and the low-molecular-weight PAH fluorene (FL), phenanthrene (PHE), fluoranthene (Fluo), and pyrene (Pyr) (≥80%). For PFAS, biocides, and pesticides, the frequency of values >LOQ varied largely between the individual substances. The priority substances perfluorooctane sulfonic acid (PFOS), terbutryn (TBY), diuron (DIU), and isoproturon (ISO) could be quantified in ≥70% of the samples. A total of 28 substances had less than 5% of values >LOQ. Among these were mainly biocides and pesticides, many of which are no longer approved in Germany, as well as several PFAS and PAH (Table A4.6). No final conclusion can be made regarding the contribution of WWTPs to the pollution of receiving waters for some of these substances, since the methods used for analysis were not sufficiently sensitive. Especially in the case of the biocides cybutryne, cypermethrin, dichlorvos, dicofol, heptachlor, and the flame retardant HBCDD, LOQ exceeded annual average EQS (AA-EQS). Due to a higher complexity of the matrix, LOQ were often higher for WWTP influents than for effluents. Consequently, a total of 23 substances were never analysed >LOQ in samples from WWTP influents, and 10 substances had less than 5% of values >LOQ. Among these were mainly biocides, pesticides, and PFAS (Table A4.5).

In CSO and SSO, metals and DEHP were quantified with concentrations >LOQ in 100% of the samples, PAH in ≥85% (except for naphthalene (NAP), 40% in SSOs and 82% in CSOs), and phenols ≥60% (Figure 4.3). The frequency of values >LOQ of individual PFAS in SSOs correlated with those in WWTP effluents and CSOs. For biocides, the results differed individually, probably due to differences in applications, transport pathways, and environmental behaviour (Table A4.7, Table A4.8). Pharmaceuticals, benzotriazoles, and ACE were only analysed in CSOs and were found at concentrations >LOQ in ≥84% of the samples (Figure 4.4).

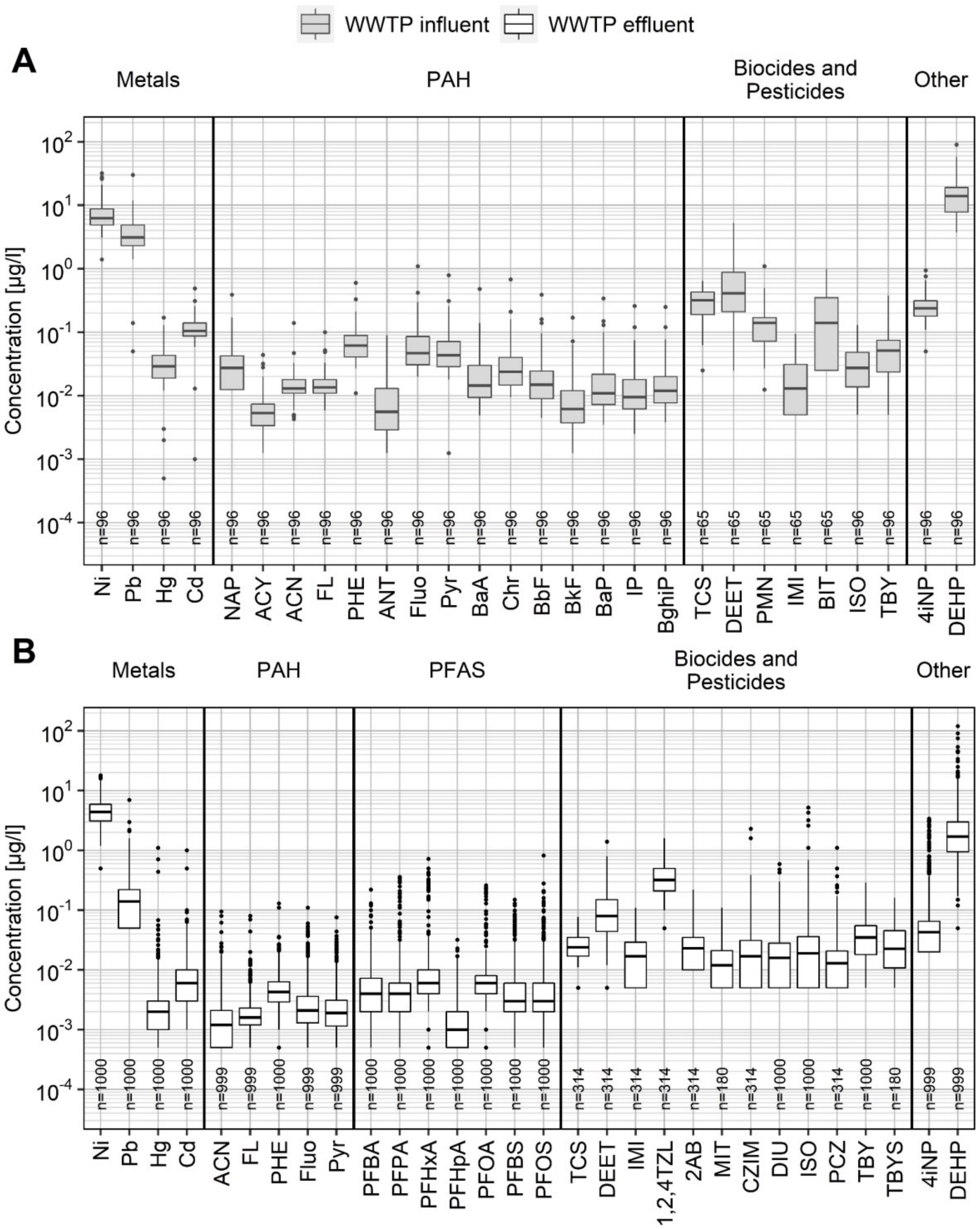

Figure 4.2: Total concentrations of substances with ≥50% values >LOQ in WWTP influents (A) and effluents (B). Values <LOQ were replaced by LOQ/2 for display. A list of substances including LOQs and abbreviations can be found in Table A4.3.

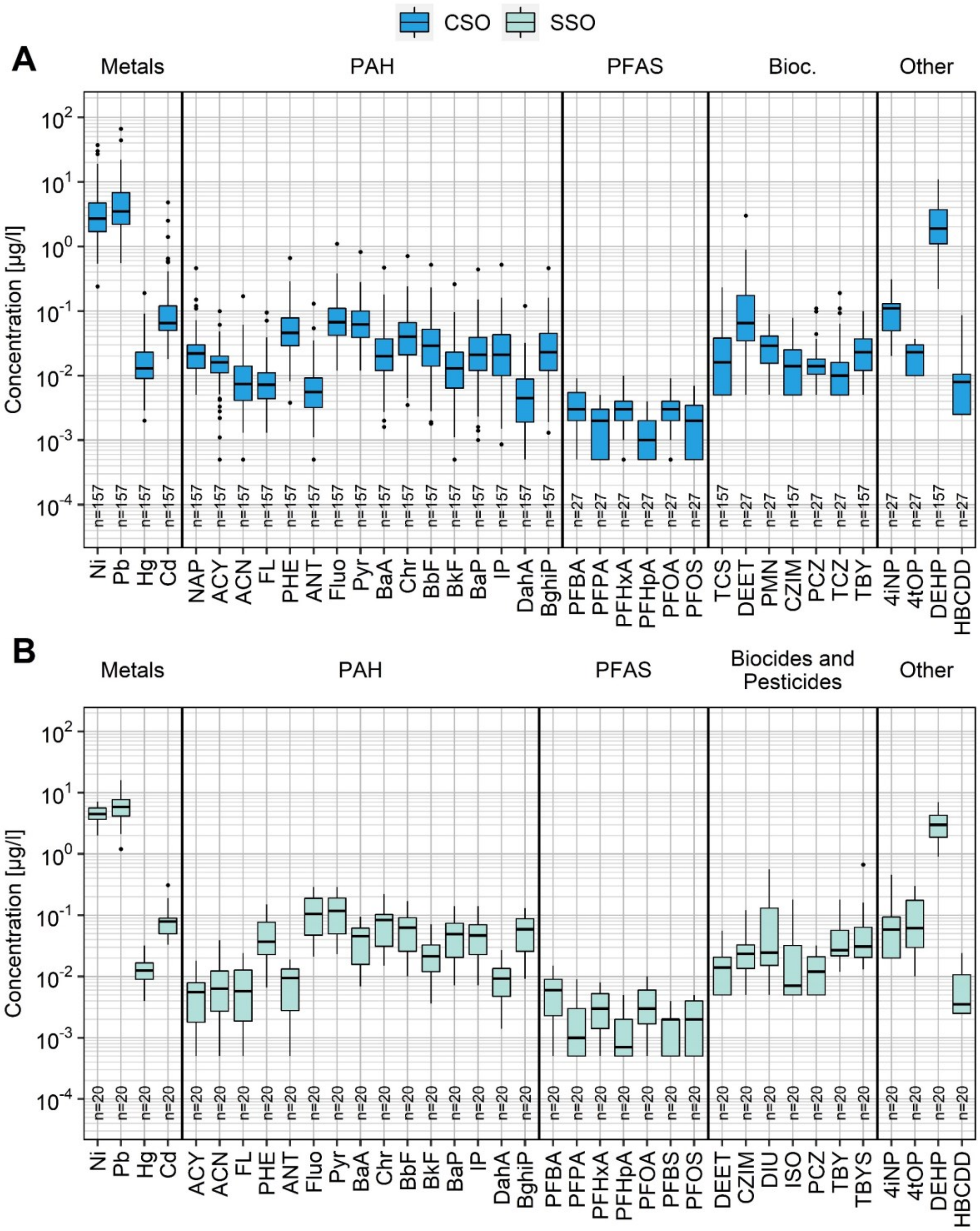

Figure 4.3: Total concentrations of substances with ≥50% values >LOQ in CSO (A) and SSO (B). Values <LOQ were replaced by LOQ/2 for display. A list of substances including LOQs and abbreviations can be found in Table A4.3.

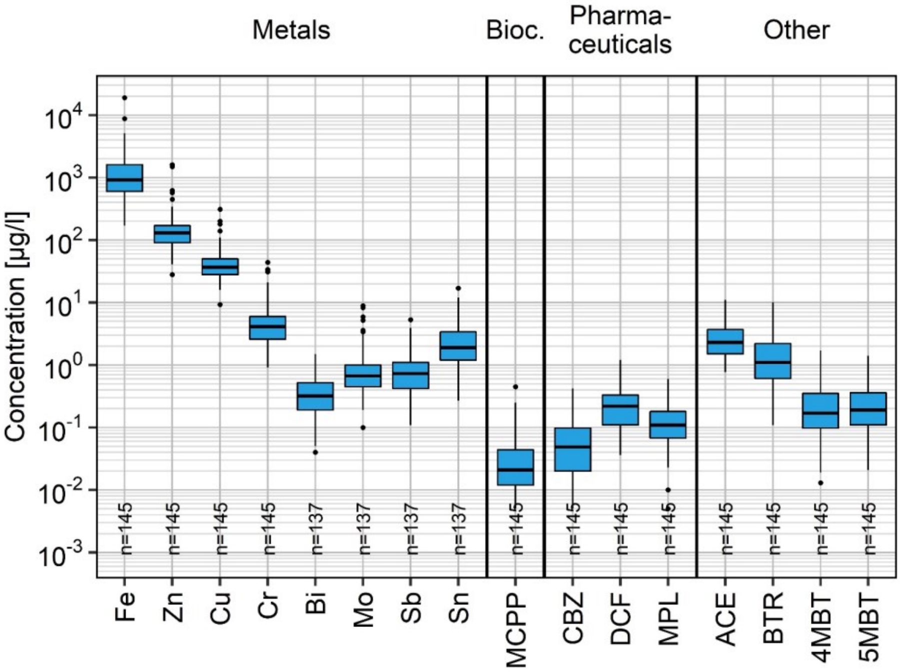

Figure 4.4: Total concentrations of additional substances analysed in CSO with ≥50% values >LOQ. Values <LOQ were replaced by LOQ/2 for display. A list of substances including LOQs and abbreviations can be found in Table A4.3.

4.3.2 Substance Concentrations and Comparison with Literature Data

Despite the composite sampling approaches, concentrations ranged across one up to three orders of magnitude for individual substances (Figure 4.2 – Figure 4.4). Concentrations in WWTP influents, effluents, CSOs, and SSOs did not follow normal distributions, but often approached lognormal distributions instead. Consequently, the median was used as an adequate central value. An overview of median concentrations and 80% interquantile ranges of selected substances from all substances groups is found in Table 4.1. The complete results for all substances are reported in the Appendix (Table A4.5–Table A4.8). Water quality parameters are also reported in the Appendix (Table A4.10–Table A4.13).

Several studies from Baden-Württemberg (Lambert *et al.* 2014; Sacher and Thoma 2014; LUBW 2019b), Austria (Clara *et al.* 2017b; Clara *et al.* 2017a), and other European regions (Loos *et al.* 2012), which were conducted with comparable methodology and a similar selection of substances, were used to compare the substance concentrations. For these studies, comparisons were possible on the basis of single values. WWTP effluent concentrations showed good agreement with the literature data, e.g. for metals, DEHP, and the biocides diethyltoluamide (DEET), DIU, ISO, and TBY. Similar concentration ranges were also found for PAH, PFAS and phenols, but the results were more variable and had more values <LOQ in the datasets.

For CSOs and SSOs, less literature data were available than for WWTPs, both in terms of the number of facilities sampled and sample sizes. Because single values were not available for most studies, comparisons were made using the reported central values (preferably medians) and ranges. With few exceptions (e.g. Cr, Fe), significant differences of substance concentrations between CSO sites in this study were found (Kruskal-Wallis-test, $p < 0.05$). Therefore, when comparing the resulting median concentrations and ranges to published data from other sites collected with different methods, both confirmatory and deviating results may be expected. Good agreement with other studies from Germany and Austria (Clara *et* *al.* 2014; Christoffels *et al.* 2016; Engelmann *et al.* 2016; Launay *et al.* 2016b) was found for metals, pharmaceuticals, benzotriazoles, DEHP, and ACE. More heterogeneous results were found for PAH, biocides, and pesticides. Mutzner *et al.* (2020) reported ranges of time-weighted average concentrations obtained by passive sampling of 95 events at 20 CSOs in Switzerland. These were comparable to our results for benzotriazole (BTR), carbamazepine (CBZ), and diclofenac (DCF), but considerably higher for the biocides carbendazim (CZIM), DIU, and mecoprop (MCPP). However, values <LOQ were excluded for summarisation by the authors, and results were stated to be likely overestimated due to the correction factors applied (Mutzner *et al.* 2020). Results from CSOs in France were comparable for metals (Becouze-Lareure *et al.* 2019) and tended to be higher for PAH and biocides (Gasperi *et al.* 2012; Paijens *et al.* 2021). Mean concentrations of diclofenac in British CSOs were very close to our results (Kay *et al.* 2017).

SSO concentrations were compared to stormwater concentrations measured at sites in Germany (Wicke *et al.* 2021), Austria (Clara *et al.* 2014), France (Zgheib *et al.* 2012; Becouze-Lareure *et al.* 2019), and Sweden (Björklund *et al.* 2009; Kalmykova *et al.* 2013). Wicke *et al.* (2021) reported concentrations in stormwater runoff from five catchments of 2.6-37 ha with contrasted land uses in Berlin. Concentrations of metals and PAH tended to be higher than shown by our results. Good agreement was found for metals and DEHP with few results of samples collected in storm sewers in two catchments in Austria, while PAH concentrations were lower (Clara *et al.* 2014). Swedish results for PAH and DEHP were close to ours, but not for phenols (Björklund *et al.* 2009; Kalmykova *et al.* 2013).

Considering the variability expected due to differences between regions, sewer systems, and sampling methods, good agreement with literature data was found for CSO and SSO concentrations. Nevertheless, most existing studies analysed stormwater that was discharged untreated, while the samples in this study were collected from sedimentation facilities. This may especially affect the concentration of pollutants adsorbed to particles. Since in Germany, SSOs without treatment are more common, more data on these direct SSOs should be acquired.

Table 4.1: Median total concentrations and 80% interquantile ranges (in brackets) of selected substances in WWTP influents, effluents, CSOs, SSOs, and removal rates in WWTPs. Removal rates were calculated based on influent and effluent concentration pairs from five selected WWTP and do not necessarily correspond to the relation of median influent and effluent concentrations shown in the table.

Group	Parameter	WWTP influent (µg/l)	WWTP effluent (µg/l)	Removal rate	CSO (µg/l)	SSO (µg/l)
No. of sites		5	29–49	3–5	6–12	2
No. of samples		65–96	314–1,000	11–95	27–157	20
Metals	Nickel (Ni)	6.25 (3.95 – 15)	4.4 (2.3–7.6)	0.47 (0.05–0.73)	2.7 (0.98–7.34)	4.5 (3.18–6.5)
	Lead (Pb)	3.1 (1.85–6.5)	0.14 (<0.1–0.33)	0.97 (0.86–0.99)	3.5 (1.46–11)	5.9 (2.82–11.4)
	Mercury (Hg)	0.029 (0.015–0.064)	0.002 (<0.001–0.005)	0.93 (0.78–0.98)	0.013 (0.007–0.034)	0.012 (0.0077–0.029)
	Cadmium (Cd)	0.11 (0.068–0.18)	0.006 (0.002–0.015)	0.93 (0.87–0.97)	0.065 (0.035–0.19)	0.079 (0.045–0.14)

Group	Parameter	WWTP influent (µg/l)	WWTP effluent (µg/l)	Removal rate	CSO (µg/l)	SSO (µg/l)
No. of sites		5	29–49	3–5	6–12	2
No. of samples		65–96	314–1,000	11–95	27–157	20
PAH	Naphthalene (NAP)	0.028 (<0.025–0.052)	<0.01 (<0.01–0.018)	0.83 (0.58–0.9)	0.022 (<0.01–0.051)	<0.01 (<0.01–0.026)
	Phenanthrene (PHE)	0.062 (0.032–0.12)	0.0043 (0.002–0.0098)	0.95 (0.89–0.98)	0.046 (0.017–0.13)	0.037 (0.0095–0.089)
	Benzo(a)pyrene (BaP)	0.011 (0.0057–0.058)	<0.0005 (<0.0005–0.0012)	0.98 (0.95–1)	0.021 (0.0051–0.067)	0.05 (0.011–0.081)
	Benzo(ghi)perylene (BghiP)	0.012 (0.006–0.052)	<0.0005 (<0.0005–0.001)	0.98 (0.96 – 1)	0.023 (0.0064–0.075)	0.059 (0.015–0.12)
Phenols	4-iso-nonylphenol (4iNP)	0.24 (0.15–0.5)	0.043 (<0.04–0.18)	0.88 (0.27–0.95)	0.11 (<0.04–0.17)	0.058 (<0.04–0.12)
	4-tert.-octylphenol (4tOP)	<0.05 (<0.05–0.052)	<0.02 (<0.02–0.033)	0.82 (0.71–0.86)	0.023 (<0.02–0.032)	0.062 (<0.02–0.26)
PFAS	Perfluorobutyric acid (PFBA)	<0.01 (<0.01–0.024)	0.004 (0.001–0.012)	0.77 (0.51–0.94)	0.003 (0.001–0.0064)	0.006 (<0.001–0.011)
	Perfluorooctanoic acid (PFOA)	<0.01 (<0.01–0.012)	0.006 (<0.001–0.011)	0.56 (0.29–0.95)	0.003 (<0.001–0.0044)	0.003 (<0.001–0.0081)
	Perfluorooctane sulfonic acid (PFOS)	<0.01 (<0.01–0.018)	0.003 (<0.001–0.011)	0.76 (0.27–0.85)	0.002 (<0.001–0.0044)	0.002 (<0.001–0.0041)
Biocides and pesticides	Triclosan (TCS)	0.32 0.12–0.51	0.024 (0.012–0.046)	0.92 (0.83–0.97)	0.016 (<0.01–0.062)	<0.01 (<0.01)
	Diethyltoluamide (DEET)	0.41 (0.16–1.56)	0.08 (0.026–0.27)	0.78 (0.30–0.97)	0.065 (0.018–0.49)	0.014 (<0.01–0.034)
	Permethrin (PMN)	0.14 (0.037–0.23)	<0.01 (<0.01)	0.96 (0.91–0.98)	0.029 (<0.01–0.047)	<0.01 (<0.01)
	Imidacloprid (IMI)	0.013 (<0.01–0.05)	0.017 (<0.01–0.043)	0 (-0.4–0.31)	<0.01 (<0.01)	<0.01 (<0.01)
	Carbendazim (CZIM)	<0.05 (<0.05–0.061)	0.017 (<0.01–0.055)	0.27 (0.05–0.76)	0.014 (<0.01–0.041)	0.024 (0.011–0.046)
	Diuron (DIU)	<0.01 (<0.01–0.03)	0.016 (<0.01–0.043)	0.07 (-0.61–0.33)	<0.01 (<0.01–0.037)	0.024 (<0.01–0.27)
	Isoproturon (ISO)	0.028 (<0.01–0.063)	0.019 (<0.01–0.066)	0.07 (-0.37–0.56)	<0.01 (<0.01–0.04)	<0.01 (<0.01–0.066)
	Terbutryn (TBY)	0.052 (0.012–0.11)	0.035 (<0.01–0.086)	0.26 (-0.05–0.58)	0.023 (<0.01–0.06)	0.027 (0.02–0.087)
Pharmaceuticals	Carbamazepine (CBZ)	Not analysed	Not analysed	Not analysed	0.049 (<0.01–0.18)	Not analysed
	Diclofenac (DCF)	Not analysed	Not analysed	Not analysed	0.22 (0.078–0.47)	Not analysed
Other organic substances	Di-(2-ethylhexyl)phthalate (DEHP)	14 (5.15–26.5)	1.7 (0.56–6.4)	0.91 (0.78–0.97)	1.9 (0.56–6.7)	3 (1.54–5.91)
	Hexabromocyclododecanes (HBCDD)	<0.01 (<0.01–0.018)	<0.005 (<0.005)	0.81 (0.75–0.91)	0.008 (<0.005–0.016)	<0.005 (<0.005–0.015)
	Acesulfame (ACE)	Not analysed	Not analysed	Not analysed	2.3 (1.2–4.8)	Not analysed

4.3.3 Relation of Concentrations between Sampling Points and to EQS

Figure 4.5 displays the concentrations of selected substances in WWTP influents, effluents, CSOs, and SSOs in relation. TCS is an example of a wastewater-associated substance. The highest TCS concentrations were analysed in WWTP influents while concentrations in stormwater (SSO) were <LOQ (0.01 µg/l). Similar results were obtained for DEET, 1,2-benzisothiazolin-3(2H)-on (BIT), permethrin (PMN), and imidacloprid (IMI). In contrast, the concentrations of benzo(ghi)perylene (BghiP) in SSO systematically exceeded WWTP influent concentrations. Likewise, median concentrations of most PAH, lead, 4-tert.-octylphenol (4iNP), and DIU were highest in SSOs. For other metals, as well as the biocides TBY and CZIM, SSOs and WWTP influents showed a similar concentration range. Significant input of these substances into UWS occurs with stormwater runoff. For PAH and 4iNP, street runoff (traffic) is known to be one important source (Björklund 2010; Wicke *et al.* 2021). DIU, TBY, and CZIM in stormwater runoff originate from leaching of building materials (Burkhardt *et al.* 2007; Burkhardt *et al.* 2012; Paijens *et al.* 2021).

CSO concentrations were typically found in a plausible range between wastewater (i.e. WWTP influent) and stormwater (SSO) concentrations. The ACE-based median mixing ratio across all samples was 16.4 (95% confidence interval: 8.6-25.0) corresponding to a stormwater content of 94%. This result complies well with the ratios of average WWTP influent and CSO concentrations of other wastewater-related substances like triclosan (TCS). However, for substances with significant input through stormwater, e.g. BghiP and TBY, these simple mixing assumptions do not produce consistent results. It can be concluded that mobilisation and transport processes are too complex and result in highly variable concentrations in both stormwater runoff and wastewater. This means that CSO concentrations cannot be reliably predicted for each individual compound by assuming a mixing of wastewater and stormwater.

WWTP effluent concentrations of PFOS, DEHP, benzo(a)pyrene (BaP), and TCS frequently exceeded AA-EQS. For these substances, the receiving water quality depends largely on the dilution capacity. SSO and CSO median concentrations of the PAH BghiP, BaP, indeno(1,2,3-cd)pyrene (IP), chrysene (Chr), and benzo(b)fluoranthene (BbF) exceeded WWTP effluent concentrations by factors of ≥100 and ≥50, respectively. This means that despite non-continuous activity, emissions from SSOs and CSOs contribute a significant share to total PAH emissions from urban areas (Nickel and Fuchs 2019). CSO and SSO concentrations of BghiP, BbF, and benzo(k)fluoranthene (BkF) can potentially be highly relevant to MAC-EQS (maximum acceptable concentration EQS) exceedance in receiving waters, considering that due to event composite sampling, maximum concentrations were not captured.

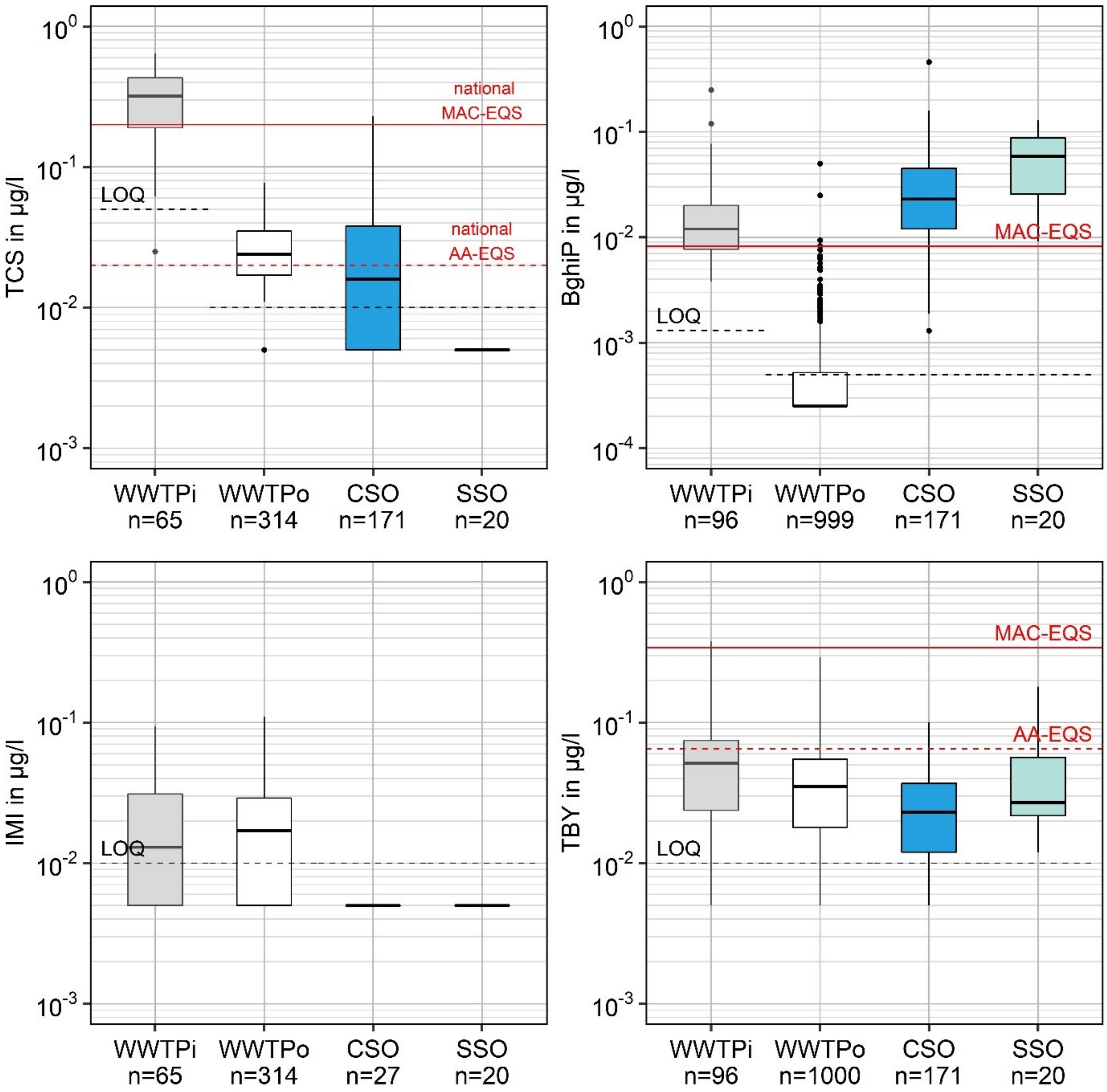

Figure 4.5: Total concentrations of triclosan (TCS), benzo(ghi)perylen (BghiP), imidacloprid (IMI), and terbutryn (TBY) in WWTP influent (WWTPi), WWTP effluent (WWTPo), combined sewer overflow (CSO), and stormwater outfall (SSO).

4.3.4 Removal Rates in WWTPs

The removal rates estimated in five selected WWTPs are shown in Figure 4.6. All removal rates are also summarised in the Appendix (Table A4.9). Overall, median removal rates (Table 4.1) were comparable to literature data and often in the upper range of reported values (Luo *et al.* 2014; Margot *et al.* 2015). Of the substances considered in this study, mainly those with a high sorption affinity showed good removal in WWTPs. The removal of metals was very high (median ≥90%) with the exceptions of zinc (86%) and nickel (47%). Likewise, all PAH were removed efficiently. Except for NAP, FL, and acenaphthylene (ACY), median PAH removal was ≥90% and varied within narrow ranges only (Figure 4.6). Removal increased with PAH molecule size and resulting hydrophobicity. Another example of predominantly particle-bound substances with very high removal was TCS (92%). The concentration drop from WWTP influent to effluent is clearly visible for both TCS and BghiP in Figure 4.5. On the contrary, substances whose elimination can be expected to depend mainly on biodegradation showed more variable, often poor and sometimes negative removal rates, e.g. several biocides including DIU (Figure 4.6). For most substances considered in this study, negative values can be regarded as outliers resulting from concentration variability or uncertainties in sampling and analysis. However, for some biocides (e.g. DIU) poor or negative removal has been observed before (e.g. Paijens *et al.* 2021) and could be due to transformation of metabolites or transformation products during wastewater treatment (Köck-Schulmeyer *et al.* 2013). Negative removal due to biotransformation of precursors has also been reported for PFAS (Murakami *et al.* 2009). However, these explanations could not be verified based on our results.

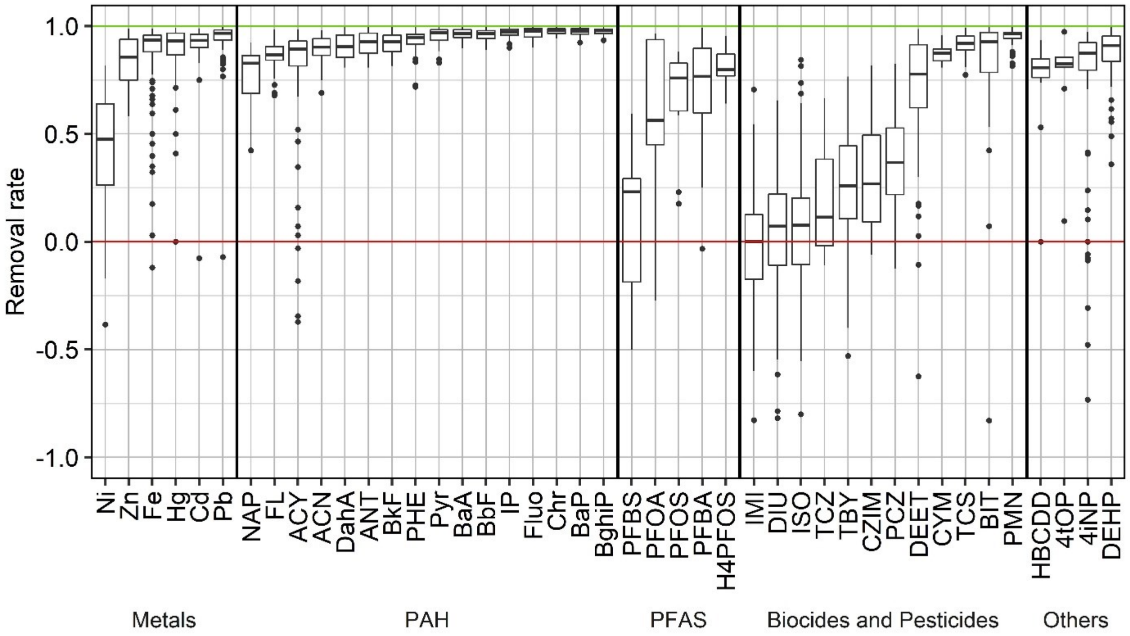

Figure 4.6: Removal rates of pollutants in five WWTPs. For better overview, outliers below -1 were excluded for nickel, PFBS, H4PFOS, IMI, BIT, DIU, and ISO (≤3 values each). A list of substances and abbreviations can be found in Table A4.3.

4.3.5 Variability between Sites and Samples

For most micropollutants, considerable concentration variability was observed both between sampling sites and between samples at each site. To compare the concentration variability resulting from differences between the sites to the variability between samples, the CV of site median concentrations and the arithmetic mean CV of concentrations of single samples at each site were considered (Table A4.14). Figure 4.7 shows the effluent concentrations of each WWTP of two example substances with different origins and environmental behaviour (particulate or dissolved transport). From the example of DEHP, it can be seen that site median concentrations fall within a comparably narrow range. Temporal variability at each site (mean CV: 1.1) exceeded the differences between site medians (CV: 0.61). This finding can be attributed to the ubiquitous occurrence of DEHP and high removal rates in WWTPs due to the sorption affinity of the substance. The biocide CZIM, known to leach off building facades exposed to rainfall (Burkhardt *et al.* 2007) and attributed to dissolved transport and poor removal in WWTP (Margot *et al.* 2015) showed more site-specific concentrations. Differences between the sampling sites (CV: 1.6) were more pronounced than temporal variability at each site (mean CV: 0.54). This means that characteristics of the catchment (e.g. type or age of building materials used, rainfall characteristics) or the WWTP (removal performance) might systematically cause increased or decreased concentrations. The removal of CZIM, which depends mainly on biodegradation (Margot *et al.* 2015), was found to be low (median: 27%) and highly variable (80% interquantile: 4.5-76%). However, considering the five WWTPs selected for detailed investigation, CZIM removal rates are not sufficient to explain site-to-site effluent concentration differences.

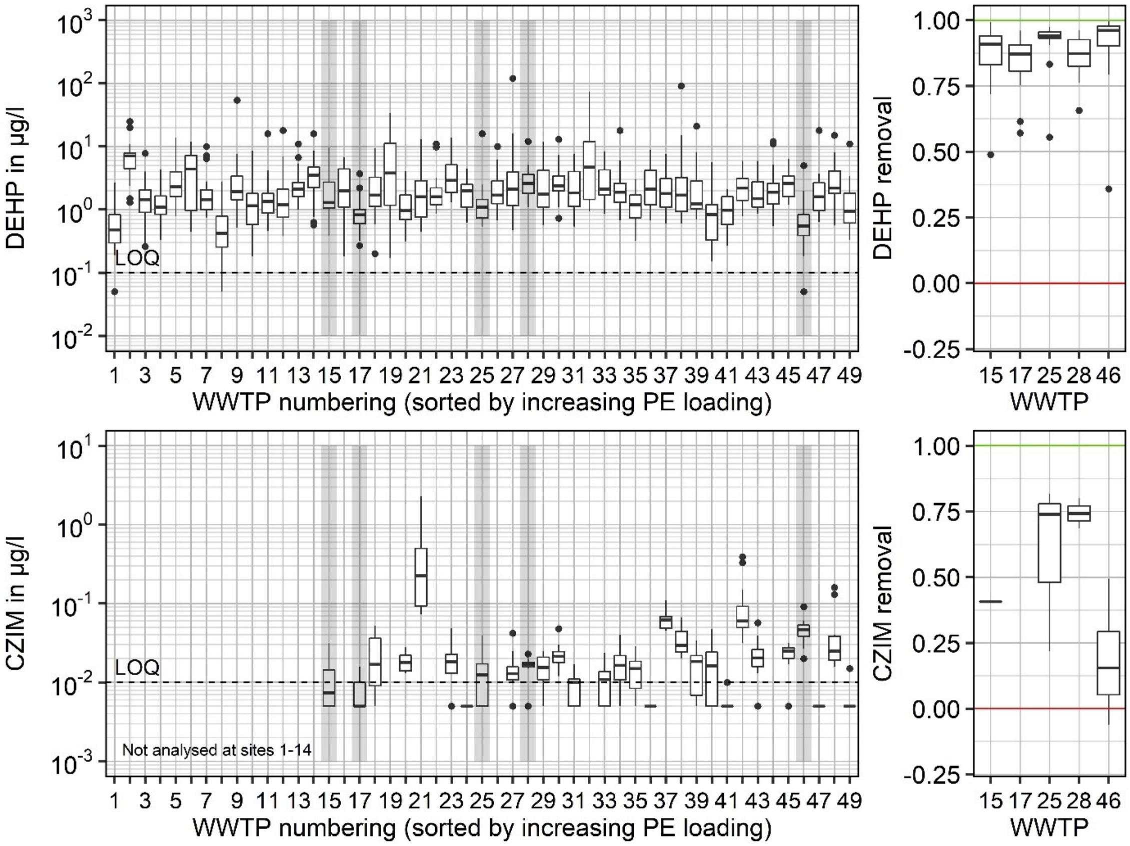

Figure 4.7: Total concentrations of di-(2-ethylhexyl)phthalate (DEHP) and carbendazim (CZIM) in WWTP effluents (left) and removal rates (right) in five WWTPs selected for detailed investigation (grey shading).

Few substances showed the differentiated behaviour of these examples. Substances with comparably low overall concentration variability in WWTP effluents included TCS and the ubiquitous metal nickel (both CV of site medians and mean CV of samples at each site ≤0.39). Very high variability was observed for most PFAS, some of which showed high variability between sites. In CSOs, all PAH showed lower variability between sites than between events. CZIM concentrations were again more influenced by site-specific differences. For other substances, neither variability between sites nor between events was dominant.

Given the size of the datasets, the impacts of documented catchment characteristics and hydraulic conditions on concentrations in WWTP effluents and CSOs were investigated by correlation analysis and visual inspection of scatterplots. This included testing for the impact of population density and flow on WWTP effluent concentrations, and population density, land use, event volume, and maximum flow on CSO concentrations. Overall, despite the large volume of data, none of the catchment characteristics could be identified as a main factor for WWTP effluent or CSO concentrations. Meaningful results were found for few individual substances only (Figure A4.2–Figure A4.3). The relationships found cannot be considered unambiguous or transferable. Similarly, the influence of hydraulic conditions was not systematic and could only be confirmed for part of the WWTPs or CSOs, respectively (Figure A4.4–Figure A4.5).

Seasonal trends were found for several PAHs in both WWTP effluents and CSOs (Figure A4.6–Figure A4.7). During the winter months, the frequency of values >LOQ was higher and/or concentrations were elevated. This was expected due to increased primary emissions caused by heating and increased deposition caused by reduced wind speeds and lower humidity (Manzetti 2013). For 4iNP, few PFAS (e.g. perfluoro-n-nonanoic acid (PFNA), perfluorodecanoic acid (PFDA), and perfluorooctanoic acid (PFOA)), and biocides (e.g. DIU, ISO), counter-directional seasonal trends with increased concentrations in summer and autumn months were found in WWTP effluents. For PFAS, this may be due to increased precipitation in summer, as significant loads of PFAS may originate from street runoff (Murakami *et al.* 2009; Müller *et al.* 2011). Elevated concentrations of PFAS in summer months or during the wet season have been reported for WWTP influents in Australia (PFNA, PFOA) (Nguyen *et al.* 2019) and sludge samples from WWTPs in China (total concentrations of perfluorinated compounds) (Na *et al.* 2020). However, higher concentrations of PFAS could not be related to higher WWTP inflow. Therefore, a conclusive assessment of these effects was not possible. In case of the biocides, the increased concentrations in summer could be due to higher temperature and precipitation which in turn may promote increased release and wash-off (Burkhardt *et al.* 2012). The seasonal trends could also reflect the main application periods of biocides and pesticides. In CSO, seasonal trends were found for the agricultural herbicides terbuthylazine and metolachlor, which were mainly detected in concentrations >LOQ from May to August. The trends underline the importance of long-term monitoring.

Overall, the variability of substance concentrations in UWS, the lack of adequate explanations for concentration differences, as well as seasonal trends of certain substances need to be taken into account for the collection and use of representative monitoring data. Generally, a large sample size from each sampling site is required to capture as much of the variability as possible. Therefore, for the objective of deriving representative concentrations, long-term monitoring of individual sites should be prioritised over the inclusion of additional sampling sites. However, for substances with high site-to-site differences, also sampling of multiple sites will be needed for a comprehensive assessment.

4.3.6 Volume-weighted Site Mean Concentrations

Volume-weighted SMCs are considered to be the most appropriate quantity for the calculation of long-term loads (Mourad *et al.* 2005; May and Sivakumar 2013). SMCs were calculated for WWTP effluents, CSOs, and SSOs, if volume data was available. This was possible for up to 49 WWTPs, 11 CSOs, and both SSOs. Median values of the resulting SMC distributions of selected substances are reported in Table 4.2. SMC ranges and information on the number of sites considered are reported for all substances in the Appendix (Table A4.15–Table A4.17).

For substances with a high frequency of values >LOQ, the median SMC can be considered a reliable summary value that integrates considerable spatial and temporal variability. It represents a cross-section of the hydrological and topographical conditions, the urban areas, and the technical states of UWS found in Germany. As such, it qualifies to be used as representative input data for estimation of average substance emissions in large areas such as river basins, if no specific data are available. A median SMC >LOQ could be evaluated for 39% of substances analysed in WWTP effluents, 52% of substances analysed in CSO, and

48% of substances analysed in SSO. Median SMCs were close to the overall medians of the single values (Table 4.1) or slightly higher in most cases.

Table 4.2: Medians of volume-weighted site mean concentrations of selected substances in WWTP effluents, CSOs, and SSOs.

Group	Parameter	WWTP effluent (µg/l)	CSO (µg/l)	SSO (µg/l)
Metals	Nickel (Ni)	4.27	3.09	4.71
	Lead (Pb)	0.16	4.01	6.69
	Mercury (Hg)	0.0022	0.014	0.015
	Cadmium (Cd)	0.0066	0.067	0.088
PAH	Naphthalene (NAP)	<0.01	0.023	<0.01
	Phenanthrene (PHE)	0.0043	0.057	0.055
	Benzo(a)pyrene (BaP)	<0.0005	0.025	0.059
	Benzo(ghi)perylene (BghiP)	<0.0005	0.024	0.074
Phenols	4-iso-nonylphenol (4iNP)	0.04	<0.04	0.087
	4-tert.-octylphenol (4tOP)	<0.02	<0.02	0.12
PFAS	Perfluorobutyric acid (PFBA)	0.0057	0.002	0.0053
	Perfluorooctanoic acid (PFOA)	0.0058	0.001	0.0031
	Perfluorooctane sulfonic acid (PFOS)	0.0039	<0.001	0.0019
Biocides and pesticides	Triclosan (TCS)	0.027	0.024	<0.01
	Diethyltoluamide (DEET)	0.098	0.058	0.015
	Permethrin (PMN)	<0.01	0.015	<0.01
	Imidacloprid (IMI)	0.018	<0.01	<0.01
	Carbendazim (CZIM)	0.016	0.014	0.029
	Diuron (DIU)	0.02	<0.01	0.1
	Isoproturon (ISO)	0.02	0.011	0.024
	Terbutryn (TBY)	0.032	0.028	0.039
Pharmaceuticals	Carbamazepine (CBZ)	Not analysed	0.067	Not analysed
	Diclofenac (DCF)	Not analysed	0.25	Not analysed
Other organic substances	Di-(2-ethylhexyl)phthalate (DEHP)	2.6	2.51	3.43
	Hexabromocyclododecanes (HBCDD)	<0.005	<0.005	0.0059
	Acesulfame (ACE)	Not analysed	2.53	Not analysed

4.3.7 Per Capita Loads

Based on the SMCs, annual per capita loads from WWTPs and CSOs were evaluated. These are considered a suitable basis for a comparison of the relative contribution of these pathways to total load from UWS to receiving waters. The per capita loads varied considerably between sites. In addition to site-to-site concentration differences, this might be due to uncertainties of the volume and population data used for the calculations (Table A4.18). The highest median per capita loads of priority substances from WWTPs were found for nickel (324 mg/capita/year), DEHP (176 mg/capita/year), and lead (9.8 mg/capita/year). For metals, DIU (1.23 mg/capita/year), and ISO (1.32 mg/capita/year), median per capita loads were in the same order of magnitude but 8-55% lower than emission factors used for E-PRTR (European Pollutant Release and Transfer Register) reporting in the Netherlands which are based on the sampling of six representative WWTPs (Baltussen 2019). Mercury loads from WWTPs (0.17 mg/capita/year) were lower than reported for Switzerland (0.57 mg/capita/year) (Suess *et al.* 2020) and Austria (0.84-0.95 mg/capita/year) (Clara *et al.* 2014), but loads of nickel and cadmium were within ±25% of the Austrian results. Biocide loads matched well with values reported for the Paris conurbation for DIU and TBY, but were one order of magnitude higher for ISO (Paijens *et al.* 2021). The differences may be due to methodological differences in both the data collection and the calculation of the loads, but are also influenced by national differences in substance occurrence and use patterns, sewer systems, and wastewater treatment. Overall, the good comparability with average per capita loads from WWTPs in other European countries shows that a reliable new database has been established for Germany.

To assess the relative importance of CSOs, the loads were normalised to the median load from WWTPs (Figure 4.8). The most pronounced differences were found for biocides and PAH. Biocide loads from WWTPs exceeded CSO loads by one order of magnitude. Paijens *et al.* (2021) also found that WWTPs were the main pathway for biocides compared to CSOs. However, CSO loads of lead, cadmium, mercury, and PAH were in the same range or higher than WWTP loads. CSO loads of high-molecular-weight PAH exceeded WWTP loads by up to one order of magnitude. PAH are efficiently removed in WWTPs and effluent concentrations were often <LOQ. Therefore, a significantly higher load from CSOs than from WWTPs can also be assumed for PAH not shown in Figure 4.8 due to values <LOQ, e.g. BghiP (Table A4.18). The importance of CSOs for the emission of metals and PAH has been reported previously (Clara *et al.* 2014; Launay *et al.* 2016b; Becouze-Lareure *et al.* 2019) and can be confirmed based on our results.

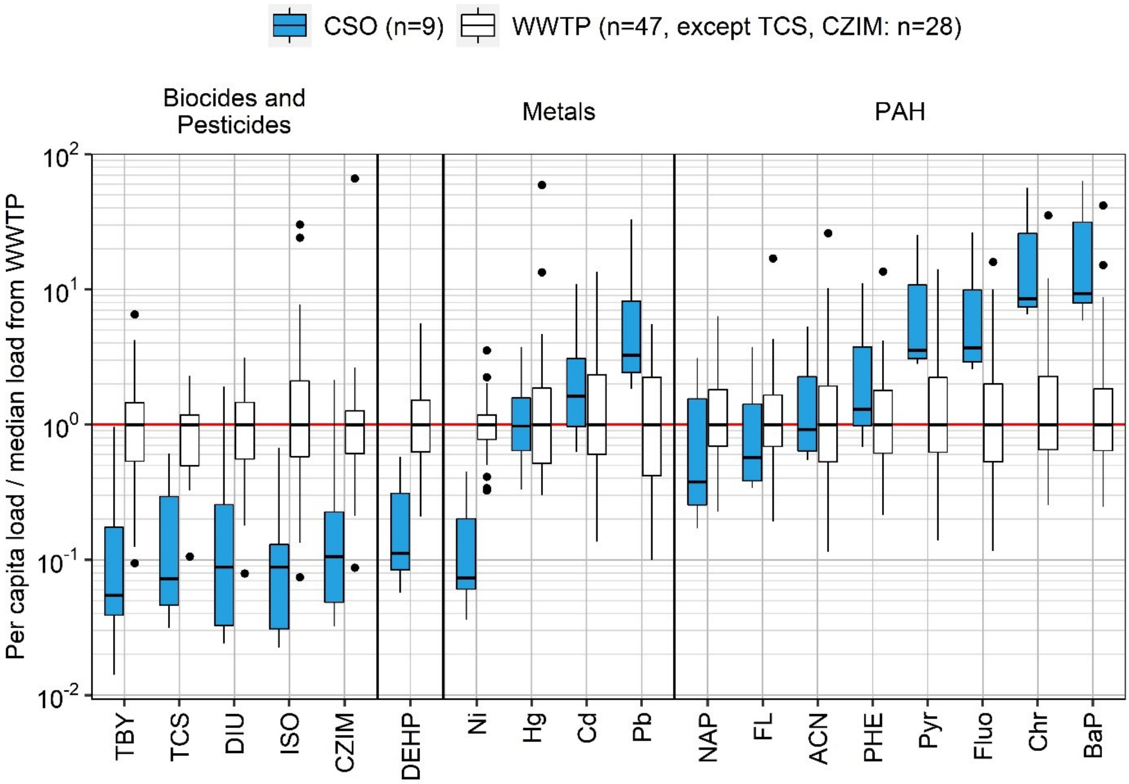

Figure 4.8: Annual per capita loads of selected substances from WWTPs and CSOs, normalised to the median load from WWTPs. Only substances with ≥25% of SMCs >LOQ are shown. A list of substances and abbreviations can be found in Table A4.3.

4.4 Conclusions

A comprehensive dataset of pollutant concentrations in German UWS is available from recently completed monitoring projects. For WWTP effluents and CSOs, it represents one of the largest datasets regarding the number of sites sampled with harmonised methodology and the total number of samples. Due to sensitive analytical methods, many substances could be analysed in concentrations >LOQ in a high percentage of samples. The data provide a consistent and reliable information base on pollutant occurrence and concentrations, which was previously not available for many substances. The reported median values of distributions of volume-weighted SMCs integrate considerable spatial and temporal variability and can be used as representative input data for estimation of average substance emissions, if no site-specific data are available. Thus, the data will contribute to the development of strategies to reduce emissions, taking into account not only WWTPs but also stormwater-related discharges.

The results confirm the ubiquity of several priority pollutants in both wastewater and stormwater. From an overall perspective, the relation of concentrations between WWTPs, CSOs, and SSOs can be explained primarily by the main areas of application and origin and the environmental behaviour (i.e. removal in WWTP due to adsorption or biodegradation) of individual substances. This means that monitoring in UWS could focus on indicator substances representing different expressions of these characteristics or new pollutants that cannot be characterised yet. Removal rates of particle-bound pollutants in conventional WWTPs were high, but additional measures are needed in order to improve the removal of other substances, e.g. biocides and PFAS, or to reduce effluent concentrations of DEHP, PFOS, and TCS which might cause EQS exceedances depending on dilution in receiving waters. CSO were confirmed as an important pathway of metals and PAH to receiving waters when compared to WWTPs on the basis of annual per capita loads.

Despite the applied composite sampling approaches that provided integration of short-term dynamics, high concentration variability at each sampling point was observed. The impact of catchment characteristics, hydraulic conditions, and seasonal trends on concentrations was investigated, but showed meaningful results for few substances only. The number of relevant influencing factors is huge. It is therefore highly questionable whether it will be possible to map their complex combined impacts on concentrations in UWS comprehensively. This underlines the need of comprehensive monitoring data for a representative assessment of long-term average conditions, which is required for quantifying substance emissions. Generally, long-term monitoring and a large sample size from each sampling site are required to capture as much of the variability as possible. For the objective of deriving representative concentrations, long-term monitoring of individual sites should therefore be prioritised over the inclusion of additional sampling sites. To account for the uncertainties associated with the variability of measured data, probabilistic modelling can be used and provide a sound basis for informed management planning.

4.5 Research Data

The full dataset of substance concentrations and accompanying data is available under https://doi.org/10.35097/449 (Nickel *et al.* 2021a).

4.6 Funding

The monitoring was financed by the federal states of Germany and was technically and administratively supported by the Federal Environment Agency (Umweltbundesamt – UBA). The additional monitoring of 10 combined sewer overflows in Bavaria was financed by the Bavarian State Ministry of the Environment and Consumer Protection (Bayerisches Staatsministerium für Umwelt und Verbraucherschutz).

4.7 Acknowledgements

We would like to thank the operators of the investigated wastewater treatment plants and sewer systems for their valuable support. Many thanks to the Federal Environment Agency (Umweltbundesamt – UBA), the Bavarian Environment Agency (Bayerisches Landesamt für Umwelt – LfU), and our partner Bioplan Landeskulturgesellschaft for their excellent cooperation. The authors would also like to thank Astrid Thoma, Snezhina Toshovski, and Maria Kaiser for coordinating the monitoring, and the technical staff of TZW for their excellent laboratory work. Thanks to Heidemarie Knierim for proofreading the manuscript.

5 Urban Water Balance Approach for the Assessment of Emissions from Wastewater Systems

5.1 Introduction

Wet weather discharges from urban wastewater systems (UWS) are increasingly in the focus of water pollution management. As wastewater treatment is continuously improved, stormwater outfalls and combined sewer overflows (CSOs) could become major pressures on receiving water body quality. To manage surface water pollution from UWS effectively, a holistic assessment of the emissions from both wastewater and stormwater treatment is needed[13].

In contrast to the standard monitoring of wastewater treatment plants (WWTPs), there is a lack of data on the occurrence, flow volumes and quality of wet weather discharges from sewer systems. Modelling approaches are needed to estimate emissions from CSOs. Detailed process-based urban-hydrological models are not applicable for area-wide estimation of CSO emissions in river basins due to missing input and calibration data or computational restrictions. However, water balance methods with a moderate data-demand and reduced spatial and temporal resolution can provide reasonable near-realistic estimates of the flow volumes in UWS. These can be combined with representative quality data to provide a preliminary emission assessment as a basis for identifying priority areas for detailed investigation.

For this purpose, the urban water balance (UWB) approach developed by Fuchs and Hahn (1999), Nafo and Geiger (2004) and LUBW (2019a) is considered to be a suitable basis. The UWB provides a robust estimate of annual CSO volume using monitoring data existing by standard in many catchments today. However, the approach needs to be adapted to account for the proportion of wastewater discharged via CSOs past wastewater treatment.

Assessments of pollutant emissions must take into account the sources of substances (stormwater or wastewater) and their environmental behaviour in UWS. Against this background, the proportion of wastewater discharged via CSOs was recently proposed as an emission target value for regulating the discharge of wastewater-borne substances from combined sewer systems (DWA 2021; Schmitt 2021). Likewise, the proportion of stormwater runoff in CSOs can be considered a proxy for emissions of stormwater-related substances (Schmitt 2021).

Thus, in the following sections, the UWB is developed further, tested on a catchment for verification, and combined with new water quality data to estimate substance emissions.

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[13] Sentence adopted from: Nickel, J. P., Sacher, F. and Fuchs, S. 2021 Up-to-date monitoring data of wastewater and stormwater quality in Germany. Water Research, 202, 117452. https://doi.org/10.1016/j.watres.2021.117452.

5.2 Materials and Methods

5.2.1 Urban Water Balance Approach

The UWB approach described in the following is based on the previous works of Nafo and Geiger (2004), LUBW (2019a), and Fuchs *et al.* (2020a; 2021). The spatial resolution of the UWB is defined by WWTP catchments, which result from the sum of all areas connected to an individual WWTP. Each WWTP catchment is considered as a simplified system with one central CSO facility (Figure 5.1). The temporal resolution of the balance results is annual. The required input data includes WWTP inflow volumes (daily values), precipitation data (hourly values), and the impervious area in the catchment.

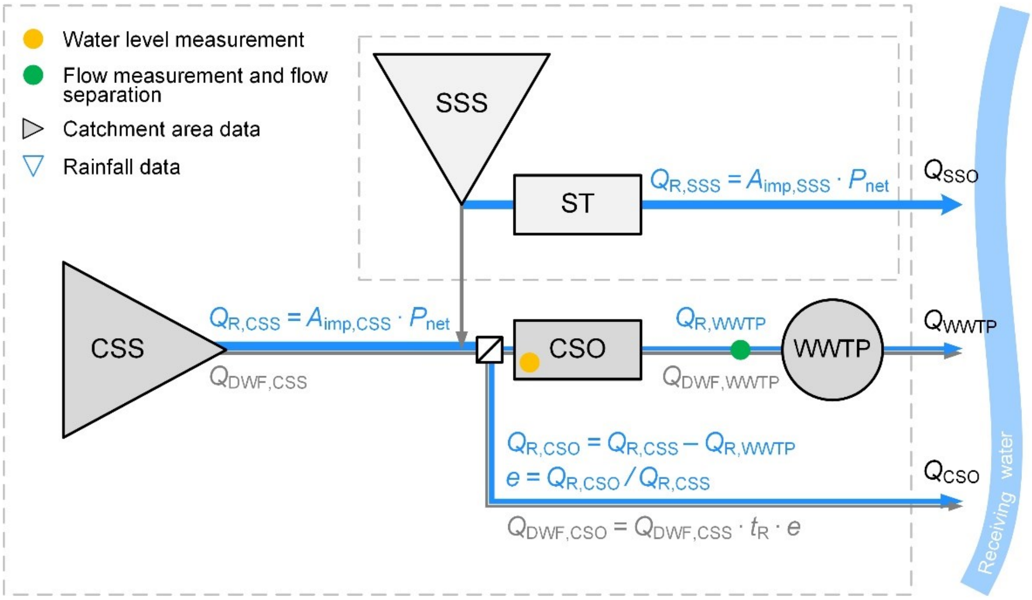

Figure 5.1: Scheme of the urban water balance approach (modified from Fuchs *et al.* 2021): CSS – combined sewer system, SSS – separate sewer system, ST – stormwater treatment, CSO – combined sewer overflow, WWTP – wastewater treatment plant. Symbols are explained in Table 5.1.

The general idea of the UWB is to balance the inflows and outflows of the combined sewer system in a WWTP catchment with a four-step approach:

1. Dry and wet weather flow separation of daily WWTP inflow data,
2. Stormwater runoff calculation based on precipitation data and impervious area,
3. Stormwater balance,
4. Estimation of dry weather flow (DWF)[14] content in CSOs.

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[14] The term dry weather flow (DWF) is used to describe the sum of the flow components wastewater (including domestic, commercial, and industrial wastewater) and infiltration water in the sewer system.

Table 5.1: Symbols used in the formulas.

Symbol	Explanation (Unit)
$A_{\mathrm{imp,CSS}}$	Connected impervious area in the combined sewer system (ha)
$A_{\mathrm{imp,SSS}}$	Connected impervious area in the separate sewer system (ha)
e	Overflow rate (-)
P	Precipitation (mm/year)
P_{net}	Net precipitation (mm/year)
Q_{CSO}	Total combined sewer overflow volume (m^3/year)
$Q_{\mathrm{DWF,CSO}}$	Dry weather flow content in combined sewer overflows (m^3/year)
$Q_{\mathrm{DWF,CSS}}$	Dry weather flow in the combined sewer system (m^3/year)
$Q_{\mathrm{R,CSO}}$	Stormwater runoff in combined sewer overflows (m^3/year)
$Q_{\mathrm{R,CSS}}$	Stormwater runoff in the combined sewer system (m^3/year)
$Q_{\mathrm{R,SSS}}$	Stormwater runoff in the separate sewer system (m^3/year)
$Q_{\mathrm{R,WWTP}}$	Stormwater runoff treated in the wastewater treatment plant (m^3/year)
Q_{SSO}	Total separate sewer outfall volume (m^3/year)
Q_{WWTP}	Total wastewater treatment plant effluent volume (m^3/year)
t_{R}	Effective rainfall duration, i.e. annual duration of rainfall exceeding the conveyance capacity of the sewer system (h/year)
Ψ_{m}	Mean annual runoff coefficient (-)

First, dry weather flow (DWF) is estimated by flow separation of daily WWTP inflow data. For the study catchment, local precipitation data allowed to identify dry weather days by excluding all days with rainfall or rainfall on the previous day. The mean DWF of all dry weather days was then assumed for all days with rainfall or rainfall on the previous day. If local precipitation data is not available, daily WWTP inflow data can be analysed using the moving minimum method which was developed to quantify infiltration water (Weiß *et al.* 2002; Fuchs *et al.* 2003). In practice, the moving minimum is calculated for a period of 21 days. However, it is known that shorter periods result in increased DWF estimates (Fuchs *et al.* 2003). Thus, the length of the moving minimum period is considered as an adjustable variable in this study using the precipitation-based flow separation as a benchmark. The daily flows are summarised to annual flow volumes of dry weather flow ($Q_{\mathrm{DWF,CSS}}$) and stormwater runoff treated in the WWTP ($Q_{\mathrm{R,WWTP}}$).

Secondly, the stormwater runoff in the combined sewer system ($Q_{\mathrm{R,CSS}}$) is estimated based on the connected impervious area ($A_{\mathrm{imp,CSS}}$) and net precipitation (P_{net}) (Equation 5.1). Net precipitation is calculated from total precipitation (P) data using a mean annual runoff coefficient (Ψ_{m}) (Equation 5.2). The mean runoff coefficient is meant to include all losses and describe the direct runoff entering the UWS. It is considered as a second adjustable variable and may be expected in a range of 0.45–0.75 when considering the WWTP catchment as a whole.

$$Q_{\mathrm{R,CSS}} = A_{\mathrm{imp,CSS}} \cdot P_{\mathrm{net}} \tag{5.1}$$

$$P_{\mathrm{net}} = P \cdot \Psi_{\mathrm{m}} \tag{5.2}$$

In the third step, a balance of the stormwater in- and outflows of the combined sewer system is used to calculate the stormwater runoff discharged by CSOs ($Q_{\mathrm{R,CSO}}$) (Equation 5.3). The ratio of stormwater discharged by CSOs ($Q_{\mathrm{R,CSO}}$) and stormwater treated at the WWTP ($Q_{\mathrm{R,WWTP}}$) is called the overflow rate (e) (Equation 5.4).

$$Q_{\mathrm{R,CSO}} = Q_{\mathrm{R,CSS}} - Q_{\mathrm{R,WWTP}} \tag{5.3}$$

$$e = Q_{\mathrm{R,CSO}} / Q_{\mathrm{R,CSS}} \quad (5.4)$$

Lastly, to estimate the DWF content in CSOs ($Q_{\mathrm{DWF,CSO}}$), the effective rainfall duration (t_{R}) is used, i.e. the annual duration of periods with rainfall leading to runoff entering the sewer system. During these periods, a complete mixing of dry weather flow and stormwater runoff is assumed. Consequently, the overflow rate (e) can be applied to the DWF volume present in the system during these periods. This volume is calculated based on the mean DWF ($Q_{\mathrm{DWF,CSS}}$) and the effective rainfall duration (t_{R}) (Equation 5.5). The effective rainfall duration can be estimated from precipitation time series by applying a threshold value. If no local precipitation data is available, raster data (Winterrath *et al.* 2018) could be used to derive typical values for the investigated area. The sum of stormwater runoff in CSOs ($Q_{\mathrm{R,CSO}}$) and dry weather flow content in CSOs ($Q_{\mathrm{DWF,CSO}}$) results in the total combined sewer overflow volume (Q_{CSO}) (Equation 5.6).

$$Q_{\mathrm{DWF,CSO}} = Q_{\mathrm{DWF,CSS}} \cdot t_{\mathrm{R}} \cdot e \quad (5.5)$$

$$Q_{\mathrm{CSO}} = Q_{\mathrm{R,CSO}} + Q_{\mathrm{DWF,CSO}} \quad (5.6)$$

The discharge from separate sewer outfalls (Q_{SSO}) is calculated using Equation 5.1 and the connected impervious area in the separate sewer system ($A_{\mathrm{imp,SSS}}$). No storage volume is considered for the separate sewer system.

5.2.2 Catchment Description

The test catchment is located in the metropolitan region of Stuttgart in Northern Baden-Württemberg. It has a total of 355 ha of impervious area connected to the WWTP, 322 ha (91%) of which are drained by a combined sewer system and 33 ha (9%) by a separate sewer system. The combined sewer system comprises 14 CSOs with storage tanks (total storage volume 4,818 m^3) and 3 direct CSOs without storage volume.

Daily WWTP flow volume measurements and hourly precipitation data were available as well as a complete one-year-record of quality-checked water level measurements at 14 of 17 CSOs which were used for the hydraulic determination of the flow volumes passing the CSO weirs (Fuchs *et al.* 2021). Thus, the measurement data available represented 93% of the total impervious area connected to the combined sewer system (Table 5.2). For a complete balance, the remaining data gaps were filled by assuming a specific CSO volume of 164 mm/year, based on the area-weighted average specific CSO volume calculated from the CSOs with measurements.

Table 5.2: Measured CSO data from 2017. Values in brackets were estimated assuming an average specific CSO volume of 164 mm/year.

CSO-ID	Impervious area (ha)	CSO Volume (m³)	CSO Duration (h)	Max. Flow (l/s)
S1	4.02	661	3.1	194
S2	40.39	78,415	86.2	3,227
S3	6.71	5,691	10.3	451
S4	4.84	5,022	20.5	307
S5	9.5	37,591	59.3	3,424
S6	4.03	3,174	9.6	1,661
S7	33.93	55,932	79.7	4,474
S8	40.71	45,312	68.6	4,361
S9	50.87	107,147	85.9	3,459
S10	11.08	(18,176)[a]	- [a]	- [a]
S11	56.04	98,613	85.6	7,204
S12	9.11	1,822	4.8	658
S13	21.4	46,380	100.3	1,243
S14	16,3	2,833	9.7	624
D1	5.92	(9,711)[b]	- [a]	- [a]
D2	4.68	(7,677)[a]	- [a]	- [a]
D3	2.46	(4,035)[a]	- [a]	- [a]
Sum, only measurements	**297.85**	**488,593**		
Sum, including estimates	**321.99**	**528,192**		

[a] Not measured.

[b] Incomplete record. 5,041 m³ measured starting from July.

5.2.3 Sensitivity Analysis of the Volume Balance

The sensitivity of the UWB approach to three main input variables was investigated, i.e. the length of the moving minimum period, the mean runoff coefficient, and the threshold value used to derive the effective rainfall duration. To this end, a global sensitivity analysis was conducted using the sensobol R package (Puy *et al.* 2022). The relative contributions of the three input variables to the variability of the CSO volume were analysed using a sampling matrix consisting of uniform distributions of the variables within the following limits:

- Length of the moving minimum period: 3–21 days
- Mean runoff coefficient: 0.45–0.75
- Threshold value used to derive the effective rainfall duration: 0.5–2 l/(s·ha)

Other catchment data were assumed to be correct and fixed, i.e. impervious area data, precipitation and WWTP inflow data series.

5.2.4 Quality Data and Emission Estimates

To estimate substance emissions, the hydrological results of the UWB were combined with the new quality monitoring dataset (Nickel *et al.* 2021a). As no local quality data was available from the study catchment, the distribution of volume-weighted site mean concentrations (SMCs) of other sites was used as representative data for WWTPs, CSOs, and stormwater outfalls (SSOs). The SMCs were assumed to be entirely representative of the concentration variability at the individual sites, and the distribution of the SMCs was assumed to be representative of other non-monitored sites. Due to the overall CSO quality data scarcity, this can be considered the best available estimate for non-monitored CSOs in Germany.

For the presentation of the results, substances were selected that had high data availability (number of sites, number of samples), a high quality of quantification (≥50% of samples >LOQ in WWTP effluents, CSOs, and SSOs), and represented contrasted groups of substances with different sources and environmental behaviour in UWS. The source of a substance (i.e. initial release to either wastewater or stormwater) and its environmental behaviour (i.e. susceptibility to removal processes, especially in WWTPs) are main factors defining the transport and fate of micropollutants in UWS and their emission pathways to receiving waters. Accordingly, the magnitude of the relative contribution of emission pathways from UWS could be transferred to other substances with comparable sources and physico-chemical properties (Table 5.3).

Table 5.3: Physico-chemical and fate properties of selected substances.

Substance	CAS-No.	Log P_{OW} *	Water solubility (mg/l) *	Henry constant (Pa·m³/mol) *	Half-life in water (days) *
Fluoranthene	206-44-0	5.2	0.26	0.90	13–42 [a]
Triclosan	3380-34-5	4.8	10	$5.1 \cdot 10^{-4}$	60 [b]
Terbutryn	886-50-0	3.7	25	$1.2 \cdot 10^{-3}$	60 [c]

* Source: ChemIDplus (2020) except [a] ECHA (2018), [b] Halden and Paull (2005), [c] Hachoumi *et al.* (2021)

Fluoranthene (Fluo) is a substance of the group of polycyclic aromatic hydrocarbons (PAH) and listed as a priority substance (European Commission 2013). PAH are ubiquitous, persistent, atmospheric pollutants which bind to particles and deposit onto surfaces (UBA 2016). They are mainly produced during incomplete combustion of organic matter (Manzetti 2013), fossil fuels and can be part of oils added to rubbers and plastics (UBA 2016). It can be assumed that both stormwater and wastewater are input pathways of Fluo into urban drainage systems, but stormwater runoff from streets is the predominant one. Removal rates of Fluo in WWTPs are high and can be attributed to adsorption (Margot 2015).

Triclosan (TCS) is an antimicrobial biocide mainly used as a preservative in personal care products or for disinfection in health facilities (SCCS 2010). Therefore, the main input of TCS into urban drainage systems can be attributed to wastewater. In fact, TCS monitoring data did only meet the criterion of ≥50% of samples >LOQ in WWTP effluents and CSOs. In SSOs, all values were <LOQ. Therefore, TCS emissions from SSOs were neglected for this study. The fate of TCS in WWTPs is characterized by a high removal rates (Luo *et al.* 2014). The main removal mechanism is adsorption and solids removal but partial biodegradation can be expected (Margot 2015). TCS is not listed as a priority substance but has been recommended for prioritisation due to its widespread use and the risks associated with its emission (Ohe *et al.* 2012).

Terbutryn (TBY) is a biocide known to leach of construction materials, e.g. facades, with stormwater (Burkhardt *et al.* 2007; Paijens *et al.* 2021). However, also releases from indoor applications to wastewater have been reported (Wieck *et al.* 2016, 2018). It is listed as a priority substance (European Commission 2013). Due to its good solubility in water, low volatility and moderate adsorption to particles, removal rates in WWTPs are low to moderate (Margot 2015; Fuchs *et al.* 2020c).

In addition to these organic pollutants, the heavy metal **mercury** (Hg) was selected due to its high relevance as an ubiquitous pollutant accounting for the poor chemical status of many European surface waters (Kristensen *et al.* 2018). As the physico-chemical and fate properties of mercury depend on its chemical form, it is not included in Table 5.3. Mercury is mainly emitted into air from the burning of fossil fuels, distributed over wide distances and transformed to various chemical forms (Marnane 2018; Ruhwedel 2021). An important source of mercury to UWS is surface runoff from streets. As mercury is mainly transported in the particulate phase, removal rates in WWTPs are high (Margot 2015; Fuchs *et al.* 2020c).

To account for the variability of the SMCs, a stochastic approach was used. Lognormal distributions were fitted to the SMCs of the selected substances using the R package fitdistrplus (Delignette-Muller and Dutang 2015; R Core Team 2021). For each substance, 29–49 SMC values (based on 313–989 event mean concentrations) were available for WWTPs (Table A4.15), and 11 SMC values (based on 143 event mean concentrations) for CSOs (Table A4.16). The Kolmogorov-Smirnov test was used to assess the goodness-of-fit (Kolmogorov 1933; R Core Team 2021). For SSOs, a uniform distribution was used as only two SMC values (based on 18 event mean concentrations) were available (Table A4.17). Concentrations were sampled from the fitted lognormal (WWTPs and CSOs) or uniform distributions (SSO) and multiplied by the UWB flow volumes after verification by the measurements in the study catchment to calculate substance emissions. To account for the measurement uncertainty of WWTP flow volume, a volume error randomly sampled from a normal distribution with a mean of 0 and a standard deviation of 5% was applied. For CSOs and SSOs, a higher standard deviation of 20% was used since higher measurement uncertainty can be expected for the flow volumes in sewer systems derived from water level measurements (Bertrand-Krajewski and Bardin 2002; Nickel and Fuchs 2020). A total of 10^6 repetitions were carried out to determine the distribution of the substance emissions.

5.3 Results

5.3.1 Water Balance

5.3.1.1 Wet and Dry Weather Flow Separation

The precipitation-based separation of dry weather flow from total WWTP inflow data resulted in higher dry weather flow estimates than the 21-day moving minimum method. This is because the 21-day moving minimum indicates considerable stormwater runoff even during longer periods without rainfall (Figure 5.2). Shorter moving minimum periods result in increased dry weather flow estimates. Using the precipitation-based separation as a benchmark, an optimum was found for a 4-day moving minimum (Figure 5.3). However, the transferability of this variable to other catchments has to be further analysed.

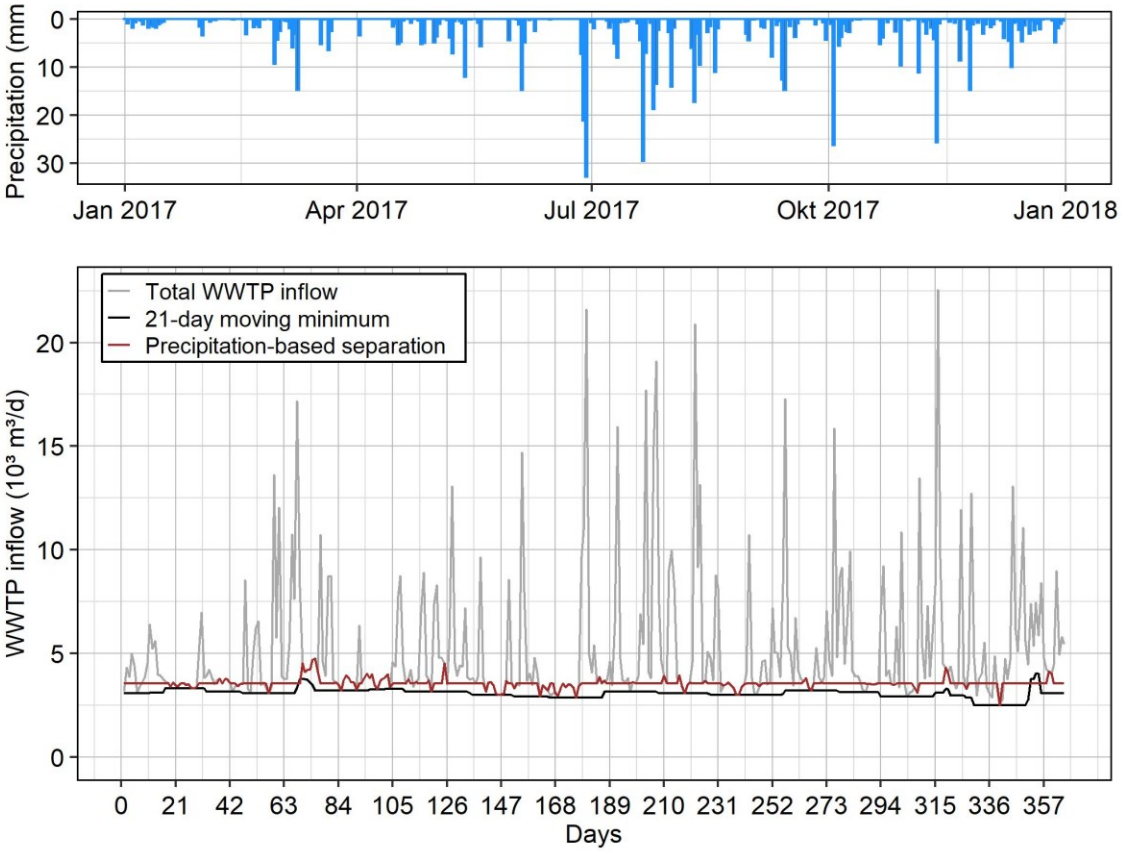

Figure 5.2: Precipitation-based separation of dry weather flow in WWTP inflow vs. using the 21-day moving minimum method.

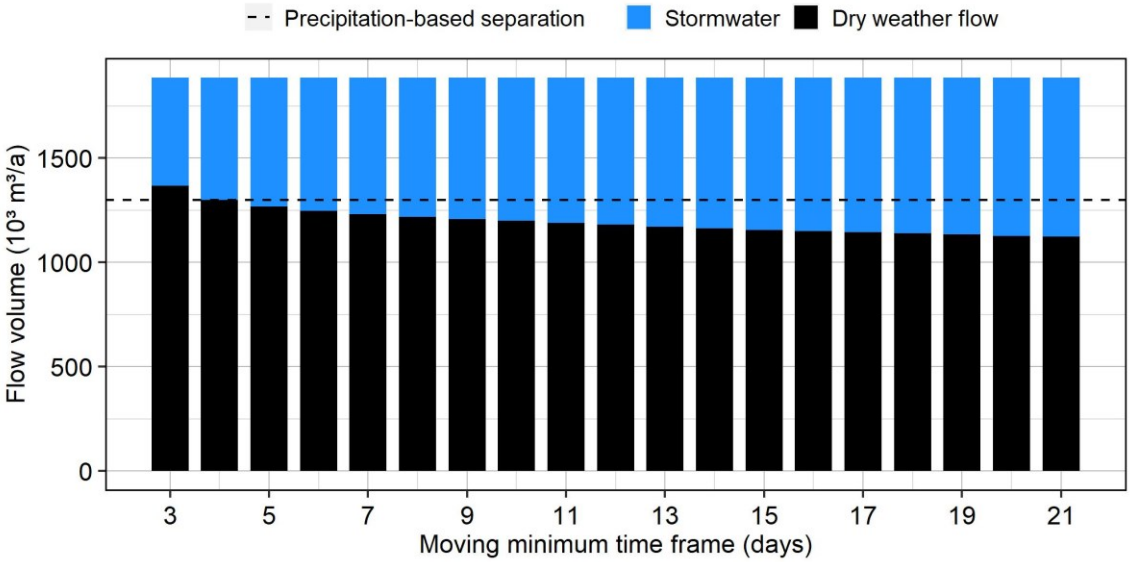

Figure 5.3: Wet and dry weather flow separation using different moving minimum time frames compared to precipitation-based separation of daily WWTP inflow values.

5.3.1.2 Mean Runoff Coefficient

As a process-based determination is not possible due to the large number of influencing factors and the lack of data, annual stormwater runoff is calculated based on the impervious area and total annual precipitation by applying a mean runoff coefficient. This mean runoff coefficient is meant to include all losses and describe the direct runoff entering the UWS. Table 5.4 shows the UWB results for mean runoff coefficients (Ψ_m) varied between 0.45 and 0.7. Using the measured CSO volume as a target value (Table 5.2), a Ψ_m of 0.5 was the closest match. This finding may be due to high surface losses but could also indicate an overestimation of impervious area in the catchment. The resulting overflow rate *e* of 0.46 is within a reasonable range used by German design guidelines (ATV-A 128E 1992). In addition, the calculated mixing ratio of stormwater to wastewater (*m*) in CSO is comparable to the average value of 16.4 estimated from quality monitoring data (chapter 4.3.3). The transferability of the mean runoff coefficient to other catchments may depend on the topography, land use, and on the quality of impervious area and rainfall data used as input. It can be considered a calibration variable that has to be tested with data from other study catchments.

Table 5.4: Urban water balance results for different runoff coefficients. *m* = mixing ratio, *%DWF* = proportion of annual dry weather flow discharged via CSOs. Other symbols are explained in Table 5.1.

Ψ_m	P_{net}	$Q_{R,CSS}$	$Q_{R,CSO}$	*e*	$Q_{DWF,CSO}$	Q_{CSO}	*m*	*%DWF*
0.45	302	971,640	386,236	0.40	24,179	410,415	16.0	1.9%
0.50	335	1,079,600	494,196	0.46	27,844	522,040	17.7	2.1%
0.55	369	1,187,560	602,156	0.51	30,842	632,999	19.5	2.4%
0.60	402	1,295,520	710,116	0.55	33,341	743,457	21.3	2.6%
0.65	436	1,403,480	818,076	0.58	35,455	853,532	23.1	2.7%
0.70	469	1,511,440	926,037	0.61	37,267	963,304	24.8	2.9%

5.3.1.3 Effective Rainfall Duration

The effective rainfall duration (t_R) was estimated by counting hours with rainfall exceeding a threshold value of 1 l/(s·ha) using local precipitation data (Figure 5.2). The threshold value was equal to the conveyance capacity of the sewer system, i.e. the maximum inflow to the WWTP, and referred to the impervious area in the combined sewer system. German WWTPs are usually designed to treat 1–2 l/(s·ha) of rainfall runoff (Dittmer 2017). This simple approach neglected surface storage losses but resulted in an effective rainfall duration of 410 hours which was close to the area-weighted average duration of impoundment of the CSO storage facilities equipped with measurement of 469 hours (durations of individual CSO facilities ranged from 27 to 857 hours). This shows that the effective rainfall duration, representing a simple estimate from precipitation time series, is suitable to describe the annual duration of periods with rainfall leading to runoff entering the sewer system. Using the effective rainfall duration and the overflow rate, the dry weather flow content in CSOs ($Q_{DWF,CSO}$) was estimated (Table 5.4). The proportion of total annual dry weather flow discharged by CSOs resulted in a close range of 1.9–2.9% depending on the runoff coefficient used (Table 5.4).

5.3.2 Sensitivity Analysis of the Volume Balance

Due to the simplicity of the UWB approach, it was already evident from the results in Table 5.4 that the mean runoff coefficient had a large impact on the CSO volume and could be expected to be the most sensitive parameter. This was confirmed by the sensitivity analysis (Table 5.5, additional information in Figure A5.1). Considering a wide range of 0.45–0.75, the mean runoff coefficient accounted for 89% of the uncertainty in the resulting CSO volume. There were no second order effects due to the simplicity of the model (all indices ≤0.001). These results underline the importance of both, a reliable impervious area data basis and careful selection of the runoff coefficients when applying the UWB to new areas. Additional investigations are recommended to derive reasonable values, as in this study only one catchment and one year of data were available for verification.

Table 5.5: First order (S_i) and total order (T_i) Sobol' sensitivity indices (in brackets: 95%-confidence interval).

Parameter	**S_i**	**T_i**
Length of the moving minimum period	0.115 (0.103–0.127)	0.115 (0.103–0.127)
Mean runoff coefficient	0.885 (0.870–0.896)	0.885 (0.870–0.896)
Effective rainfall duration threshold value	0.001 (0.001–0.001)	0.001 (0.001–0.001)

5.3.3 Substance Emissions

The first bar in Figure 5.4 shows the relative contribution of WWTP (75%), CSOs (21%) and SSOs (4%) to the total wastewater flow volume to receiving waters in the study catchment resulting from the UWB after verification by the CSO measurements. The contribution to total substance emissions resulting from multiplication with the respective median of volume-weighted SMCs is shown in the other bars (Figure 5.4). Wastewater-related TCS is mainly emitted from the WWTP. Nevertheless, the contribution of CSOs to the total emission (19%) substantially exceeds the proportion of total dry weather flow discharged by CSOs (2.1%) due to the high removal rates in WWTP. On the contrary, more than 60% of Hg and 90% of Fluo are emitted from CSOs and SSOs. This estimation shows distinct differences between the substances but does not account for the uncertainties resulting from concentration variability.

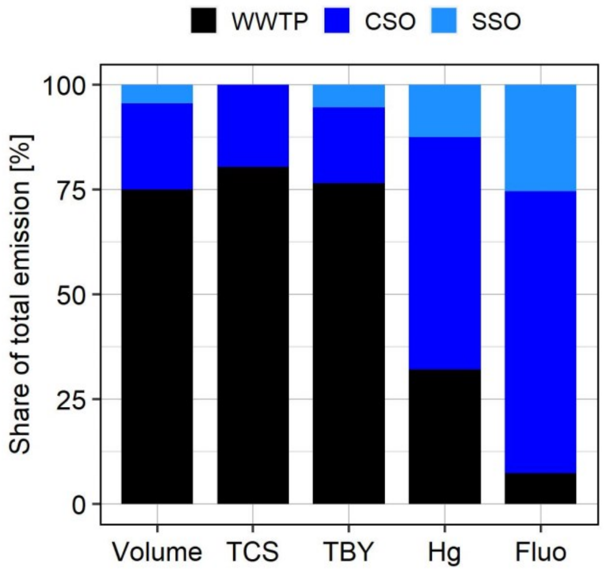

Figure 5.4: Contributions of wastewater treatment plants (WWTP), combined sewer overflows (CSO), and stormwater outfalls (SSO) to total substance emissions resulting from applying the median of site mean concentrations to the volume balance of the test catchment: TCS = Triclosan, TBY = Terbutryn, Hg = Mercury, Fluo = Fluoranthene.

The stochastic calculation was used to evaluate and visualise these uncertainties. An acceptable lognormal fit (Kolmogorov-Smirnov test $p>0.05$) was found for the SMCs of all substances in WWTP effluents and CSOs (Table A5.1, Figure A5.2). For SSOs, uniform distributions were used. TCS emissions from SSOs were not calculated since all values were <LOQ. The results of the stochastic calculation are shown in Figure 5.5. The greater the distance between the cumulative density functions and the steeper the curves, the more significant are the differences between the emission pathways and the more reliable are the estimates. For example, 38–86% of Fluo emissions could be attributed to CSOs, 10–45% to SSOs, and 1.3–35% to WWTPs considering 95%-confidence intervals. Measures to mitigate Fluo emissions from UWS in the catchment should focus on a detailed assessment of the CSOs. The main emission pathway of TCS in the catchment is the WWTP. For TBY and Hg, 95%-confidence intervals largely overlap (Table 5.6). Despite these wide confidence intervals, the stochastic approach allows a more informed decision making by acknowledging the existing uncertainties in the estimates.

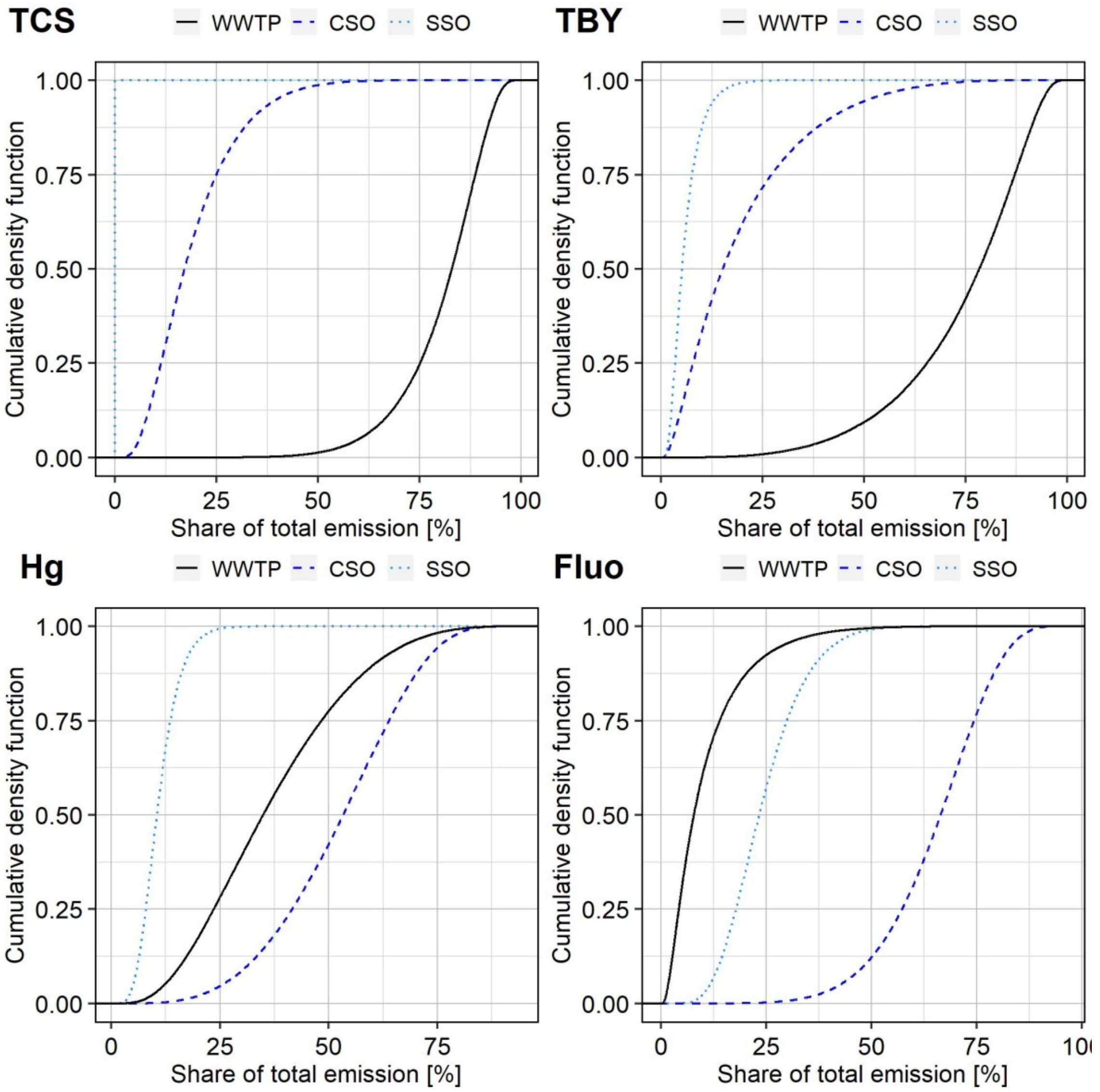

Figure 5.5: Distributions of the contributions of wastewater treatment plants (WWTP), combined sewer overflows (CSO), and stormwater outfalls (SSO) to total substance emissions resulting from applying fitted distributions of site mean concentrations (Figure A5.2) to the volume balance of the test catchment: TCS = Triclosan, TBY = Terbutryn, Hg = Mercury, Fluo = Fluoranthene.

Table 5.6: 95%-confidence intervals of stochastic emission estimates (share of total emission in %).

Substance	WWTP	CSO	SSO
Triclosan (TCS)	59–97	3.1–41	Not calculated
Terbutryn (TBY)	41–98	0.5–51	0.9–13
Mercury (Hg)	7.5–69	23–80	3.4–20
Fluoranthene (Fluo)	0.4–29	40–87	8.5–42

5.4 Discussion

The UWB approach needs little input data, is completely transparent, and can be readily applied to other WWTP catchments. The required input data includes impervious area data and standard monitoring data (daily WWTP inflow and hourly precipitation data) which are either available at river basin level or could be collected by the authorities with reasonable effort. As such, the UWB is a suitable approach for estimating near-realistic regionalised annual emissions from UWS at river basin level.

The UWB results showed good agreement with both measured data (CSO volume and duration of impoundment of CSO storage facilities) and standard design values (overflow rate and mixing ratio of stormwater and wastewater in CSO), when using adjusted input variables. The CSO volume estimates were shown to be most sensitive to the mean runoff coefficient which is central to the simplified rainfall-runoff calculation and represents the most important variable. Therefore, the input data for precipitation and impervious area as well as the realistic consideration of surface losses are of particular importance.

Generally, rainfall-runoff modelling is subject to a high degree of uncertainty. "*The main model input – precipitation is uncertain due to the limited number of available observations and the high spatio-temporal variability*" (Bárdossy *et al.* 2022). The common practice of assuming uniform spatial distribution of rainfall in the catchment may lead to significant error (Cristiano *et al.* 2017; Maier *et al.* 2020). Also land cover data (here: impervious area) may introduce error due to highly heterogeneous urban surface cover and the presence of sub-areas with different types of connection (Ravagnani *et al.* 2009). This information should ideally be determined precisely by the municipalities or sewer system operators, taking into account the local sewer network characteristics. If such data is not available at river basin level, sewer system statistics and high resolution land cover data may be used instead, e.g. Copernicus high resolution imperviousness geodata (EEA 2018).

Thus, the accuracy of UWB estimates is limited by a typically rather imprecise data situation. However, this also underlines that the use of more detailed modelling approaches is not currently indicated at river basin level and that these are unlikely to improve the reliability of predictions without additional detailed input data. Further improvement of the data basis available for modelling wet weather discharges from UWS is generally advisable. In this regard, the evaluation of UWB results, such as overflow rate or mixing ratio, might be used to support the identification of catchments with clearly implausible input data.

To adequately take into account surface losses, further validation of the mean runoff coefficient in study areas with a reliable data situation is recommended. In this study, data of one individual study catchment was considered. Due to the general lack of adequate monitoring data on CSO activities, a validation of the UWB in additional catchments was not possible. Therefore, it is yet to be investigated whether the adjusted runoff coefficient could be transferred to other catchments in the area or whether certain catchment characteristics could be used to develop a transfer function. The further validation of the UWB and the investigation of the area-wide transferability of the input variables is the subject of ongoing studies (Ganatsas 2022). There is a continued need to equip more CSOs with measurement systems and produce quality-checked validation data. This is essential to continuously improve the UWB approach and the state of knowledge on CSOs in general.

A new central output of the UWB is the proportion of DWF discharged via CSOs. In perspective, this quantity could be used as an emission target value for regulating the discharge of wastewater-borne substances from combined sewer systems (DWA 2021; Schmitt 2021). Likewise, the proportion of stormwater runoff in CSOs can be considered a proxy for emissions of stormwater-related substances (Schmitt 2021).

Locally, these volume-based quantities could be determined more accurately than actual substance emissions using calibrated hydrological simulations (DWA 2021; Schmitt 2021). The UWB is now suited to provide a first estimate of the proposed emission target values to prioritise catchments for detailed assessment.

LUBW (2019a) have implemented a preliminary version of the UWB in the river basin model METRIS-BW used for modelling phosphorous emissions in the federal state of Baden-Württemberg. A federal database of municipal wastewater and stormwater treatment facilities provided input data. As an alternative to daily WWTP data, LUBW (2019a) used annual total WWTP inflow and annual dry weather flow data pre-evaluated according to standardised 21-day moving minimum methods (Weiß *et al.* 2002; Fuchs *et al.* 2003). The results were used to identify water bodies that should be prioritised for measures to reduce nutrient emissions from sewer systems (LUBW 2019a; Fuchs *et al.* 2020a). This included water bodies that had both a moderate to bad ecological status in terms of macrophytes and phytobenthos, and more than 50% of phosphorous emissions from sewer systems (sum of CSOs and SSOs).

Such strategy recommendations can also be derived for micropollutants using representative quality monitoring data. The UWB provides a basis for assessing the contribution of CSOs to the total emissions in water bodies that fail to achieve good chemical status, i.e. environmental quality standards or no effect concentrations are exceeded. Due to the overall CSO quality data scarcity, the new dataset (Nickel *et al.* 2021a) can be considered an eligible basis for non-monitored CSOs in Germany. As more data becomes available, the transferability of the data, which originate primarily from southern Germany, should be further reviewed.

It was demonstrated that the uncertainties associated with both the UWB and the use of representative quality data are considerable. Furthermore, with its monitoring-based approach, the UWB is primarily a retrospective instrument and has limited possibilities to consider measure scenarios, e.g. increased sewer storage volume or wastewaster treatment capacity. However, the results allow for a robust screening level assessment of the importance of CSOs as an emission pathway of pollutants in WWTP catchments. Stochastic approaches can be used to point out and acknowledge the uncertainty resulting from the use of representative data but still allow to derive informed strategy recommendations. Thus, the UWB is to be understood primarily as a prioritisation instrument meant to achieve capacity to act. As a next step, a site-specific problem definition and detailed assessment of prioritised WWTP catchments are required before measures can be effectively implemented. This will have to include a review of locally available CSO monitoring data and in most cases additional targeted monitoring of CSOs, i.e. flow volumes or at least frequency and duration. The UWB can be applied to individual CSO facilities if measurements of the flow conveyed from the facility to the WWTP are available (Fuchs *et al.* 2020a). Alternatively, results of WWTP catchments might be disaggregated to allow further prioritisation of individual CSO facilities based on CSO duration measurements. This underlines the usefulness of the further installation of measurement equipment at CSOs and the importance of monitoring data to support a targeted and effective optimisation of combined sewer systems. The monitoring can then be complemented by calibrated hydrological simulation, providing higher temporal and spatial resolution, e.g. to consider measure scenarios. Suspect screening with passive samplers might be an efficient approach to generate an overview of local CSO quality (Mutzner *et al.* 2020).

6 General Discussion

CSOs impose hydraulic, physical, and chemical pressures on receiving water ecosystems. There is a continuing need for further research to improve the overall understanding and assessment of these pressures in order to adequately address CSOs in water quality management. This thesis aimed to contribute to improving the emission-oriented assessment of CSOs as a pathway of chemical pollution from urban areas to receiving water bodies. Considering the general data scarcity on CSOs, e.g. in comparison to WWTPs, this involved studying CSO quality as well as to investigate approaches for generalisation, transfer and area-wide assessment. More specifically, this involved to expand the data on CSO quality with a focus on micropollutants using a strategically harmonised LVS sampling, analyse the observed concentration variability, and build a consistent dataset qualified to be used as representative data. Finally, these data were integrated into an UWB approach applicable for regionalised emission modelling at river basin level to support the prioritisation of areas for detailed assessment.

6.1 CSO Monitoring, Data Quality and Data Availability

There is no standardised monitoring of CSOs. Despite increasing research efforts, the availability of data on their activity, quantity, and quality is still limited. The further implementation of water level or flow monitoring at CSOs is essential to improve the assessment of these discharges and refine models. It is also a prerequisite for any water quality monitoring of CSOs.

Water quality monitoring in UWS is challenging and cost-intensive due to high spatial and temporal variability and a high number of potentially relevant substance groups. Comprehensive monitoring needs to cover both variability between sites and temporal variability at each site. Integrating sampling methods and long observation periods at individual sites are required to collect representative data in an efficient way. Unless the objective is to study short-time concentration fluctuations, event-based analysis of CSOs represents a practicable compromise between temporal resolution and analytical costs. Volume-proportional event composite samples are suitable to quantify the EMC and the event load, provided that the event is sufficiently represented in the sample. Annual emitted loads can be estimated by aggregating event mean concentrations to volume-weighted site mean concentrations.

LVS are an increasingly used sampling system in line with this monitoring strategy. To ensure comparability with other studies, the comparability of EMCs analysed in LVS composite samples to EMCs estimated from conventional autosampler pollutographs was demonstrated with a focus on the key water quality parameter total suspended solids. LVS were also shown to come with specific advantages, i.e. the flexibility to sample widely varying event volumes and durations and the option to conduct detailed particle analyses using the collected solids. However, future applications of LVS should be accompanied by further research on the characteristics of the sampling system to explain differences in particle analyses between homogenised and sedimented LVS subsamples.

The monitoring carried out contributed new original data on CSO quality confirming the occurrence and quantifying the concentrations of various priority substances and other micropollutants originating from both wastewater and stormwater runoff. The data were merged with WWTP and SSO quality data to provide a consistent and comparable basis for the assessment of these three main emission pathways from UWS.

Detailed documentation of methods and accessibility of raw data, including accompanying data, are essential to ensure comparability and re-usability. Thus, all data have been processed and made publicly available including accompanying data to maximise the usefulness for further work in this area (Nickel *et al.* 2021a). It would be desirable to extend this database to substance groups that have been under-represented in this work, e.g. pharmaceuticals and other mobile substances with unknown or various sources in UWS, as well as to collect additional data on SSOs, using the same harmonised sampling strategies.

6.2 Understanding or Accepting Concentration Variability?

Despite the applied composite sampling approaches that provided integration of short-term dynamics, substance concentrations vary significantly between events (temporally) and between different sites (spatially)[15]. Correlating patterns can be observed for groups of substances with similar sources and environmental behaviour in UWS (i.e. susceptibility to removal processes). This insight can be used as a starting point to structure and address in a general way the plethora of different substances potentially relevant to aquatic ecosystems.

Explanatory approaches for concentration differences based on catchment properties (e.g. land use, population density) or hydraulic conditions (e.g. volume, intensity) would be highly desirable to improve the understanding of concentration variability in CSOs and predict concentration levels at non-monitored sites. However, although the new dataset includes a large number of CSO sites and events analysed using consistent methodology, few meaningful relationships were found and none of the tested characteristics could be identified as main drivers of concentration differences. While a tendency of increased concentrations of several substances in urban catchments versus rural catchments was found based on a qualitative categorisation of the catchments, this could not be clearly confirmed using quantitative variables, e.g. population density. Such single conventional parameters are only of limited use to adequately describe the complexity of the processes determining the discharge quality in catchments and UWS (Liu *et al.* 2015). Moreover, since the data were collected at the outlets of entire catchments, it can be assumed that the influence of contrasting catchment characteristics is partly levelled out and pollutant sources are not necessarily reflected in the outlet concentrations. Only sampling with higher spatial resolution might allow concentrations to be linked to land use patterns (Spahr *et al.* 2020; Wicke *et al.* 2021). However, it seems highly unlikely that it will be possible to map the complex combined impacts of influencing factors on CSO concentrations and derive transferable predictive functions considering the current technical and financial limitations of CSO sampling and micropollutant analysis[15]. This means accepting an inherent stochastic and unpredictable concentration variability that has to be accounted for in the assessment of CSOs. Thus, for current emission modelling at river basin level, the use of representative concentrations (and their uncertainty ranges) without regional differentiation is appropriate. If possible, simple V × C (volume × concentration) approaches should be preferred to applying surface potentials or other emission factors to avoid introducing additional uncertainty due to these quantities (e.g. impervious area, population). The results of such assessments are not suited to predict the impact of CSOs in individual catchments

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[15] Sentence partly adopted from: Nickel, J. P., Sacher, F. and Fuchs, S. 2021 Up-to-date monitoring data of wastewater and stormwater quality in Germany. *Water Research*, 202, 117452. https://doi.org/10.1016/j.watres.2021.117452.

since local specifics and conditions are not accounted for. Neither can water protection measures be derived solely on this basis. However, they contribute to improving the understanding of the potential importance of CSOs to receiving water quality and provide a basis for prioritisation and further detailed assessment.

6.3 Modelling Emissions from CSOs

The quantitative determination of the flow volumes in UWS is the prerequisite for estimating pollutant emissions discharged from CSOs. The use of detailed urban-hydrological models is limited to the local scale due to missing input and calibration data or computational restrictions. Only simple urban water balance approaches with a moderate data-demand and reduced spatial and temporal resolution are currently applicable for the area-wide estimation of emissions in river basins. Increased monitoring of CSO flow volumes is needed to improve the knowledge of CSO activities and refine these approaches. The successive installation of water level sensors at overflow weirs for hydraulic discharge determination will play an important role in this context.

The UWB approach presented in this work relies on measurement data from WWTPs and rainfall gauges that are already available by standard in many catchments. The calculation steps are straightforward and transparent and the results can be verified and refined using CSO data as they become increasingly available. Since the data required for more detailed modelling approaches are typically not available, they cannot be expected to be more reliable or advantageous.

The CSO volume estimates were shown to be most sensitive to the mean runoff coefficient which is central to the simplified rainfall-runoff calculation and represents the most important variable. Therefore, the input data for precipitation and impervious area as well as the realistic consideration of surface losses are of particular importance for obtaining realistic results. Further validation of the UWB and the area-wide transferability of the input variables failed due to a lack of test catchments with adequate CSO data and is still needed. In perspective, monitoring data will be available for more CSOs. In Baden Württemberg, there is a new legal requirement to equip all CSO tanks with measurement devices by 2025. Bavaria is currently preparing similar requirements. This will allow the UWB to be successively validated and strategically improved or eventually partially replaced by measured data.

With its monitoring-based approach, the UWB is primarily a retrospective instrument and has limited possibilities to consider measure scenarios, e.g. increased sewer storage volume or wastewaster treatment capacity. However, the results allow for a robust screening level assessment of the importance of CSOs as an emission pathway of pollutants in WWTP catchments. In addition, the UWB is suited to provide a first estimate of recently proposed volume-based emission target values, i.e. the proportion of wastewater discharged via CSOs. Thus, against the background of low availability of quantitative data on CSOs, the UWB represents a valuable prioritisation instrument to support a targeted and effective optimisation of combined sewer systems.

6.4 Importance of Chemical Pollution from CSOs to Water Protection

Chemical pollution from CSOs can cause acute and long-term effects in aquatic ecosystems. Acute effects result from short-term exceedances of ecotoxicologically critical concentrations. CSO concentrations of the priority substances benzo(b)fluoranthene, benzo(ghi)perylene, and benzo(k)fluoranthene frequently exceeded MAC-EQS (≥20% of the EMCs). Acute risk potentials from CSOs have been identified for other individual substances as well (Mutzner *et al.* 2020). Consequently, CSO might indeed contribute to acute adverse effects of micropollutants in receiving waters depending on the local dilution potential. While actual local exposure needs to be analysed on-site with high temporal resolution, especially small streams can be subject to both hydraulic and chemical risks from CSOs (Becouze-Lareure *et al.* 2016; Fuchs *et al.* 2020a). Moreover, risk assessments based on individual substances or few target analytes may underestimate the combined risk of chemical mixtures, analytically undetected compounds, and transformation products (Brack *et al.* 2018; Brack *et al.* 2019; Spahr *et al.* 2020).

With regard to many micropollutants, long-term risks due to the accumulated impact of emitted loads are the main concern. The potential contribution of CSOs to long-term risks in water bodies can be assessed if emissions are reliably quantified. In this work, the contribution of CSOs to total emissions from UWS was assessed from a local (comparison of per capita loads of individual monitored CSOs and WWTPs in chapter 4), a national (rough wastewater balance for Germany in chapter 3) and a regionalised catchment-based perspective (urban water balance approach in chapter 5). In all three cases, the results can be summarised as follows: CSOs are a major emission pathway for substances with stormwater-related input to UWS and/or high removal rates in WWTPs, e.g. due to adsorption and solids removal. This includes several ubiquitous, persistent, bioaccumulative, and toxic (uPBT) substances often causing failure to achieve good chemical status of surface waters, e.g. heavy metals and PAHs. Conventional WWTPs without advanced micropollutant treatment are a major emission pathway for substances with predominantly dissolved transport and poor removal rates in WWTPs, e.g. due to partial biodegradation. This includes for example several priority biocides. Similar results have been found by other authors (Clara *et al.* 2014; Launay *et al.* 2016b; Becouze-Lareure *et al.* 2019; Paijens *et al.* 2021). The differences between these pathways can be quite pronounced depending on the UWS considered and will be shifted by implementing advanced micropollutant treatment at more WWTPs.

It should be noted that emission pathways from UWS other than WWTPs, CSOs, and SSOs were not considered in this work, e.g. households not connected to wastewater treatment, households not connected to sewer systems (Fuchs *et al.* 2017a), or sewer exfiltration (Nguyen and Venohr 2021). For a complete picture, the UWB and representative monitoring data should be implemented in a substance emission model covering all other pathways, e.g. as in Figure 6.1 (LUBW 2019a; Fuchs *et al.* 2021).

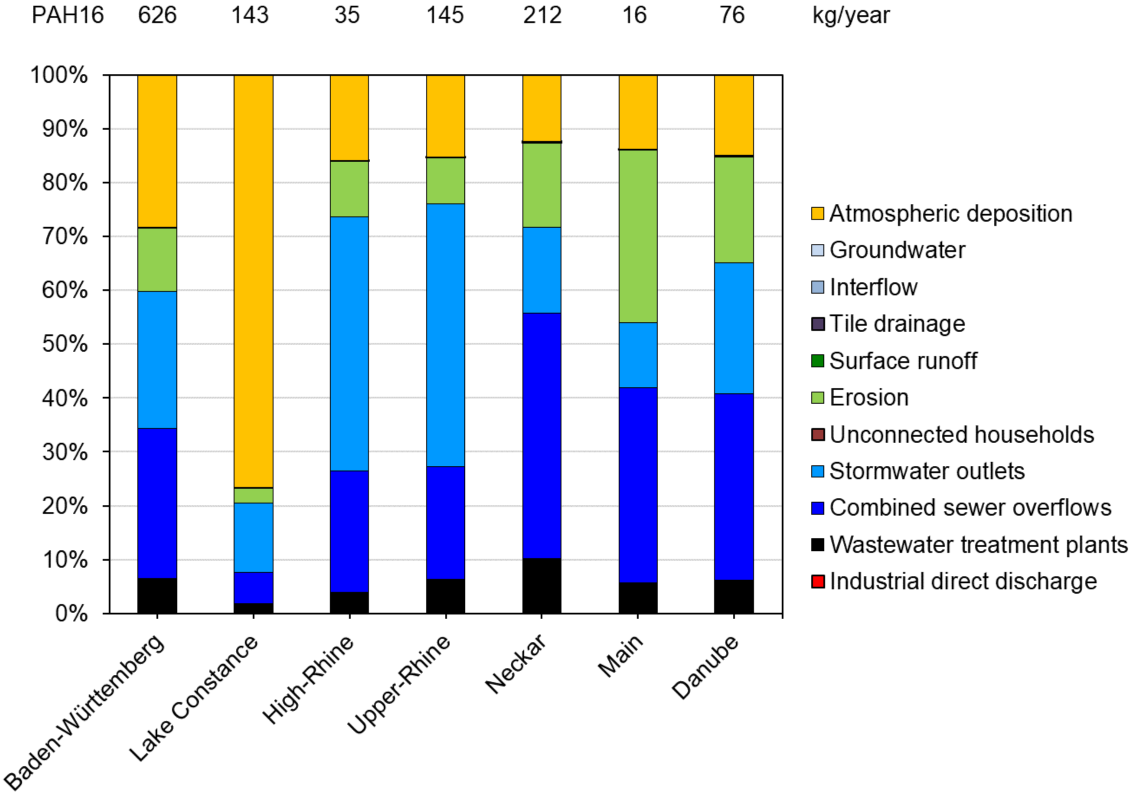

Figure 6.1: Emissions of PAH16 into surface water bodies in Baden-Württemberg: Total emissions (kg/year) and relative contributions of different pathways (Fuchs *et al.* 2021).

6.5 Outlook: Mitigation of Emissions from UWS

There are no universal measures to mitigate micropollutant emissions from UWS. Different categories of substances with different sources and very different environmental behaviour must be considered individually. Precautionary strategies are needed to minimise the entry of chemicals into the water cycle in the first place, since the technical possibilities of wastewater treatment and drinking water treatment are limited, and extremely costly (Pistocchi *et al.* 2022b). Combinations of advanced treatment processes are needed to remove all classes of chemicals (Fatta-Kassinos *et al.* 2016).

The further implementation of advanced wastewater treatment will not eliminate but increasingly reduce emissions of micropollutants from WWTPs (Pistocchi *et al.* 2022a). This could rapidly shift the ratio of emissions from WWTPs and CSOs. Emissions of stormwater-transported substances can already be significantly higher from CSOs and SSOs (e.g. Figure 6.1). Thus, emissions from both wastewater and stormwater treatment have to be regarded. To mitigate micropollutant emissions from UWS effectively, measures at different levels of action have to be combined: substance-specific source-control measures to reduce the initial pollution of the flows, stormwater management measures in catchments and optimisation of sewer systems to reduce CSOs and SSOs and increase the proportion of wastewater (and stormwater) undergoing treatment before discharge, and finally, end-of-pipe measures to improve treatment.

Source-control measures must include ending the use of hazardous substances, the development of eco-friendly substitutes, and the implementation of risk reduction measures in product authorisation processes (UBA 2018) to ensure proper application and disposal of medicinal products, biocides, pesticides, and other chemicals. Potential gaps in risk assessment procedures need to be closed (Wieck *et al.* 2016). Researchers should continue to identify specific sources of pollutants to support the development of targeted source-control measures (Müller *et al.* 2020).

Decarbonisation of energy production may also be regarded as a source-control measure for reducing chemical pollution of water bodies. With coal combustion being the main source of primary emissions of mercury (Ruhwedel 2021), phasing-out the use of coal will be decisive to reach WFD goals.

A reduction of CSOs can be achieved by providing more storage volume in sewer systems (grey solutions), or by water-sensitive urban development aimed at reducing or delaying the direct stormwater runoff into sewer systems. Water-sensitive urban development has a high potential to reduce both hydraulic and chemical pressures on water bodies from CSOs and includes all kinds of so-called blue-green solutions, i.e. systems for stormwater storage and use, evaporation (e.g. green roofs, facade greening) and infiltration (e.g. swales, trenches, permeable surfaces) which all have synergistic effects in terms of climate change adaptation (e.g. drinking water savings, groundwater recharge, urban cooling, reduced urban flooding risk, biodiversity). Green solutions are estimated to be more cost-effective than grey solutions for widespread implementation (Quaranta *et al.* 2022b) and can be considered as “no-regret” options due to their additional benefits (Quaranta *et al.* 2021). Municipalities should incorporate these solutions consequently into their urban development plans and implement them proactively in public projects. Further development of legal requirements, incentives/funding, as well as technical guidance are needed to also induce more private investments and control quality. The materials used in green systems and their construction need to be assessed and optimised to avoid the unwanted release of pollutants (Hachoumi *et al.* 2021). Decentralised stormwater treatment needs to be improved and consistently implemented where needed to prevent the transfer of dissolved pollutants to surface water or groundwater (Bork *et al.* 2021). Furthermore, management plans for the pollutant depots formed in decentralized treatment systems have to be developed.

Sewer system operators should continue to install measurement devices in sewer systems to improve the understanding of their functioning. The existing systems can be optimised with respect to minimising wet weather discharges or according to the ecological requirements of receiving waters. Sewer system optimisation may include sewer rehabilitation to minimise infiltration water in order to restore capacities for stormwater, static optimisation of flow regulators to reduce overflows into particularly sensitive water bodies (Bachmann-Machnik *et al.* 2021) or real time control (Botturi *et al.* 2020; van der Werf *et al.* 2022). The effect of optimisation measures may be limited and depends largely on local conditions, but implementation can be very cost-effective compared to other measures (Quaranta *et al.* 2022b). In combined sewer systems, the treatment of increased combined sewage flows in WWTPs may substitute additional storage volume in the sewer system. A bypass can be used to protect sensitive process stages (Günther 2019). Retention and partial treatment of stormwater in WWTPs is a major advantage of combined over separate sewer systems. Additional capacity to decrease the occurrence and magnitude of CSOs may even be provided by meshed sewer system structures (Reyes-Silva *et al.* 2020).

End-of-pipe measures for CSOs include upgrading of existing storage and sedimentation tanks to state-of-the-art standards and optimising existing mechanical treatment processes, e.g. by reducing the design surface loading rate to avoid remobilisation of sediments (Fuchs *et al.* 2019b) or retrofitting lamella elements in sedimentation tanks (Fuchs *et al.* 2014; Kemper 2016). Effective additional treatment of wet weather discharges from CSOs and SSOs can be achieved with retention soil filters or more generally, constructed wetlands (Brunsch *et al.* 2020; Rizzo *et al.* 2020). In an European-scale assessment of CSO management options, treatment with constructed wetlands was estimated to be more cost-effective than both grey and green measures to prevent CSOs (Quaranta *et al.* 2022b). However, constructed wetlands require comparatively large areas which are often not available in densely built-up urban areas.

Due to the different benefits, implications and limitations, an optimal combination of blue-green solutions, grey solutions, system optimisation, and end-of-pipe measures has to be found depending on the local conditions in individual catchments, and taking into account the ecological requirements of the receiving waters (e.g. existing deficits, hydraulic capacity, dilution ratio).

This work contributes to the updating and expansion of knowledge on chemical pollution from combined sewer systems. The results and approaches of this work can be applied to identify areas where measures to mitigate emissions from CSOs may be required as a priority. For this purpose, the UWB approach and the new data are recommended for implementation into a substance emission model. This will support river basin managers in defining priority areas for a detailed assessment. The detailed assessments of catchments will in most cases require additional local monitoring programmes to derive an optimally adapted planning of measures. This underlines the usefulness of the further installation of measurement equipment at CSOs and the importance of monitoring data to support a targeted and effective optimisation of combined sewer systems. Where water quality monitoring of CSOs is indicated, the practical insights of the sampling carried out in this work can contribute to further improve the sampling methods used, as well as the reliability and comparability of the monitoring results.

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Appendix

Supplementary Material to Chapter 2

Chapter 2 and the supplementary material have been published in Water: Nickel, J. P. and Fuchs, S. 2021 Large-Volume Samplers for Efficient Composite Sampling and Particle Characterization in Sewer Systems. *Water*, 13(20), 2831. https://doi.org/10.3390/w13202831

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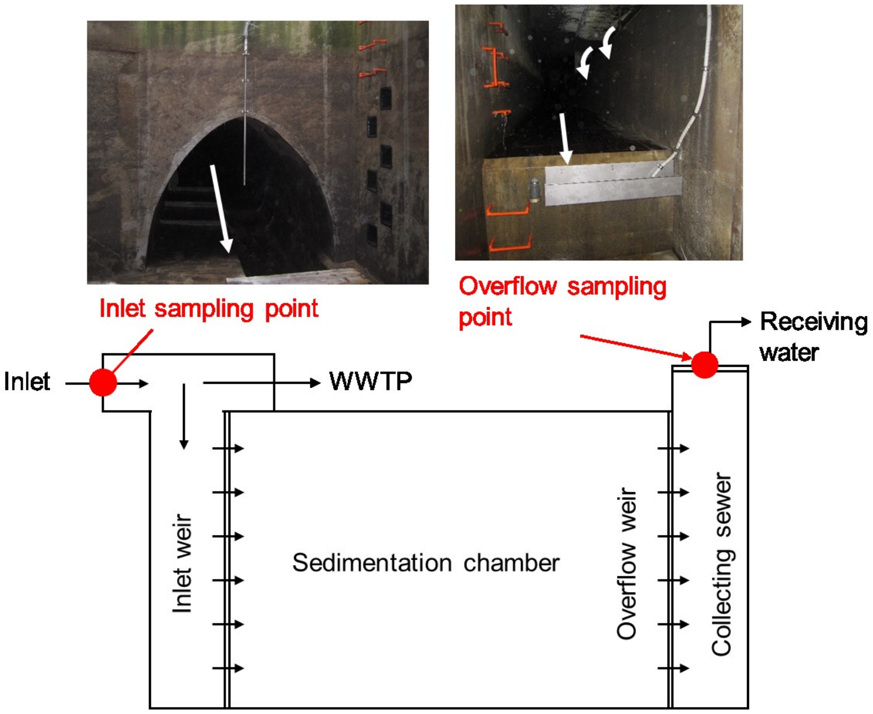


Figure A2.1: Sketch of CSO facility SED06 with sampling points.

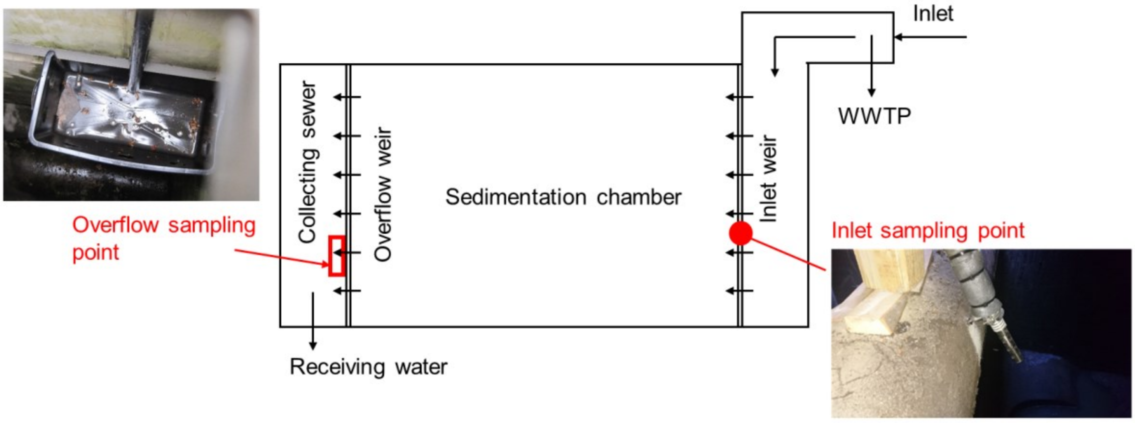


Figure A2.2: Sketch of CSO facility SED02 with sampling points.

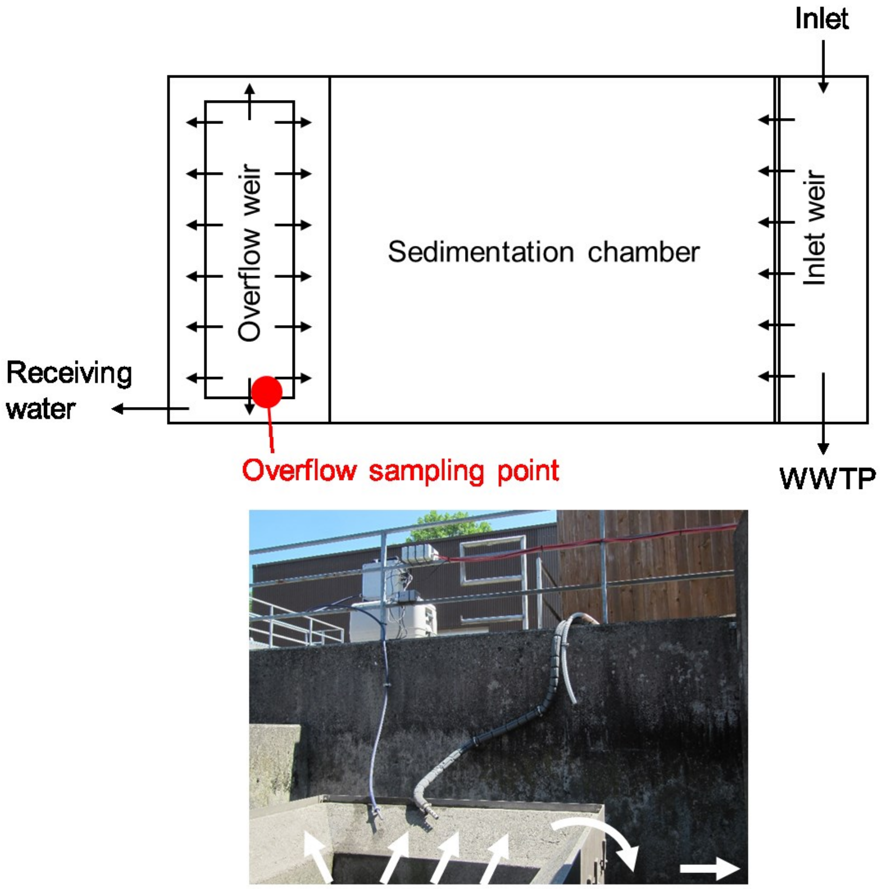


Figure A2.3: Sketch of CSO facility SED05 with sampling point.

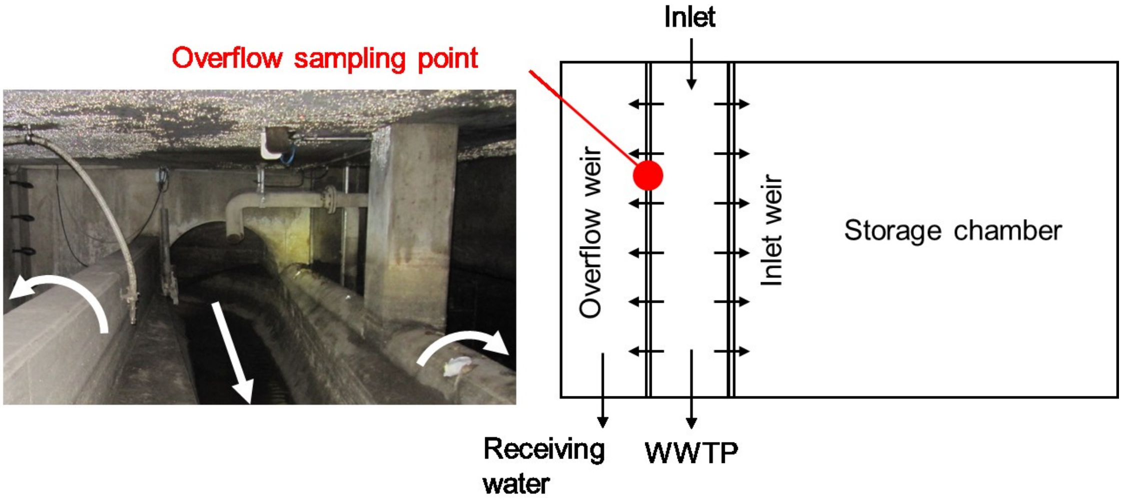
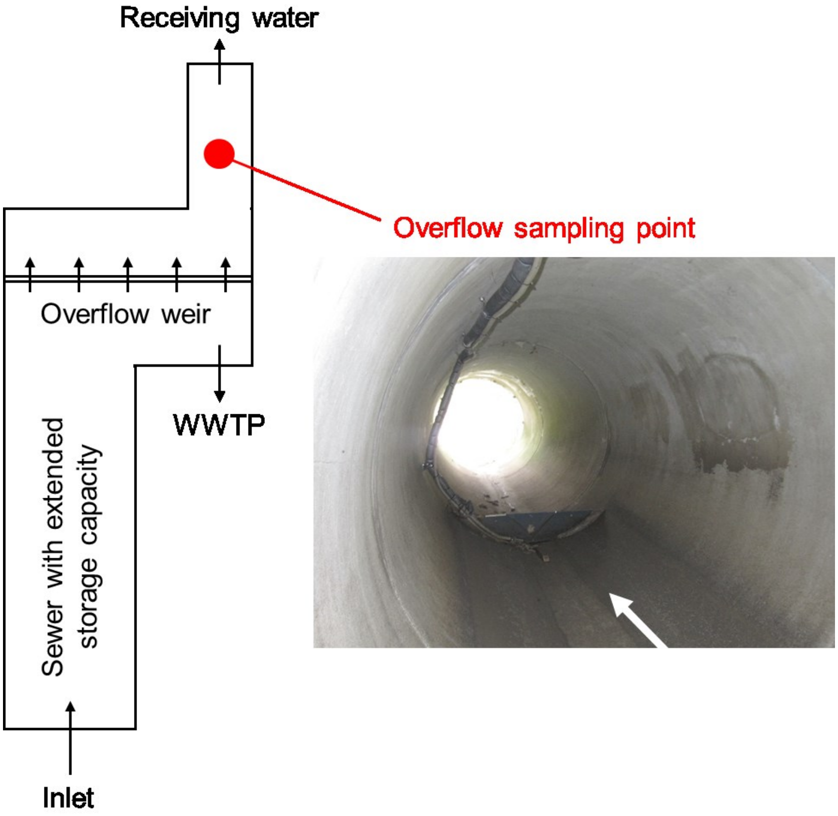


Figure A2.4: Sketch of CSO facility FFR02 with sampling point.



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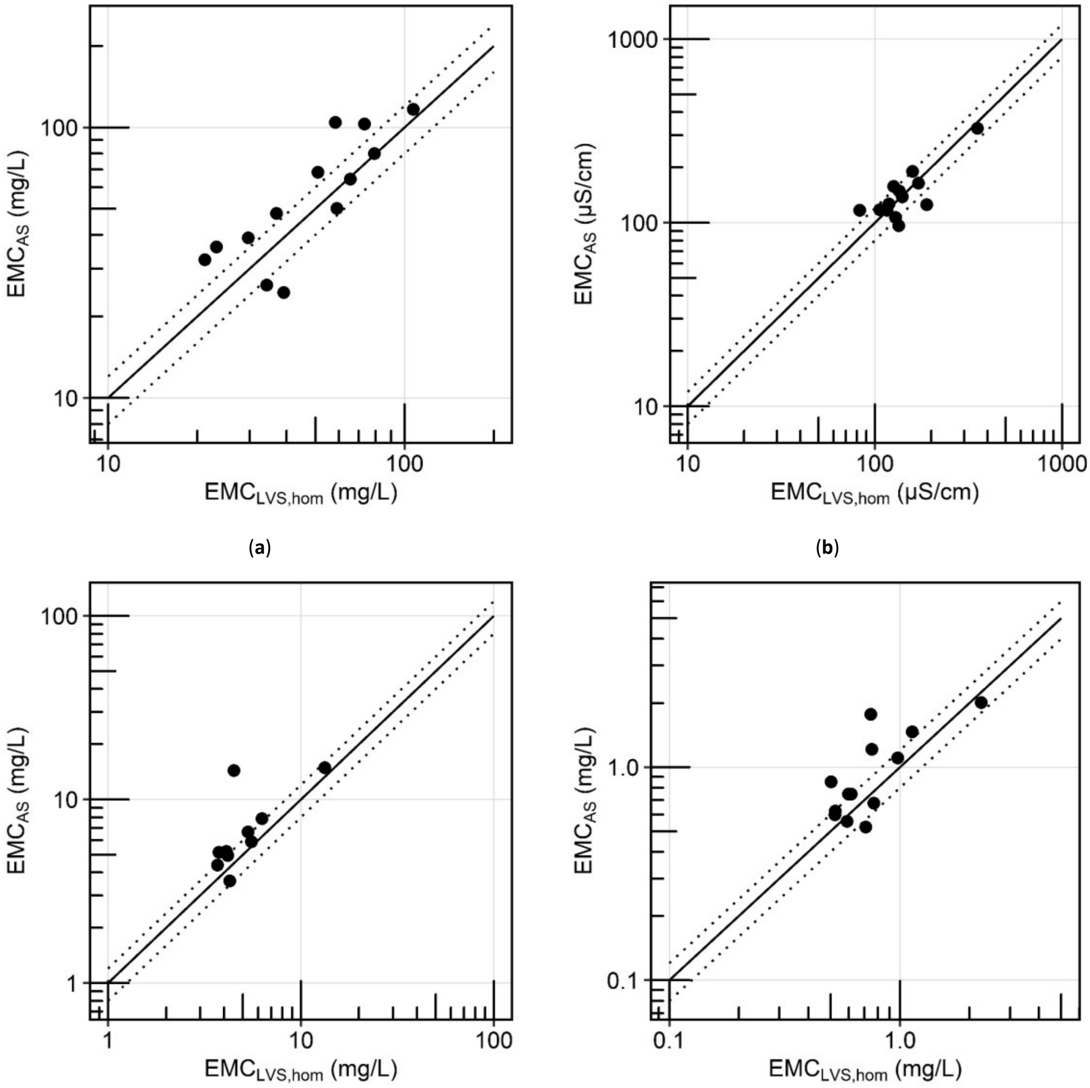

(**a**) (**b**)

(**c**) (**d**)

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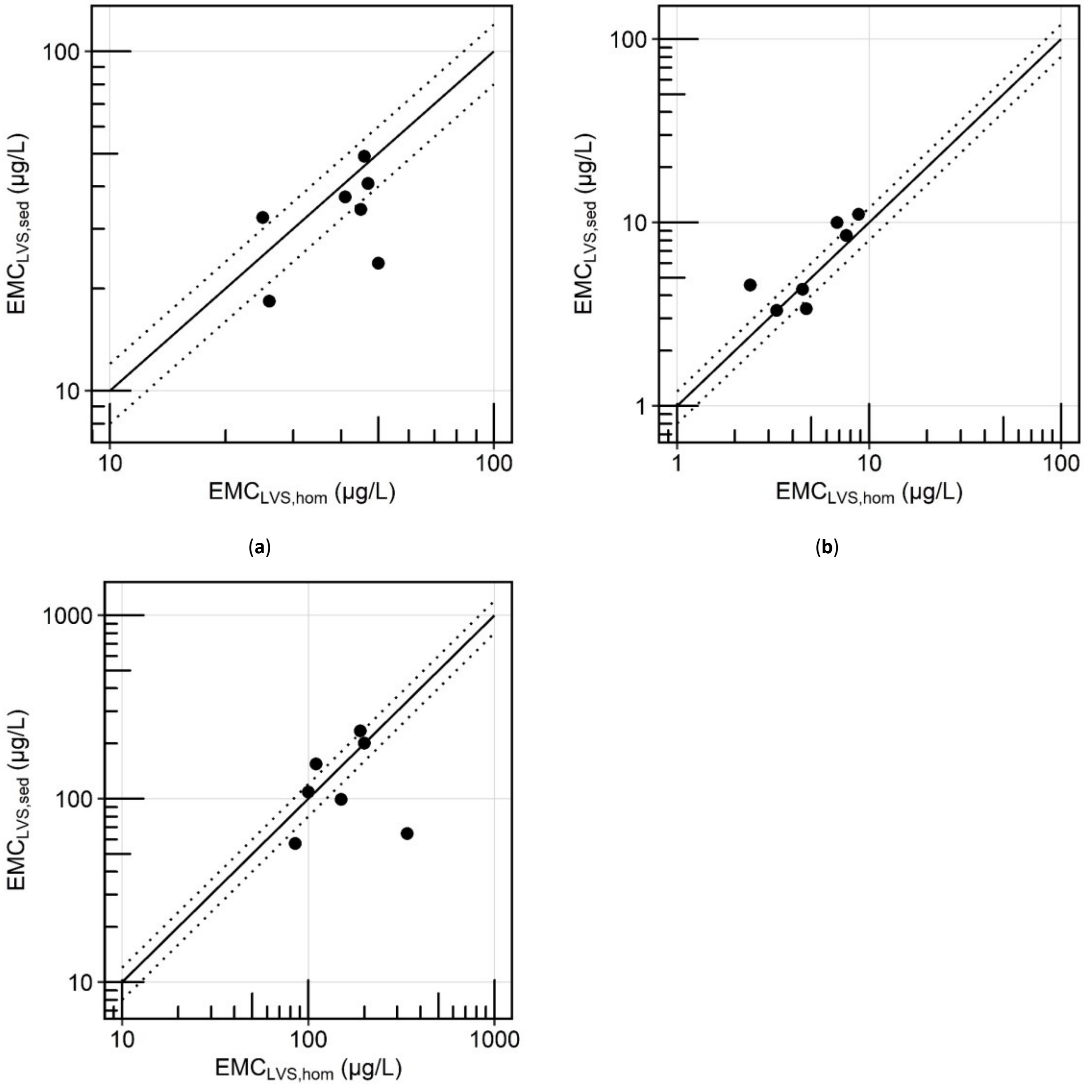

(**a**)

(**b**)

(**c**)

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Table A2.1. Analytical methods used for water samples.

Parameter(s)	**Analytical Method**
Conductivity	EN 27888-C8
TSS	DIN 38409-H2
LOI	DIN 38409-H2
COD	DIN 38409-H41-H44
TNb	EN ISO 11905-1
TP, PO4-P	DIN 38405 D11-4
Metals	Inductively coupled plasma with mass spectrometry (ICP-MS) (DIN EN ISO 17294) after microwave digestion with addition of acid

Table A2.2: Analytical methods used for sediment samples.

Parameter(s)	Analytical Method
Sieving analysis	DIN 18123:2011-04
Dry mass	DIN 38409-H1
LOI	DIN 38409-H2
TP	DIN 38405 D11-4 (after perchloric acid digestion, in-house method)
Metals	Inductively coupled plasma with mass spectrometry (ICP-MS) (DIN EN ISO 17294) after microwave digestion with addition of acid

Table A2.3: Summary of analytical results of homogenized LVS samples.

Parameter	Unit	Inlet			Overflow		
		n	Median	Min-Max	n	Median	Min-Max
TSS	mg/l	5	77.0	45.0–137	20	43.3	16.3–109
TSS63	mg/l	5	50.4	23.3–108	20	30.1	6.5–82.4
LOI <63 µm	%	5	41	33–68	20	59	38–77
LOI 63–2,000 µm	%	5	65	57–82	20	69	49–88
pH	-	5	6.4	6.1–6.7	20	6.5	6.1–6.9
Conductivity	µS/cm	5	134	83–220	20	151	92–353
COD	mg/l	5	98.2	37–116	20	54.7	21.2–129
TNb	mg/l	5	Not analyzed		20	5.3	3.69–13.3
TP	mg/l	5	0.8	0.50–1.52	20	0.7	0.52–2.25
PO_4-P	mg/l	5	Not analyzed		20	0.3	0.22–1.33

Table A2.4: Summary of analytical results of sedimented LVS samples.

Parameter	Unit	Inlet			Overflow		
		n	Median	Min-Max	n	Median	Min-Max
TSS	mg/l	5	73.0	46.4–120	11	62.8	33.5–126
TSS63	mg/l	5	65.3	37.3–84.1	11	44.9	25.5–110
LOI <63 µm	%	5	36	22–49	11	41	27–55
LOI 63–2,000 µm	%	5	83	76–86	11	75	24–92
Supernatant							
pH	-	5	6.6	6.6–6.7	11	6.7	6.4–7.1
Conductivity	µS/cm	5	149	94–204	11	148	91–281
Particle-bound pollutants							
TP <63 µm	µg/mg	5	5.29	3.03–8.78	11	6.96	3.95–8.32
TP 63–2,000 µm	µg/mg	5	2.09	1.63–2.62	11	2.47	1.52–7.05
Cu <63 µm	µg/mg	5	0.34	0.24–0.42	11	0.48	0.26–0.85
Cu 63–2,000 µm	µg/mg	5	0.18	0.02–0.22	7	0.32	0.20–1.0
Pb <63 µm	µg/mg	5	0.078	0.070–0.097	11	0.09	0.058–0.12
Pb 63–2,000 µm	µg/mg	5	0.063	0.030–0.069	7	0.073	0.031–0.20
Zn <63 µm	µg/mg	5	1.10	0.82–1.70	11	1.90	0.032–2.5
Zn 63–2,000 µm	µg/mg	5	0.73	0.60–0.95	7	1.60	0.57–2.9

Table A2.5: Summary of analytical results of individual autosampler samples.

Parameter	Unit	Inlet			Overflow		
		n	Median	Min-Max	n	Median	Min-Max
TSS	mg/l	24	38.8	18–112	215	36.9	7.86–257
pH	-	24	6.4	6.3–6.6	215	6.5	6.2–7.1
Conductivity	µS/cm	24	97	73–147	215	143	2.4–436
COD	mg/l	24	38.2	30.3–119	215	47.1	11.5–257
TP	mg/l	24	0.6	0.44–1.58	215	0.8	0.27–9.49
TNb	mg/l	24	4	3.31–8.13	192	5.5	2.72–21.7

Table A2.6: Summary of analytical results of autosampler EMCs.

Parameter	Unit	Inlet			Overflow		
		n	Median	Min-Max	n	Median	Min-Max
TSS	mg/l	2	53.5	43.9–63.1	11	39.6	24.8–122
Conductivity	µS/cm	2	107	96.3–117	11	138	107–326
COD	mg/l	2	56.2	48.0–64.4	11	50.2	24.5–117
TP	mg/l	2	0.80	0.75–0.85	11	0.70	0.52–2.01
TNb	mg/l	2	5.1	4.5–5.7	10	5.5	3.6–14.9

Supplementary Material to Chapter 4

Chapter 4 and the supplementary material have been published in Water Research: Nickel, J. P., Sacher, F. and Fuchs, S. 2021 Up-to-date monitoring data of wastewater and stormwater quality in Germany. *Water Research*, 202, 117452. https://doi.org/10.1016/j.watres.2021.117452

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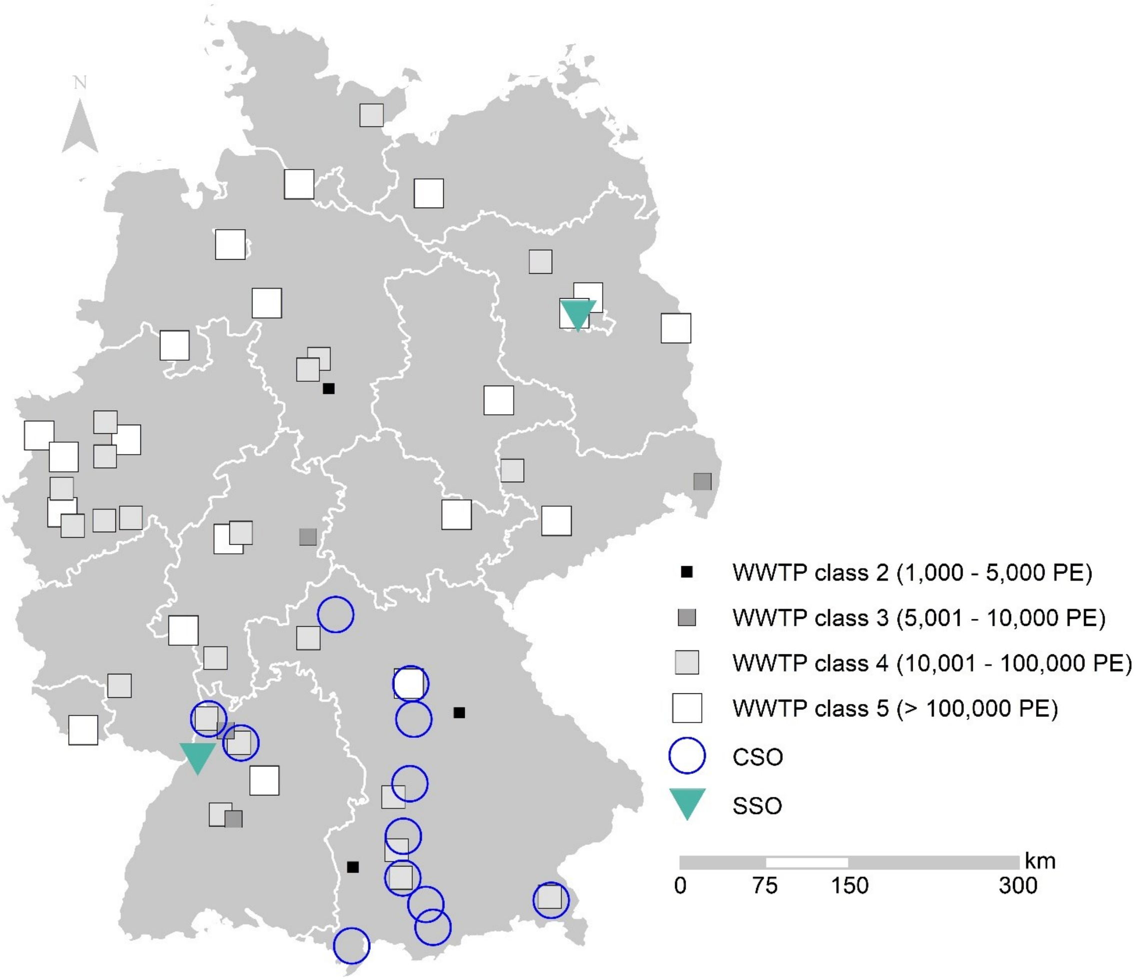


Figure A4.1: Sampling locations in the federal states of Germany. WWTP = wastewater treatment plant, PE = population equivalents, CSO = combined sewer overflow, SSO = stormwater outfall.

Table A4.1: Characteristics of wastewater treatment plants selected for sampling. Grey shading indicates WWTPs selected for detailed investigation.

ID	Size class *	Capacity (PE)	Share of combined system	Population density of municipality in km^{-2} **	Number of effluent / influent samples
WWTP01	2	1,500	0.00	39	12
WWTP02	2	3,800	0.28	44	21
WWTP03	2	5,000	0.50	NA	18
WWTP04	3	7,500	0.80	79	23
WWTP05	3	8,000	0.10	79	12
WWTP06	4	36,000	0.30	185	13
WWTP07	4	19,000	0.05	285	20
WWTP08	3	9,000	0.72	306	24
WWTP09	3	10,000	0.85	281	24
WWTP10	4	15,900	0.82	199	22
WWTP11	4	18,000	1.00	153	24

ID	Size class *	Capacity (PE)	Share of combined system	Population density of municipality in km^{-2} **	Number of effluent / influent samples
WWTP12	4	33,000	0.32	236	20
WWTP13	4	28,000	0.55	341	24
WWTP14	4	26,000	0.50	954	22
WWTP15	4	35,000	0.00	410	12 / 12
WWTP16	4	27,000	0.50	618	24
WWTP17	4	31,350	0.80	243	32 / 32
WWTP18	4	35,833	0.68	738	23
WWTP19	4	44,000	0.00	101	12
WWTP20	4	30,000	0.52	784	26
WWTP21	4	55,500	0.90	352	23
WWTP22	4	55,000	0.90	624	24
WWTP23	4	50,000	0.95	588	24
WWTP24	4	64,000	0.22	258	20
WWTP25	4	64,000	0.60	499	20 / 18
WWTP26	4	70,000	NA	414	26
WWTP27	5	120,000	0.26	394	19
WWTP28	5	149,073	0.00	349	12 / 12
WWTP29	4	100,000	0.98	762	18
WWTP30	4	99,000	0.70	416	23
WWTP31	5	145,000	0.59	334	26
WWTP32	4	99,000	0.68	179	24
WWTP33	5	120,000	1.00	634	23
WWTP34	5	155,000	0.45	615	21
WWTP35	5	135,000	0.95	1,080	24
WWTP36	5	160,000	0.10	490	17
WWTP37	5	210,000	0.72	968	23
WWTP38	5	200,000	0.30	43	22
WWTP39	5	250,000	0.03	1,372	12
WWTP40	5	270,000	0.84	1,442	25
WWTP41	5	400,000	0.72	1,117	21
WWTP42	5	400,000	0.87	2,202	24
WWTP43	5	705,000	0.91	2,090	19
WWTP44	5	1,200,000	1.00	1,645	16
WWTP45	5	860,000	0.05	56	15
WWTP46	5	1,200,000	0.92	3,052	25 / 24
WWTP47	5	840,000	0.54	139	12
WWTP48	5	1,000,000	0.62	1,741	23
WWTP49	5	1,600,000	0.81	4,055	12

* Class based on capacity: class 2: 1,000 – 5,000 PE, class 3: 5,001 – 10,000 PE, class 4: 10,001 – 100,000 PE, class 5: > 100,000 PE.

** Data source: IOER Monitor © Leibniz Institute of Ecological Urban and Regional Development.

Table A4.2: Characteristics of combined sewer overflows and stormwater outfalls selected for sampling.

Type	ID*	Total catchment area in ha	Population density in ha^{-1} (total area)	Directly connected area in ha	Share of traffic areas	Share of industrial and commercial areas	Imperviousness (direct area)	Storage volume in m³	Throttled flow to WWTP in $l \cdot s^{-1}$	Number of samples
CSO	FFR01	191.4	24	77.7	0.15	0.19	0.27	1,100	60	13
CSO	FFR02	73.1	34	73.1	0.20	0.09	0.40	457	35	21
CSO	SED01	44.2	17	44.2	0.13	0.09	0.17	168	9	17
CSO	SED02	126.9	27	39.3	0.16	0.04	0.51	597	64	12
CSO	SED03	287.3	56	108.2	0.19	0.23	0.39	3,788	240	10
CSO	SED04	129.9	69	129.9	0.13	0.13	0.48	825	128	16
CSO	SED05	791.2	49	345.7	0.19	0.11	0.23	1,325	500	15
CSO	SED06	1,845	34	1,845	0.18	0.20	0.15	5,700	650	15
CSO	SED07	633,0	NA	38.7	NA	NA	0.67	1,652	242	4
CSO	SED08	442.0 (imperv.)	NA	0	NA	NA	NA	1,414	330	8
CSO	SES01	3,848	42	116.7	0.16	0.17	0.37	4,074	1,845	9
CSO	SES02	314.1	49	221.3	0.20	0.16	0.66	1,456	330	31
SSO	SED09	122.6	NA	122.6	NA	NA	0.40	650	NA	10
SSO	SED10	70.0	NA	70.0	NA	NA	0.43	325	NA	10

* FFR = first flush retention tank, SED = sedimentation tank, SES = sewer with extended storage

Table A4.3: List of substances analysed in wastewater treatment plant influent, effluent, combined sewer overflow (CSO) and stormwater outfall (SSO). If no limit of quantification (LOQ) is reported, the substance was not analysed in the respective medium.

Abbreviation	Substance	CAS-No.	LOQ in µg/l				EQS in µg/l	
			Influent	Effluent	CSO	SSO	AA	MAC
Artificial sweeteners								
ACE	Acesulfame	55589-62-3	-	-	0.05	-	-	-
Benzotriazoles								
4MBT	4-Methylbenzotriazole	29878-31-7	-	-	0.01	-	-	-
5MBT	5-Methylbenzotriazole	136-85-6	-	-	0.01	-	-	-
BTR	Benzotriazole	95-14-7	-	-	0.01	-	-	-
Biocides and Pesticides								
1,2,4TZL	1,2,4-Triazole	288-88-0	0.5	0.1	0.1	0.1	-	-
2AB	2-Aminobenzimidazole	934-32-7	0.1	0.02	0.02	0.02	-	-
ACF	Aclonifen	74070-46-5	0.01	0.01	0.01	0.01	0.12	0.12
ATR	Atrazin	1912-24-9	0.01	0.01	0.01	0.01	0.6	2
BDF	Brodifacoum	56073-10-0	0.05	0.01	0.01	0.01	-	-
BFX	Bifenox	42576-02-3	0.004	0.004	0.004	0.004	0.012	0.04
BIT	1,2-Benzisothiazolin-3(2H)-on	2634-33-5	0.05	0.01	0.01	0.01	-	-
CBT	Cybutryne	28159-98-0	0.005	0.005	0.005	0.005	0.0025	0.016
cHCE	cis-Heptachlor epoxide	1024-57-3	0.01	0.004	0.004	0.004	$2 \cdot 10^{-7}$	0.0003
CYM	Cypermethrin	52315-07-8	0.013	0.005	0.005	0.005	$8 \cdot 10^{-5}$	0.0006
CZIM	Carbendazim	10605-21-7	0.05	0.01	0.01	0.01	-	-
DCS	Diclosan	3380-30-1	0.05	0.01	0.01	0.01	-	-
DCV	Dichlorvos	62-73-7	0.05	0.01	0.01	0.01	0.0006	0.0007
DEET	Diethyltoluamide	134-62-3	0.05	0.01	0.01	0.01	-	-

Abbreviation	**Substance**	**CAS-No.**	**LOQ in µg/l**				**EQS in µg/l**	
			Influent	**Effluent**	**CSO**	**SSO**	**AA**	**MAC**
DFTL	Difethialon	104653-34-1	0.05	0.01	0.01	0.01	-	-
DIF	Dicofol	115-32-2	0.05	0.02	0.02	0.02	0.0013	-
DIU	Diuron	330-54-1	0.01	0.01	0.01	0.01	0.2	1.8
HC	Heptachlor	76-44-8	0.01	0.004	0.004	0.004	$2\cdot10^{-7}$	0.0003
IMI	Imidacloprid	105827-78-9/ 138261-41-3	0.01	0.01	0.01	0.01	-	-
ISO	Isoproturon	34123-59-6	0.01	0.01	0.01	0.01	0.3	1
IZL	Imazalil	35554-44-0	0.05	0.01	0.01	0.01	-	-
MCPP	MCPP (Mecoprop)	93-65-2	-	-	0.01	-	-	-
MDCS	Methyl-Diclosan	4640-07-7	0.025	0.01	0.01	0.01	-	-
MET	Metolachlor	51218-45-2	-	-	0.01	-	-	-
MIT	2-Methyl-3-isothiazolinon	2682-20-4	0.05	0.01	0.01	0.01	-	-
MTCS	Methyl-Triclosan	4640-01-1	0.025	0.01	0.01	0.01	-	-
OIT	2-Octyl-3-isothiazolinon	26530-20-1	0.05	0.01	0.01	0.01	-	-
PCZ	Propiconazole	60207-90-1	0.05	0.01	0.01	0.01	-	-
PLN	Prallethrin	103065-19-6	0.05	0.01	0.01	0.01	-	-
PMN	Permethrin	52645-53-1	0.025	0.01	0.01	0.01	-	-
PMNS	Permethric acid	55701-05-8	0.25	0.05	0.05	0.05	-	-
QNX	Quinoxyfen	124495-18-7	0.05	0.01	0.01	0.01	0.15	2.7
TBA	Terbuthylazine	5915-41-3	-	-	0.01	-	-	-
TBY	Terbutryn	886-50-0	0.01	0.01	0.01	0.01	0.065	0.34
TBYD	Terbutryn-desethyl	30125-65-6	0.05	0.01	0.01	0.01	-	-
TBYS	Terbutryn-sulfoxide	82985-33-9	0.05	0.01	0.01	0.01	-	-
TCS	Triclosan	3380-34-5	0.05	0.01	0.01	0.01	-	-
TCZ	Tebuconazol	107534-96-3	0.05	0.01	0.01	0.01	-	-
tHCE	trans-Heptachlor epoxide	28044-83-9	0.01	0.004	0.004	0.004	$2\cdot10^{-7}$	0.0003
THIA	Thiabendazol	148-79-8	0.05	0.01	0.01	0.01	-	-
Industrial chemicals								
HBCDD	Hexabromocyclododecanes	not applicable	0.01	0.005	0.005	0.005	0.0016	0.5
Metals								
Bi	Bismuth	7440-69-9	-	-	0.01	-	-	-
Cd	Cadmium	7440-43-9	0.002	0.002	0.002	0.002	≤ 0.08	≤ 0.45
Cr	Chrome	7440-47-3	-	-	0.1	-	-	-
Cu	Copper	7440-50-8	-	-	1	-	-	-
Fe	Iron	7439-89-6	20	20	5	-	-	-
Hg	Mercury	7439-97-6	0.001	0.001	0.001	0.001	-	0.07
Mo	Molybdenum	7439-98-7	-	-	0.01	-	-	-
Ni	Nickel	7440-02-0	1	1	0.1	1	4	34
Pb	Lead	7439-92-1	0.1	0.1	0.1	0.1	1.2	14
Sb	Antimony	7440-36-0	-	-	0.1	-	-	-
Sn	Tin	7440-31-5	-	-	0.1	-	-	-
Zn	Zinc	7440-66-6	20	20	5	-	-	-
PFAS								
H4PFOS	1H,1H,2H,2H-Perfluoroctansulfonic acid	27619-97-2	0.01	0.001	0.001	0.001	-	-
PFBA	Perfluorobutyric acid	375-22-4	0.01	0.001	0.001	0.001	-	-
PFBS	Perfluorobutanesulfonic acid	375-73-5	0.01	0.001	0.001	0.001	-	-
PFDA	Perfluorodecanoic acid	335-76-2	0.01	0.001	0.001	0.001	-	-
PFDoA	Perfluorododecanoic acid	307-55-1	0.01	0.001	0.001	0.001	-	-
PFDS	Perfluorodecane sulfonic acid	335-77-3	0.01	0.001	0.001	0.001	-	-

Abbreviation	Substance	CAS-No.	LOQ in µg/l				EQS in µg/l	
			Influent	Effluent	CSO	SSO	AA	MAC
PFHpA	Perfluoro-n-heptanoic acid	375-85-9	0.01	0.001	0.001	0.001	-	-
PFHpS	Pentadecafluoro-1-heptanesulfonic acid	375-92-8	0.01	0.001	0.001	0.001	-	-
PFHxA	Perfluorohexanoic acid	307-24-4	0.01	0.001	0.001	0.001	-	-
PFHxS	Perfluorohexanesulfonic acid	355-46-4	0.01	0.001	0.001	0.001	-	-
PFNA	Perfluoro-n-nonanoic acid	375-95-1	0.01	0.001	0.001	0.001	-	-
PFOA	Perfluorooctanoic acid	335-67-1	0.01	0.001	0.001	0.001	-	-
PFOS	Perfluorooctane sulfonic acid	1763-23-1	0.01	0.001	0.001	0.001	0.00065	36
PFPA	Perfluoropentanoic acid	2706-90-3	0.01	0.001	0.001	0.001	-	-
PFPeS	Perfluoropentane-1-sulfonic acid	2706-91-4	0.01	0.001	0.001	0.001	-	-
PFUnA	Perfluoro-n-undecanoic acid	2058-94-8	0.01	0.001	0.001	0.001	-	-
Pharmaceuticals								
CBZ	Carbamazepine	298-46-4	-	-	0.01	-	-	-
DCF	Diclofenac	15307-86-5	-	-	0.01	-	-	-
MPL	Metoprolol	37350-58-6	-	-	0.01	-	-	-
Phenols								
4iNP	4-iso-nonylphenol	84852-15-3	0.1	0.04	0.04	0.04	0.3	2
4tOP	4-tert.-octylphenol	140-66-9	0.05	0.02	0.02	0.02	0.1	-
Plasticisers								
DEHP	Di-(2-ethylhexyl)phthalate	117-81-7	0.25	0.1	0.1	0.1	1.3	-
Polycyclic aromatic hydrocarbons (PAH)								
ACN	Acenaphthene	83-32-9	0.0025	0.001	0.001	0.001	-	-
ACY	Acenaphthylene	208-96-8	0.0025	0.001	0.001	0.001	-	-
ANT	Anthracene	120-12-7	0.0025	0.001	0.001	0.001	0.1	0.1
BaA	Benzo(a)anthracene	56-55-3	0.0025	0.001	0.001	0.001	-	-
BaP	Benzo(a)pyrene	50-32-8	0.0013	0.0005	0.0005	0.0005	0.00017	0.27
BbF	Benzo(b)fluoranthene	205-99-2	0.0025	0.001	0.001	0.001	-	0.017
BghiP	Benzo(ghi)perylene	191-24-2	0.0013	0.0005	0.0005	0.0005	-	0.0082
BkF	Benzo(k)fluoranthene	207-08-9	0.0025	0.001	0.001	0.001	-	0.017
Chr	Chrysene	218-01-9	0.0025	0.001	0.001	0.001	-	-
DahA	Dibenz(ah)anthracene	53-70-3	0.0025	0.001	0.001	0.001	-	-
FL	Fluorene	86-73-7	0.0025	0.001	0.001	0.001	-	-
Fluo	Fluoranthene	206-44-0	0.0025	0.001	0.001	0.001	0.0063	0.12
IP	Indeno(1,2,3-cd)pyrene	193-39-5	0.0013	0.0005	0.0005	0.0005	-	-
NAP	Naphthalene	91-20-3	0.025	0.01	0.01	0.01	2	130
PHE	Phenanthrene	85-01-8	0.0025	0.001	0.001	0.001	-	-
Pyr	Pyrene	129-00-0	0.0025	0.001	0.001	0.001	-	-

Table A4.4: Analytical methods. Additional details are available in Fuchs *et al.* (2020c), Fuchs *et al.* (2020b), and Nickel and Fuchs (2020).

Parameter(s)	**Analytical method**
Mercury	Microwave digestion with addition of acid followed by Atomic fluorescence spectrometry (DIN EN ISO 17852)
Other metals	Microwave digestion with addition of acid followed by inductively coupled plasma with mass spectrometry (ICP-MS) (DIN EN ISO 17294)
PAH, DEHP	Liquid-liquid extraction with cyclohexane followed by gas chromatography with tandem mass spectrometry (GC-MS/MS)
Permethrin, methyl-triclosan, methyl-diclosan	Liquid-liquid extraction with cyclohexane followed by gas chromatography with tandem mass spectrometry (GC-MS/MS)
Brodifacoum und difethialon	Offline enrichment in rotary vacuum concentrator followed by liquid chromatography with tandem mass spectrometry (HPLC-MS/MS)
2-Aminobenzimidazol, 1,2-benzisothiazolin-3(2H)-on (BIT), 2-methyl-3isothiazolinon (MIT), 1,2,4-triazol	Direct injection to liquid chromatography with tandem mass spectrometry (HPLC-MS/MS)
Other biocides and pesticides	Online solid-phase extraction followed by liquid chromatography with tandem mass spectrometry (HPLC-MS/MS)
Benzotriazoles	Online solid-phase extraction followed by liquid chromatography with tandem mass spectrometry (HPLC-MS/MS)
Pharmaceuticals	Online solid-phase extraction followed by liquid chromatography with tandem mass spectrometry (HPLC-MS/MS)
HBCDD	Liquid-liquid extraction with cyclohexane followed by gas chromatography with mass spectrometry (GC-MS)
PFAS	Solid-phase extraction followed by liquid chromatography with tandem mass spectrometry (HPLC-MS/MS)
Acesulfame	Solid-phase extraction followed by liquid chromatography with tandem mass spectrometry (HPLC-MS/MS)
Conductivity	EN 27888 - C 8
$K_{a4.3}$	EN 29963 - 1 - H 7
TSS	DIN 38409 - H 2
COD	ISO 6060-1989, DIN 38409 - H41-H44
TNb	EN ISO 11905-1
NH_4-N	WWTP effluent samples: Continuous flow analysis (CFA) and spectrometric detection (DIN EN ISO 11732) WWTP influent/CSO/SSO samples: DIN 38406 E 5
NO_3-N	WWTP effluent samples: Ion chromatography (DIN EN ISO 10304-1) WWTP influent/CSO/SSO samples: Diazo method
TP, PO_4-P	DIN EN ISO 6878

Table A4.5: Statistical summary of micropollutant concentrations in WWTP influents.

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10th – 90th percentile)	Unit
Metals						
Fe	5	96	1	0.89	0.56 - 2.42	mg/l
Zn	5	96	1	0.17	0.11 - 0.33	mg/l
Ni	5	96	1	6.25	3.95 - 15	µg/l
Pb	5	96	0.99	3.1	1.85 - 6.5	µg/l
Hg	5	96	0.99	0.029	0.015 - 0.064	µg/l
Cd	5	96	0.99	0.11	0.068 - 0.18	µg/l
PAH						
NAP	5	96	0.58	0.028	< 0.025 - 0.052	µg/l
ACY	5	96	0.86	0.0054	< 0.0025 - 0.012	µg/l
ACN	5	96	1	0.013	0.0072 - 0.024	µg/l
FL	5	96	1	0.014	0.008 - 0.022	µg/l
PHE	5	96	1	0.062	0.032 - 0.12	µg/l
ANT	5	96	0.82	0.0056	< 0.0025 - 0.021	µg/l
Fluo	5	96	1	0.047	0.025 - 0.14	µg/l
Pyr	5	96	0.99	0.044	0.023 - 0.12	µg/l
BaA	5	96	1	0.014	0.0066 - 0.058	µg/l
Chr	5	96	1	0.024	0.012 - 0.084	µg/l
BbF	5	96	1	0.015	0.007 - 0.064	µg/l
BkF	5	96	0.92	0.0062	0.0029 - 0.027	µg/l
BaP	5	96	1	0.011	0.0057 - 0.058	µg/l
IP	5	96	1	0.0096	0.0048 - 0.047	µg/l
DahA	5	96	0.43	< 0.0025	< 0.0025 - 0.012	µg/l
BghiP	5	96	1	0.012	0.006 - 0.052	µg/l
Phenols						
4iNP	5	96	0.99	0.24	0.15 - 0.5	µg/l
4tOP	5	96	0.11	< 0.05	< 0.05 - 0.052	µg/l
PFAS						
PFBA	5	96	0.25	< 0.01	< 0.01 - 0.024	µg/l
PFPA	5	96	0.01	< 0.01	< 0.01 (max. 0.05)	µg/l
PFHxA	5	96	0.06	< 0.01	< 0.01 (max. 0.067)	µg/l
PFHpA	5	96	0.031	< 0.01	< 0.01 (max. 0.027)	µg/l
PFOA	5	96	0.11	< 0.01	< 0.01 - 0.012	µg/l
PFNA	5	96	0.01	< 0.01	< 0.01 (max. 0.051)	µg/l
PFDA	5	96	0.021	< 0.01	< 0.01 (max. 0.024)	µg/l
PFUnA	5	96	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
PFDoA	5	96	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
PFBS	5	96	0.18	< 0.01	< 0.01 - 0.035	µg/l
PFPeS	5	96	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
PFHxS	5	96	0.021	< 0.01	< 0.01 (max. 0.022)	µg/l
PFHpS	5	96	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
PFOS	5	96	0.12	< 0.01	< 0.01 - 0.018	µg/l
PFDS	5	96	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
H4PFOS	5	96	0.1	< 0.01	< 0.01 (max. 0.58)	µg/l
Biocides and Pesticides						
DCS	5	65	0.046	< 0.05	< 0.05 (max. 0.073)	µg/l
MDCS	5	65	0	< 0.025	< 0.025 (max. < 0.025)	µg/l
TCS	5	65	0.98	0.32	0.12 - 0.51	µg/l
MTCS	5	65	0	< 0.025	< 0.025 (max. < 0.025)	µg/l
IZL	5	65	0	< 0.05	< 0.05 (max. < 0.05)	µg/l
BDF	5	65	0	< 0.05	< 0.05 (max. < 0.05)	µg/l
DIF	5	96	0	< 0.05	< 0.05 (max. < 0.05)	µg/l
DEET	5	65	0.98	0.41	0.16 - 1.56	µg/l
DFTL	5	65	0	< 0.05	< 0.05 (max. < 0.05)	µg/l
HC	5	96	0	< 0.01	< 0.01 (max. < 0.01)	µg/l

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10th – 90th percentile)	Unit
cHCE	5	96	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
tHCE	5	96	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
PMN	5	65	0.94	0.14	0.037 - 0.23	µg/l
PMNS	5	65	0	< 0.25	< 0.25 (max. < 0.25)	µg/l
PLN	5	65	0	< 0.05	< 0.05 (max. < 0.05)	µg/l
DCV	5	96	0	< 0.05	< 0.05 (max. < 0.05)	µg/l
IMI	5	65	0.63	0.013	< 0.01 - 0.05	µg/l
1,2,4TZL	5	65	0.046	< 0.5	< 0.5 (max. 0.92)	µg/l
BIT	5	65	0.66	0.14	< 0.05 - 0.55	µg/l
2AB	5	65	0	< 0.1	< 0.1 (max. < 0.1)	µg/l
MIT	5	32	0.19	< 0.05	< 0.05 - 0.072	µg/l
OIT	5	65	0	< 0.05	< 0.05 (max. < 0.05)	µg/l
CZIM	5	65	0.29	< 0.05	< 0.05 - 0.061	µg/l
CBT	5	96	0	< 0.025	< 0.025 (max. < 0.025)	µg/l
CYM	5	96	0.16	< 0.013	< 0.013 - 0.018	µg/l
DIU	5	96	0.45	< 0.01	< 0.01 - 0.03	µg/l
ISO	5	96	0.82	0.028	< 0.01 - 0.063	µg/l
PCZ	5	65	0.25	< 0.05	< 0.05 - 0.086	µg/l
TCZ	5	65	0.25	< 0.05	< 0.05 - 0.091	µg/l
TBY	5	96	0.93	0.052	0.012 - 0.11	µg/l
TBYD	5	32	0	< 0.05	< 0.05 (max. < 0.05)	µg/l
TBYS	5	32	0.06	< 0.05	< 0.05 (max. 0.05)	µg/l
THIA	5	65	0.015	< 0.05	< 0.05 (max. 0.053)	µg/l
ACF	5	96	0.01	< 0.05	< 0.05 (max. 0.098)	µg/l
ATR	5	96	0.01	< 0.01	< 0.01 (max. 0.03)	µg/l
BFX	5	96	0	< 0.02	< 0.02 (max. < 0.02)	µg/l
QNX	5	96	0	< 0.05	< 0.05 (max. < 0.05)	µg/l
Other organic substances						
DEHP	5	96	1	14	5.15 - 26.5	µg/l
HBCDD	5	96	0.38	< 0.01	< 0.01 - 0.018	µg/l

Table A4.6: Statistical summary of micropollutant concentrations in WWTP effluents.

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10th – 90th percentile)	Unit
Metals						
Fe	5	100	1	0.07	0.02 - 0.44	mg/l
Zn	5	100	0.96	0.03	< 0.02 - 0.041	mg/l
Ni	49	1000	1	4.4	2.3 - 7.6	µg/l
Pb	49	1000	0.68	0.14	< 0.1 - 0.33	µg/l
Hg	49	1000	0.89	0.002	< 0.001 - 0.005	µg/l
Cd	49	1000	0.93	0.006	0.002 - 0.015	µg/l
PAH						
NAP	49	999	0.43	< 0.01	< 0.01 - 0.018	µg/l
ACY	49	999	0.3	< 0.001	< 0.001 - 0.0017	µg/l
ACN	49	999	0.63	0.0012	< 0.001 - 0.0044	µg/l
FL	49	999	0.86	0.0016	< 0.001 - 0.0037	µg/l
PHE	49	1000	0.97	0.0043	0.002 - 0.0098	µg/l
ANT	49	999	0.038	< 0.001	< 0.001 (max. 0.013)	µg/l
Fluo	49	999	0.83	0.0021	< 0.001 - 0.0062	µg/l
Pyr	49	999	0.8	0.0019	< 0.001 - 0.0056	µg/l
BaA	49	999	0.14	< 0.001	< 0.001 - 0.0012	µg/l
Chr	49	999	0.33	< 0.001	< 0.001 - 0.0022	µg/l
BbF	49	999	0.15	< 0.001	< 0.001 - 0.0014	µg/l
BkF	49	999	0.046	< 0.001	< 0.001 (max. 0.038)	µg/l
BaP	49	999	0.33	< 0.0005	< 0.0005 - 0.0012	µg/l

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10th – 90th percentile)	Unit
IP	49	999	0.23	< 0.0005	< 0.0005 - 0.00092	µg/l
DahA	49	999	0.014	< 0.001	< 0.001 (max. 0.014)	µg/l
BghiP	49	999	0.27	< 0.0005	< 0.0005 - 0.001	µg/l
Phenols						
4iNP	49	999	0.57	0.043	< 0.04 - 0.18	µg/l
4tOP	49	999	0.27	< 0.02	< 0.02 - 0.033	µg/l
PFAS						
PFBA	49	1000	0.91	0.004	0.001 - 0.012	µg/l
PFPA	49	1000	0.89	0.004	< 0.001 - 0.013	µg/l
PFHxA	49	1000	0.98	0.006	0.002 - 0.018	µg/l
PFHpA	49	1000	0.58	0.001	< 0.001 - 0.004	µg/l
PFOA	49	1000	0.9	0.006	< 0.001 - 0.011	µg/l
PFNA	49	1000	0.16	< 0.001	< 0.001 - 0.001	µg/l
PFDA	49	1000	0.24	< 0.001	< 0.001 - 0.002	µg/l
PFUnA	49	1000	0.002	< 0.001	< 0.001 (max. 0.001)	µg/l
PFDoA	49	1000	0.004	< 0.001	< 0.001 (max. 0.006)	µg/l
PFBS	49	1000	0.88	0.003	< 0.001 - 0.013	µg/l
PFPeS	49	1000	0.016	< 0.001	< 0.001 (max. 0.005)	µg/l
PFHxS	49	1000	0.33	< 0.001	< 0.001 - 0.004	µg/l
PFHpS	49	1000	0.016	< 0.001	< 0.001 (max. 0.006)	µg/l
PFOS	49	1000	0.84	0.003	< 0.001 - 0.011	µg/l
PFDS	49	1000	0	< 0.001	< 0.001 (max. < 0.001)	µg/l
H4PFOS	49	1000	0.23	< 0.001	< 0.001 - 0.003	µg/l
Biocides and Pesticides						
DCS	29	314	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
MDCS	29	314	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
TCS	29	314	0.96	0.024	0.012 - 0.046	µg/l
MTCS	29	314	0.013	< 0.01	< 0.01 (max. 0.012)	µg/l
IZL	29	314	0.08	< 0.01	< 0.01 (max. 0.027)	µg/l
BDF	29	314	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
DIF	49	999	0	< 0.02	< 0.02 (max. < 0.02)	µg/l
DEET	29	314	0.98	0.08	0.026 - 0.27	µg/l
DFTL	29	314	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
HC	49	999	0	< 0.004	< 0.004 (max. < 0.004)	µg/l
cHCE	49	999	0	< 0.004	< 0.004 (max. < 0.004)	µg/l
tHCE	49	999	0	< 0.004	< 0.004 (max. < 0.004)	µg/l
PMN	29	314	0.003	< 0.01	< 0.01 (max. 0.011)	µg/l
PMNS	29	314	0.1	< 0.05	< 0.05 (max. 0.096)	µg/l
PLN	29	314	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
DCV	49	1000	0.004	< 0.01	< 0.01 (max. 0.52)	µg/l
IMI	29	314	0.74	0.017	< 0.01 - 0.043	µg/l
1,2,4TZL	29	314	0.94	0.32	0.15 - 0.69	µg/l
BIT	29	314	0.31	< 0.01	< 0.01 - 0.036	µg/l
2AB	29	314	0.6	0.023	< 0.02 - 0.05	µg/l
MIT	29	180	0.57	0.012	< 0.01 - 0.032	µg/l
OIT	29	314	0.013	< 0.01	< 0.01 (max. 0.042)	µg/l
CZIM	29	314	0.72	0.017	< 0.01 - 0.055	µg/l
CBT	49	1000	0.035	< 0.005	< 0.005 (max. 0.059)	µg/l
CYM	49	999	0	< 0.005	< 0.005 (max. < 0.005)	µg/l
DIU	49	1000	0.71	0.016	< 0.01 - 0.043	µg/l
ISO	49	1000	0.7	0.019	< 0.01 - 0.066	µg/l
PCZ	29	314	0.63	0.013	< 0.01 - 0.057	µg/l
TCZ	29	314	0.35	< 0.01	< 0.01 - 0.046	µg/l
TBY	49	1000	0.89	0.035	< 0.01 - 0.086	µg/l
TBYD	29	180	0.11	< 0.01	< 0.01 - 0.011	µg/l
TBYS	29	180	0.77	0.022	< 0.01 - 0.079	µg/l
THIA	29	314	0.15	< 0.01	< 0.01 - 0.011	µg/l

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10th – 90th percentile)	Unit
ACF	49	1000	0.001	< 0.01	< 0.01 (max. 0.041)	µg/l
ATR	49	1000	0.041	< 0.01	< 0.01 (max. 0.15)	µg/l
BFX	49	1000	0	< 0.004	< 0.004 (max. < 0.004)	µg/l
QNX	49	1000	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
Other organic substances						
DEHP	49	999	1	1.7	0.56 - 6.4	µg/l
HBCDD	49	1000	0.008	< 0.005	< 0.005 (max. 0.047)	µg/l

Table A4.7: Statistical summary of micropollutant concentrations in CSOs.

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10th – 90th percentile)	Unit
Metals						
Fe	10	145	1	920	410 - 2,800	µg/l
Zn	10	145	1	130	68 - 256	µg/l
Cu	10	145	1	37	23.4 - 71.4	µg/l
Ni	12	157	1	2.7	0.98 - 7.34	µg/l
Pb	12	157	1	3.5	1.46 - 11	µg/l
Cr	10	145	1	4.1	1.9 - 10.6	µg/l
Hg	12	157	1	0.013	0.007 - 0.034	µg/l
Cd	12	157	1	0.065	0.035 - 0.19	µg/l
Bi	10	137	1	0.32	0.11 - 0.74	µg/l
Mo	10	137	1	0.67	0.3 - 1.7	µg/l
Sb	10	137	1	0.73	0.28 - 1.8	µg/l
Sn	10	137	1	1.9	0.74 - 5.04	µg/l
PAH						
NAP	12	157	0.82	0.022	< 0.01 - 0.051	µg/l
ACY	12	157	0.99	0.016	0.0072 - 0.026	µg/l
ACN	12	157	0.99	0.0074	0.0024 - 0.024	µg/l
FL	12	157	1	0.0072	0.0029 - 0.017	µg/l
PHE	12	157	1	0.046	0.017 - 0.13	µg/l
ANT	12	157	0.97	0.0056	0.0019 - 0.018	µg/l
Fluo	12	157	1	0.067	0.029 - 0.19	µg/l
Pyr	12	157	1	0.062	0.025 - 0.15	µg/l
BaA	12	157	1	0.02	0.0055 - 0.072	µg/l
Chr	12	157	1	0.04	0.012 - 0.11	µg/l
BbF	12	157	1	0.029	0.0071 - 0.094	µg/l
BkF	12	157	0.99	0.013	0.0028 - 0.043	µg/l
BaP	12	157	1	0.021	0.0051 - 0.067	µg/l
IP	12	157	1	0.021	0.0049 - 0.072	µg/l
DahA	12	157	0.89	0.0045	< 0.001 - 0.014	µg/l
BghiP	12	157	1	0.023	0.0064 - 0.075	µg/l
Phenols						
4iNP	6	27	0.78	0.11	< 0.04 - 0.17	µg/l
4tOP	6	27	0.59	0.023	< 0.02 - 0.032	µg/l
PFAS						
PFBA	6	27	0.93	0.003	0.001 - 0.0064	µg/l
PFPA	6	27	0.59	0.002	< 0.001 - 0.004	µg/l
PFHxA	6	27	0.85	0.003	< 0.001 - 0.0054	µg/l
PFHpA	6	27	0.52	0.001	< 0.001 - 0.0024	µg/l
PFOA	6	27	0.89	0.003	< 0.001 - 0.0044	µg/l
PFNA	6	27	0.15	< 0.001	< 0.001 - 0.001	µg/l
PFDA	6	27	0.41	< 0.001	< 0.001 - 0.0024	µg/l
PFUnA	6	27	0	< 0.001	< 0.001 (max. < 0.001)	µg/l
PFDoA	6	27	0	< 0.001	< 0.001 (max. < 0.001)	µg/l
PFBS	6	27	0.48	< 0.001	< 0.001 - 0.0028	µg/l

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10th – 90th percentile)	Unit
PFPeS	6	27	0	< 0.001	< 0.001 (max. < 0.001)	µg/l
PFHxS	6	27	0.037	< 0.001	< 0.001 (max. 0.001)	µg/l
PFHpS	6	27	0	< 0.001	< 0.001 (max. < 0.001)	µg/l
PFOS	6	27	0.67	0.002	< 0.001 - 0.0044	µg/l
PFDS	6	27	0	< 0.001	< 0.001 (max. < 0.001)	µg/l
H4PFOS	6	27	0.22	< 0.001	< 0.001 - 0.003	µg/l
Pharmaceuticals						
CBZ	10	145	0.84	0.049	< 0.01 - 0.18	µg/l
DCF	10	145	1	0.22	0.078 - 0.47	µg/l
MPL	10	145	0.99	0.11	0.039 - 0.29	µg/l
Biocides and Pesticides						
DCS	6	27	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
MDCS	6	27	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
TCS	12	157	0.68	0.016	< 0.01 - 0.062	µg/l
MTCS	6	27	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
IZL	6	27	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
BDF	6	27	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
DIF	6	27	0	< 0.02	< 0.02 (max. < 0.02)	µg/l
DEET	6	27	0.96	0.065	0.018 - 0.49	µg/l
DFTL	6	27	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
HC	6	27	0	< 0.004	< 0.004 (max. < 0.004)	µg/l
cHCE	6	27	0	< 0.004	< 0.004 (max. < 0.004)	µg/l
tHCE	6	27	0	< 0.004	< 0.004 (max. < 0.004)	µg/l
PMN	6	27	0.81	0.029	< 0.01 - 0.047	µg/l
PMNS	6	27	0	< 0.05	< 0.05 (max. < 0.05)	µg/l
PLN	6	27	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
DCV	6	27	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
IMI	6	27	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
1,2,4TZL	6	27	0	< 0.1	< 0.1 (max. < 0.1)	µg/l
BIT	6	27	0.19	< 0.01	< 0.01 - 0.032	µg/l
2AB	6	27	0	< 0.02	< 0.02 (max. < 0.02)	µg/l
MIT	6	27	0.07	< 0.01	< 0.01 (max. 0.023)	µg/l
OIT	6	27	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
CZIM	12	157	0.66	0.014	< 0.01 - 0.041	µg/l
CBT	6	27	0	< 0.005	< 0.005 (max. < 0.005)	µg/l
CYM	6	27	0.15	< 0.005	< 0.005 - 0.01	µg/l
DIU	12	157	0.47	< 0.01	< 0.01 - 0.037	µg/l
ISO	12	157	0.41	< 0.01	< 0.01 - 0.04	µg/l
PCZ	6	27	0.78	0.014	< 0.01 - 0.04	µg/l
TCZ	6	27	0.52	0.01	< 0.01 - 0.076	µg/l
TBY	12	157	0.81	0.023	< 0.01 - 0.06	µg/l
TBYD	6	27	0.037	< 0.01	< 0.01 (max. 0.011)	µg/l
TBYS	6	27	0.3	< 0.01	< 0.01 - 0.018	µg/l
THIA	6	27	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
ACF	6	27	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
ATR	12	157	0.013	< 0.01	< 0.01 (max. 0.045)	µg/l
BFX	6	27	0	< 0.004	< 0.004 (max. < 0.004)	µg/l
MCPP	10	145	0.82	0.021	< 0.01 - 0.088	µg/l
MET	10	145	0.23	< 0.01	< 0.01 - 0.03	µg/l
QNX	6	27	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
TBA	10	145	0.33	< 0.01	< 0.01 - 0.12	µg/l
Other organic substances						
ACE	10	145	1	2.3	1.2 - 4.8	µg/l
BTR	10	145	1	1.1	0.39 - 2.76	µg/l
4MBT	10	145	1	0.17	0.05 - 0.5	µg/l
5MBT	10	145	1	0.19	0.053 - 0.43	µg/l
DEHP	12	157	1	1.9	0.56 - 6.7	µg/l

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10th – 90th percentile)	Unit
HBCDD	6	27	0.56	0.008	< 0.005 - 0.016	µg/l
HOI	10	145	0.81	0.22	0.1 - 0.59	mg/l

Table A4.8: Statistical summary of micropollutant concentrations in SSOs.

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10th – 90th percentile)	Unit
Metals						
Ni	2	20	1	4.5	3.18 - 6.5	µg/l
Pb	2	20	1	5.9	2.82 - 11.4	µg/l
Hg	2	20	1	0.012	0.0077 - 0.029	µg/l
Cd	2	20	1	0.079	0.045 - 0.14	µg/l
PAH						
NAP	2	20	0.4	< 0.01	< 0.01 - 0.026	µg/l
ACY	2	20	0.95	0.0056	0.0012 - 0.01	µg/l
ACN	2	20	0.9	0.0064	0.0014 - 0.016	µg/l
FL	2	20	0.85	0.0058	< 0.001 - 0.016	µg/l
PHE	2	20	1	0.037	0.0095 - 0.089	µg/l
ANT	2	20	0.9	0.0098	0.0013 - 0.015	µg/l
Fluo	2	20	1	0.11	0.031 - 0.24	µg/l
Pyr	2	20	1	0.12	0.038 - 0.23	µg/l
BaA	2	20	1	0.046	0.011 - 0.077	µg/l
Chr	2	20	1	0.083	0.024 - 0.15	µg/l
BbF	2	20	1	0.062	0.015 - 0.11	µg/l
BkF	2	20	1	0.022	0.0062 - 0.052	µg/l
BaP	2	20	1	0.05	0.011 - 0.081	µg/l
IP	2	20	1	0.047	0.01 - 0.096	µg/l
DahA	2	20	1	0.0093	0.0019 - 0.02	µg/l
BghiP	2	20	1	0.059	0.015 - 0.12	µg/l
Phenols						
4iNP	2	20	0.7	0.058	< 0.04 - 0.12	µg/l
4tOP	2	20	0.85	0.062	< 0.02 - 0.26	µg/l
PFAS						
PFBA	2	20	0.85	0.006	< 0.001 - 0.011	µg/l
PFPA	2	20	0.6	0.001	< 0.001 - 0.0041	µg/l
PFHxA	2	20	0.75	0.003	< 0.001 - 0.0071	µg/l
PFHpA	2	20	0.5	< 0.001	< 0.001 - 0.0031	µg/l
PFOA	2	20	0.8	0.003	< 0.001 - 0.0081	µg/l
PFNA	2	20	0.3	< 0.001	< 0.001 - 0.002	µg/l
PFDA	2	20	0.45	< 0.001	< 0.001 - 0.005	µg/l
PFUnA	2	20	0	< 0.001	< 0.001 (max. < 0.001)	µg/l
PFDoA	2	20	0	< 0.001	< 0.001 (max. < 0.001)	µg/l
PFBS	2	20	0.65	0.002	< 0.001 - 0.003	µg/l
PFPeS	2	20	0.05	< 0.001	< 0.001 (max. 0.001)	µg/l
PFHxS	2	20	0	< 0.001	< 0.001 (max. < 0.001)	µg/l
PFHpS	2	20	0	< 0.001	< 0.001 (max. < 0.001)	µg/l
PFOS	2	20	0.65	0.002	< 0.001 - 0.0041	µg/l
PFDS	2	20	0	< 0.001	< 0.001 (max. < 0.001)	µg/l
H4PFOS	2	20	0.25	< 0.001	< 0.001 - 0.0011	µg/l
Biocides and Pesticides						
DCS	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
MDCS	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
TCS	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
MTCS	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
IZL	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
BDF	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10^{th} – 90^{th} percentile)	Unit
DIF	2	20	0	< 0.02	< 0.02 (max. < 0.02)	µg/l
DEET	2	20	0.65	0.014	< 0.01 - 0.034	µg/l
DFTL	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
HC	2	20	0	< 0.004	< 0.004 (max. < 0.004)	µg/l
cHCE	2	20	0	< 0.004	< 0.004 (max. < 0.004)	µg/l
tHCE	2	20	0	< 0.004	< 0.004 (max. < 0.004)	µg/l
PMN	2	20	0.05	< 0.01	< 0.01 (max. 0.017)	µg/l
PMNS	2	20	0	< 0.05	< 0.05 (max. < 0.05)	µg/l
PLN	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
DCV	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
IMI	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
1,2,4TZL	2	20	0	< 0.1	< 0.1 (max. < 0.1)	µg/l
BIT	2	20	0.05	< 0.01	< 0.01 (max. 0.017)	µg/l
2AB	2	20	0	< 0.02	< 0.02 (max. < 0.02)	µg/l
MIT	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
OIT	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
CZIM	2	20	0.95	0.024	0.011 - 0.046	µg/l
CBT	2	20	0	< 0.005	< 0.005 (max. < 0.005)	µg/l
CYM	2	20	0.05	< 0.005	< 0.005 (max. 0.0052)	µg/l
DIU	2	20	0.9	0.024	< 0.01 - 0.27	µg/l
ISO	2	20	0.5	< 0.01	< 0.01 - 0.066	µg/l
PCZ	2	20	0.6	0.012	< 0.01 - 0.024	µg/l
TCZ	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
TBY	2	20	1	0.027	0.02 - 0.087	µg/l
TBYD	2	20	0.25	< 0.01	< 0.01 - 0.023	µg/l
TBYS	2	20	1	0.031	0.015 - 0.15	µg/l
THIA	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
ACF	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
ATR	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
BFX	2	20	0	< 0.004	< 0.004 (max. < 0.004)	µg/l
QNX	2	20	0	< 0.01	< 0.01 (max. < 0.01)	µg/l
Other organic substances						
DEHP	2	20	1	3	1.54 - 5.91	µg/l
HBCDD	2	20	0.5	< 0.005	< 0.005 - 0.015	µg/l

Table A4.9: Statistical summary of WWTP removal rates.

Parameter	No. of sites	No. of samples	Median	80 % interquantile range (10^{th} – 90^{th} percentile)
Metals				
Fe	5	92	0.93	0.64 - 0.97
Zn	5	92	0.86	0.67 - 0.96
Ni	5	94	0.47	0.05 - 0.73
Pb	5	93	0.97	0.86 - 0.99
Hg	5	93	0.93	0.78 - 0.98
Cd	5	93	0.93	0.87 - 0.97
PAH				
NAP	5	54	0.83	0.58 - 0.9
ACY	5	81	0.89	0.46 - 0.95
ACN	5	94	0.9	0.82 - 0.96
FL	5	94	0.87	0.79 - 0.93
PHE	5	94	0.95	0.89 - 0.98
ANT	5	77	0.93	0.83 - 0.98
Fluo	5	94	0.98	0.93 - 0.99
Pyr	5	93	0.97	0.91 - 0.99
BaA	5	94	0.97	0.92 - 0.99

Parameter	No. of sites	No. of samples	Median	80 % interquantile range (10th – 90th percentile)
Chr	5	94	0.98	0.96 - 0.99
BbF	5	94	0.97	0.93 - 0.99
BkF	5	86	0.93	0.85 - 0.98
BaP	5	94	0.98	0.95 - 1
IP	5	94	0.97	0.94 - 0.99
DahA	5	40	0.91	0.83 - 0.97
BghiP	5	94	0.98	0.96 - 1
Phenols				
4iNP	5	93	0.88	0.27 - 0.95
4tOP	4	11	0.82	0.71 - 0.86
PFAS				
PFBA	5	24	0.77	0.51 - 0.94
PFPA	1	1	0.86	0.86 - 0.86
PFHxA	3	6	-0.012	-0.46 - 0.62
PFHpA	3	3	0.91	0.83 - 0.97
PFOA	4	11	0.56	0.29 - 0.95
PFNA	1	1	0.99	0.99 - 0.99
PFDA	1	2	0.97	0.96 - 0.98
PFBS	3	17	0.12	-1.3 - 0.42
PFHxS	2	2	0.72	0.51 - 0.93
PFOS	3	12	0.76	0.27 - 0.85
H4PFOS	3	10	0.79	0.29 - 0.94
Biocides and pesticides				
DCS	1	3	0.92	0.92 - 0.93
TCS	5	62	0.92	0.83 - 0.97
DEET	5	62	0.78	0.3 - 0.97
PMN	5	59	0.96	0.91 - 0.98
IMI	5	40	0	-0.4 - 0.31
1,2,4TZL	2	3	-0.25	-0.3 - 0.18
BIT	5	41	0.92	0.53 - 0.98
MIT	2	6	0.55	0.18 - 0.75
CZIM	4	18	0.27	0.045 - 0.76
CYM	3	15	0.88	0.82 - 0.91
DIU	4	42	0.071	-0.61 - 0.33
ISO	5	77	0.071	-0.37 - 0.56
PCZ	3	16	0.37	0.12 - 0.69
TCZ	3	15	0.11	-0.08 - 0.58
TBY	5	87	0.26	-0.046 - 0.58
TBYS	1	2	-0.73	-0.74 - -0.72
THIA	1	1	0.74	0.74 - 0.74
ACF	1	1	0.58	0.58 - 0.58
ATR	1	3	0.92	0.92 - 0.93
Other organic substances				
DEHP	5	94	0.91	0.78 - 0.97
HBCDD	5	35	0.81	0.75 - 0.91

Table A4.10: Statistical summary of water quality parameters in WWTP influents.

Parameter	**No. of sites**	**No. of samples**	**Freq. > LOQ**	**Median**	**80 % interquantile range (10th – 90th percentile)**	**Unit**
Conductivity	5	96	1	1,274	804 - 2,077	µS/cm
$K_{a4.3}$	5	96	1	7.14	4.35 - 11	mmol/l
TSS	5	96	1	172	108 – 287	mg/l
COD	5	96	1	356.5	186 - 688	mg/l
COD_{sol}	5	96	1	139	65 - 285	mg/l
TNb	5	96	1	77.3	40.3 - 174	mg/l

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10^{th} – 90^{th} percentile)	Unit
TNorg	5	96	1	47.6	22.2 - 95.3	mg/l
NH_4-N	5	96	1	29.3	15.3 - 78.25	mg/l
NO_3-N	5	96	1	0.11	0.04 - 1.97	mg/l
NO_2-N	5	32	0.81	0.04	0.01 - 0.63	mg/l
TP	5	96	1	6.58	2.70 - 11.4	mg/l
PO_4-P	5	96	1	4.04	1.57 - 6.97	mg/l

Table A4.11: Statistical summary of water quality parameters in WWTP effluents.

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10^{th} – 90^{th} percentile)	Unit
Conductivity	5	100	1	1,049	758 - 1,630	µS/cm
$K_{a4.3}$	5	100	1	2.52	1.8 - 3.47	mmol/l
COD	5	100	1	22.9	12.8 - 38.1	mg/l
TNb	5	99	1	8.84	4.1 - 21.1	mg/l
TN_{org}	5	100	0.37	1.4	1.4 - 9.3	mg/l
NH_4-N	49	1001	0.95	0.45	0.06 - 2.40	mg/l
NO_3-N	49	1001	1	5.06	1.19 - 9.84	mg/l
NO_2-N	5	33	0.91	0.09	0.02 - 0.17	mg/l
TP	5	100	1	0.32	0.1 - 0.6	mg/l

Table A4.12: Statistical summary of water quality parameters in CSOs.

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10^{th} – 90^{th} percentile)	Unit
pH	12	167	1	6.7	6.4 - 7	-
Conductivity	12	167	1	190	106 - 329	µS/cm
$K_{a4.3}$	6	20	1	1.85	0.9 - 2.71	mmol/l
TSS	12	168	0.99	53	23.6 - 152.4	mg/l
COD	12	168	1	63	28.3 - 142	mg/l
COD_{sol}	6	20	1	29	17.6 - 60.3	mg/l
TNb	12	168	1	6.21	3.75 - 11.6	mg/l
NH_4-N	6	23	1	5.67	2.13 - 11.02	mg/l
NO_3-N	6	23	0.7	0.20	0.07 - 0.40	mg/l
TP	12	167	1	1.02	0.51 - 2.05	mg/l
PO_4-P	12	167	1	0.45	0.24 - 1.03	mg/l

Table A4.13: Statistical summary of water quality parameters in SSOs.

Parameter	No. of sites	No. of samples	Freq. > LOQ	Median	80 % interquantile range (10^{th} – 90^{th} percentile)	Unit
pH	2	20	1	6.8	6.5 - 7.3	-
Conductivity	2	20	1	340	100 – 1.652	µS/cm
$K_{a4.3}$	2	18	1	0.93	0.65 - 2.21	mmol/l
TSS	2	19	1	36.7	15.0 - 56.2	mg/l
COD	2	20	1	42.1	27.2 - 58.8	mg/l
COD_{sol}	2	19	1	19.3	11.5 - 35.7	mg/l
TNb	2	20	1	3.29	1.78 - 4.39	mg/l
NH_4-N	2	20	1	0.49	0.14 - 1.80	mg/l
NO_3-N	2	20	1	0.96	0.54 - 1.86	mg/l
TP	2	20	1	0.25	0.13 - 0.35	mg/l
PO_4-P	2	20	0.6	0.05	0.025 - 0.116	mg/l

Table A4.14: Coefficients of variation (CV) of site medians and of samples per site for selected micropollutants (only shown if analysed at ≥ 10 sites with ≥ 50 % values > LOQ).

Group	Parameter	WWTP effluent		CSO	
		CV of site medians	Mean CV of samples per site	CV of site medians	Mean CV of samples per site
Metals	Ni	0.36	0.33	0.65	0.80
	Pb	0.55	0.67	0.76	0.76
	Hg	0.48	0.80	0.85	0.67
	Cd	0.63	0.70	1.78	0.77
PAH	NAP	-	-	0.46	0.81
	ACY	-	-	0.33	0.47
	ACN	0.86	0.69	0.59	0.83
	FL	0.47	0.48	0.4	0.71
	PHE	0.5	0.49	0.41	0.68
	ANT	-	-	0.49	0.76
	Fluo	1.21	0.62	0.4	0.65
	Pyr	1.13	0.64	0.37	0.65
	BaA	-	-	0.52	0.79
	Chr	-	-	0.48	0.74
	BbF	-	-	0.52	0.77
	BkF	-	-	0.54	0.80
	BaP	-	-	0.51	0.79
	IP	-	-	0.54	0.82
	DahA	-	-	0.55	0.84
	BghiP	-	-	0.48	0.77
Phenols	4iNP	2.13	0.52	-	-
PFAS	PFBA	0.68	1.02	-	-
	PFPA	2.07	0.54	-	-
	PFHxA	2.72	0.4	-	-
	PFHpA	1.25	0.71	-	-
	PFOA	2.77	0.58	-	-
	PFBS	1.77	0.51	-	-
	PFOS	1.79	0.71	-	-
Biocides and pesticides	TCS	0.39	0.29	0.72	0.88
	DEET	0.63	0.72	-	-
	IMI	0.66	0.46	-	-
	1,2,4TZL	0.5	0.36	-	-
	2AB	0.53	0.44	-	-
	MIT	0.79	0.66	-	-
	CZIM	1.6	0.54	0.71	0.54
	DIU	0.57	0.86	-	-
	ISO	0.95	0.95	-	-
	PCZ	1.24	0.51	-	-
	TBY	0.63	0.62	0.69	0.59
Pharmaceuticals	CBZ	-	-	0.94	0.53
	DCF	-	-	0.41	0.53
Other organic substances	ACE	-	-	0.41	0.37
	DEHP	0.61	1.08	0.70	0.70

Table A4.15: Statistical summary of volume-weighted site mean concentrations in WWTP effluents.

Parameter	No. of sites	No. of samples considered	Median	80 % interquantile range (10th – 90th percentile)	Unit
Metals					
Fe	5	93	0.067	0.039 - 0.4	mg/l
Zn	5	93	0.027	< 0.02 - 0.044	mg/l
Ni	49	989	4.27	2.81 - 6.68	µg/l

Parameter	No. of sites	No. of samples considered	Median	80 % interquantile range (10th – 90th percentile)	Unit
Pb	49	989	0.16	< 0.1 - 0.3	µg/l
Hg	49	989	0.0022	0.0014 - 0.0052	µg/l
Cd	49	989	0.0066	0.0033 - 0.014	µg/l
PAH					
NAP	49	988	< 0.01	< 0.01 - 0.012	µg/l
ACY	49	988	< 0.001	< 0.001	µg/l
ACN	49	988	0.0012	< 0.001 - 0.0054	µg/l
FL	49	988	0.0018	0.0012 - 0.0036	µg/l
PHE	49	989	0.0043	0.003 - 0.011	µg/l
ANT	49	988	< 0.001	< 0.001	µg/l
Fluo	49	988	0.0023	< 0.001 - 0.0073	µg/l
Pyr	49	988	0.0024	< 0.001 - 0.0056	µg/l
BaA	49	988	< 0.001	< 0.001	µg/l
Chr	49	988	< 0.001	< 0.001 - 0.0021	µg/l
BbF	49	988	< 0.001	< 0.001	µg/l
BkF	49	988	< 0.001	< 0.001	µg/l
BaP	49	988	< 0.0005	< 0.0005	µg/l
IP	49	988	< 0.0005	< 0.0005	µg/l
DahA	49	988	< 0.001	< 0.001	µg/l
BghiP	49	988	< 0.0005	< 0.0005	µg/l
Phenols					
4iNP	49	988	0.04	< 0.04 - 0.21	µg/l
4tOP	49	988	< 0.02	< 0.02 - 0.026	µg/l
PFAS					
PFBA	49	989	0.0057	0.0025 - 0.011	µg/l
PFPA	49	989	0.0041	0.0013 - 0.012	µg/l
PFHxA	49	989	0.006	0.0028 - 0.016	µg/l
PFHpA	49	989	0.0013	< 0.001 - 0.0031	µg/l
PFOA	49	989	0.0058	0.0031 - 0.0093	µg/l
PFNA	49	989	< 0.001	< 0.001	µg/l
PFDA	49	989	< 0.001	< 0.001 - 0.0014	µg/l
PFUnA	49	989	< 0.001	< 0.001	µg/l
PFDoA	49	989	< 0.001	< 0.001	µg/l
PFBS	49	989	0.0032	0.0013 - 0.012	µg/l
PFPeS	49	989	< 0.001	< 0.001	µg/l
PFHxS	49	989	< 0.001	< 0.001 - 0.0036	µg/l
PFHpS	49	989	< 0.001	< 0.001	µg/l
PFOS	49	989	0.0039	0.0016 - 0.013	µg/l
PFDS	49	989	< 0.001	< 0.001	µg/l
H4PFOS	49	989	< 0.001	< 0.001 - 0.0033	µg/l
Biocides and Pesticides					
DCS	29	313	< 0.01	< 0.01	µg/l
MDCS	29	313	< 0.01	< 0.01	µg/l
TCS	29	313	0.027	0.016 - 0.044	µg/l
MTCS	29	313	< 0.01	< 0.01	µg/l
IZL	29	313	< 0.01	< 0.01	µg/l
BDF	29	313	< 0.01	< 0.01	µg/l
DIF	49	988	< 0.02	< 0.02	µg/l
DEET	29	313	0.098	0.054 - 0.19	µg/l
DFTL	29	313	< 0.01	< 0.01	µg/l
HC	49	988	< 0.004	< 0.004	µg/l
cHCE	49	988	< 0.004	< 0.004	µg/l
tHCE	49	988	< 0.004	< 0.004	µg/l
PMN	29	313	< 0.01	< 0.01	µg/l
PMNS	29	313	< 0.05	< 0.05	µg/l
PLN	29	313	< 0.01	< 0.01	µg/l
DCV	49	989	< 0.01	< 0.01	µg/l

Parameter	No. of sites	No. of samples considered	Median	80 % interquantile range (10th – 90th percentile)	Unit
IMI	29	313	0.018	< 0.01 - 0.038	µg/l
1,2,4TZL	29	313	0.35	0.16 - 0.59	µg/l
BIT	29	313	< 0.01	< 0.01	µg/l
2AB	29	313	0.023	< 0.02 - 0.045	µg/l
MIT	29	179	< 0.01	< 0.01 - 0.024	µg/l
OIT	29	313	< 0.01	< 0.01	µg/l
CZIM	29	313	0.016	< 0.01 - 0.048	µg/l
CBT	49	989	< 0.005	< 0.005	µg/l
CYM	49	988	< 0.005	< 0.005	µg/l
DIU	49	989	0.02	< 0.01 - 0.037	µg/l
ISO	49	989	0.02	< 0.01 - 0.06	µg/l
PCZ	29	313	0.012	< 0.01 - 0.047	µg/l
TCZ	29	313	< 0.01	< 0.01 - 0.049	µg/l
TBY	49	989	0.032	0.013 - 0.066	µg/l
TBYD	29	179	< 0.01	< 0.01	µg/l
TBYS	29	179	0.024	< 0.01 - 0.072	µg/l
THIA	29	313	< 0.01	< 0.01	µg/l
ACF	49	989	< 0.01	< 0.01	µg/l
ATR	49	989	< 0.01	< 0.01	µg/l
BFX	49	989	< 0.004	< 0.004	µg/l
QNX	49	989	< 0.01	< 0.01	µg/l
Other organic substances					
DEHP	49	988	2.6	1.09 - 5.74	µg/l
HBCDD	49	989	< 0.005	< 0.005	µg/l

Table A4.16: Statistical summary of volume-weighted site mean concentrations in CSOs.

Parameter	No. of sites	No. of samples considered	Median	80 % interquantile range (10th – 90th percentile)	Unit
Metals					
Fe	10	141	1285	893 - 1813	µg/l
Zn	10	141	137	85.5 - 196	µg/l
Cu	10	141	39.1	29.7 - 56.3	µg/l
Ni	11	143	3.09	2.43 - 5.06	µg/l
Pb	11	143	4.01	3.35 - 8.62	µg/l
Cr	10	141	4.82	3.72 - 6.48	µg/l
Hg	11	143	0.014	0.011 - 0.021	µg/l
Cd	11	143	0.067	0.054 - 0.11	µg/l
Bi	10	133	0.35	0.14 - 0.58	µg/l
Mo	10	133	0.66	0.47 - 1.95	µg/l
Sb	10	133	0.78	0.45 - 1.09	µg/l
Sn	10	133	2.41	1.67 - 3.56	µg/l
PAH					
NAP	11	143	0.023	0.012 - 0.038	µg/l
ACY	11	143	0.015	0.012 - 0.021	µg/l
ACN	11	143	0.011	0.0065 - 0.017	µg/l
FL	11	143	0.0084	0.0066 - 0.012	µg/l
PHE	11	143	0.057	0.028 - 0.079	µg/l
ANT	11	143	0.0069	0.0041 - 0.0096	µg/l
Fluo	11	143	0.077	0.053 - 0.14	µg/l
Pyr	11	143	0.064	0.057 - 0.11	µg/l
BaA	11	143	0.025	0.018 - 0.039	µg/l
Chr	11	143	0.043	0.035 - 0.08	µg/l
BbF	11	143	0.033	0.024 - 0.079	µg/l
BkF	11	143	0.015	0.011 - 0.034	µg/l
BaP	11	143	0.025	0.018 - 0.051	µg/l

Parameter	**No. of sites**	**No. of samples considered**	**Median**	**80 % interquantile range (10th – 90th percentile)**	**Unit**
IP	11	143	0.023	0.017 - 0.057	µg/l
DahA	11	143	0.0055	0.0033 - 0.0098	µg/l
BghiP	11	143	0.024	0.018 - 0.056	µg/l
Phenols					
4iNP	5	14	< 0.04	< 0.04 - 0.16	µg/l
4tOP	5	14	< 0.02	< 0.02 - 0.024	µg/l
PFAS					
PFBA	5	14	0.002	0.0013 - 0.005	µg/l
PFPA	5	14	< 0.001	< 0.001 - 0.003	µg/l
PFHxA	5	14	0.002	< 0.001 - 0.0058	µg/l
PFHpA	5	14	< 0.001	< 0.001 - 0.0024	µg/l
PFOA	5	14	0.001	< 0.001 - 0.0045	µg/l
PFNA	5	14	< 0.001	< 0.001	µg/l
PFDA	5	14	< 0.001	< 0.001 - 0.002	µg/l
PFUnA	5	14	< 0.001	< 0.001	µg/l
PFDoA	5	14	< 0.001	< 0.001	µg/l
PFBS	5	14	< 0.001	< 0.001 - 0.002	µg/l
PFPeS	5	14	< 0.001	< 0.001	µg/l
PFHxS	5	14	< 0.001	< 0.001	µg/l
PFHpS	5	14	< 0.001	< 0.001	µg/l
PFOS	5	14	< 0.001	< 0.001 - 0.0032	µg/l
PFDS	5	14	< 0.001	< 0.001	µg/l
H4PFOS	5	14	< 0.001	< 0.001	µg/l
Pharmaceuticals					
CBZ	10	141	0.067	0.015 - 0.12	µg/l
DCF	10	141	0.25	0.15 - 0.32	µg/l
MPL	10	141	0.12	0.058 - 0.28	µg/l
Biocides and Pesticides					
DCS	5	14	< 0.01	< 0.01	µg/l
MDCS	5	14	< 0.01	< 0.01	µg/l
TCS	11	143	0.024	0.01 - 0.027	µg/l
MTCS	5	14	< 0.01	< 0.01	µg/l
IZL	5	14	< 0.01	< 0.01	µg/l
BDF	5	14	< 0.01	< 0.01	µg/l
DIF	5	14	< 0.02	< 0.02	µg/l
DEET	5	14	0.058	0.019 - 0.19	µg/l
DFTL	5	14	< 0.01	< 0.01	µg/l
HC	5	14	< 0.004	< 0.004	µg/l
cHCE	5	14	< 0.004	< 0.004	µg/l
tHCE	5	14	< 0.004	< 0.004	µg/l
PMN	5	14	0.015	< 0.01 - 0.045	µg/l
PMNS	5	14	< 0.05	< 0.05	µg/l
PLN	5	14	< 0.01	< 0.01	µg/l
DCV	5	14	< 0.01	< 0.01	µg/l
IMI	5	14	< 0.01	< 0.01	µg/l
1,2,4TZL	5	14	< 0.1	< 0.1	µg/l
BIT	5	14	< 0.01	< 0.01 - 0.018	µg/l
2AB	5	14	< 0.02	< 0.02 - < 0.02	µg/l
MIT	5	14	< 0.01	< 0.01	µg/l
OIT	5	14	< 0.01	< 0.01	µg/l
CZIM	11	143	0.014	< 0.01 - 0.042	µg/l
CBT	5	14	< 0.005	< 0.005	µg/l
CYM	5	14	< 0.005	< 0.005	µg/l
DIU	11	143	< 0.01	< 0.01 - 0.041	µg/l
ISO	11	143	0.011	< 0.01 - 0.036	µg/l
PCZ	5	14	0.013	< 0.01 - 0.018	µg/l
TCZ	5	14	0.011	< 0.01 - 0.013	µg/l

Parameter	No. of sites	No. of samples considered	Median	80 % interquantile range (10th – 90th percentile)	Unit
TBY	11	143	0.028	< 0.01 - 0.065	µg/l
TBYD	5	14	< 0.01	< 0.01	µg/l
TBYS	5	14	< 0.01	< 0.01 - 0.021	µg/l
THIA	5	14	< 0.01	< 0.01	µg/l
ACF	5	14	< 0.01	< 0.01	µg/l
ATR	11	143	< 0.01	< 0.01	µg/l
BFX	5	14	< 0.004	< 0.004	µg/l
MCPP	10	141	0.031	0.017 - 0.077	µg/l
MET	10	141	< 0.01	< 0.01	µg/l
QNX	5	14	< 0.01	< 0.01	µg/l
TBA	10	141	< 0.01	< 0.01 - 0.051	µg/l
Other organic substances					
ACE	10	141	2.53	1.67 - 3.77	µg/l
BTR	10	141	1.25	0.71 - 2.58	µg/l
4MBT	10	141	0.21	0.073 - 0.39	µg/l
5MBT	10	141	0.21	0.11 - 0.32	µg/l
DEHP	11	143	2.51	1.25 - 3.83	µg/l
HBCDD	5	14	< 0.005	< 0.005 - 0.0082	µg/l
HOI	10	141	0.26	0.2 - 0.5	mg/l

Table A4.17: Statistical summary of volume-weighted site mean concentrations in SSOs.

Parameter	No. of sites	No. of samples considered	Median	Min	Max	Unit
Metals						
Ni	2	18	4.71	4.60	4.83	µg/l
Pb	2	18	6.69	5.68	7.69	µg/l
Hg	2	18	0.015	0.012	0.018	µg/l
Cd	2	18	0.088	0.076	0.101	µg/l
PAH						
NAP	2	18	< 0.01	< 0.01	0.013	µg/l
ACY	2	18	0.0063	0.0061	0.0064	µg/l
ACN	2	18	0.0093	0.0070	0.0116	µg/l
FL	2	18	0.0074	0.0065	0.0082	µg/l
PHE	2	18	0.055	0.044	0.067	µg/l
ANT	2	18	0.011	0.010	0.011	µg/l
Fluo	2	18	0.14	0.10	0.17	µg/l
Pyr	2	18	0.14	0.11	0.17	µg/l
BaA	2	18	0.05	0.047	0.054	µg/l
Chr	2	18	0.098	0.088	0.108	µg/l
BbF	2	18	0.076	0.074	0.077	µg/l
BkF	2	18	0.031	0.030	0.032	µg/l
BaP	2	18	0.059	0.058	0.060	µg/l
IP	2	18	0.062	0.061	0.063	µg/l
DahA	2	18	0.012	0.012	0.013	µg/l
BghiP	2	18	0.074	0.069	0.079	µg/l
Phenols						
4iNP	2	18	0.087	0.034	0.141	µg/l
4tOP	2	18	0.12	0.034	0.204	µg/l
PFAS						
PFBA	2	18	0.0053	0.0042	0.0064	µg/l
PFPA	2	18	0.0015	0.0012	0.0017	µg/l
PFHxA	2	18	0.0028	0.0024	0.0032	µg/l
PFHpA	2	18	0.0011	< 0.001	0.0013	µg/l
PFOA	2	18	0.0031	0.0018	0.0044	µg/l
PFNA	2	18	< 0.001	< 0.001	< 0.001	µg/l

Parameter	No. of sites	No. of samples considered	Median	Min	Max	Unit
PFDA	2	18	< 0.001	< 0.001	< 0.001	µg/l
PFUnA	2	18	< 0.001	< 0.001	< 0.001	µg/l
PFDoA	2	18	< 0.001	< 0.001	< 0.001	µg/l
PFBS	2	18	0.0017	0.0013	0.0021	µg/l
PFPeS	2	18	< 0.001	< 0.001	< 0.001	µg/l
PFHxS	2	18	< 0.001	< 0.001	< 0.001	µg/l
PFHpS	2	18	< 0.001	< 0.001	< 0.001	µg/l
PFOS	2	18	0.0019	0.0013	0.0025	µg/l
PFDS	2	18	< 0.001	< 0.001	< 0.001	µg/l
H4PFOS	2	18	< 0.001	< 0.001	< 0.001	µg/l
Biocides and Pesticides						
DCS	2	18	< 0.01	< 0.01	< 0.01	µg/l
MDCS	2	18	< 0.01	< 0.01	< 0.01	µg/l
TCS	2	18	< 0.01	< 0.01	< 0.01	µg/l
MTCS	2	18	< 0.01	< 0.01	< 0.01	µg/l
IZL	2	18	< 0.01	< 0.01	< 0.01	µg/l
BDF	2	18	< 0.01	< 0.01	< 0.01	µg/l
DIF	2	18	< 0.02	< 0.02	< 0.02	µg/l
DEET	2	18	0.015	< 0.01	0.024	µg/l
DFTL	2	18	< 0.01	< 0.01	< 0.01	µg/l
HC	2	18	< 0.004	< 0.004	< 0.004	µg/l
cHCE	2	18	< 0.004	< 0.004	< 0.004	µg/l
tHCE	2	18	< 0.004	< 0.004	< 0.004	µg/l
PMN	2	18	< 0.01	< 0.01	< 0.01	µg/l
PMNS	2	18	< 0.05	< 0.05	< 0.05	µg/l
PLN	2	18	< 0.01	< 0.01	< 0.01	µg/l
DCV	2	18	< 0.01	< 0.01	< 0.01	µg/l
IMI	2	18	< 0.01	< 0.01	< 0.01	µg/l
1,2,4TZL	2	18	< 0.1	< 0.1	< 0.1	µg/l
BIT	2	18	< 0.01	< 0.01	< 0.01	µg/l
2AB	2	18	< 0.02	< 0.02	< 0.02	µg/l
MIT	2	18	< 0.01	< 0.01	< 0.01	µg/l
OIT	2	18	< 0.01	< 0.01	< 0.01	µg/l
CZIM	2	18	0.029	0.018	0.040	µg/l
CBT	2	18	< 0.005	< 0.005	< 0.005	µg/l
CYM	2	18	< 0.005	< 0.005	< 0.005	µg/l
DIU	2	18	0.1	0.015	0.189	µg/l
ISO	2	18	0.024	< 0.01	0.044	µg/l
PCZ	2	18	0.012	< 0.01	0.019	µg/l
TCZ	2	18	< 0.01	< 0.01	< 0.01	µg/l
TBY	2	18	0.039	0.033	0.045	µg/l
TBYD	2	18	< 0.01	< 0.01	< 0.01	µg/l
TBYS	2	18	0.067	0.021	0.113	µg/l
THIA	2	18	< 0.01	< 0.01	< 0.01	µg/l
ACF	2	18	< 0.01	< 0.01	< 0.01	µg/l
ATR	2	18	< 0.01	< 0.01	< 0.01	µg/l
BFX	2	18	< 0.004	< 0.004	< 0.004	µg/l
QNX	2	18	< 0.01	< 0.01	< 0.01	µg/l
Other organic substances						
DEHP	2	18	3.43	2.61	4.26	µg/l
HBCDD	2	18	0.0059	< 0.005	0.0094	µg/l

Table A4.18: Annual per capita loads from WWTPs and CSOs, and the percentage of site mean concentrations (SMCs) >LOQ used for the calculation. SMCs <LOQ were replaced by LOQ/2. Per capita loads are not reported if <25% of SMCs were >LOQ.

Group	**Substance**	**WWTP (n=47, except TCS, CZIM: n=28)**		**CSO (n=9)**	
		Median load (80 % interquantile) [mg·capita^{-1}·year^{-1}]	Percentage of SMC > LOQ [%]	Median load (80 % interquantile) [mg·capita^{-1}·year^{-1}]	Percentage of SMC > LOQ [%]
Metals	Ni	323.51 (177 - 547)	100	23.82 (13 - 90.8)	100
	Pb	9.83 (2.41 - 40.6)	70	32.09 (21.7 - 146)	100
	Hg	0.17 (0.067 - 0.45)	100	0.17 (0.075 - 0.39)	100
	Cd	0.45 (0.21 - 1.59)	98	0.73 (0.31 - 2.24)	100
PAH	NAP	0.43 (0.22 - 1.27)	28	0.16 (0.093 - 0.8)	89
	ACY	-	9	0.17 (0.075 - 0.62)	100
	ACN	0.08 (0.029 - 0.36)	60	0.08 (0.051 - 0.3)	100
	FL	0.12 (0.05 - 0.31)	94	0.07 (0.044 - 0.26)	100
	PHE	0.31 (0.16 - 0.87)	100	0.41 (0.27 - 2.26)	100
	ANT	-	0	0.05 (0.035 - 0.22)	100
	Fluo	0.17 (0.045 - 0.64)	89	0.62 (0.47 - 3.74)	100
	Pyr	0.14 (0.027 - 0.5)	85	0.50 (0.41 - 2.82)	100
	BaA	-	6	0.20 (0.14 - 1.05)	100
	Chr	0.04 (0.021 - 0.2)	28	0.33 (0.27 - 2.04)	100
	BbF	-	6	0.28 (0.19 - 1.49)	100
	BkF	-	2	0.14 (0.084 - 0.68)	100
	BaP	0.02 (0.0098 - 0.13)	28	0.18 (0.14 - 1.05)	100
	IP	-	11	0.22 (0.13 - 1.04)	100
	DahA	-	0	0.05 (0.025 - 0.2)	89
	BghiP	-	17	0.21 (0.16 - 1.1)	100
	TCS	2.01 (0.77 - 3.08)	100	0.15 (0.079 - 0.72)	89

Group	Substance	WWTP (n=47, except TCS, CZIM: n=28)		CSO (n=9)	
		Median load (80 % interquantile) [$mg \cdot capita^{-1} \cdot year^{-1}$]	Percentage of SMC > LOQ [%]	Median load (80 % interquantile) [$mg \cdot capita^{-1} \cdot year^{-1}$]	Percentage of SMC > LOQ [%]
Biocides and Pesticides	CZIM	1.12 (0.28 - 2.19)	75	0.12 (0.04 - 0.76)	67
	DIU	1.23 (0.4 - 2.79)	72	0.11 (0.035 - 0.95)	44
	ISO	1.32 (0.26 - 5.41)	74	0.12 (0.035 - 0.89)	44
	TBY	2.55 (0.78 - 5)	94	0.14 (0.076 - 1.04)	78
Others	ACE	-	-	22.15 (9.52 - 70.5)	100
	DEHP	175.95 (72.7 - 425)	100	19.72 (10.1 - 65.1)	100

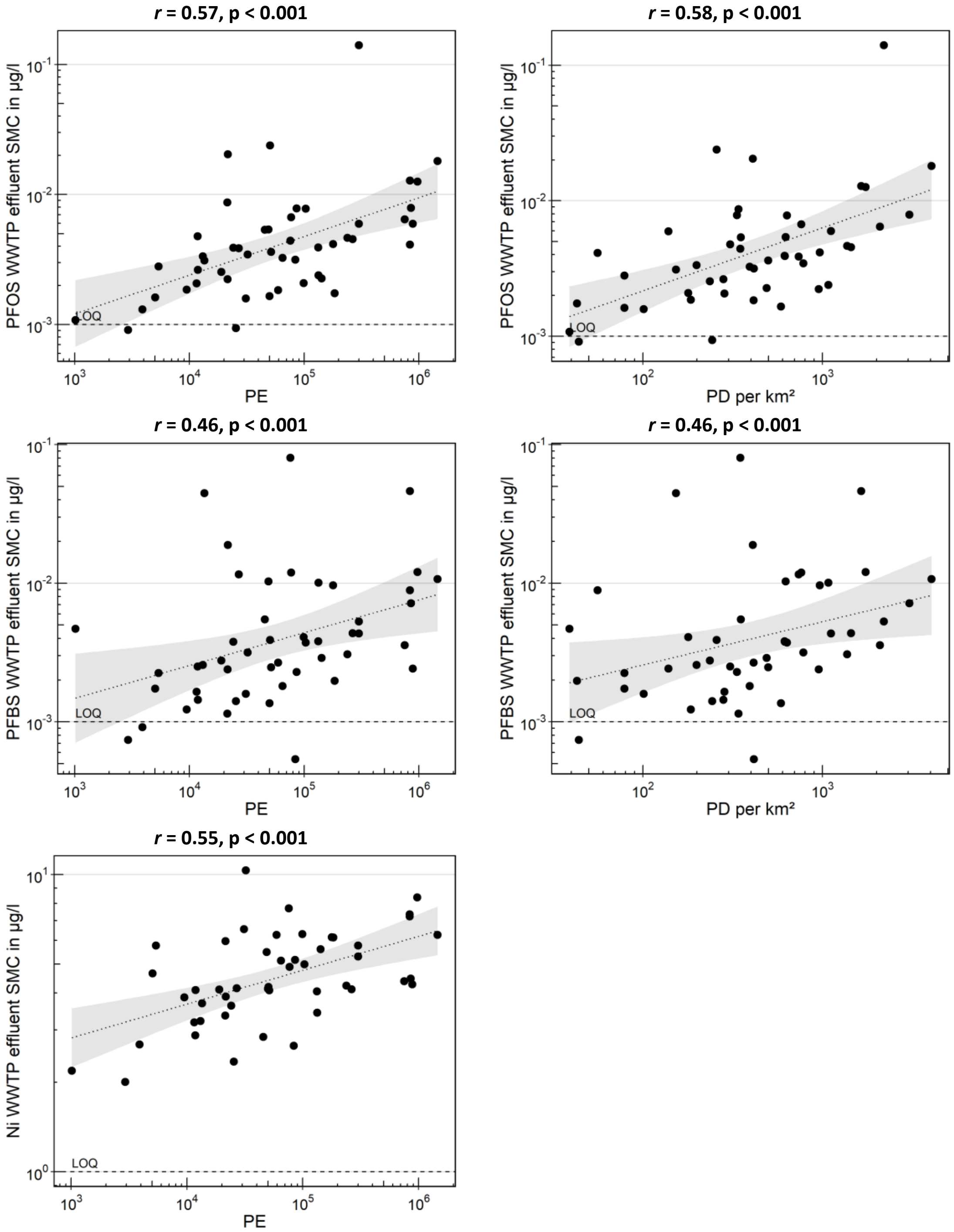
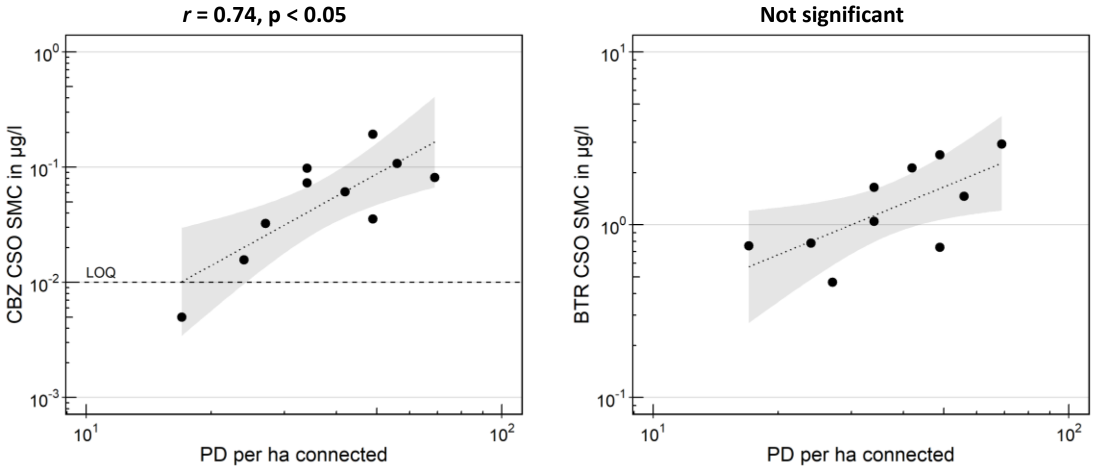


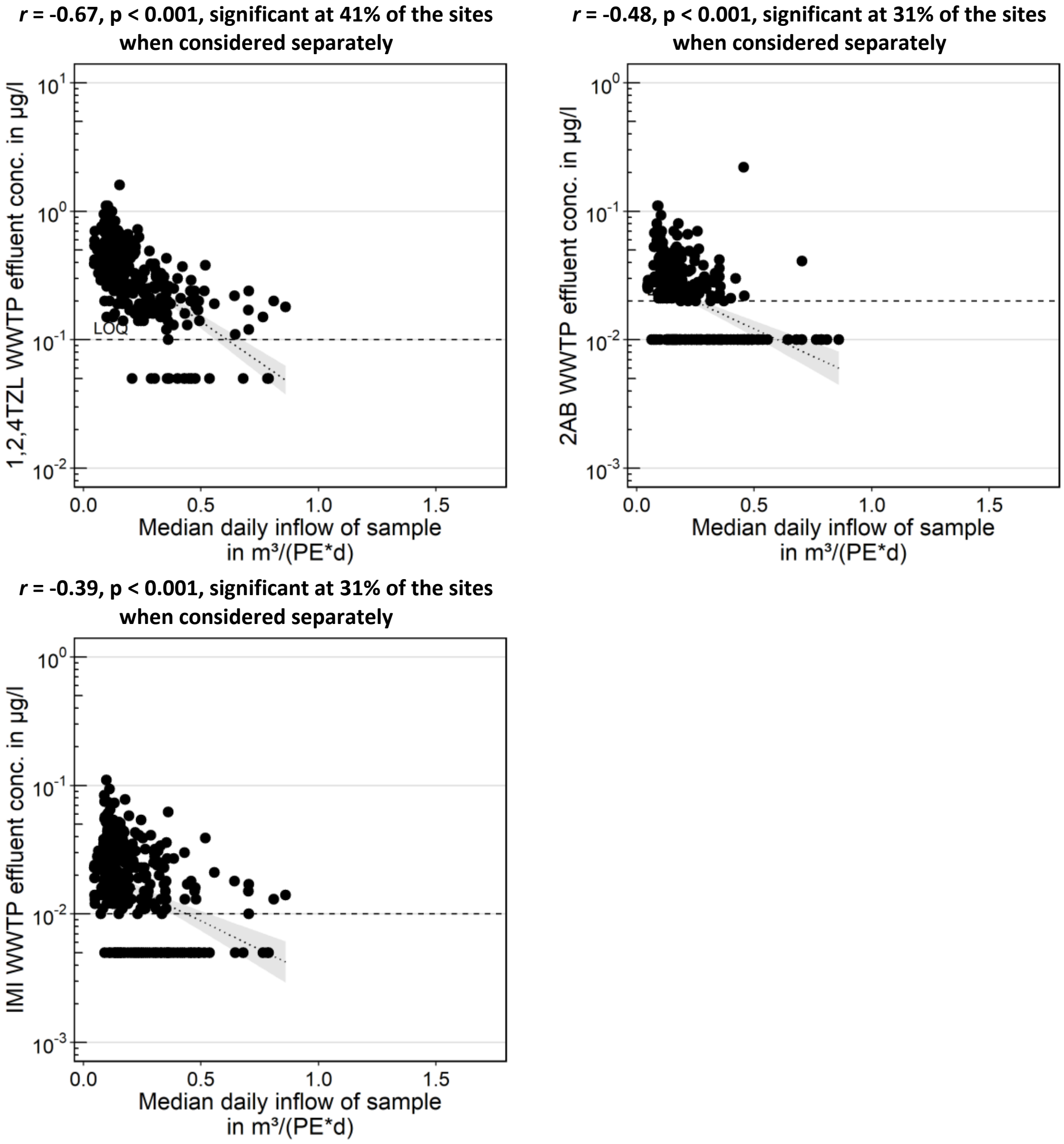
Figure A4.2: Spearman rank correlations between the number of population equivalents (PE) connected to the WWTP (left) or the average population density (PD) of the municipality (right) and WWTP effluent site mean concentrations (SMC): PFOS, PFBS, and Ni. Only substances analysed at ≥10 sites with ≥50% values >LOQ were tested.



r = 0.74, p < 0.05

Not significant

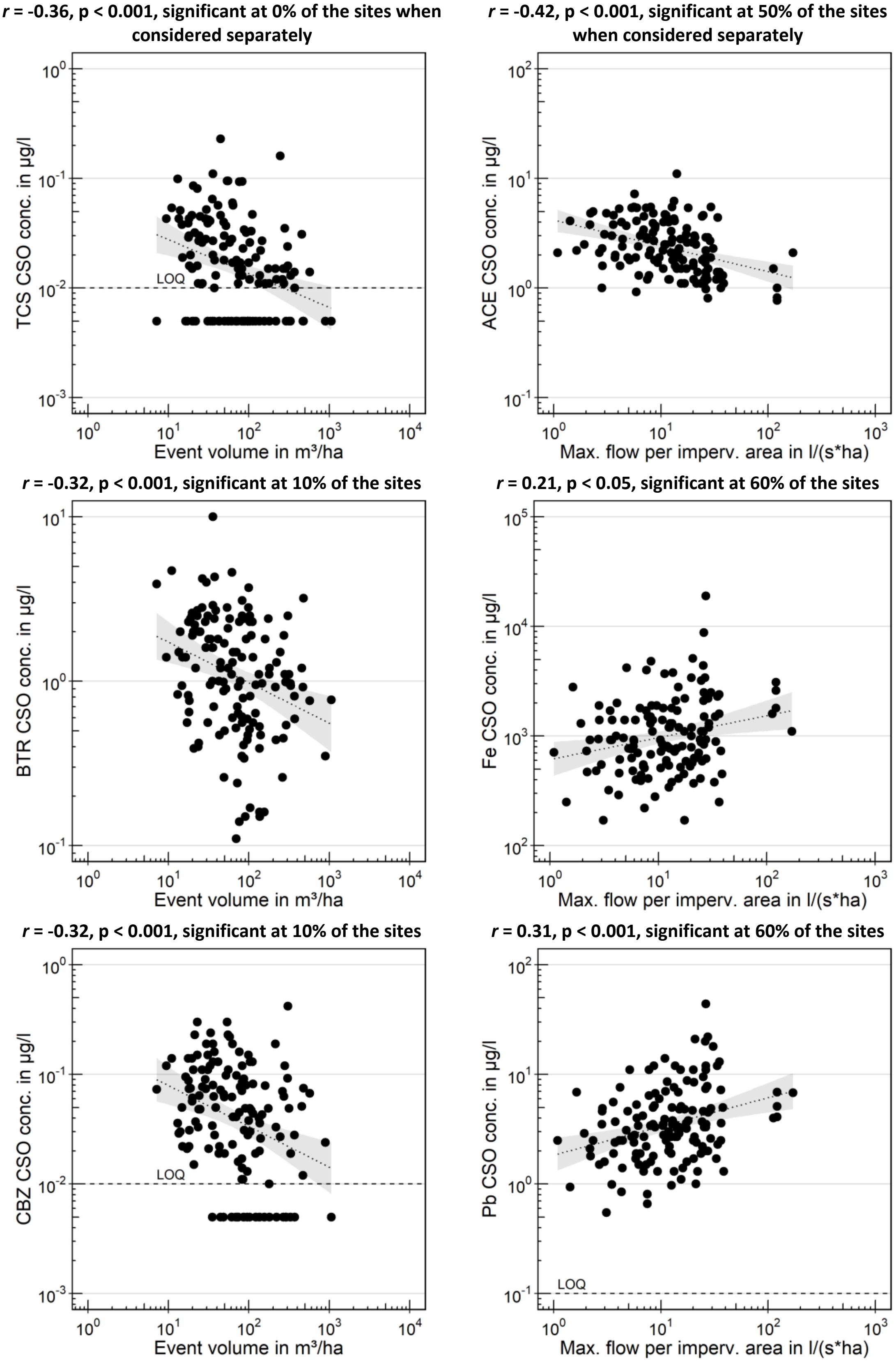
Figure A4.3: Spearman rank correlations between population density (PD) and CSO site mean concentrations (SMC): CBZ and BTR. Only substances analysed at ≥10 sites with ≥50% values >LOQ were tested.


***r* = -0.67, p < 0.001, significant at 41% of the sites when considered separately**

***r* = -0.48, p < 0.001, significant at 31% of the sites when considered separately**

***r* = -0.39, p < 0.001, significant at 31% of the sites when considered separately**

Figure A4.4: Spearman rank correlations between median daily inflow (m³/PE) into the WWTP and WWTP effluent concentrations: 1,2,4TZL, 2AB, and IMI. Only substances analysed at ≥10 sites with ≥50% values >LOQ were tested.



r = -0.36, p < 0.001, significant at 0% of the sites when considered separately

r = -0.42, p < 0.001, significant at 50% of the sites when considered separately

r = -0.32, p < 0.001, significant at 10% of the sites

r = 0.21, p < 0.05, significant at 60% of the sites

r = -0.32, p < 0.001, significant at 10% of the sites

r = 0.31, p < 0.001, significant at 60% of the sites

Figure A4.5: Spearman rank correlations between event volume (left) or maximum flow (right) and CSO concentrations: TCS, BTR, CBZ, ACE, Fe, and Pb. Only substances analysed at ≥10 sites with ≥50% values >LOQ were tested.

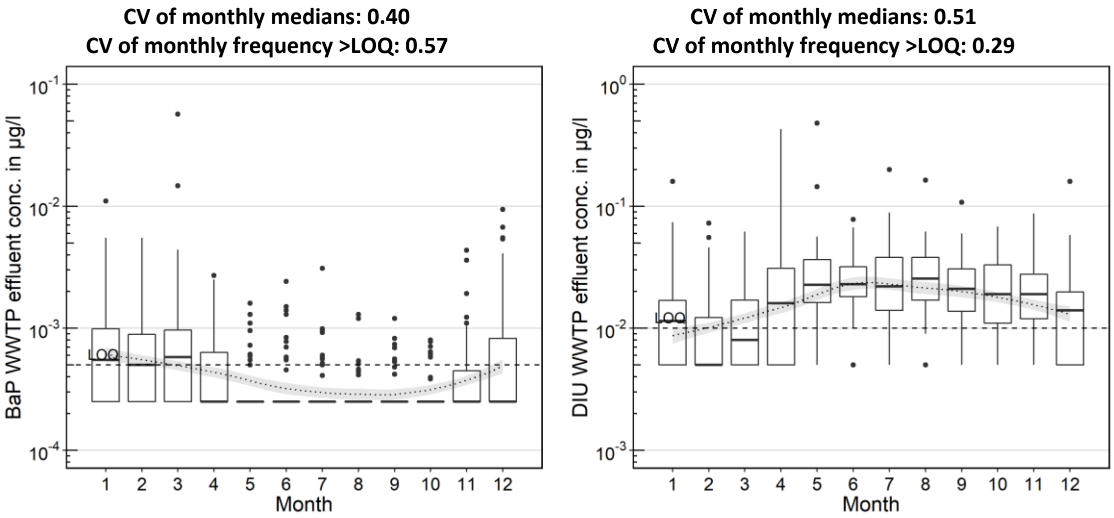


Figure A4.6: Seasonal trends of WWTP effluent concentrations grouped by the month of sampling: BaP and DIU. The coefficient of variation (CV) of monthly medians and the CV of the monthly frequency of values >LOQ were assessed. Significant concentration differences between months were identified using the Kruskal-Wallis test, and trends were identified by visual inspection of plots. Only substances analysed during at least 10 months with ≥5% of values >LOQ were tested.

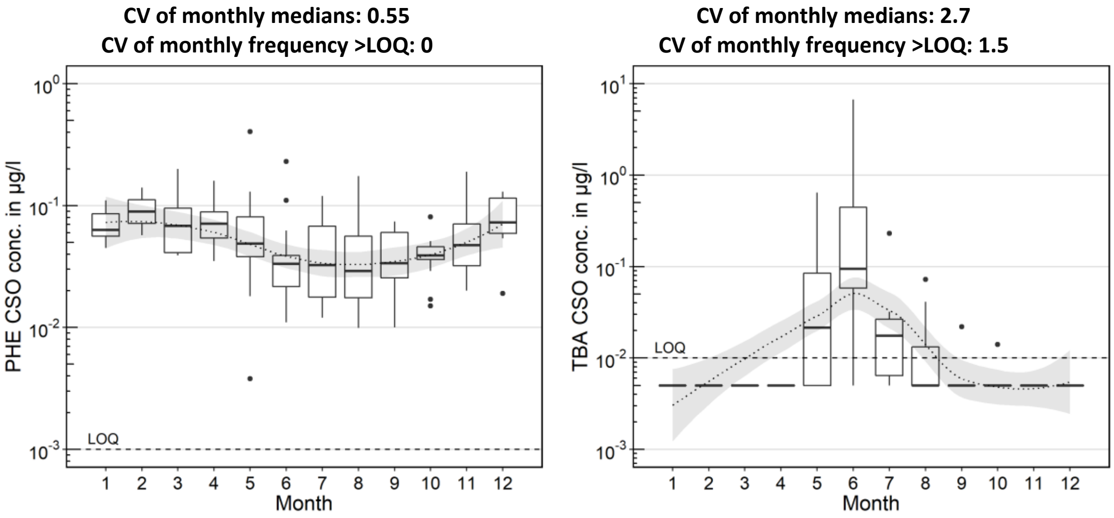


Figure A4.7: Seasonal trends of CSO concentrations grouped by the month of sampling: PHE and TBA. The coefficient of variation (CV) of monthly medians and the CV of the monthly frequency of values >LOQ were assessed. Significant concentration differences between months were identified using the Kruskal-Wallis test, and trends were identified by visual inspection of plots. Only substances analysed during at least 10 months with ≥5% of values >LOQ were tested.

Supplementary Material to Chapter 5

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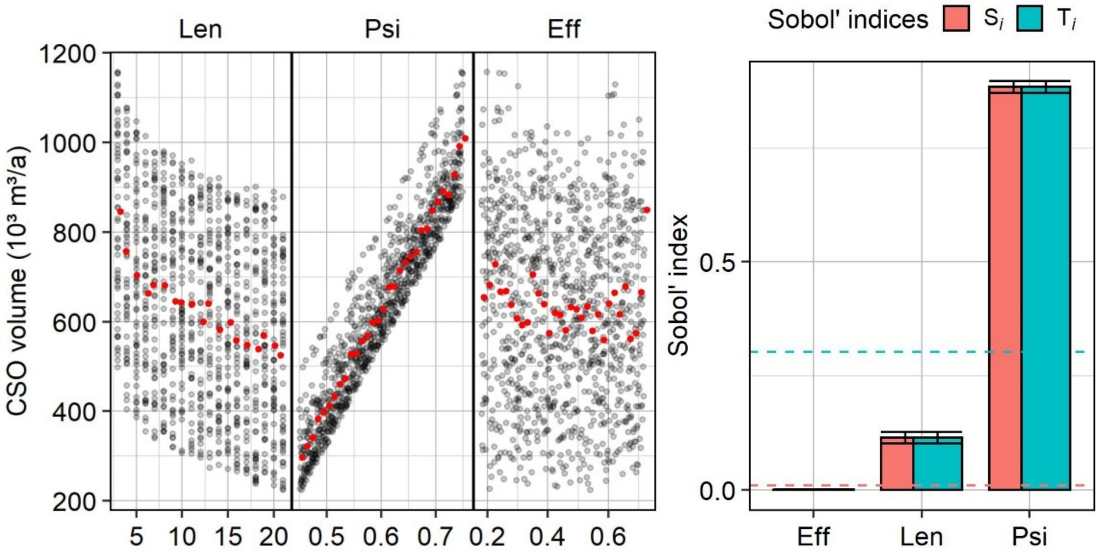

Figure A5.1: Sensitivity analysis results: Scatterplots of input parameters versus annual CSO volume resulting from the UWB (left), and Sobol' indices with 95%-confidence intervals (right). Len = Length of the moving minimum period (days), Psi = Mean runoff coefficient, Eff = Effective rainfall duration threshold value (mm/hour). The red dots show the mean CSO volume in a bin of model runs resulting from fixing the respective input parameter to the possible values in its uncertainty range while the other parameters are left to vary (Puy *et al.* 2022).

Table A5.1: Lognormal (lnorm) and uniform (unif) distributions fitted to site mean concentrations in wastewater treatment plant effluents (WWTPo), combined sewer overflows (CSO). KS test = Kolmogorov-Smirnov test.

Substance	**Compo-nent**	**Fit**	**KS test**	**Parameter Estimates**		**Standard Error**		**Limits of uniform distribution**	
			p	**Meanlog**	**SDlog**	**Meanlog**	**SDlog**	**Min.**	**Max.**
Triclosan	WWTP	lnorm	0.999	-3.67	0.38	0.07	0.05	-	-
	CSO	lnorm	0.406	-3.94	0.56	0.17	0.12	-	-
	SSO	unif	-	-	-	-	-	0	0
Terbutryn	WWTP	lnorm	0.403	-3.46	0.69	0.10	0.07	-	-
	CSO	lnorm	0.958	-3.79	0.86	0.26	0.18	-	-
	SSO	unif	-	-	-	-	-	0.033	0.045
Mercury	WWTP	lnorm	0.130	-5.92	0.77	0.11	0.08	-	-
	CSO	lnorm	0.893	-4.18	0.28	0.09	0.06	-	-
	SSO	unif	-	-	-	-	-	0.012	0.018
Fluoranthene	WWTP	lnorm	0.687	-5.98	0.89	0.13	0.09	-	-
	CSO	lnorm	0.379	-2.52	0.43	0.13	0.09	-	-
	SSO	unif	-	-	-	-	-	0.103	0.169

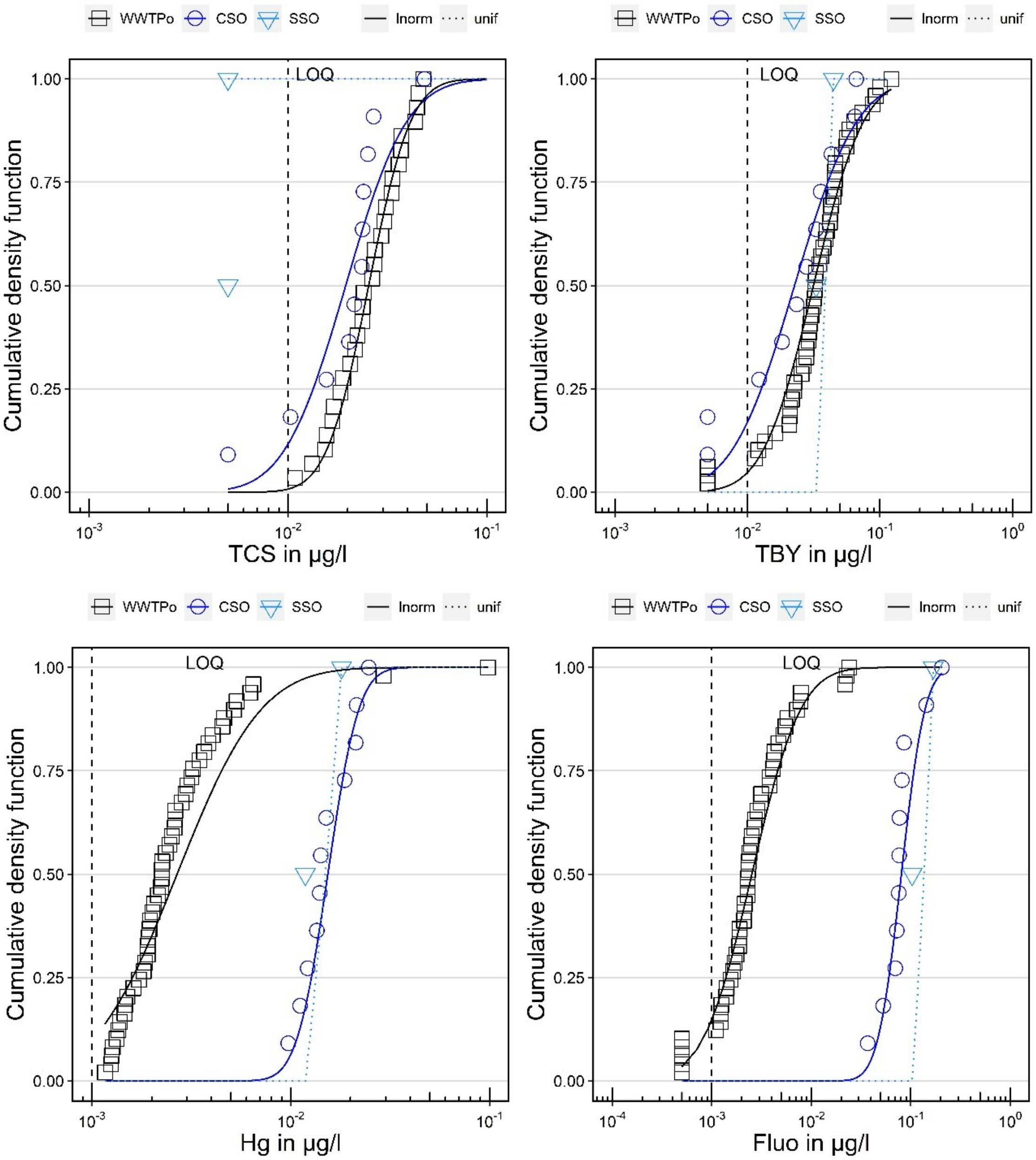

Figure A5.2: Empirical cumulative density functions of site mean concentrations in wastewater treatment plant effluents (WWTPo), combined sewer overflows (CSO), and stormwater outfalls (SSO) with fitted lognormal (lnorm) and uniform (unif) distributions: TCS = Triclosan, TBY = Terbutryn, Hg = Mercury, Fluo = Fluoranthene.