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Preface

The implementation of the Water Framework Directive requires that good chemical and ecological status of streams is ensured. An important factor that may hinder such a status is emissions of wet weather discharges from urban areas, notably combined sewage containing both domestic sewage and storm water.

The Danish Environmental Protection Agency has requested that the Technical University of Denmark and Aarhus University make a joint assessment of the state-of-the-art on knowledge of the impacts of emissions of combined sewage during wet weather in a Danish context. An additional purpose, based on this assessment, is to define operational criteria for these emissions that will ensure compliance with the requirements of the Water Framework Directive. The focus should be placed on emissions of organic matter and associated oxygen demand and ammonia. The criteria for compliance should be based on measurements taken in the stream that receives the emissions.

This report serves as a background technical document for a main report that is available in Danish. The authors would like to thank Associate Professor Poul Løgstrup Bjerg for a detailed revision and commenting of the report and Professor Peter Steen Mikkelsen for the fruitful discussions on the report content.

The authors,
Kongens Lyngby, January 2018

Content

1. Introduction

Combined sewage is a mixture of domestic sewage and stormwater runoff. Combined sewage is typically conveyed away from urban areas through underground sewer systems and treated at wastewater treatment plants (WWTP). However, during medium and large storms the underground sewer systems are overloaded and, to protect the city assets from uncontrolled flooding, several emergency outlets are built along the network. These outlets, denoted as combined sewer overflows, ensure that excess water is discharged into nearby streams and other surface waters during periods of overloading. Similar structures are located at WWTPs to divert any flows exceeding the maximum treatment capacity of the plant (the so-called bypass flows). On an annual basis only a minor fraction of the total combined sewage volume is discharged through these structures, but during very extreme storms the magnitude of wet discharges can result in a manifold flow increase to the overall river flow compared to dry weather conditions. Together with emissions from separate stormwater systems, these emissions are denoted as wet weather discharges.

Wet weather discharges were studied intensively both nationally and internationally in the period from 1975–2000. It was recognized that especially emissions from combined sewage during wet weather heavily impacted small creeks and lakes (Eriksson et al., 2007a; Kjølholt et al., 2001). Large measurement campaigns were initiated to quantify these emissions and to establish causal relationships between the emissions and impacts. Impacts were often divided into physical changes (erosion, deposition), aesthetical pollution, eutrophication, pathogenic pressure, oxygen depletion, toxic and/or xenobiotic components, and changes in the ecosystem (community dynamics) within and around the surface water.

The implementation of related environmental legislation in Denmark and across the EU during the period 1987–2000 mainly focused on continuous emissions. Construction of wastewater treatment plants for industrial emissions, as well as domestic sewage has reduced the annual loadings to surface waters substantially during the last decades. The enactment of the Water Framework Directive (2000/60/CE), however, moved the focus from single discharge points to a more holistic evaluation of the ecological status of the receiving water body. Although not directly addressed, intermittent discharges play an important role in affecting the overall quality of the receiving water body. Some surface waters have clearly improved their status thanks to the implementation of these environmental legislations and the construction of treatment plants, while other surface waters still struggle to achieve the desired quality standard.

In general, the following types of measures are considered to further improve the chemical and/or ecological status:

- Reduction of emissions from continuous sources (e.g. waste water treatment plants, industrial emissions, agriculture).
- Reduction of emissions from intermittent (e.g. wet weather) sources.
- Change in land use and/or banning of specific compounds in the area.
- Change in (base) flow of surface water.
- Biomanipulation of the aquatic ecosystem to favour its transition to a better ecological status.
- Changes in hydromorphological (physical) conditions (river aeration, re-meandering, etc).

Furthermore, urban areas are affected by processes that are intensifying the pressure on receiving water bodies caused by wet-weather discharges. These processes include increasing urbanization and subsequently impermeabilization of existing urban areas, which lead to a rise in the runoff flows and volumes. Changes in rainfall patterns caused by climate change can also contribute to more frequent and/or greater wet-weather discharges. These changes might contribute to deteriorate the current status of receiving water bodies, requiring additional measures.

This report revisits the importance of wet weather discharges, notably combined sewer overflows, in relation to the goal of achieving good chemical and ecological status of surface waters. The report mainly focuses on the discharges of ammonium/ammonia, organic matter, and the resulting oxygen depletion, as based on a review of the existing scientific literature, they cause the most evident negative impacts on the water bodies, and it is possible to quantify cause-effect relationships between discharges and the status of the receiving water body.

- Chapter 2 defines all the elements of the integrated urban water system that are considered in the report, and outlines our understanding of how the different elements interact, which may affect the chemical and ecological status of the receiving water body as a consequence of wet weather discharges.
- Chapter 3 discusses our current understanding of the pollutants discharged through wet weather discharges, providing an overview of existing measurements and comparing them to environmental quality standards for good chemical status.
- Chapter 4 describes the indicators that are used to evaluate the impacts of wet weather discharges on the ecological status of the receiving water body. A specific focus is given to identifying a link between insufficient ecological status and existing stressors, including combined sewer overflows.
- Chapter 5 takes a holistic perspective by exploring our understanding of the causal relationships existing between wet weather emissions and good ecological status, including stress-factors affecting the ecological status other than wet weather discharges.
- Chapter 6 describes the state-of-the art in relation to the monitoring of water quality (both at discharge points and the receiving water body).
- Chapter 7 provides an overview of current regulation approaches for overflow discharges and water quality criteria at the international level.
- Chapter 8 illustrates the different modelling approaches that can be used as tools to interpret the integrated measurements coming from monitoring programs, and thus to support future decision-making (i.e. next generation regulations).
- Chapter 9 then proposes a procedure to establish operational guidelines for the regulation of wet weather discharges from urban areas.

2. System schematization

The discharge from Combined Sewer Overflows (CSO) cannot be effectively regulated without proper consideration of the entire integrated urban water system, including attention to the state of the 'natural' receiving water body. The need for an integrated approach is one of the key principles of the EU Water Framework Directive (WFD - European Commission, 2000) and this is also reflected in the elements that are considered in this report (Figure 1).

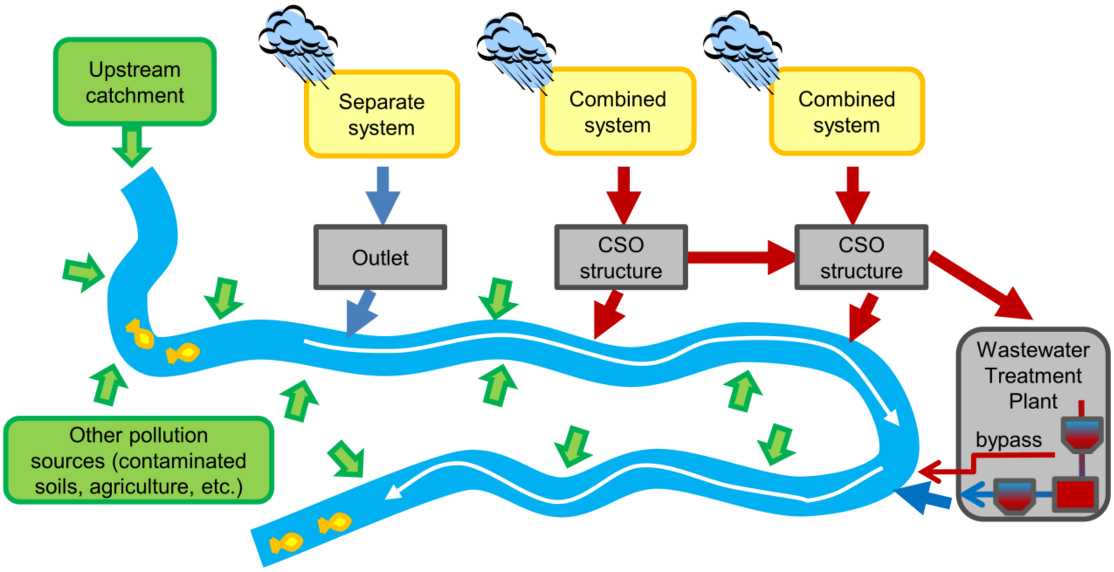
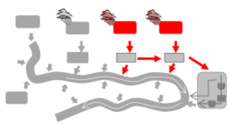


Figure 1. Conceptualization of the system considered in this report. The status of the receiving water body is affected by wet weather discharges from combined systems (brown arrows), other discharges from point sources in urban areas (separate systems, wastewater treatment plant - dark blue arrows) together with other pollution sources such as contaminated sites, drainage of agricultural areas and diffuse pollution (green arrows).



Combined Sewer Overflows are elements in the combined sewer network that discharge to the receiving water body when the network flow capacity is exceeded. The combined sewer network collects waste- and stormwater from urban areas (combined systems) and conveys these flows to the *WasteWater Treatment Plant* (WWTP, lately also defined as WRRF – Water Resource Recovery Facility). Discharges from CSOs are caused by medium/heavy rainfall events, generating runoff flows that exceed the existing capacity of the drainage network (e.g. Figure 2). The threshold for CSO events depends on the physical characteristics of the system, such as size of the drained catchment, the dimensions of the pipes, the available storage volume, etc. The CSO pollution levels depend on the wastewater and stormwater composition. The first is affected by the number of inhabitants and by the contribution of industrial activities in the drained catchments, which can contribute to increasing loads of e.g. specific micropollutants (deriving from production activities) or organic matter (as in the case of food processing industries).

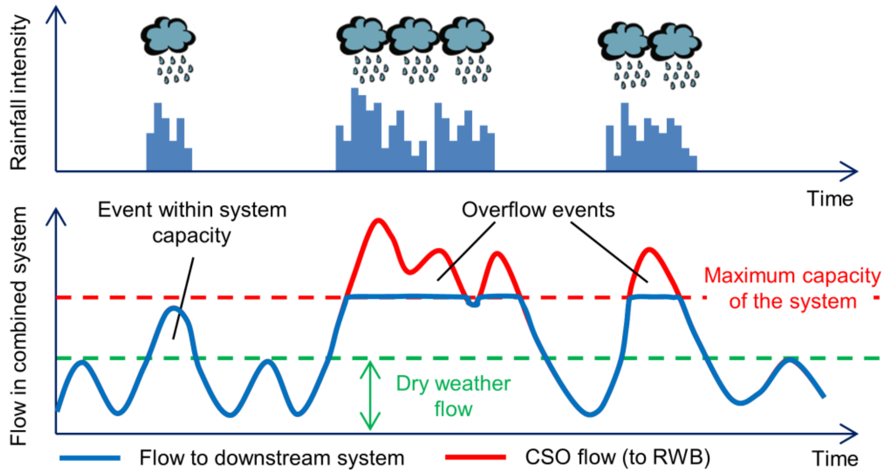
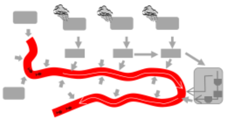


Figure 2. Schematic representation of flow in a combined sewer overflow structure during dry and wet weather periods.

Stormwater mainly acts as a dilution factor, given the generally lower concentrations for a great range of typical pollutants (with exceptions for some heavy metals and PAHs). Depending on the characteristics of the system, stormwater also drives the resuspension of sediments that have accumulated in the drainage network (thereby also affecting those pollutants which have a strong tendency to bind to particles).



CSO discharges can impact the quality of the *Receiving Water Body (RWB)*, which – according to the WFD – should be able to maintain good quality status. This is expressed in terms of both chemical and ecological conditions, which depends on the classification of the water body. For example, the WFD defines different environmental objectives for artificial and heavily modified water bodies, recognizing the inherent difficulty in re-establishing a good status in those RWBs. For chemical status, indicators are expressed as threshold concentrations: in the WFD, these are defined as maximum allowable concentrations (MAC) and annual average concentrations (AA). The relationship between rain events, CSO events and the subsequent exceedance of different chemical indicators is notably not linear, as schematized in Figure 3.

The Danish legislation (BEK 439 19/05/2016 - Miljø- og Fødevareministeriet, 2016) also defines quality criteria for sediments, which is relevant for wet weather discharges, since a great number of pollutants in CSOs have a strong tendency to sorb to particles (cf. section 5.3.3).

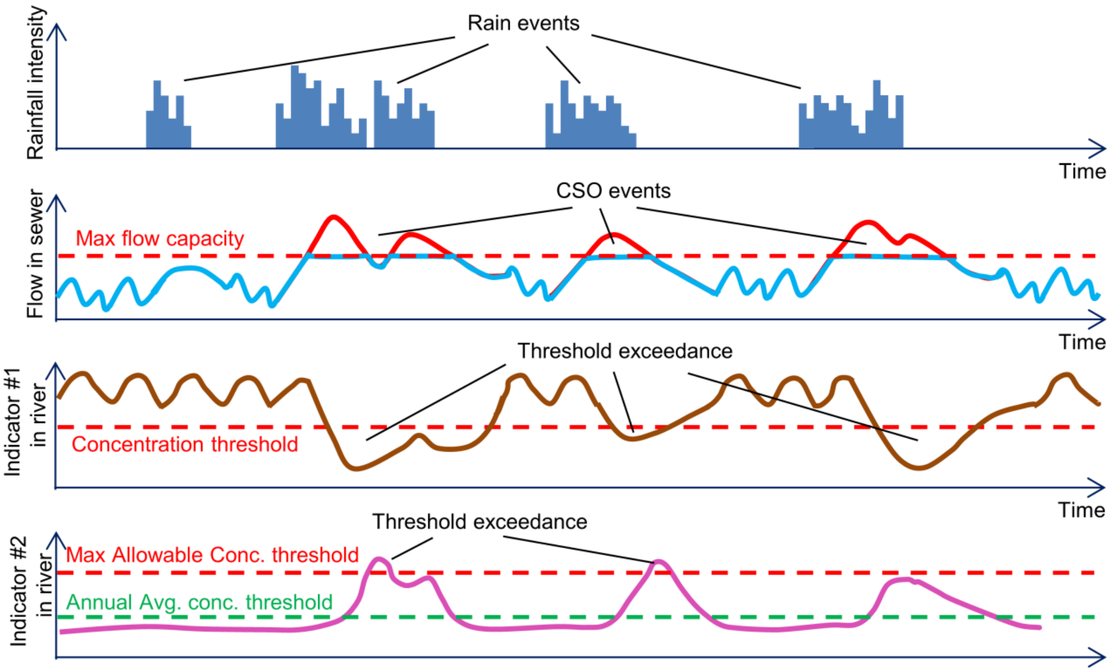
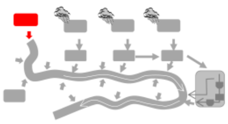


Figure 3. Schematic representation of the relationship between rain events (a: four events), causing CSO discharges to the RWB (b: three events) and therefore an exceedance of thresholds for two different chemical indicators (c: three events; d: two MAC exceedance events, three AA exceedance events).



The Receiving Water Body usually originates from *rural catchments* located upstream of the urban areas. In these rural areas, runoff is generated with a slower response compared to urban areas and, together with any existing activities and pollutant sources within the rural areas, will define the background concentration present in the RWB as it flows into the downstream urban areas (see Chapter 5). Usually, runoff from rural areas is responsible for the greater part of the flow in the RWB. However, in highly urbanized areas or in certain periods of the year, flows from urban areas (discharge from WWTPs and CSOs) can represent the principal contributor to the RWB flow. For example, the anthropogenic contribution represents the greater fraction of summer flows for some rivers in Northern Zealand (Denmark), as in the case of Usserød Å (Figure 4). In this case, a fraction ranging from 43% to 67% of the dry weather flow in July was due to the WWTP effluent, while wet weather discharges from urban areas contributed only to an additional 30%-50% flow (occurring only 3% of the time).

A similar situation is presented by Langeveld et al. (2013a) for the Dommel river (The Netherlands), where the WWTP effluent contributed almost 50% of the river summer flow in dry weather. The influence of the upstream rural areas is therefore an essential feature in properly defining the water quality status of any RWB and thus for enabling a robust evaluation of the impact of discharges from urban areas.

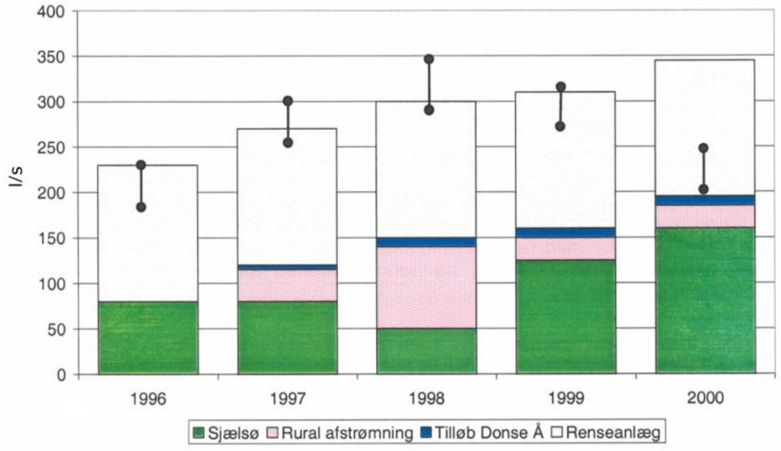
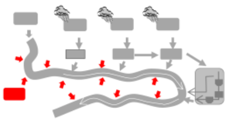
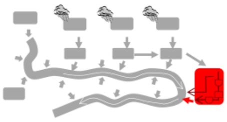


Figure 4. Estimated contribution of different sources to the dry weather flow in Userød Å in July (PH Consult, 2000): Sjælsø lake (green), runoff from rural areas (pink), contribution from the Donse Å stream (blue), and WWTP (white). Black lines represent measured flows, showing the deviation between measured and estimated total flows.



Other pollution sources may affect the quality of rural runoff: unwanted washout of nutrients from fields or leaching of pesticides from farmland may affect the RWB quality before the CSO discharge point. The pollutant loading from rural areas can be so high that the CSO contribution to the entire pollutant load will be limited, or conversely, the upstream conditions of the RWB can be so good (in terms of flow, chemical and ecological status) that CSO discharges will not cause any perceptible deterioration of the RWB status. The latter was the case for the Userød Å (PH Consult, 2000), where the good water quality originating from Sjælsø Lake resulted in a negligible impact for any CSO discharges in the upper stream reaches compared to the lower reaches.



During wet periods, WWTPs operate at the limit of their design capacity. The increased hydraulic load to the plant results in a lower hydraulic residence time and in a reduced effect of the settling processes within secondary clarifiers. This can result in an overall decrease in the WWTP removal performance. For example, Bowes et al. (2012) measured an increase in phosphorous effluent concentration after a prolonged rainy period (several weeks) in a plant that was otherwise capable of fulfilling effluent discharge limits (also after short storm events). Moreover, when the design capacity is exceeded, flow of untreated or partially treated wastewater (i.e. treatment encompasses only physical processes, skipping any biological treatment) will be discharged directly into the RWB (the so-called *bypass).* Depending on the physical configuration of the WWTP, bypass flow can be mixed with the treated effluent or discharged from a separate outlet. These characteristics are relevant for monitoring and regulation purposes, since it should be possible to distinguish this rain-induced flow from the plant effluent.

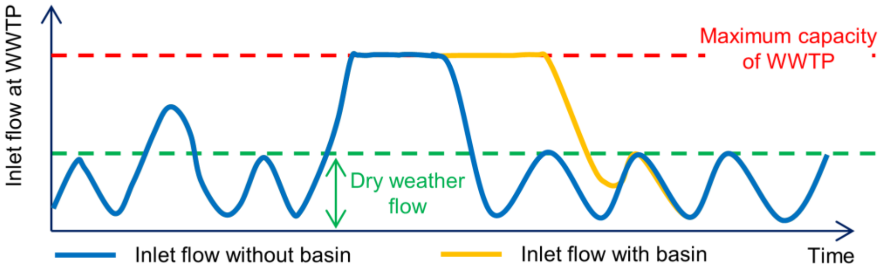
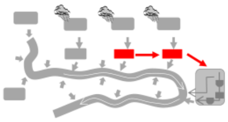
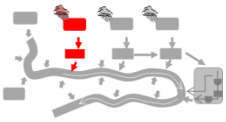


Figure 5. Schematic representation of inlet flow at a WWTP in a system with and without detention basins in the upstream system.

The quality of bypass flows depends on the point where the flow is diverted: bypass after the primary treatment (but before the biological treatment) will have different characteristics than a bypass taking place at the WWTP inlet (which can be considered similar to a CSO).



Detention basins are common infrastructural solutions to reduce CSO volumes: excess water is stored during rain events to avoid direct discharges to the RWB, which is subsequently conveyed to the WWTP. However, the emptying of these basins can result in an increased duration of high hydraulic loads to the WWTP (Figure 5) and/or in the creation of sudden pollution peaks at the WWTP inlet (e.g. Tik et al., 2015) resulting in an overall reduction in WWTP performance (e.g. Langeveld et al., 2013).



Another infrastructural option to reduce CSO volumes is the separation of wastewater and stormwater flows (catchment separation). This eliminates the cause for the overloading of the sewer system, avoiding CSO discharges. Stormwater runoff is discharged to the RWB after a certain degree of treatment. This depends on the local discharge requirements, since discharge from separate systems is not explicitly regulated by existing regulations. Whilst average pollutant concentrations are lower in separate stormwater systems than in CSOs for the majority of pollutants, the total discharged volume will be greater, i.e. it is possible that – depending on the local conditions (e.g. catchment area, capacity of the existing combined system) – the total pollutant loads from separate systems may ultimately exceed those from CSO structures.

3. Urban water discharges

3.1 Discharges characterization

3.1.1 Chemical water quality criteria

This section provides an overview of the measured pollution levels from wet weather discharges (Combined Sewer Overflows and WWTP bypass) based on internationally available data. The focus is on chemical parameters, i.e. chemical indicators which are listed by the current environmental legislations.

Since possible infrastructural options to reduce CSO discharges can affect other elements of the urban drainage/wastewater system, discharges from separate systems and wastewater treatment plants (WWTP) operating during wet weather periods are also included in this overview. In fact, a possible option to reduce CSO is catchment disconnection: by constructing a separate stormwater collection system it is possible to reduce the total overflow volume, but untreated discharges from separate systems can pose a higher risk to the receiving water.

Similarly, detention basins represent a widespread option to reduce CSO volumes and pollutant loads directly discharged to the natural water. However, the stored wastewater volumes are sent to the downstream WWTP, increasing the duration of high inflow events (see Figure 5). This can negatively affect the plant removal performance during wet weather periods (as shown in the early studies of Rauch and Harremoës, 1996; Hansen et al., 1993; Lijklema et al., 1993) and thus, together with bypass flows, pose a new risk to the receiving water body. Therefore, typical pollution levels for discharges from separate stormwater systems and wet weather discharges from WWTPs are also provided in Sections 3.4 and 3.5, respectively. This additional information allows for a holistic evaluation of impacts from both CSOs and their alternatives.

Typical pollutant concentrations are listed for a range of typical water quality criteria, including priority pollutants and new emerging contaminants (Table 1). Ranges for pollutants explicitly listed in these legislations have been compared against existing Emission Level Values (ELV) and Environmental Quality Standards (EQS) defined by existing legislation.

Table 1. Chemical water quality parameters investigated in the report.

Category	Typical indicators[1]	Legislation reference
Traditional pollutants	Organic matter (BOD_5, COD) Nutrients (Total P, Total N, NH_3-N) Solids (SS)	Wastewater discharge: – BEK 726 01/06/2016 – EU Directive 91/271/EEC
Priority substances	Heavy metals, Industrial chemicals, Pesticides/ Biocides/Herbicides, Flame retardants and plasticisers, Polycyclic aromatic hydrocarbons (PAHs), Polychlorinated biphenyls (PCBs)	Environmental Quality Standards – BEK 439 19/05/2016 – EU Directive 2000/60/EC, 2008/105/EC, 2013/39/EU
Emerging pollutants	Pharmaceuticals Endocrine disruptors Artificial sweeteners Personal care products	EU Watch List: – EU directive 2013/39/EU – Carvalho et al. (2015)

[1] See Appendix A for the complete list

Additionally, data for selected emerging pollutants (i.e. those initially considered in the elaboration of the EU watch list - cf. Carvalho et al., 2015) are also listed. In order to screen between the over 160 substances listed by the current Danish regulation (BEK 439 19/05/2016, Miljø- og Fødevareministeriet, 2016), priority substances have been classified according to the potential threat they might pose to the chemical status of the receiving water body (as defined by the EQS).

The following assumptions and criteria have been used in this screening (Table 2):

- *Assumption:* Discharges from urban areas will be diluted to a certain degree, i.e. measured concentrations at discharge points are expected to be higher than in the receiving waters. Therefore, the comparison between measured concentrations and EQS will result in a conservative evaluation of the influence of wet weather discharges on the RWB status.
- *Criterion #1*: if measured concentrations are always below the EQS, the discharge is not expected to threaten the chemical status of the natural water body (i.e. it represents a negligible threat);
- *Criterion #2:* if only extreme concentrations (values above mean/median) are above the EQS, these thresholds are expected to be exceeded only in extreme events (i.e. there is a low threat);
- *Criterion #3:* when measured concentrations are above the Annual Average EQS (AA-EQS), discharges are expected to regularly threaten the good chemical status, when dilution is not important and/or background concentrations are high (i.e. there is a potential threat);
- *Criterion #4:* when measured concentrations are above the Maximum Allowed Concentration EQS (MAC-EQS), discharges will threaten the chemical status of the river when dilution is not important and/or background concentrations are high (i.e. there is a high threat).

Table 2. Criteria used to identify critical pollutant discharges based on literature data and existing EQS values.

Classification		Criterion	Rationale
Negligible threat to good status		All available measurements below EQS	Even with high CSO concentrations and low dilution, EQS will not be exceeded
Low potential threat to good status		Maximum measured concentrations above MAC-EQS or AA-EQS, but mean/median[2] below AA-EQS (i.e. EQS can be exceeded in extreme events)	EQS will be exceeded only in extreme events (e.g. with low dilution or high CSO concentrations)
Potential threat to good status		Mean/median concentrations above AA-EQS (i.e. the majority of EMC values exceed AA-EQS)	AA-EQS can be exceeded in case of low dilution or high background concentrations
High potential threat to good status		Mean/median concentrations above MAC-EQS (i.e. the majority of EMC values exceed MAC-EQS)	EQS are expected to be exceeded in the majority of cases, with few exceptions (e.g. high dilution or low background concentrations)

[2] Median is used for a few of the extremely high measurements, which affect the calculation of the average concentration.

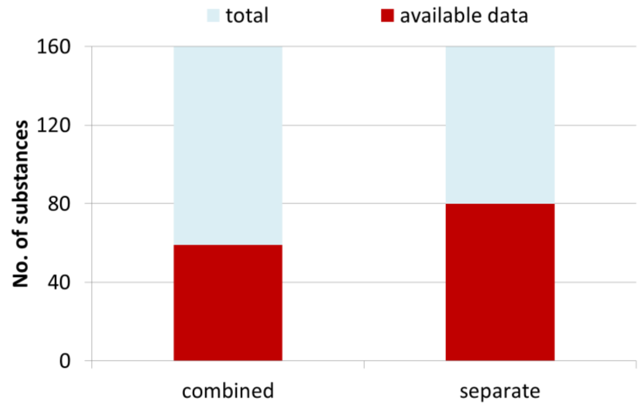


Figure 6. Comparison between substances listed in environmental legislation (BEK 439 19/05/2016) and number of substances for which measurements are available.

This screening is quite general and it has some important limitations:

- Site-specific characteristics are not considered. These include dilution, land use in the upstream catchment, and background concentrations in the recipient.
- The characterization focuses on concentrations, i.e. pollutant loads are not taken into consideration. Also, depending on the source, concentrations are listed as event mean values (based on several measurements – see Figure 7) or as single measurements (which have more extreme ranges).
- Only the water phase is considered, i.e. legislation with existing EQS values for sediment quality has not been included in the screening. Also, most of concentrations are reported as total concentrations, while EQS are defined for some pollutants for the bioavailable (i.e. dissolved) fraction.
- The number of available measurements is not considered: this affects both the estimation of mean/median values, as well as the minimum-maximum values. In some cases, this can also affect the screening process: for example with *Criterion #1,* as the probability of measuring high concentrations increases with the number of available measurements.

Due to these limitations, the screening only allows the identification of groups of substances based on their potential to threaten the good ecological status. The available information in fact does not allow for a complete evaluation of the expected environmental risk, which would require a more detailed analysis. Measurements for several priority substances and emerging pollutants are limited (Figure 6): only 37% of the priority substances listed in BEK 439 19/05/2016 have been measured in CSOs (50% for separate systems). Thus, the overall discharge impact could be underestimated.

3.2 Discharge variability

Information on the quality of urban discharges is commonly provided as event mean concentrations (EMC) and, when sufficient measurements are available, as Site Mean Concentrations (SMC). This format is explained by the monitoring techniques that are often used to monitor water quality: water samples are collected by automatic samplers, which then provide a discrete representation of a dynamic process (with consequent loss of information about the dynamic behaviour of pollutant concentrations – see the scheme shown in Figure 7). ELV exceedance needs to be quantified for specific discharge points, i.e. SMCs are necessary to account for the variability between different catchments (linked to the variability in pollution sources). There are different suggestions on the number of measured events that are necessary to quantify a SMC: a range between 6-12 EMCs has been suggested (Maniquiz-Redillas et al., 2013; May and Sivakumar, 2009), while Mourad et al. (2005) considered measurement uncertainties and could not provide a general suggestion valid for all events and pollutants. These results should be taken into account when designing monitoring campaigns aiming at estimating pollution levels for a specific catchment (see also Section 6.1).

To fully exploit the information conveyed by these measurements, it is important to distinguish between the dynamic behaviour of different pollutants in combined systems:

- *Dissolved pollutants* (such as ammonia) show an easily predictable pattern: pollutants commonly found in wastewater flows are diluted by the stormwater volume. Their concentration behaviour in the discharged water thus follows the flow pattern, i.e. higher stormwater flows will increase dilution and pollutant concentrations will decrease.
- *Particulate pollutants* (often lumped by the TSS indicator) show a higher variability, which is related to factors such as pollutant sources, sediment accumulation and resuspension in the sewer network, antecedent dry periods, etc. It is therefore difficult to provide a general description of their behaviour: Metadier and Bertrand-Krajewski (2012), for example, showed how pollutographs could be subdivided into three main groups based on their behaviour, but without identifying a strong correlation with hydraulic factors such as flow rate and rainfall intensity.

The highly variable behaviour of TSS (and thereby for all the priority substances with a strong tendency to sorb to particles) should be taken into account when evaluating the potential impact of urban discharges.

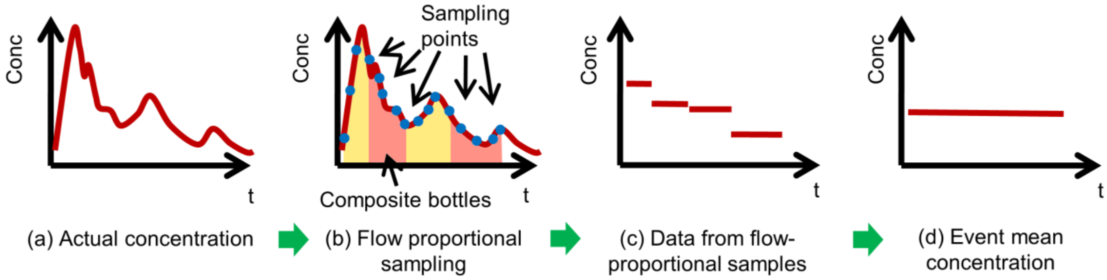


Figure 7. Scheme showing how the actual pollutant concentration (a) is commonly measured by automatic samplers (b), resulting in a series of measurements for a single event (c), which are then used to calculate an average event value (d) .

Online sensors (e.g. Brzezińska et al., 2016; Metadier and Bertrand-Krajewski, 2012; Dirckx et al., 2011) allow for a better estimation of total pollutant load distributions, as well as acute toxicity caused by sudden concentration peaks. A lognormal distribution is commonly observed for EMCs (Rossi et al., 2005; Van Buren et al., 1997a; Harremoës, 1988), with variations between separate and combined systems. Metadier and Bertrand-Krawjeski (2012), for example, subtracted the wastewater contribution in order to obtain a log-normal distribution of TSS and COD event loads from a combined system. This suggests that the log-normal distribution of pollutant loads is mainly linked to the natural variability of the rainfall/runoff processes causing CSO events, and is thereby easier to observe in discharges from separate systems.

Available measurements differ in their collection methods and they are often reported in a heterogeneous manner: EMCs are often provided as averages and ranges (minimum and maximum values), with additional information (coefficient of variations, standard deviation) available only in a limited number of studies. It is therefore difficult to analyse and compare these data and to estimate typical distributions. Therefore, only minimum and maximum values are reported here in order to provide general information about the pollution level that is expected from urban discharges.

3.3 Discharges from Combined Sewer Overflows

3.3.1 Traditional pollutants

Measured ranges for traditional pollutant measurements are listed in Table 3, based on the monitoring campaigns listed in Appendix A). Although the majority of the data used to compile Table 3 have been collected in the last decade, little variations in the concentration ranges (mainly for the COD and TSS intervals) are noticed compared to the values listed in the review presented in Arnbjerg-Nielsen et al. (2000). This shows how the available data in the early 2000s were sufficiently representative to grasp the pollutant variability in CSO discharges and to provide a good estimation of the pollution ranges. Results from measurement campaigns carried out with new measurement techniques (i.e. online sensors - e.g. Metadier and Bertrand-Krajewski, 2012) show some discrepancies for some extreme values and average COD concentrations (Table 4), but these differences can be described by natural variability, site specific characteristics (e.g. the data collected by online sensors listed in Table 4 refer to a single sampling site), and the number of monitored events.

Table 3. Measured EMC ranges for traditional pollutants in CSO against maximum values allowed by Danish legislation for discharge from WWTP with capacity above 2000 PE (BOD and COD) and 5000 PE (Ntot and Ptot) (BEK 726 01/06/2016 - Miljø- og Fødevareministeriet, 2016b) and European legislation (91/271/EEC).

Parameter	Min [mg/l]	Max [mg/l]	Limit (ELV) [mg/l]
BOD5	2	286	<15
COD	16*	1354*	<75
N-TKN	0,48	46*	<8
N-NH4	3,3*	22,2*	
Ptot	0,31	8,3	<8
TSS	13*	1934*	<35

*Values differing from previous intervals listed in Arnbjerg-Nielsen et al. (2000). Ammonia was not included in that review.

Table 4. Comparison between ranges estimated based on traditional monitoring techniques and by using online sensors (as in Metadier and Bertrand-Krajewski, 2012)

Measured Pollutant	Monitoring method	No of Data/Events	Measured concentrations [mg/l]		
			Min	Mean	Max
TSS	Traditional	>100	19	304	1184
	Online	239	13	260	1433
COD	Traditional	>96	34	365	1078
	Online	239	16	441	1354

The comparison with the maximum discharge limits for discharges from WWTP (Table 3) shows that EMCs are usually exceeding these thresholds. Moreover, it should be noticed that local authorities can define more stringent limits according to the sensitivity of the receiving water body.This is the case for ammonium, where local regulations typically define limits around 1-3 mg/l.

3.3.2 Priority substances

As shown in Figure 6, information on priority substances in CSO discharges is quite limited (59 substances out of the 160 listed by current legislation). This is due both to the practical challenges in monitoring CSO events and to the difficulties in monitoring Priority Substances, which are commonly present in low concentration ranges (on the order of µg/l or below). In fact, data availability is greater for heavy metals, followed by PAHs, while few EMCs (<5) are usually available for pesticides and other substances (see Figure 8). In some cases, pollutant ranges listed in Danish literature (dark blue in Figure 8) show smaller intervals than international data (light blue in Figure 8), but no clear pattern can be seen. Also, the width of the ranges, expressed as minimum and maximum measured values, can also depend on the number of monitored events (i.e. a greater number of monitored events will likely result in wider ranges, as a consequence of the natural discharge variability, as discussed in Section 3.2).
Overall, 14 groups of substances showed a high potential for impacting the chemical status of receiving waters (Table 5), since their measured EMC ranges were above both the AA-EQS and MAC-EQS. These include heavy metals (e.g. copper, zinc), PAHs, and pesticides. Another 12 groups of substances indicated a potential to threaten the chemical status. Given the different characteristics of these substances, a direct relationship between traditional pollutants and these priority substances can be established only for specific cases. For example, PAHs have a strong tendency to sorb, so their presence and concentration behaviour can be correlated to TSS. Conversely, toxic effects for copper and zinc are related to the bioavailable (dissolved) fraction, and fractionation of these substances depends on different chemical-physical factors.

3.3.3 Other emerging pollutants

Among the 39 candidate substances on the EU watchlist (Carvalho et al., 2015), only 6 have been detected so far in CSO discharges. These substances include pesticides (e.g. glyphosate), as well as pharmaceuticals (such as diclorofenac and ibuprofen). However, the number of available studies (Launay et al., 2016; Gasperi et al., 2008) is limited and further data collection is needed before an impact assessment could be done.

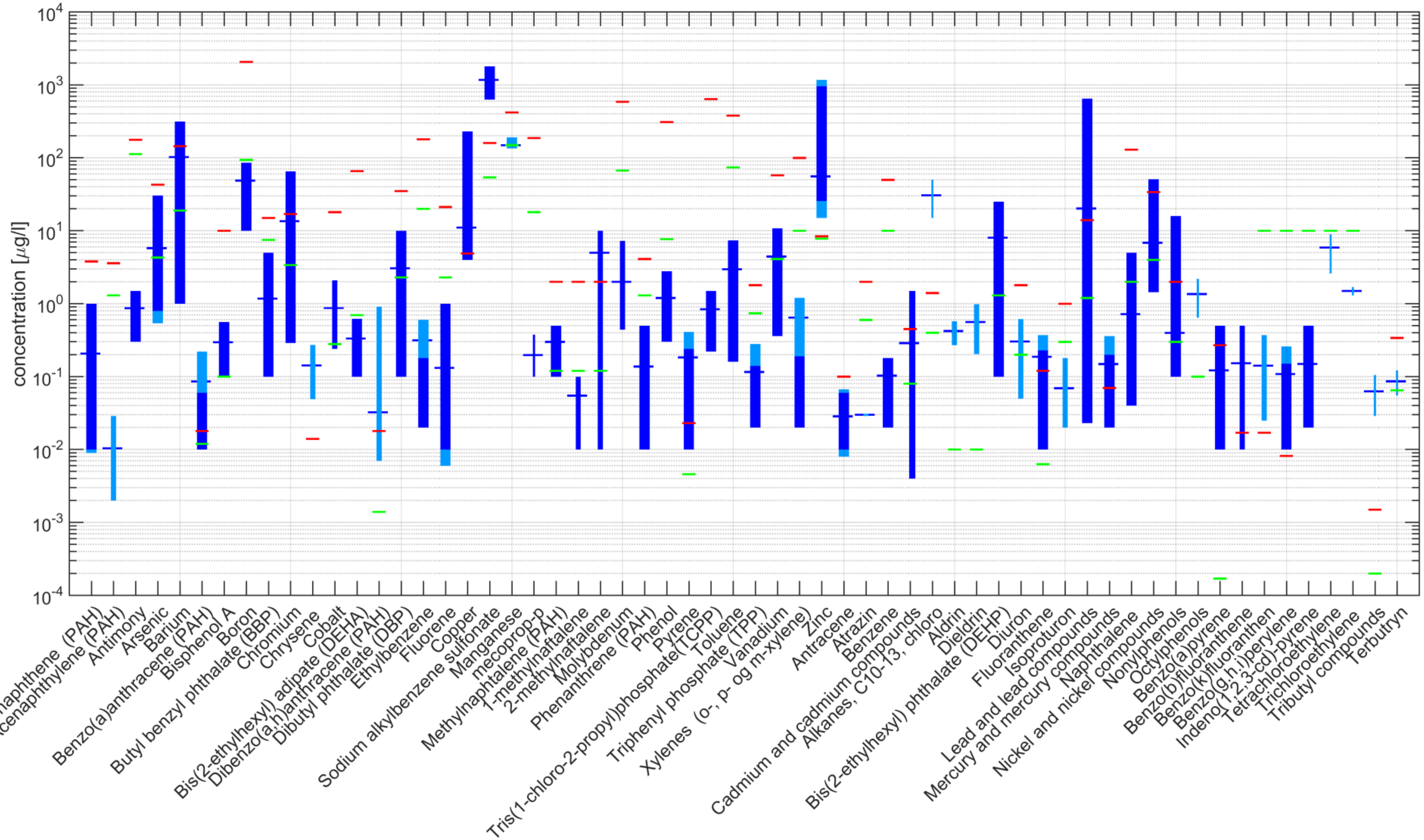


Figure 8. Concentration ranges for priority substances measured in Combined Sewer Overflows (blue lines, expressed as minimum and maximum value), median/mean value used in the screening (blue horizontal lines), AA-EQS (green horizontal lines) and MAC-EQS (red horizontal lines). The thickness of the blue line is proportional to the number of available measurements (thinnest line: n<5, thickest line: n>15). Dark blue: data from Danish studies. Light blue: all available measurements in international literature. For further details, see Appendix A.

Table 5. Comparison of measured concentration ranges for priority substances in combined systems against their Environmental Quality Standards, along with the estimated threat to good chemical status (see Table 3) and number of available measurements. Substances with light blue background are classified as "priority hazardous pollutants"[3]. Only substances posing a potential or highly potential threat to the good chemical status are listed here; the complete list of analysed substances is available in Appendix A.

CAS number[4]	Substance	AA-EQS[5] [µg/l]	MAC-EQS[6] [µg/l]	Minimum and maximum measured concentrations [µg/l] (dissolved in brackets)		Threat to good chemical status	Available measurements [events]
				All available data	Danish data		
7440-38-2	Arsenic	4,3[7]	43	0,54-30,6	0,80-30,6		>15
56-55-3	Benzo(a)anthracene (PAH)	0,012	0,018	0,01-0,22	0,01-0,06		>15
80-05-7	Bisphenol A	0,1	10	0,10-0,56	0,10-0,56		>15
7440-47-3	Chromium Cr VI	3,4	17	0,29-65,2	0,29-65,2		>15
	Cr III	4,9	124				
218-01-9	Chrysene	0,014	0,014	0,049-0,273			5-15
7440-48-4	Cobalt	0,28[7]	18	0,24-2,10	0,24-2,10		5-15
53-70-3	Dibenzo(a,h)anthracene (PAH)	0,0014	0,018	0,007-0,91			5-15
84-74-2	Dibutyl phthalate (DBP)	2,3	35	0,1-10	0,1-10		>15
7440-50-8	Copper	1[7,8] 4,9[9]	2[7] 4,9[9]	4-230 (2,17-23)	4-230 (2,17-23)		>15
68411-30-3	Sodium alkylbenzene sulfonate	54	160	630-1800	630-1800		>15

[3] Substances whose emissions, according to the Water Framework Directive, should be must cease or be phased out
[4] CAS: Chemical Abstracts Service.
[5] Expressed as annual concentration. The value refers to the sum concentration for all the isomers unless differently specified.
[6] Expressed as the highest allowed concentration.
[7] EQS is expressed as this value added to the natural background concentration.
[8] EQS applies to the bioavailable concentration.
[9] EQS applies to the total concentration, irrespective of the total natural background concentration.

CAS number[4]	Substance	AA-EQS[5] [µg/l]	MAC-EQS[6] [µg/l]	Minimum and maximum measured concentrations [µg/l] (dissolved in brackets)		Threat to good chemical status	Available measurements [events]
				All available data	Danish data		
90-12-0 91-57-6 28804-88-8 28652-77-9	Methylnaphtalene (PAH), including: 1-methylnaphtalene 2- methylnaphtalene Dimethylnaphthalene, mixture of isomers methylnaphtalene	Σ = 0,12	Σ = 2	0,1-0,5 0,01-0,1 0,01-10	0,1-0,5 0,01-0,1 0,01-10		>15
129-00-0	Pyrene	0,0046	0,023	0,01-0,41	0,01-0,24		>15
7440-66-6	Zinc	7,8[7,8] 3,1[7,10]	8,4[7]	15-1177 (3,03-128)	25,6-962 (3,03-128)		>15
85535-84-8	Alkanes, C10-13, chloro[11]	0,4	1,4	15-50			<5
309-00-2 60-57-1 72-20-8 465-73-6	Organochloride pesticides aldrin dieldrin endrin isoendrin	Σ = 0,01	not applied	0,27-0,574 0,204-0,98			<5
117-81-7	Bis(2-ethylhexyl) phthalate (DEHP)	1,3	not applied	0,7-25	1-25		>15
206-44-0	Fluoranthene	0,0063	0,12	0,01-0,373	0,01-0,23		>15
7439-92-1	Lead and lead compounds	1,2[8]	14	0,023-650	0,023-650		>15
7440-02-0	Nickel and nickel compounds	4[8]	34	1,44-50,9 (1,02-17,2)	1,44-50,9 (1,02-17,2)		>15

[10] This EQS is valid for soft water (H<24 mg CaCO3/l).
[11] There is no indicator parameter for these substances. The indicator parameter is defined based on the analysis methodology.

CAS number[4]	Substance	AA-EQS[5] [µg/l]	MAC-EQS[6] [µg/l]	Minimum and maximum measured concentrations [µg/l] (dissolved in brackets)		Threat to good chemical status	Available measurements [events]
				All available data	Danish data		
84852-15-3	Nonylphenols (4-nonylphenol)	0,3	2,0	0,1-16 (0,086-0,63)	0,1-16		>15
140-66-9	Octylphenols	0,1	not applied	0,645-2,19			<5
50-32-8	Benzo(a)pyrene	1,7 × 10-4	0,27	0,01-0,5	0,01-0,5		>15
205-99-2	Benzo(b)fluoranthene	[12]	0,017	0,01-0,5	0,01-0,5		5-15
207-08-9	Benzo(k)fluoranthene	[12]	0,017	0,025-0,371			5-15
191-24-2	Benzo(g,h,i)perylene	[12]	8,2 × 10-3	0,01-0,259	0,01-0,15		>15
36643-28-4	Tributyl compounds	0,0002	0,0015	0,029-0,105			<5
886-50-0	Terbutryn	0,065	0,34	0,055-0,122			<5

[12] For this group of priority substances, polyaromatic hydrocarbons (PAH), the EQS for biota and the corresponding EQS for the concentration of benzo(a)pyrene are applied. Benzo(a)pyrene can be used as marker for the entire PAH group and therefore, only benzo(a)pyrene needs to be monitored when comparing the EQS for biota and corresponding EQS for water.

3.4 Discharges from Separate Stormwater systems

Discharges from separate systems show a higher variability compared to combined systems, i.e. there is a larger spread between minimum and maximum values. For example, the coefficients of variation for EMCs measured by Metadier and Bertrand-Krawjeski (2012) increased from 0.61 (COD) and 0.73 (TSS) for combined systems to 0.71 (COD) and 1.07 (TSS) for separate systems. This high variability can be explained by the missing effects of the wastewater flow, whose pollutant concentrations tend to be more stable and consequently may flatten the extremes caused by rainfall-runoff driven processes (such as resuspension of sediments and other particulate pollutants). Generally, average concentrations tend to be lower in separate systems for a greater number of pollutants, and a similar pattern can be observed for discharged event loads. However, this depends on the pollutant sources: for a large number of heavy metals, for example, measured concentration ranges in separate systems are higher than in combined systems. Also, extreme event loads can be higher for separate systems, due to the high event variability.

When considering catchment disconnection as a solution to reduce CSO impacts, it should be considered that the total load from separate systems can exceed the total load from CSO structures. In fact, disconnection will result in greater volumes directly discharged to the natural waters, with a potential increase in the impact. For example, Wicke et al. (2016) calculated that the larger fraction of priority substances discharged from the city of Berlin to the receiving water originates from separate systems rather than WWTPs (although the discharged stormwater volume from separate systems is about one third of the treated wastewater coming from combined systems).

The measured EMC for traditional pollutants are listed in Table 6. Median values are generally below discharge limits for wastewater (cf. Table 3), with the exception of TSS. This suggests that traditional pollutants from stormwater systems represent a risk to the chemical status only for extreme events. Specifically, ammonia sources are not present in stormwater systems (unless in case of cross-connections with combined systems), i.e. acute toxicity due to ammonia is negligible for separate systems. Concerns can be raised about COD maximum concentrations, but the major issue is usually linked to TSS concentrations. Particles are a major carrier for several priority substances with a strong tendency to sorb, and they can be used as a proxy for several of these pollutants.

Table 6. Measured EMC ranges for traditional pollutants in separate systems.

Parameter	Min [mg/l]	Median [mg/l]*	90% quantiles [mg/l][13]	Max [mg/l]
BOD5	0,15	12	81,4	490
COD	0,5	69	417	3000
N-TKN	0,008	2,9	7,75	53
N-NH4	Not available	Not available	Not available	Not available
Ptot	0,005	0,27	1,35	5,6
TSS	0,006	68,1	714	6143

[13] These values are estimated based on heterogeneous data found in the literature (often reported as average values or ranges), so they represent an overestimation of actual values and they are presented here only to provide an indication of the EMC magnitude

Only 11 substances (among the 80 measured in stormwater systems - Figure 9) showed ranges that were always above the MAC-EQS (see Appendix A for the complete analysis). Similar to the CSO concentrations, these substances include heavy metals and PAHs. The majority of measured substances showed ranges mainly below the MAC-EQS, with 18 substances with ranges also below the AA-EQS.

Importantly, the variability in the measured EMCs is greater than for CSOs: this is linked both to the intrinsic variability of stormwater pollution at each site, as well as to the variability between the different catchments (and related pollution sources) where literature data were collected. For example, the lowest concentrations are typically measured in low pollution areas (e.g. systems collecting roof runoff, parks, green areas), while the highest concentrations are measured in runoff from highways and high traffic roads. Also, data availability is limited, with 32 substances measured in less than five monitoring campaigns. Overall, it can be concluded that discharges from separate systems can pose an acute risk to the chemical status for selected substances (heavy metals, PAHs), while they can also affect the chronic toxicity due to the size of the discharged loads.

3.5 Wet weather discharges from Wastewater Treatment Plants

Rain events have two different effects on Wastewater Treatment Plants: the increase in the hydraulic load may affect the removal performance of the plant and, when the maximum capacity of the plant is exceeded, it may result in bypass flows. The increased hydraulic load results in a decrease of the residence time within the system and thereby in a reduced removal efficiency of the various physico-chemical and biological processes. Installation of detention basins in the upstream catchment as a solution to reduce overflow discharges might increase the duration of these high-flow events at the WWTP, with a detrimental effect on the overall pollutant load discharged to the RWB.

The different treatment steps in the WWTP have different maximum capacities. When the inflow to the plant reaches these limits, the exceeding flow is diverted and directly discharged to the RWB (the so-called bypass flows). Depending on the plant configuration, bypass flows can originate at different points (see Figure 10): e.g. before entering the plant, after a primary treatment, or before entering the biological treatment. Depending on the origin of the bypass flow, the pollutant levels can change: pollutant concentrations in the bypass at the WWTP inlet will be similar to those measured in CSOs, while lower pollution levels can be expected for other bypass flows.

Depending on the configuration of the plant, bypass flows can have independent discharge points, or they can be mixed with the plant effluent. This is relevant when looking at regulation and emission limit values. WWTP discharges are in fact strictly regulated, but the major focus is on dry weather discharges, which represent the greater fraction of the plant operation time. Wet weather discharges typically fall within the allowed exceedances. For example, the EU Urban Waste Water directive (91/271/EEC) lists the number of samples that are allowed to exceed discharge limits, implying a lower removal in a limited number of cases (e.g. 25 exceedances over an entire year). At the Danish level, the number of allowed exceedances is specified in the discharge permit for each plant. However, it can be argued that independent discharges (e.g. from weirs located at the plant inlet, before any form of treatment) can be categorized as CSO discharges, requiring different regulations.

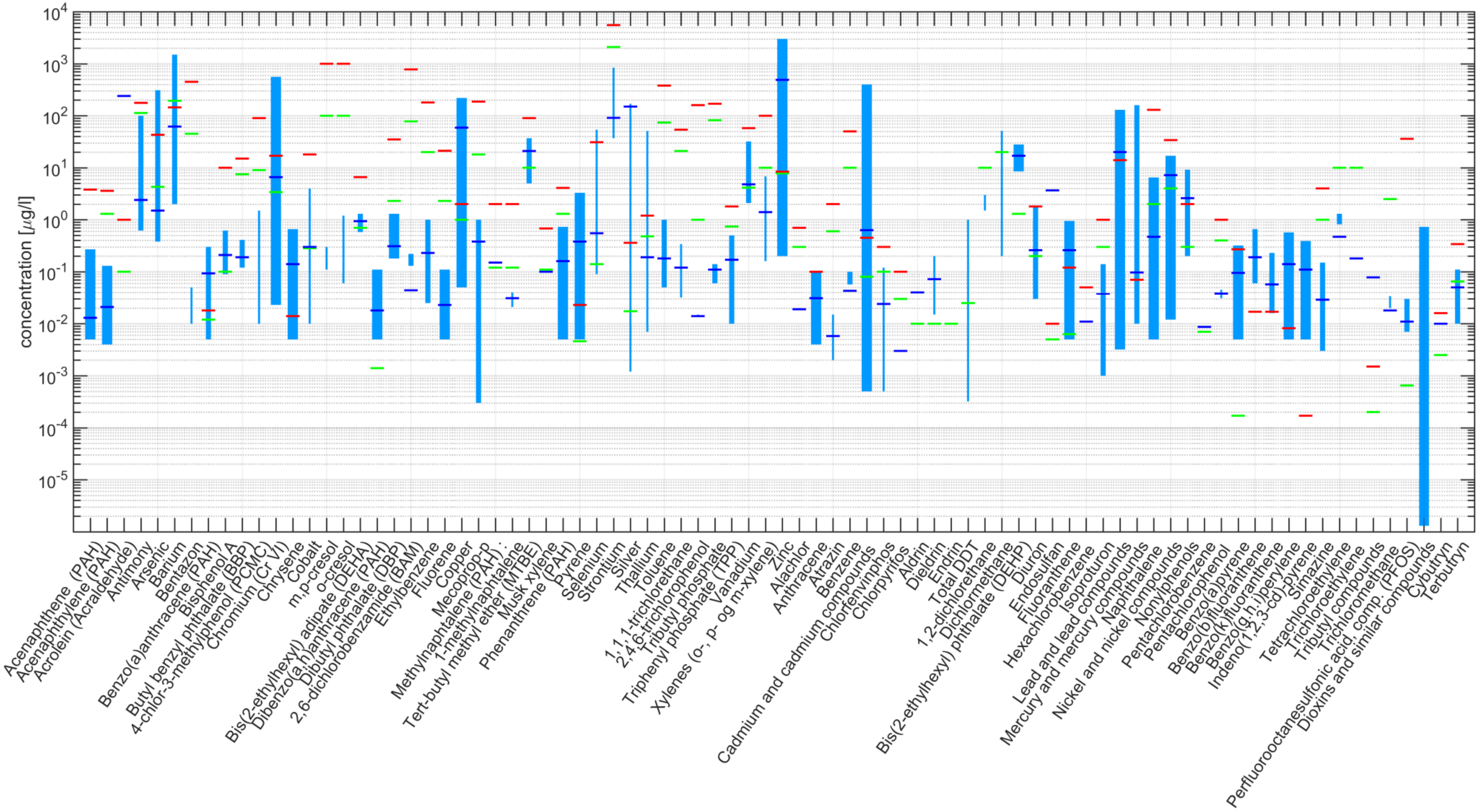


Figure 9. Concentration ranges for priority substances measured in separate stormwater systems (blue lines, expressed as minimum and maximum value), median/mean value used in the screening (blue horizontal lines), AA-EQS (green horizontal lines) and MAC-EQS (red horizontal lines). The thickness of the blue line is proportional to the number of available measurements (thinnest line: n<5, thickest line: n>15). For further details, see Appendix A.

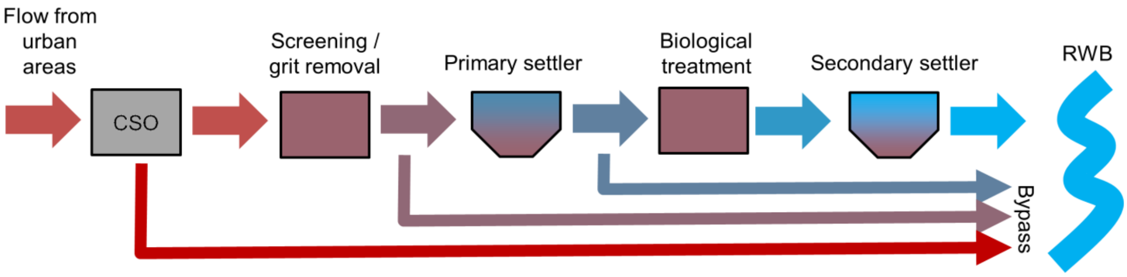


Figure 10. Schematization of the various possible locations for bypass flow to occur in a classical WWTP with biological treatment. Bypass discharges to RWBs can be mixed with the WWTP effluent or have independent discharge points.

Table 7. Comparison between values from Rukovets and Mitchell (2010) and legislation limits.

Parameter	Wet Weather concentration [mg/l]				Removal [%]	
	Limit (BEK726 01/06/2016)	Measured			Limit (91/271/EEC)	Measured Average
		Average	Min	Max		
BOD5	<15	22-24	9	30	70-90	77-81
TSS	<35	20-29	13	33	90	71-89

Data on WWTP wet weather discharges are limited. Information about traditional pollutants is sparse: two key American studies (Gray, 2010; Rukovets and Mitchell, 2010) analysed blended effluents (mix of effluents from treatment lines and bypass) from WWTPs, with a specific focus on pathogen concentrations and health risks posed by the wet weather events. These studies show how both traditional pollutants (Table 7) and pathogen concentrations increase during wet weather events. However, both studies did not provide strong conclusions, since the effect on pathogens depends on the plant-specific configuration and operation, and a limited increase in the estimated number of infections was estimated.

Goodson (2013) analysed the removal of priority substances and emerging pollutants during dry and wet weather operation of a WWTP. Removal of these substances depends on their physico-chemical characteristics, and this also affects their removal during wet weather events. No significant difference in removal between dry and wet period was found for the majority of the substances, with some exceptions for PAHs. The latter, in fact, were mostly removed in the secondary clarifier, the unit of a traditional WWTP whose performance is most sensitive to high flow conditions.

Additional studies focused on measuring the effect of WWTP operation during wet weather operations. Bowes et al. (2012) measured phosphorous concentrations at the outlet of the Marlborough WTTP with a high-frequency sensor (measurements were taken at 30-minute intervals). The monitoring campaign showed how the WWTP was generally complying with effluent limits, also after rain events. However, a prolonged rainy period resulted in an increase of measured concentrations due to a deterioration of the WWTP removal performance after such a long period of high inlet flows.

Faber and Bierl (2012) investigated the toxicity of WWTP effluent during wet weather events, but they could not find a significant impact of wastewater flow on toxicity. Also, they observed a decrease in toxicity for some organic fractions, which was explained by the dilution caused by the stormwater flow at the WWTP inlet. Boënne et al. (2014) utilized an online monitoring station in the Witte Nete river to monitor the effect of rain events and capacity overloading on the local WWTP. Compared to the traditional monitoring (grab samples carried out by the local environmental authority), the online measurements revealed higher ammonia peaks and lower oxygen levels. This monitoring approach was found to be more appropriate for fully evaluating the impact of WWTP discharges on the receiving water bodies.

4. Ecological indicators for determining impacts from wet weather discharges from urban areas

4.1 Defining ecological indicators under the WFD

According to the European WFD, Danish streams should meet the obligatory ecological quality requirements (good ecological quality), defined as a slight deviation from the undisturbed or least disturbed reference scenario. Moreover, the WFD states that the current ecological status must not be deteriorated (European Commission, 2000). The ecological status is quantified using biological quality elements. According to the national water plans 2015-2021, the biological quality elements comprise freshwater plants, fish, macroinvertebrates and benthic algae. The ecological status is assessed as the deviation from the reference scenario or least disturbed conditions (i.e. Ecological Quality Ratio; EQR), which are defined for each type of water body. In order to simplify freshwater management, five ecological quality classes (high, good, moderate, poor, and bad) have been established based on intercalibrated EQR thresholds.

In Denmark, freshwater plants, macroinvertebrates, and fish are currently used as ecological quality elements, and ecological indices exist for these. The group of benthic algae is intended to get included in the national water plans 2015-2021, but the corresponding ecological index is not yet fully developed. The ecological status based on freshwater plants is quantified using the Danish Stream Plant Index (DSPI) and reflects especially physical disturbances, such as weed cutting and anthropogenic changes in the physical stream dimensions, and eutrophication (Baattrup-Pedersen and Larsen, 2013). The use of freshwater plants as ecological indicators is restricted to stream types 2 and 3 (i.e. catchment size > 10 km^2). The ecological status based on macroinvertebrates is quantified using the Danish Stream Fauna Index (DSFI) reflecting especially effects of untreated wastewater (leading to reduced oxygen concentrations) and anthropogenic changes in the physical stream dimensions and substrate composition (Miljøstyrelsen, 1998).

The Danish Fish Index for Streams (DFIS) is used to assess the ecological quality of streams based on the natural production of salmonid fish in small streams (width < 2m) and on the taxonomic composition of fish communities in larger streams (width > 2m) (Kristensen et al., 2014). The DFIS reflects especially changes in the physical stream dimensions (e.g. channelization and dredging) and substrate composition and migration barriers (i.e. dams and fish farms), but may also reflect pollution leading to reduced oxygen concentrations (Kristensen et al., 2014) as well as intense weed cutting (Bach et al., 2016). Since the benthic algae index is still under evaluation and the DSPI cannot be applied in stream type 1, we focus strictly on the macroinvertebrates and fish as ecological indicators for scrutinising ecological effects of urban water discharges. Note, however, that the DFIS has not yet been intercalibrated with comparable EU member states; hence using the DFIS to quantify ecological status should be done with care.

In addition to the legislative requirements enforced through the European WFD, the Danish streams provide habitats for a number of species with specific protection goals as defined in Annex II of the European Habitats Directive. The conservation status of these species must be "favourable" and the populations of these species should be monitored to guide the sufficient protection of the species and their habitats. In Denmark, 14 species of fish, one species of dragonflies and two species of mussels are mentioned in Annex II.

4.2 State of the art: Ecological effects from discharges from urban areas

In order to present an overview of the state-of-the-art in terms of ecological effects from discharges from urban areas, we performed a literature search for peer reviewed articles containing information on both biological communities or populations and some quantified measure of stressor level from urban water discharges. The literature search was based on the following key words: (stream* OR river*), (*invertebrate* OR fish*), and (industr* OR wastewater* OR wwtp*). Using these keywords in combination revealed that 737 articles matched the search criteria. However, a majority of these studies were conducted in Asia (especially China and India), South America (especially Brazil), and Africa. These studies have not been included in the subsequent review of existing literature due to several parameters which are not comparable to Danish conditions (i.e. resident biota, chemical mixture composition, and urban water management and treatment). Moreover, a large number of studies have focused on chemical or biological markers of pollution (e.g. bioaccumulation, gene expression, enzymatic activity, and behavioural responses) in fish or benthic biofilm. While biomarkers for chemical pollution may provide useful information for some research aims, such endpoints cannot, and have never been, translated into measures for ecological quality (i.e. ecological indices) or other community-based endpoints. Hence, for the purpose of this review, biomarker and chemical marker studies were omitted from the search list. Applying these additional selection criteria, 23 articles matched the search and selection criteria and were reviewed. A full overview table of these studies is presented in Appendix B.

The literature search was matched with articles published from 1998 to date and spans a wide range of temporal and spatial resolutions in quantifications of discharges from urban areas and complexities of ecological endpoints, including a gradient in replication and sampling intensity. None of the existing studies attempted identifying effect-based threshold values for water quality or quantity. Moreover, in all but one study by Münze et al. (2017) quantifications of chemical concentrations in urban water discharges were based on grab samples, whereas Münze et al. (2017) used passive samplers (Chemcatcher®) to quantify time weighted means of pesticide concentrations. Due to the consistent lack of chemical concentration data with higher temporal resolution, threshold concentrations cannot be obtained from a meta-analysis of these studies, since the potential temporal variations in effluent concentrations, induced especially by heavy rain events, have not been covered.

While a number of the studies have applied various ecological indices, formally used for stream management to pinpoint that discharges from urban areas can reduce index scores, none of the studies have addressed WFD requirements nor established risks of not meeting the obligatory ecological quality criteria (i.e. good ecological status). In the studies that show reduced index scores downstream of urban discharge points, these effects could generally not be coupled with specific chemical or hydrological characteristics of discharges from urban areas.

However, Münze et al. (2017) showed that the SPEcies At Risk (SPEAR) index, specifically targeting effects of pesticides, was significantly reduced downstream of WWTP effluents mainly due to insecticide inputs that were specifically related to the WWTP effluents. In contrast, Bunzel et al. (2013) also showed that SPEAR index values were significantly reduced downstream of WWTP effluents, but this reduction could not be coupled with pesticide concentrations in the effluents.

The majority of studies do not include quantifications of anthropogenic chemicals, but are based on DO, nitrogen, and phosphorous compounds. This is a logical consequence of the majority of European ecological indices, based on macroinvertebrates and fish, targeting effects of pollution with easily degradable organic matter (causing reduced oxygen concentrations). Interestingly, general effects of toxicants (i.e. organic chemicals such as pesticides and inorganic substances such as heavy metals) appear to be mainly driven by organismal sizes with smaller-sized animals being more sensitive to toxicant stress (Wiberg-Larsen et al., 2016; Buchwalter et al., 2008). Importantly, macroinvertebrate species that are highly sensitive to reduced oxygen concentrations are comprised of both larger and smaller species. Hence, although toxicant concentrations in urban water effluents may significantly change the macroinvertebrate community composition towards lower abundances or eradication of species sensitive to these toxicants, this effect will not necessarily be detectable using the traditional macroinvertebrate indices (Wiberg-Larsen et al., 2016).

The studies that integrate several decades of monitoring data reveal substantial improvements in ecological quality due to more comprehensive and improved wastewater treatment and management (Appendix B). However, none of these studies link the ecological improvements to specific urban water management initiatives (e.g. specific treatment technologies, reduction of CSOs, or stormwater management strategies). In contrast, several studies failed to clearly quantify the negative effects of discharges from urban areas when the upstream river systems were heavily modified. In fact, Burdon et al. (2016) showed that the habitat quality of upstream river sections was a more important driver of Saprobic Index (SI) scores than measured water quality or the proportional contribution of WWTPs to the overall stream discharge. The potential for environmental filters acting at different spatial and temporal scales to influence the ecological responses to changed/improved urban water management is discussed in detail in Chapter 5.

4.3 Delimitation of chemical indicators for discharges from urban areas

4.3.1 Characterising physico-chemical impacts of urban discharges in streams

Discharges from urban areas lead to a number of physico-chemical changes in RWBs, and these changes are particularly intense during wet weather discharges (see also chapter 3). These changes include, but are not limited to, hydraulic stress, reduced oxygen concentrations (increased BOD_5), increased transport of fine sediment (TSS), increased concentrations of ionised ammonium, unionised ammonia, and various macronutrients, as well as increased concentrations of heavy metals and anthropogenic toxic chemicals (see also Chapter 3). The actual physico-chemical impact of discharges from urban areas on the RWB depends on: i) base flow discharge of the RWB (i.e. dilution potential), ii) quantity of discharged wastewater (i.e. volume of wet weather discharges), iii) physico-chemical characteristics of the discharges, and iv) temporal exposure pattern to the wastewater (see also Chapter 3).

4.3.2 Identifying chemical indicators for ecological effects

Priority substances in discharges from urban areas (e.g. pesticides and heavy metals) may have strong effects on stream biota and related ecosystem functions, depending on the composition of compounds (e.g Bunzel et al., 2013; Englert et al., 2013). Nevertheless, the complexity of chemical mixtures and the temporal variability in exposure regimes make ecological effects of toxic chemicals from CSOs extremely difficult to predict (see also Chapter 3). However, in Chapter 3, we pinpointed heavy metals as one group of toxicants that frequently exceed regulatory thresholds. Nevertheless, as mentioned above, there is currently no knowledge addressing the link between heavy metal pollution and ecological quality. Therefore, although heavy metals, especially copper, would be useful chemical indicators for urban water discharges, this cannot be linked to ecological quality based on the current knowledge.

Other important characteristics of wet weather discharges are increased concentrations of ammonia and reduced oxygen concentrations (in part caused by higher BOD_5). Both the DSFI and the DFIS are based on indicator species that have high sensitivity or tolerance to these pressures. Consequently, the currently used ecological indices for fish and macroinvertebrates should be applicable to detect the effects of increased concentrations of ammonia and reduced oxygen concentrations. Below, we briefly review the state-of-the-art in terms of impacts of ammonia and easily degradable organic matter on fish and macroinvertebrates.

4.3.3 Ammonia

The total amount of ammonium (total-ammonium) is comprised of unionised ammonia and ionised ammonium, and the equilibrium concentrations depend on several factors, especially pH and temperature. Increased temperature and increasing pH both increase the fraction of unionised ammonia.

Laboratory studies show that fish are more sensitive to ammonia compared to macroinvertebrates and plants (Crabtree et al., 2012). However, some large species of mussels appear to have comparably high sensitivities (Crabtree et al., 2012). Hence, concentrations of unionised ammonia that are considered as safe for the most sensitive species of fish should additionally be safe for other freshwater organisms. Sublethal effects of unionised ammonia on fish include permanent physiological damages in gill structures generating reduced growth rates (Milne et al., 2000). Sublethal effects on macroinvertebrates (e.g. catastrophic drift) appear to occur at concentrations similar to those causing sublethal effects on salmonid fish (Crabtree et al., 2012).

In general, salmonid fish species are more sensitive to unionised ammonia compared to cyprinid fish species (Milne et al., 2000). Laboratory studies additionally show that especially the time between repeated exposures is an important governing factor for the overall effect of unionised ammonia on salmonid fish (Milne et al., 2000). When the recurrence frequency of exposure exceeds one per week, the influence of exposure repetition on the mortality in salmonid fish steeply increases (Crabtree et al., 2012). In other words, recovery time is a highly important factor in determining the ecological effects of unionised ammonia. Based on the current knowledge, threshold criteria for no-effects have been developed for urban streams in England (UPM2 standards) differentiating between exposure duration, frequency, and concentration (see Section 7.2).

Importantly, field-based studies reveal strong correlations between concentrations of ionised ammonium and numerous species of freshwater macroinvertebrates in Danish streams. Population densities of sensitive species decrease, especially mayflies (Ephemeroptera) and stoneflies (Plecoptera), whereas densities of tolerant species increase with increasing concentrations (annual average) of ionised ammonium (Friberg et al., 2010). Most of the species showing population responses to ionised ammonium concentrations are positive quality indicators in the DSFI (Friberg et al., 2010). Friberg et al. (2010) additionally showed that population densities of several sensitive and tolerant macroinvertebrate species were strongly altered at unionised ammonium concentrations around 0.2 mg/L.

4.3.4 Dissolved oxygen

The vast majority of stream dwelling organisms use oxygen for respiratory purposes, including all organism groups that are used for assessing ecological quality in streams (plants, macroinvertebrates, fish, and benthic algae). Due to the predominance of turbulent flow and the generally small size of Danish streams (compared to the global scale), oxygen concentrations in Danish streams can be expected to be comparable across the entire cross-sectional area of the streams. However, oxygen concentrations undergo diurnal fluctuations driven by oxygen production by primary producers (mainly plants and algae) during daylight hours, and by oxygen consumption due to respiratory processes by all stream dwelling organisms.

The overall respiratory capacity of the stream ecosystem strongly depends on the total amount of easily degradable organic material (measured as BOD_5), which is often correlated to wet weather discharges of untreated or partially treated wastewater (see also Chapter 3). A multitude of studies document that fish, and especially macroinvertebrates, are particularly sensitive to low oxygen concentrations (Crabtree et al., 2012). Hence, threshold concentrations for oxygen which are sufficiently protective to macroinvertebrates can additionally be expected to sufficiently protect other organism groups in streams (Crabtree et al., 2012). However, salmonid larvae and juveniles may be more sensitive than most macroinvertebrate species and require particular attention in terms of management of urban water discharges (Elshout et al., 2013).

Oxygen concentrations in stream water define the upper limit for metabolic requirements of the stream organisms. In other words, a certain amount of oxygen is necessary for sustaining the basal physiological processes, and this oxygen threshold concentration varies among species. In general, macroinvertebrates are more sensitive than fish to low oxygen concentrations, especially species with a preference for riffle habitats (low water depth, coarse substrate, and high current velocities) require high oxygen concentrations to sustain their metabolic requirements. In particular, these sensitive species belong to the mayflies (Ephemeroptera) and stoneflies (Plecoptera) (Crabtree et al., 2012). Moreover, salmonid fish are more sensitive than cyprinids to low oxygen concentrations (Crabtree et al., 2012). Concentration-response curves reveal that the mortality increases rapidly with decreasing oxygen concentrations for most species (see also Section 7.2.2), meaning that small variations in oxygen concentrations can prompt significantly different effects, depending on the specific oxygen requirements of the organism (Seager et al., 2000).

Low oxygen concentrations prompt active escape behaviour in macroinvertebrates as well as in fish, where oxygen concentrations < 4 mgL^{-1} strongly increase these behavioural responses (i.e. catastrophic drift in macroinvertebrates and active swimming in fish) (Crabtree et al., 2012). In fact, behavioural responses occur approximately at the same concentrations as mortality (Crabtree et al., 2012). In contrast to ammonia, the influence of exposure concentrations is the primary factor governing effects with exposure frequency and time between exposures being less important (Crabtree et al., 2012).

Similar to ammonia-N, UPM2 standards for DO have been implemented for urban streams in England providing a generic guideline for concentrations, duration of exposure, and time between exposures, and the threshold concentrations are based on the current knowledge as reviewed by Crabtree et al. (2012) (see Section 7.2).

Field studies reveal that population densities of sensitive, as well as tolerant macroinvertebrate species are strongly correlated to measured BOD_5 in open land streams (annual average), reflecting availability of oxygen (e.g. Friberg et al., 2010). Friberg et al. (2010) found strongly declining population densities of several sensitive macroinvertebrate species at BOD_5 concentrations > 1.5 mgL^{-1}. As such, the currently applied threshold concentrations for BOD_5 for high and good ecological status in Danish streams are 1.4 and 1.8 mgL^{-1} (annual average) (Miljøstyrelsen, 2015). However, both macroinvertebrate and fish communities can cope with higher oxygen stress for shorter periods in time (Crabtree et al., 2012). Overall, oxygen concentration levels and the duration of low-concentration events are more important than the recurrence frequency of low-concentration events in terms of magnitude of ecological effects (Crabtree et al., 2012).

4.3.5 Linking ammonia and dissolved oxygen to currently used ecological indicator tools for Danish streams

Macroinvertebrates - DSFI

The DSFI quantifies the ecological quality based on a set of indicator species characterised by high sensitivity or tolerance to low oxygen concentrations, and the final index value (fauna class) is categorical ranging from 1 to 7. Fauna class 7 represents high ecological quality, and fauna classes 5 and 6 represent good ecological quality. The index is semi-quantitative, meaning that each indicator species, in most cases, counts as long as > 1 individual is found in the fauna sample (Miljøstyrelsen, 1998).

Since the DSFI targets pollution effects of easily degradable organic matter, the index is well equipped to capture the effects of low oxygen concentrations governed by wet weather discharges. Critically low oxygen concentrations will decrease both the abundance and species richness of macroinvertebrate taxa sensitive to low oxygen concentrations, and conversely increase both the abundance and species richness of macroinvertebrate taxa with high tolerance to low oxygen concentrations (e.g. Burdon et al., 2016; Bunzel et al., 2013).

Additionally, the DSFI index should respond to increased concentrations of ionised ammonium, since multiple species, acting as positive indicators for ecological quality in the DSFI index, show strong negative correlations to measured concentrations of ionised ammonium (Friberg et al., 2010). However, the DSFI index additionally responds to intense weed cutting (depending on the weed cutting method and frequency) (Bach et al., 2016), ochre pollution (due to a lowering of the groundwater tables, mainly occurring in Western Jutland), and reduced habitat quality (Baattrup-pedersen et al., 2016). As such, streams rarely obtain good or high ecological quality, measured with the DSFI, when subjected to weed cutting (full cutting of the main flow channel with a frequency > 1 time per year) (Bach et al., 2016), ochre pollution, or when the physical habitat quality is low (relative value for habitat quality: < 0.29 measured with the Danish Habitat Quality Index) (Baattrup-pedersen et al., 2016), irrespective of the oxygen conditions. Hence, low index scores determined with the DSFI are context dependent and need to be interpreted as such.

Fish – DFIS

The DFIS is subdivided into two constituent parts; DFISa and DFISt. DFISa is based on the community composition of fish, whereas the DFISt is based on the density of naturally produced juvenile trouts (*Salmo trutta*) and juvenile salmon (*Salmo salar*) (Kristensen et al., 2014). DFISt is intended for use in small streams (catchment area < 10 km^2), whereas DFISa is intended for larger ones (catchment area > 10 km^2).

Since both DFIS indices respond to pollution with easily degradable organic matter (resulting in low oxygen concentrations), both could be considered suitable for capturing the effects of wet weather discharges that result in reduced oxygen concentrations in the RWB. Moreover, since salmonid fish are highly sensitive to unionised ammonia and since salmonid fish constitute the backbone of the DFISt and are the dominant positive indicator in the DFISa (Kristensen et al., 2014), both indices could additionally be considered as suitable for capturing the effects of urban water discharges that result in increased concentrations of unionised ammonia.

However, similar to macroinvertebrates, the two DFIS indices additionally respond to other stressors than just reduced oxygen concentrations and increased concentrations of unionised ammonia. Lower index values are obtained when migratory barriers exist downstream in the stream system (e.g. dams and impoundments). Also, lower index values are obtained when physical conditions are impoverished, especially when coarse substrates are lacking or sparsely occurring (Kristensen et al., 2014). Therefore, similar to macroinvertebrates, low DFIS scores are context dependent and should be interpreted as such.

4.3.6 Species with specific protection goals

Freshwater species with specific protection goals generally have spatially constrained occurrence patterns. However, brook lamprey appears to occur at the broad national scale, although populations are more scattered on the Danish islands. They spawn on gravel beds and the juveniles spend the majority of time in low-flow habitats with fine and soft substrate types. Salmon, grayling and snout all mainly occur in the western part of Jutland and are all strongly threatened. For the remaining fish species, little is known in terms of their conservation status (Fredshavn et al., 2014).

The dragonfly *Ophiogomphus cecilia* is restricted to clean and larger streams with minimal impact on oxygen concentrations and mainly occurs in the five larger river systems in Jutland (e.g. River Skjern), and the conservation status of this species is favourable. The mussel *Unio crassus* has only been registered in three river systems on Funen and Zealand and has a preference for sand-dominated streams with scattered occurrence of gravel and boulders.

The other mussel species with specific protection goals, *Margaritifera margaritifera* has only been found in the Varde River where it may still have a viable population (Fredshavn et al., 2014).

In terms of the sensitivity of these species to urban water discharges, no knowledge exists in the peer reviewed literature. However, since several of the species (salmon, snout and greyling) are salmonid fish or large mussels (*Unio crassus* and *Margaritifera margaritifera*) being highly sensitive to both low oxygen concentrations and high concentrations of unionised ammonia, the specific protection of these species should be considered if they occur in the stream system in focus.

5. Influence of the environmental context for quantifying ecological impacts from wet weather discharges

This chapter provides an overview of what is currently known about the state of the upstream – typically rural – catchment area that is often considered “pristine” in the context of urban planning, as well as our understanding of the resulting impacts related to individual chemical stressor groups (e.g. pesticides; chlorinated solvents, etc.). It begins with a general overview, contextualizing the need for looking at both surface and groundwater conditions in the context of stream water quality, and includes a short overview of the natural variability of surface water chemistry. It concludes with a more focused discussion of multiple (chemical) stressor conditions, found especially in mixed land use stream systems, which are probably the most relevant when discussing impacts in a context that should include urban water discharges.

5.1 Importance of headwater streams

Surface water has been the primary freshwater supply appropriated to meet anthropogenic water demands (industrial, municipal, agricultural) worldwide (Richey et al., 2015), with some exceptions such as Denmark with a 100% groundwater-based water supply. Conventionally, the monitoring of freshwater systems for chemical and ecological status has also been limited to surface water concentrations, where the dominant focus has been on meeting specific water quality criteria – driven by a few (<50) priority chemical compounds including those responsible for eutrophication. This dates back to the 1890s when monitoring of a few European rivers commenced (e.g. Thames; Seine), which were highly polluted particularly with untreated domestic sewage (Meybeck and Helmer, 1989). Society has become increasingly reliant on groundwater, however, as surface water supplies become less reliable from both the water quantity and quality perspective leading also to its overexploitation (McKnight et al., 2012). This makes it crucial to include groundwater when discussing potential impacts to e.g. aquatic freshwater systems. Groundwater exchange has long been known to affect surface water conditions in a number of ways apart from its role in contributing to xenobiotic chemical contamination, including sustaining stream base-flows, moderating water level fluctuations, providing stable temperature habitats, and supplying nutrients and inorganic ions (Hayashi and Rosenberry, 2002).

Knowledge of the influences of headwaters, typically defined as first-order, perennial streams that can include contributions from smaller intermittent and ephemeral streams, on the water quality and flow regime of down-gradient waters is essential for ensuring the sustainable management of water resources at the river basin scale. Headwaters are intrinsically connected to landscape processes, which can influence the supply, transport and fate of water and solutes in watersheds (Alexander et al., 2007). Specifically, hydrological processes control the recharge of subsurface water stores, flow paths and residence times throughout landscapes. Groundwater is a key component of headwater flows, providing the base-flow during periods with no rain or snowmelt input and can also constitute much of the increased discharge during and immediately following storms (Hayashi and Rosenberry, 2002) in pristine systems. The dynamic coupling of hydrological and biogeochemical processes furthermore controls the chemical form, timing and fate of solute transport within the watershed, which is likely facilitated by the high density of headwater streams in the upper catchment and thus high frequency of tributary linkages to higher-order streams in river networks (Alexander et al., 2007). Considering the placement of anthropogenic land use activities such as agriculture, it has become increasingly difficult to find suitable locations in upstream catchments that are representative of "pristine" conditions, leading instead to the use of control sites documented as e.g. "least disturbed conditions" (McKnight et al., 2012; Stoddard et al., 2006).

Interestingly, a recent study of 226 small- and medium-sized streams across central and northern Europe indicated the total number of benthic invertebrate taxa were statistically significantly higher in the small streams compared to the medium streams; otherwise no differences in biological diversity existed in relation to stream size (O'Hare et al., 2015). This is indicative of the important role headwater streams play in maintaining source populations that affect the dispersal capacities of sensitive species (Haase et al., 2013). Freshwaters in general are essential for providing an array of ecosystem services, including both provisional (e.g. drinking water; food) and regulating (e.g. self-purification; nutrient cycling) services (Brauman et al., 2007; MEA, 2005).

Importantly, headwater streams are often characterized by the impairment of hydromorphological, chemical and ecological conditions which may ultimately influence the ecological conditions at downstream sites. As such, Stoll et al. (2016) showed that the ecological quality, quantified with the macroinvertebrate-based Saprobic Index, was highly dependent on the ecological status of the upstream sections. In fact, even a high quality of the hydromorphological conditions (of higher order streams) did not support high ecological quality if the upstream sites were characterized by low ecological quality. Conversely, even hydromorphologically degraded stream sites may support high ecological quality if the headwaters are characterized by high ecological quality (Stoll et al., 2016). This is relevant also for urban streams since the impact of urban water discharges on e.g. macroinvertebrate communities depends on the environmental context of the entire river system. In other words, if headwater streams support high ecological quality, this may mask some of the negative effects of chemical and hydrological disturbances from urban water discharges on the macroinvertebrate communities (Burdon et al., 2016). Conversely, if the headwater streams are characterized by low ecological and hydromorphological quality, downstream sites will have a low probability of obtaining good ecological status even if urban water discharges are conservatively managed in terms of chemical pollution and hydromorphological disturbances (Burdon et al., 2016). It should be noted that, in contrast to most other European member states, headwater streams are to some extent included in the Danish national water plans.

5.2 Variability in natural waters and legislation tie-in

Notably, continental surface water chemistry is already highly variable depending on the prevailing environmental conditions such as basin lithology, vegetation and climate. Spatial variations are known to be more pronounced in small watersheds (≤10 km^2), while this variability decreases (by at least an order of magnitude) for the larger basins (Meybeck and Helmer, 1989). In fact, for small watersheds the range of natural concentrations for most elements usually spans 2-3 orders of magnitude, with H^+, Na^+, Cl^-, SO_4^{2-} and TSS representing the most variable elements.

Natural variability thus prevents the implementation of a generic reference standard for river water, and is thus (partly) responsible for the setting of individual chemical stressor target values for compliance purposes in legislation such as the European WFD.

5.2.1 Issues associated with meeting WFD objectives

The WFD legislative approach sets very ambitious objectives for the quality and protection of European waters, including targets to integrate water quality and ecological status (von der Ohe et al., 2009), and relies on a river basin approach for water management (Jager et al., 2016; EEA, 2007). However, in Europe two six-year cycles of Member State reporting (first in 2009, then 2015) continue to show that progress in achieving good ecological status is still hampered by ambiguous results, e.g. data gaps and inconsistencies (EEA, 2012). This has resulted in an extension of the original 2015 deadline to 2027 (European Commission, 2016), and led to numerous recommendations for enabling a more efficient assessment and management (Reyjol et al., 2014) of particularly chemical contamination impacting surface water resources (Brack et al., 2017). Risk management approaches linked to river basin management plans will therefore have to deliver proactive (e.g. upstream) measures in addition to reactive (e.g. downstream) measures in order to provide a sustainable pathway for improved water resources at reduced environmental and consumptive costs.

5.2.2 Issues associated with ecological and chemical indicators

The practical implementation of the WFD has generated many new challenges, including the need to identify contamination sources and quantify their linkages to ecological impacts (McKnight et al., 2010). Moreover, fulfilling the ecological quality criterion – to ensure ecosystem integrity and not just pollution control – requires that an overall assessment of aquatic ecosystem health is made (Munoz et al., 2014; Birk et al., 2012), which is often supported by the use of qualitative indicators and/or measurement methods that can be difficult to utilize for planning and regulation purposes. This type of legislation has thus initially reinforced existing efforts to continue focusing on eliminating or reducing the effects of the (perceived) dominant stressors, which somehow implies that stressor effects can be separately quantified and will adequately represent the status of a water body. A closer look, however, reveals a paucity in the matching of ecological and chemical monitoring results, which translates into a general lack of suitable stressor-specific metrics (i.e. for single biological quality elements) that can act as a proxy for all the important stressors that may be active in a catchment thus enabling a comprehensive risk assessment (Rasmussen et al., 2013a; McKnight et al., 2012; von der Ohe et al., 2009).

Determining the chemical status of a stream is relatively straight-forward from a legislative perspective, as it has been defined in part by a set of environmental quality standards (EQS) for priority substances in the stream water (e.g. the European EQS Directive 2008/105/EC, European Commission, 2008), and in part by legislation derived within the individual (Member State) countries (e.g. Miljø- og Fødevareministeriet, 2016). In reality, however, the collection of suitable field data for comparison with EQS values is complicated, especially for mixed land use stream systems – a characteristic also commonly found in the upstream sub-catchments or headwater streams.

Specifically, the high temporal and spatial variations of the contamination dynamics create a complex picture where the distribution of contaminants will depend on a number of factors (e.g. physico-chemical properties, redox conditions, hydrological processes) leading to diverse impacts within different stream compartments, i.e. stream water, hyporheic zone and bed sediment (Sonne et al., 2017). This will be discussed further, i.e. the difficulties in translating data into understanding, within the context of multiple stressor impacts.

5.2.3 Issues associated with delineating stressor impacts

The environmental consequences associated with land use intensification, driven by urban expansion and increased agricultural production, have long been recognized as one of the main drivers for increased biodiversity loss and the impairment of ecosystem functions (Beketov et al., 2013; Matson et al., 1997). Primary pressures include hydromorphological alterations (e.g. flow regulation; water abstraction), xenobiotic (organic and inorganic) chemical inputs, coming from both diffuse sources – originating from both geogenic and anthropogenic (typically agricultural) activities, as well as point sources such as wastewater outlets and contaminated sites, and aquatic invasive species (Carpenter et al., 2011).

Hydromorphological impairments are expected to mask the impacts from xenobiotic organic compounds, particularly if the chemical stressors are evaluated independently of the ecology and prevailing environmental conditions (Buffagni et al., 2016; Rasmussen et al., 2011a). This also implies that catchment-scale stressors may counteract local management efforts, which means for example that ongoing (xenobiotic) pollution may counteract the effects of hydromorphological restoration efforts (Feld et al., 2011). In fact, attempts to quantify the ecological response to the effects of hydromorphologically-focused restoration projects often showed a less than satisfactory result, with positive restoration effects (i.e. increases in biodiversity) documented only in ca. 35-45% of the cases (Haase et al., 2013; Palmer et al., 2010; Pelley, 2000). This indicates that other factors must hinder ecosystem recovery, such as chemical stressors (Schäfer et al., 2016; Malaj et al., 2014) and/or the considerable distances that often exist between restored stream sections and undisturbed source (e.g. invertebrate) populations (Stoll et al., 2016). Notably, increasing evidence suggests that chemicals play a crucial role in defining ecological impairment at both the regional (Malaj et al., 2014; Beketov et al., 2013) and global scales (Stehle and Schulz, 2015), and thus should be seen as a stressor for stream ecosystems as equally important as invasive species (Schäfer et al., 2016; Sonne et al., submitted). Putting this knowledge in the context of urban water discharges, we therefore focus the rest of this chapter solely on the discussion of chemical stressor impacts.

5.3 Chemical stressor impacts

Throughout history, humanity has seen a number of different water pollution problems taking center stage at successive stages in their development. These issues are often linked to socio-economic development and resulting anthropogenic water quality deterioration (Meybeck and Helmer, 1989). The severity of these problems has generally been associated with river basin size, where pollution at the local scale is typically seen as having the most severe levels (due to generally reduced dilution effects). This has been attributed to the increasing modification of land use, land cover and water management (recognizing also long-range atmospheric transport of contaminants as an important pathway, see also Section 5.4) resulting in multiple chemical stressors impacting water bodies on a global scale (Yu et al., 2014; Davis et al., 2010) even in remote areas. Impairments due to chemical stressors are especially noticeable in streams and rivers (compared to e.g. lakes and marine settings), which are highly connected to their landscape via their draining systems (Fausch et al., 2010). This section thus focuses solely on freshwater ecosystems, as they experience higher extinction rates than marine and terrestrial systems (Collen et al., 2014).

5.3.1 Heavy metals

Some trace metals are essential for life such as copper and zinc, as they are required for various biochemical/physiological functions and deficiency diseases may result if there is an inadequate supply; however, high concentrations may result in cell and tissue damage (Fonseca et al., 2017). A major fraction of trace metals in aquatic systems can be traced to anthropogenic sources. Copper and zinc may also be used in place of antibiotics and as growth promoters on e.g. pig farms (Jondreville et al., 2003) and subsequently spread as manure onto agricultural fields and enter freshwater systems along with surface run-off (Formentini et al., 2015; Gräber et al., 2005). A number are used in a variety of commercial and industrial processes (e.g. Cd, Cu, Pb, Ni, Zn), or in the case of Hg, derived from the combustion of fossil fuels, namely coal, and thus spread ubiquitously throughout the environment via long-range atmospheric transport (Naik and Hammerschmidt, 2011). Other metals may occur naturally in aquifer sediment (e.g. arsenic; aluminium) and be subsequently released to freshwater systems depending on the prevailing biogeochemical processes, which could be (partly) due to the presence of other (organic) contaminants (Cozzarelli et al., 2016) or due to e.g. acidification of the aquifer (Kjøller et al., 2004).

Many metals are thus eventually mobilized to surface waters from either point or non-point sources (Li et al., 2009; Tiefenthaler et al., 2008). Distinguishing between anthropogenic and geogenic sources of metals requires insight of the governing processes in groundwater, the hyporheic zone and streams. Table 8 presents an overview for dissolved metal concentrations in Danish streams and groundwater, which are in fact comparable to concentration levels for heavy metals found in European streams (data not shown). Trace metals have long been considered common priority pollutants in urban runoff, with Cu and Pb most prevalent in e.g. the USA (Li et al., 2009). However, upstream concentrations arising from agricultural inputs are increasingly of concern as previously indicated. Pollutant behaviour is governed by its speciation, whereby they can be present in numerous physicochemical forms (soluble, adsorbed on mineral surfaces, complexed with organic matter, or precipitated/entrapped in mineral phases). Readily exchangeable forms (such as the acid reducible phase) are usually considered as immediately bioavailable species, such that much of the recent research has focused on fractionation and partitioning to interpret the potential for ecosystem impacts (Naik and Hammerschmidt, 2011; Boughriet et al., 2007; Chandra Sekhar et al., 2004).

Table 8: Detected levels for dissolved trace metals for Danish streams and groundwater from 2004-2012, including median and 90% quantile values and Danish EQS values for freshwater where existing (adapted from Sonne et al., 2017). All concentrations are in µg/L; dashes indicate data is not available; NBL stands for natural background level (to be added to EQS for determining threshold limits).

Dissolved metals	Danish streams[a]		Skjern stream (as 'reference')		Danish groundwater		Danish freshwater EQS[b]
	Median	90%	Median	90%	Median	90%	
Aluminium	0.79	1.5	-	-	2.2	12	-
Arsenic	0.73	2.0	-	-	0.54	3.4	4.3
Barium	63	82	-	-	71	200	19
Cadmium	-	-	0.034	0.04	0.011	0.16	≤0.08-0.25
Copper	1.1	2.5	0.95	1.5	0.41	4.5	1 (4.9 max)
Chromium	0.3	0.61	-	-	0.34	0.88	Cr(VI) 3.4, Cr(III) 4.9
Lead	0.23	0.63	0.08	0.69	0.03	0.075	1.2
Nickel	1.3	2.0	3.35	3.7	1.10	11	4 (NBL)
Vanadium	0.48	0.92	-	-	-	-	4.1
Zinc	4.2	14	8.9	18	3.10	41	7.8
Mercury	<0.001	0.004	0.003-0.018 (n=2)		<0.001	0.01	0.07

[a] Boutrup et al. (2015)

[b] BEK 439 19-05-2016 (Miljø- og Fødevareministeriet, 2016a)

In general, for the upstream catchment, diffuse sources of metals have been found to play a substantial role for stream quality. The study by Naik and Hammerschmidt (2011) covering three American watersheds found positive correlations between metal concentrations (Hg, Cd, Cu, Pb, Ni, Zn) and the discharge in the studied streams. Metals in general were also found to have a high affinity for suspended particles, where Hg additionally revealed an association with dissolved organic carbon (DOC). Except for Hg, metal levels did not vary seasonally in streams, and the Hg variation could be due to runoff associated with atmospheric deposition. These findings are similar to those from a Danish study covering a 16-km stream corridor in a mixed land use catchment (Sonne et al., 2017). In both studies, fairly consistent concentrations could be suggestive of a ubiquitous source, such as atmospheric deposition or weathering. Interestingly, neither study found evidence that presence or absence of a WWTP had any detectable effect on most metal concentrations, which could either mean the impact was similar across catchments, or – in the Danish case – be due to the fact that only one WWTP facility was present along the investigated stream corridor. Notably, Sonne et al. (2017) additionally found that metals from geogenic sources were likely to be enhanced locally due to the reduced conditions attributed to the presence of a large groundwater contaminant plume, leading to the increased mobilization of dissolved iron and manganese, thus affecting the dissolved concentration of e.g. arsenic.

5.3.2 Micropollutants in the water phase

The contamination of freshwater systems with thousands of chemical compounds has been recognized as one of the key environmental problems facing humanity today (Vörösmarty et al., 2010; Schwarzenbach et al., 2006). In fact, more than 85.000 chemicals are in production and use worldwide, with more than 2.200 produced in quantities exceeding 450 tonnes per year (McKnight et al., 2015). Stokstad and Grullon (2013) showed that pesticides are currently second only to fertilizers in the amount of chemicals applied and extent of use in the environment. Fenner et al. (2013) estimated ca. 1 to 2.5 million tonnes of active ingredients are used each year, predominantly in agriculture, with nearly 20.000 pesticide products entering the market since registration began in the late 1940s (Lyandres, 2012), with >1.000 currently sold annually in e.g. Denmark (Miljøstyrelsen, 2011).

Large-data studies are also now more commonplace, documenting the occurrence of organic chemicals and their potential to jeopardize the health of freshwater ecosystems. A study by Schäfer et al. (2011) on the occurrence and toxicity of >300 organic pollutants in large rivers in Germany found a trend of increasing detections for most compounds in the period considered (1994-2004), where most of the compounds responsible for aquatic toxicity were not listed as priority substances within the EU. In fact, only 2 of the 25 priority substances detected in this study occurred at levels relevant in terms of toxicity. Polycyclic aromatic hydrocarbons (PAHs) were the most frequently detected, while pesticides were the key group regarding estimated impacts to aquatic ecosystems. A similar study (1992-2001) in the USA (Gilliom, 2007), focused solely on (75) pesticides (and 8 metabolites) in streams and groundwater, found that pesticides were generally detected throughout the year (>90% of the time) in streams for catchments comprised of developed watersheds (i.e. those dominated by agricultural, urban or mixed land use) and their behaviour typically followed the (documented) patterns in land use and pesticide use. This trend, i.e. in land use correlating with pesticide use, was documented also in a later study (Vecchia et al., 2009). In Gilliom (2007), pesticides occurred in >50% of shallow groundwater wells and in 33% of the deeper (regional aquifer) wells commonly used for water supply. They furthermore compared these concentrations to both human health and aquatic benchmarks (mostly screening-level guideline values from US EPA pesticide risk assessments), finding that individual pesticides were seldom found exceeding human health guidelines, but often exceeded the benchmarks (both in stream water and bed sediment) for aquatic organisms and fish-eating wildlife. Most commonly exceeding the benchmarks in stream water were insecticides, mainly chlorpyrifos, diazinon and malathion, but also other compounds such as the herbicide atrazine banned in Europe since 1994 (McKnight et al., 2015); in sediment these were the organochlorine compounds (e.g. DDT, aldrin), which were already banned in the USA well before the study began. Notably, (aquatic) exceedances were documented in 56% of the 178 streams with developed watersheds. Looking solely at urban streams this number jumps to 83%, although a decreasing trend was seen over the entire study period (e.g. down to 64% during 1998-2000) for the pesticides sampled, and it has been assumed their uses were simply replaced by other insecticides not covered in their campaign.

An increasing body of literature, also in association with prominent EU projects (e.g. GLOBAQUA; SOLUTIONS; MARS), continues to focus on ranking multiple stressors according to their relative contribution to ecological degradation (Rico et al., 2016; Brack et al., 2015; Hering et al., 2015; Navarro-Ortega et al., 2015; Sundermann et al., 2013). It should be noted that environmentally-relevant (aqueous) concentrations detected in the field are typically very low (in the ng/L to µg/L range) for most organic micropollutants such as pesticides, pharmaceutical compounds and other industrial chemicals such as per- and polyfluoroalkyl substances (PFAS) (Banzhaf et al., 2017; Berger et al., 2017; Loos et al., 2013). The use of laboratory-derived ecotoxicity data in conjunction with measured concentration (field) data, for the assessment of the relative contribution of chemicals (and their links to ecological status), is now commonplace and can be found integrated into risk assessment approaches such as toxic units (TU) (Sprague, 1970). TU is calculated by dividing the measured concentration with the lab-derived lethal mortality concentration (LC50) for a specific chemical and species (typically 48-h LC50 value for the invertebrate *Daphnia magna*). Notably, these lab-based tests cannot reproduce the complexity of the receiving environment, nor can they provide insight on the long-term impact of continuous low-dose contamination (McKnight et al., 2015; Artigas et al., 2012; Beketov and Liess, 2012) and may thus underestimate the toxicity. Nevertheless, they can be utilized to provide a uniform assessment of the potential for detected chemical stressors to impact the stream environment, at the very least providing information on whether a disconnect exists between what is known about the chemical status in comparison with ecological status, and is thus in line with the requirements of the WFD.

In fact, the toxic units (TU) approach has become one of the more commonly used methods to support the linking of detected chemical contamination with ecological impacts (Kuzmanović et al., 2016; Rasmussen et al., 2015; Schäfer et al., 2013; McKnight et al., 2012; Höss et al., 2011) in part due to the ease with which it can be connected to an existing benthic macroinvertebrate index, the SPEcies At Risk (SPEAR) index, developed for both pesticides (Liess et al., 2008; Liess and von der Ohe, 2005) and xenobiotic organic compounds (von der Ohe and Liess, 2004). There is a growing body of literature documenting the successful combination of TU/SPEAR in providing evidence for the toxicity of dissolved-phase pesticides in headwater streams locally, regionally and globally (Stehle and Schulz, 2015; Bundschuh et al., 2014; Beketov et al., 2013; Rasmussen et al., 2011b,2013b,a; McKnight et al., 2012; Schäfer et al., 2012). Variations on this approach can also be found; for example, a recent study by Malaj et al. (2014), covering much of the European landscape (but not Denmark), analyzed >200 organic chemicals at >4.000 sites and in >90 river basins. They additionally related these concentrations to potential aquatic impacts using a threshold for acute risk (ART) and chronic risk (CRT). For determining acute impacts (ART), they compared the maximum concentration to the ART, defined as 1/10 of the LC50 for each of three standard test organisms (invertebrates, fish and algae). Similarly for chronic risk (CRT), they compared mean concentrations to the CRT, defined as 1/1000, 1/100, and 1/50 of the LC50 for invertebrates, fish and algae, respectively. Their results indicated that organic chemicals were likely to cause acute lethal and chronic long-term effects on the representative organisms in 14% and 42% of the sites, respectively. Pesticides, the biocide tributyltin, PAHs and brominated flame retardants were the major contributors to chemical risk, and their presence was related to both agricultural and urban areas in the upstream catchment.

5.3.3 Micropollutants in sediments

There is a similar body of literature (using TU/SPEAR) indicating that the sediment-bound phase may be a crucial environmental source releasing highly toxic compounds, including pesticides, trace metals and other contaminants of emerging concern (de Castro-Català et al., 2016; McKnight et al., 2015; Rasmussen et al., 2015; Wu et al., 2013; Kuivila et al., 2012; Zhao et al., 2009; Amweg et al., 2006; Warren et al., 2003), which so far has been largely overlooked in the context of environmental monitoring programs and hampered by the lack of sediment quality guidelines (but see e.g. Wolfram et al., 2012; de Deckere et al., 2011). For example, a study by Kronvang et al. (2003) found that the average number of pesticides detected in predominantly agricultural headwater stream sediments was higher than for streams draining non-agricultural catchments in Denmark, and were significantly related to catchment size, soil type and hydrological regime; several heavy metals (Cr, Cu, Pb, V and Zn) could additionally be related to urban activity and soil type. This constitutes a serious problem in general, as here too it has been identified that many chemicals lack ecotoxicological data for both sediment-bound phases and/or for the affected benthic invertebrates, despite that many toxic pollutants are known to bind preferentially to soft sediments (Höss et al., 2011). Following conventional practice, many studies now apply the equilibrium-partitioning approach to convert sediment concentrations of non-ionic organic chemicals to pore water concentrations for estimating the potential toxicity to ecosystems (McKnight et al., 2015; Hawthorne et al., 2006).

5.3.4 Organic micropollutants from urban sources

Urban biocides are also now commonly detected in upstream catchment areas, which typically contain smaller residential settlements (Bollmann et al., 2014b; Vorkamp et al., 2014; Wittmer et al., 2010). Their concentrations may actually exceed those of agricultural pesticides (Liu et al., 2015; Wittmer et al., 2011). And it is becoming apparent that some pesticides may be (long) banned for use in agriculture, but are still permitted as biocides (e.g. diuron; isoproturon) or used in both settings (e.g. propiconazole; mecoprop (restricted use); tebuconazole) thus complicating source determination for these chemicals (compare e.g. McKnight et al., 2015; with Styszko et al., 2015; Bollmann et al., 2014b). This is an important finding as biocides are often detected in conjunction with urban WWTP influent for both dry and wet weather conditions (up to 100 ng/L) (Bollmann et al., 2014a). Results from a subsequent modelling study, based on real data and encompassing both agricultural pesticide and urban biocide sources together with sewer systems and a WWTP for urban areas, highlighted the change in importance of the flow components during a rain event from urban sources – during the most intensive rain period – towards agricultural ones over a prolonged time period. Key parameters driving the model were found to be land use, pesticide application, weather and soil-related parameters (e.g. saturated water content, hydraulic conductivity, lateral distances of the drainage pipes) (Wittmer et al., 2016).

Considerable amounts of pharmaceuticals are used in human and veterinary medicine, which may not be efficiently removed from WWTPs (Osorio et al., 2016), as well as in aquaculture (fish farms) and which can be located in upstream catchment streams (Sonne et al., 2017). Accordingly, focus has broadened to include the occurrence of these additional (emerging) organic contaminants, including pharmaceuticals (e.g. antibiotics), personal care products (PCP, e.g. surfactants; endocrine disrupters (ED)) and other indicator chemicals indicative for WWTPs such as caffeine (often used as a proxy for emerging contaminants of concern) (Ebele et al., 2017; Lindim et al., 2017; Zhang et al., 2017; Geiger et al., 2016). Many of these studies contain monitoring data taken throughout a watershed, without necessarily focusing on the relevance of the sampling site's location within the catchment (i.e. upstream/downstream).
In general, these studies have shown that surfactants and EDs may pose a greater risk to freshwater organisms than pharmaceuticals, where municipal sewage was the primary source

for these chemicals. The effects of wet versus dry seasonal changes to the overall risk was compound-group specific, i.e. surfactants were highly affected. Another important but less researched source for these chemicals – within the context of this report – comes from contaminated sites, i.e. the factories producing chemicals, leading to the subsequent contamination of groundwater and the potential for re-emergence in surface water (Sonne et al., 2017).

Chlorinated solvents in general, i.e. as a compound group, have not been found to be key constituents impacting freshwater ecosystems (McKnight et al., 2010,2012) despite their global prevalence in surface water and groundwater resources (Abe et al., 2009; Troldborg et al., 2008; Chapman et al., 2007; Ellis and Rivett, 2007). This is due to their extremely high LC50 values (on the order of mg/L) across most trophic levels and to the fact that groundwater in general is not typically considered as a pathway of much importance (for any type of chemical) in ecological risk assessments, thus overlooking groundwater as a potential source of key toxic chemicals driving toxicity (Rasmussen et al., 2015; Roy and Bickerton, 2012). However, there is indication that sub-lethal effects (i.e. using 10-d chronic exposure tests for trichloroethylene and vinyl chloride – known human carcinogens) may occur on genes and proteins related to metabolism, reproduction and growth in *D. magna* at concentrations down to 0.1 µg/L (Houde et al., 2015). Potentially, this stressor will accrue more importance in the context of multiple stressors (see also Section 5.4), as mechanistic understanding of such interactions grows in the coming decade(s).

5.4 Multiple stressor conditions

Water managers need (to agree on) a set of measures for determining water body status, however, approaches capable of clarifying the many existing discrepancies between chemical and ecological status are still urgently needed. Thus, novel approaches supporting decision-makers are required that are capable of assessing multi-functionality, i.e. the achievement of environmental standards (according to EU policies) while maintaining viable and sustainable anthropogenic practices (Brauman et al., 2007). Multi-functionality represents a new challenge in particular for stakeholders operating in peri-urban environments that affect large and small countries alike on a global scale. The spatial mosaic of variable land-use types and intensities are therefore decisive in the provision of water-related ecosystem services and form synergies to other aspects of mixed land-use catchments (e.g. soil conservation; habitat protection).

It is becoming increasingly clear that mitigation measures focusing on individual stressors may not be effective in reducing ecological risks, as the majority of European streams are subjected to >2 stressors each with the potential to obstruct meeting the obligatory ecological quality requirements (Schäfer et al., 2016). The impairment of water quality from chemical stressors may originate from multiple sources, listed previously, and subsequently enter surface water via a number of contaminant-specific pathways (e.g. surface runoff; atmospheric deposition; groundwater-surface water interactions). The growing understanding of the complexity inherent in particularly mixed land use stream systems (Ding et al., 2016; Stutter et al., 2007) has shifted the focus towards risk assessment approaches at the catchment scale, as opposed to controlling isolated contamination events.

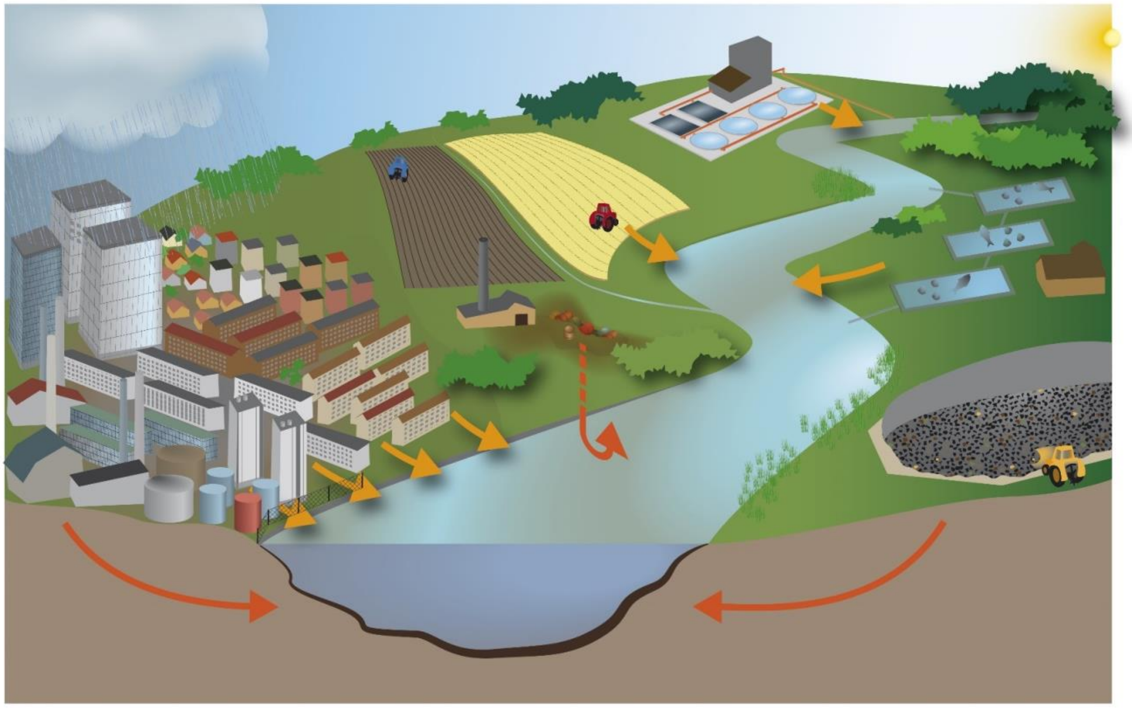


Figure 11. Conceptual sketch expanding the system conceptualization described in Figure 1 for a mixed land use stream system impacted by multiple sources from both urban (e.g. wastewater outlets, contaminated sites) and agricultural activities (e.g. crop production, fish farms). The pathways for chemical stressors to the stream are indicated with orange arrows and together represent the chemical footprint existing within these streams (adapted from Sonne et al., 2017).

Multiple stressor impacts are now obvious in most regions of Europe (Figure 11), where for headwater streams it can even be difficult to find isolated contamination events, i.e. comprised of only one stressor type such as pesticides or chlorinated solvents, thus complicating efforts to quantify stressor impacts separately (Rasmussen et al., 2013a; McKnight et al., 2012).

However, it is still a major challenge in practice to identify the sources and related impacts of (organic and inorganic) contaminants particularly at the catchment scale, due to the multitude of processes co-occurring in time and space (Sonne et al., 2017; Kuzmanović et al., 2016; Barber et al., 2006). As delineated in the previous section, chemicals in the environment are still being predominantly evaluated on an individual basis for their adverse impacts on ecosystem health, in part as little is known about how they may interact in the field. Recently, a methodology was developed in Sonne et al. (2017) for risk assessing chemical stressors in such systems. It encompasses a holistic evaluation of the chemical quality encompassing three stream compartments: stream water (SW), hyporheic zone (HZ), streambed sediment (BS), enabling a more robust linking of chemical stressors to their respective sources and obtain new knowledge about source composition and origin.

An overview of risk assessment approaches conducted in mixed land use stream systems is given in Appendix C, thus providing a first overview of the current state-of-the-art with respect to multiple stressor research. It reveals that a number of field investigations are still approaching chemical risk assessment by focusing on e.g. one compound group in one stream compartment

(SW: Ding et al., 2016; Yu et al., 2014; Wittmer et al., 2010) or multiple compound groups (SW: Kuzmanović et al., 2016; Malaj et al., 2014) in one stream compartment to locate the main sources. Many of these investigations linked chemical assessments to toxicological (lab-based estimates or approaches such as TU) and ecological descriptors (field observations) to examine potential key compounds that may impact ecological health, as discussed in Chapter 4 and Section 5.3.

A few studies have evaluated multiple compartments for one compound group (SW, suspended sediment (SS), BS: Stutter et al., 2007; SW, BS: Moon et al., 1994) or multiple groups (SW,SS: Rasmussen et al., 2013a) in order to obtain a holistic picture of the chemical quality. The physical properties of the stream system, e.g. sediment characteristics, have also been included in two BS studies (de Castro-Català et al., 2016; Höss et al., 2011) to clarify whether documented changes in benthic communities were governed by the physical habitat (i.e. grain size) rather than chemical quality. Moreover, land use data has been used as an integrated factor with different, related stressors. For example, Berger et al. (2016) used land use data to correlate observed ecological changes with poor habitat quality and eutrophication. In Höss et al. (2011), the characterization of the hydromorphological stream type (e.g. channel) was used as a proxy for chemical contamination. Data encompassing a more detailed characterization of key hydromorphological parameters (for investigated sampling stations) were only included in a few studies, e.g. Sabater et al. (2016) and Rasmussen et al. (2013a,2016b).

In general, these studies have covered a wide range of chemical stressors; however, some sources have received less attention in field-based studies of mixed land use stream systems, such as the potential impact of contaminated sites through groundwater-surface water interactions (but see e.g. Roy et al., 2017; Roy and Bickerton, 2012; McKnight et al., 2010). This is in part a result of a traditional subdivision of groundwater and surface water in risk assessment, where the enactment of the WFD and associated daughter directives was central to refocusing attention on the importance of these processes. Within this context, contaminated sites may be key overlooked sources for a large variety of contaminants, including chlorinated solvents, gasoline constituents, pharmaceuticals and other PCPs, inorganic macro-components and trace metals that may eventually find their way into surface water (Roy et al., 2016; McKnight et al., 2012; Roy and Bickerton, 2012; Christensen et al., 2001). Summing up, the main focus seems geared predominantly on SW, BS and SS in risk assessments, often without examining the chemical quality in the HZ including organisms preferring this habitat, such as meiobenthic invertebrates, and which may be a stronger indicator for ecological impairment in these systems (Roy et al., 2017; Sonne et al., submitted).

Discharges from urban areas generate a multitude of environmental impacts on stream ecosystems including a huge variety of anthropogenic chemicals, oxygen consuming organic matter, nutrients, and strongly altered hydrological regime. As discussed in Chapter 4, the current knowledge does not allow for a differentiation or ranking of individual stressors in the multi-stressor context. As discussed in Chapters 3 and 5, the current knowledge on occurrence and concentrations of the multitude of anthropogenic chemicals that may enter stream systems through urban water discharges is limited, but effects appear to be at least partly linked to the relative contribution of urban water discharges to the total stream discharge.

These effects are additionally strongly governed by the environmental context, i.e. the overall hydromorphological and ecological status of the entire stream system, in particular the upstream headwater sections. These effects are also governed, however, by other stressors (sometimes co-occurring) in addition to the stressors originating from urban water discharge. Consequently, safeguarding the ecological health of streams requires more than a stringent focus on chemical indicators for urban water discharges and should include focus on additional stressors and the overall environmental context (i.e. the recolonization potential mediating recovery after pollution or extreme hydrological events).

6. Monitoring

6.1 CSO monitoring

The collection of water quantity and quality data at overflow structures is a complex process. There is a big range of factors affecting the precision and accuracy of the collected data. These include among others: logistical difficulties in accessing monitoring sites, the harsh environment which challenges the installed equipment, and the representativeness of quantity and quality measurements. All these factors contribute to the high level of uncertainty in sewer water quality monitoring.

For example, Bertrand-Krawjeski et al. (2003) analytically derived relative uncertainties of 6-10% for flows, 25-30% for TSS concentrations and loads measured in sewer systems. The measurements performed by Ahm et al. (2016) during the AMOK project in Viby (Aarhus - see Sharma et al., 2014) showed an average deviation of 28% in the overflow volumes estimated by using the standard weir equation, which is traditionally applied in CSO monitoring. The AMOK project also compared two of the most widely applied approaches in sewer water quality monitoring: the *in-situ* and the *ex-situ* sensor installation. In the first approach (used by e.g. Alferes et al., 2014; Winkler, 2004), sensors are placed directly in the wastewater stream, with consequent requirements for continuous sensor maintenance and cleaning. The second approach (applied by Métadier and Bertrand-Krajewski, 2012) addresses the maintenance issue by placing the sensor in a controlled environment outside the sewer (a container). Wastewater is pumped to the container, where operators have easy access to the instrumentation. However, this method has an important footprint (due to the space required by the container) and the results can be affected by malfunctioning of the pump.

An investigation of the sampling settings (direction, angle and height of sampling pipe) was carried out by Larrarte and Pons (2011), who found an error below 5% in estimation of TSS concentrations (i.e. negligible). The low importance of sampling setting were confirmed in following studies (Larrarte, 2015), but Sandoval and Betrand-Krajewski (2016) argued that these estimations are valid only in high-velocity, well-mixed flows, where TSS gradients are not important. For slow-flows, Sandoval and Betrand-Krajewski (2016) provided a method to estimate TSS underestimation based on the sensor placement. Also, laboratory experiments showed the importance of sensor calibration on the measured values (Joannis et al., 2008).

The traditional sampling methods, based on automatic samplers, have been applied for decades (e.g. Aarts et al., 2013). However, this approach has several limitations: the number of available bottles (limiting the duration of the monitored period or lumping dynamic variations into the sample bottles – see Figure 7) and the number of resources needed to monitor several events (resulting in a limited number of monitored events). The development of online sensors has extended the monitoring capabilities and led to the collection of important datasets on sewer water quality (e.g. Métadier and Bertrand-Krajewski, 2012; Caradot et al., 2011; Gruber, 2004).

In some cases, CSO monitoring is required by legislation. In France, the *Arrêté du 21 juillet 2015* (JORF, 2015) requires the installation of autosurveillance systems for monitoring CSO loads. This implies the installation of both hydraulic sensors (a common practise also in

Denmark) and water quality sensors. This legislative requirement has led to the development of several tools for data validation (e.g. Bertrand-Krajewski, 2013; Métadier and Bertrand-Krajewski, 2012) to manage the large amount of information deriving from such a legislative requirement and to ensure the quality of the collected data. Altough all the existing tools for data validation are defined as "automatic" or "semi-automatic" (Alferes et al., 2013; Bertrand-Krajewski, 2013), human interaction is still necessary. For example, the EVOHE software (Bertrand-Krajewski, 2013) is one of the most advanced softwares for data validation that was explicitely developed to manage water quality data collected in sewers and CSO structures. Nevertheless, after automatic filters and advanced statistical tests are run to remove dubious measurements, an operator is still required to approve (and sometimes modify) the results of the validation process.

Online measurements can also be combined with integrated models to better assess the impacts deriving from CSO discharges. In fact, collected data (both from sensors installed at CSO structures or in the RWB) can be used for calibrating such complex models (Riechel et al., 2016; Langeveld et al., 2013a; Caradot et al., 2011).

6.2 Freshwater quality monitoring

There is a vast literature regarding river water quality monitoring: the reviews presented in Behmel et al. (2016), Khalil and Ouarda (2009), and Strobl and Robillard (2008) provide a detailed overview of methodologies and strategies to implement monitoring campaigns. At the European level, the WFD directive (Annex V) distinguishes between three types of monitoring:

- *Surveillance monitoring*, which aims (a) at providing the data to support the evaluation of the RWB impact assessment, (b) at allowing the design of future monitoring programmes, (c) at assessing the long-term changes in natural conditions, and specifically (d) those resulting from widespread anthropogenic activity.
- *Operational monitoring,* which provides the information (a) to establish the status of the RWB which has been identified as at risk of not meeting their environmental objectives, and (b) to assess any changes in the status of such RWBs resulting from the planned improvement measures.
- *Investigative monitoring* is carried out (a) to identify the causes of exceedances of the quality standards in the RWB (when those are unknown) and (b) to evaluate the effect of accidental pollution events (and thereby provide the basis for the necessary remediation).

An historical overview of monitoring approaches is provided by Horowitz (2013), which discusses them from the perspective of decreasing available financial resources. The majority of the available studies focus on larger spatial and temporal scales than those involved in urban wet-weather discharges. Nevertheless, it is possible to adapt the main concepts and findings to the specific case of short-term exposures to pollutants originating from point sources. Behmel et al. (2016) provided a general overview of the steps that are necessary to plan and optimize a monitoring campaign.

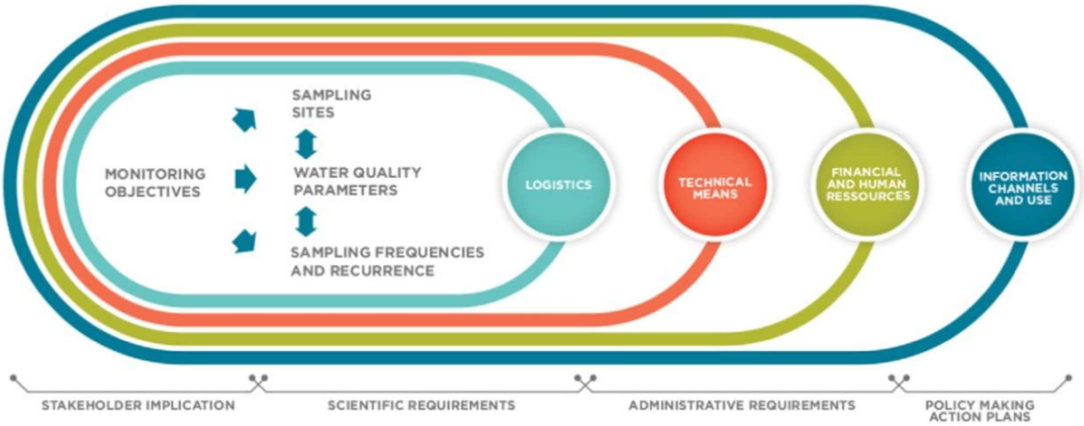


Figure 12. Diagram schematization of the steps to include in planning and optimizing a water quality monitoring campaign (from Behmel et al., 2016)

In this process, there are several factors that need to be taken into account (Figure 12): logistics (e.g. choice of accessible monitoring sites), technical means (e.g. available monitoring techniques and instrumentation), available resources, and how the collected data will influence the decision process and the approval of pollution management plans. This report, mainly considering surveillance monitoring (as defined in the WFD), focuses on the technical-scientific requirements, which include water quality parameters (see Section 3.1), choice of sampling sites, and definition of sampling frequencies and recurrences.

According to Khalil and Ouarda (2009), locations for river quality monitoring can be divided into three types of locations (Figure 13):

- *Macrolocations:* are monitoring sites that are selected to evaluate the water quality in an entire river branch, i.e. in the upstream catchment. Macrolocations assess the lumped effect of all the pollutant sources within the catchment upstream of the monitoring site. In the context of CSO regulation, macrolocations are monitoring sites placed upstream from the discharge points, and are used to provide the background status of the River Water Body.
- *Microlocations:* are sites defined to assess the impact in a well-mixed water body after a specific point-source. When looking at CSO regulations, microlocations are placed downstream from discharge points (CSO and WWTP outlets) after the mixing zone. The latter requires an assessment which can be based on ad-hoc measurements and/or modelling (with different levels of complexities (see the examples provided in Auckland Regional Council, 2010; European Communities, 2010; US EPA, 2006).
- *Representative locations:* are sites on the river transect which provide information on the lateral profile of the stream. This type of location is generally not relevant for monitoring the impact of CSO discharges.

Logistical considerations play an important role in the placement of monitoring sites, with site accessibility playing an essential role in this. As discussed by Khalil and Oarda (2009), all existing methodologies for site identification aim at minimizing the number of stations and at placing them in relevant locations in order to avoid the risk of “data rich – information poor” monitoring programmes (i.e. collection of non-representative data due to issues with location, sampling methodology and frequency).

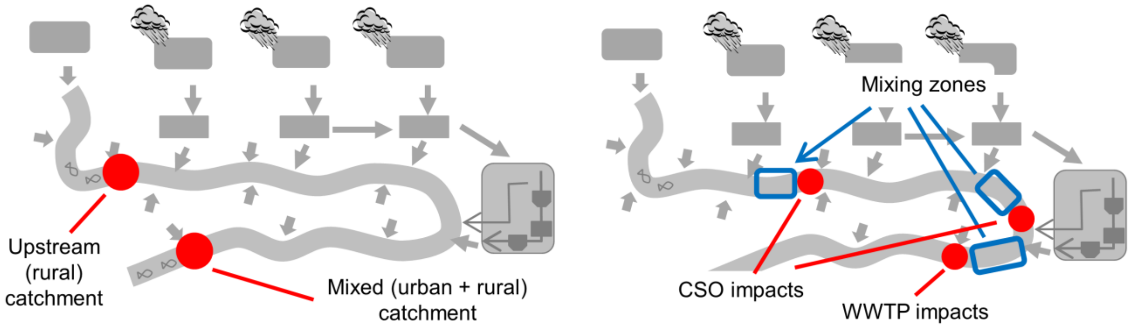


Figure 13. Example showing possible monitoring *macrolocations* (left) and *microlocations* (right) in the schematic system from Figure 1.

For example, Wagner et al. (2006) provided a list of recommendations to ensure that on-line sensors are collecting data that are representative for the entire river cross section. As pointed out by Behmel et al. (2016), there are several examples of standardized guidelines for water quality monitoring, such as those defined in the Annex V of the WFD, the Canadian Environmental Guidelines (Canadian Council of Ministers of the Environment, 1999), or in the guidelines proposed by Chapman (1996). However, these standards need to be adapted to the specific conditions of the monitored RWB. Also, new opportunities emerge from new monitoring techniques (e.g. passive samplers - Lohmann et al., 2017), on-line sensors (e.g. Escoffier et al., 2016; Boënne et al., 2014; Viviano et al., 2014), effect-based tools (Altenburger et al., 2015; Wernersson et al., 2015), and even social media and citizens participation (Zheng et al., 2017).

An evaluation of the potential for passive samplers to support monitoring programs has been carried out by Birch (2012). Specifically, the use of flow-dependent passive samplers (Birch et al., 2013a) was combined with traditional sampling techniques and water quality models (Birch et al., 2013b) to provide a better, more cost-effective overview of the RWB chemical status (see Figure 14).

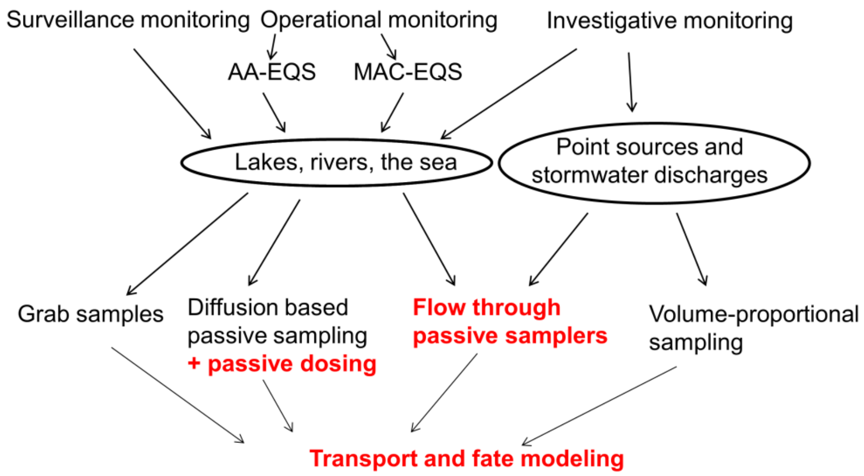


Figure 14. Schematic comparison of traditional monitoring approaches and possibilities offered by passive samplers (in red - from Birch, 2012).

High time resolution measurements are quite effective in monitoring the acute effects of urban wet weather discharges (see e.g. Blaen et al., 2016). The time resolution of these data can range from 1-5 minutes (e.g. Boënne et al., 2014; Alferes et al., 2013) to 30 minutes and even a few hours (e.g. Skeffington et al., 2015) The benefits of these monitoring approaches have been shown by Skeffington et al. (2015), who investigated how low monitoring frequencies can lead to an incorrect evaluation of the status of the RWB. Bowes et al. (2012) used high-time resolution measurements to evaluate the compliance of WWTPs with discharge limits, showing how an increase in phosphorous concentrations were originating in the catchment upstream of the urban area. Similarly, Boënne et al. (2014) measured the effect of CSO events by using online sensors placed downstream from the discharge point, and compared these data against measurements collected by traditional surveillance monitoring programs. Ivanovsky et al. (2016) and Halliday et al. (2015) monitored streams that were strongly affected by WWTP discharges, while Caradot et al. (2011) and Irvine et al. (2005) specifically targeted the effects of CSO discharges to the RWB. All available studies agree on the benefits of using high-time resolution measurements to assess the status of the RWB. However, a technical drawback was identified in the large amount of collected information generated, which might be redundant (especially in dry periods) and necessitate the application of data validation methods (e.g. Alferes et al., 2013). In this context, Blaen et al. (2016) suggested an adaptive monitoring strategy, where the frequency of data collection is defined based on the status of the monitored systems. For example, a higher frequency can be used during and in the aftermath of rain events (when there is a high risk for CSO events) and a lower frequency can be applied in dry periods, when low impacts on the monitored systems are expected.

6.3 Overview of monitoring of ecological status in DK

The EU WFD has shifted the focus to a more holistic evaluation of ecological status, quantified using biological quality elements which, according to the Danish national water plans 2015-2021, should comprise freshwater plants, fish, macroinvertebrates and benthic algae, the latter to be added within this cycle as the ecological index for algae is still under development. Denmark has ca. 60.000 km of waterways of which ca. 40.000 km are classified as artificial and thus only need to meet good ecological potential, i.e. determined solely by their chemical status. These plans require, however, that all of the remaining ca. 20.000 km of waterways are monitored for (good) ecological status. This reporting is driven by the Danish EPA, allocating an estimated 30-40 million DKK for this purpose, with data collection carried out predominantly by the Danish Centre for Environment and Energy (DCE). These waterways are currently divided into two subprograms: one comprising ca. 7.000 stations, which collect and report data under the WFD and return only index scores every 5 years, in accordance with the various biological indices (i.e. DSPI, DFIS and DSFI – see Section 4.1). Another 800 stations are used for case-based, i.e. science-based counselling purposes providing an opportunity to collect more comprehensive data. In total, these 7.800 stations can cover from several hundred meters up to several kilometres of stream stretch, with the supposition that the station is placed such that it is representative of the entire watercourse. In addition to the legislative requirements enforced through the WFD, Danish streams additionally provide habitats for a number of species with specific protection goals defined within the European Habitats Directive (i.e. fish; dragonflies; mussels); the conservation status of these species must be “favourable” and their populations should additionally be monitored to ensure their minimum requirements are being met according to species-specific technical guidance documents.

7. International experience

7.1 CSO discharge regulation

International legislation regulates CSO discharges based on different approaches (see the overview in Dirckx et al., 2011; Zabel et al., 2001), which can be grouped into Uniform Emission Standards (UES) and Environmental Quality Standards (EQS).

- UES are usually expressed as effluent concentrations. Clearly, this regulation approach derives directly from wastewater discharges, where the pollution source is relatively constant in time, with relatively limited daily, weekly and seasonal variations that can be easily modelled by periodic processes. Also, this approach does not consider dilution in the RWB. UES regulation is relatively easy to establish (since the same limit is defined for all the CSO structures), but the stochastic nature of CSO events make its evaluation more complex. Also, compliance with UES is easier to evaluate in the planning phase through application of mathematical models.
- EQS consider the status of the RWB and the environmental objectives that have been defined for it (e.g. achievement of a good ecological status). The EQS regulation thus measures the effect rather than the cause and will be site-specific, i.e. greater resources are required in the implementation phase. Compliance assessment is relatively easier in the field (since the monitored body is always accessible), but this requires complex integrated mathematical models (e.g. Holguin-Gonzalez et al., 2014; Langeveld et al., 2013) in the planning phase.

Limits can be defined by using different indicators. At the international level, several examples can be found:

- *Dilution*: CSOs are designed to handle a maximum flow $Q_{T,max}$ which is defined as *n*-times the average DWF - Dry Weather Flow (Q_m) or the peak DWF (Q_p). When the flow in the combined system reaches this threshold, the exceeding flow is discharged to the RWB (as exemplified in Figure 15);
- *Concentrations*: maximum concentration limits are defined for discharge points;
- *Loads*: a maximum yearly pollutant load is allowed from the discharge point;
- *Volumes*: the maximum allowed yearly volumes are defined as a function of the upstream catchment (e.g. reduced area);
- *Overflow Frequency*: a maximum number of overflows per year is defined.
- *Maximum discharge flow*, defined as the maximum allowed from the CSO, calculated based on the catchment area.

An overview of CSO design criteria for several EU countries is presented in Dirckx et al. (2011b) (Table 9): all the countries included in the analysis define dilution factors (i.e. maximum flow as a function of the DWF). Overflow frequency, which implicitly recognizes the natural variability of CSO events, is considered by few countries (e.g. The Netherlands: the Belgian region of Flanders).

Table 9. Overview of CSO design criteria in different European countries (Dirckx et al., 2011b).

	Throttle flow limitation ($Q_{T,max}$)	Equivalent Mean DWF (Q_m)	CSO criterion	UES or EQS approach	Pollution loading	Modelling required
Belgium (Flanders)	$6Q_p$	10	f=7	UES+	no	no
France	$3Q_p$	4–6	—	UES and EQO/EQS-	yes	yes?
Germany	$7Q_m$**	7	V=10–40 m/ha_{red}	UES	yes	no
Greece	3–$6Q_m$	3–6	—	UES+	no	no
Ireland	$6Q_m$	6	—	UES and EQO/EQS	no?	no
Italy	3–$5Q_m$	3–5	f(?)	UES	no	no
Luxemburg	$3Q_p$**	4–6	V=10–40 m/ha_{red}	UES	no	no
Netherlands	$7Q_m$	7	f=3–10 V=70 m/ha_{red}	UES+ and EQO/EQS-	no?	no
Portugal	$6Q_m$	6		UES	no	no
Spain	3–$5Q_m$	3–5		UES	no	no
UK (England & Wales)	6.5–$9Q_m$*	6.5–9		EQO/EQS	yes?	yes
UK(Scotland)	6.5–$9Q_m$*	6.5–9		EQO/EQS	yes?	yes

UES: Uniform Emission Standard

UES+: UES with some consideration of the receiving water

EQO/EQS: Environmental Quality Objective/Standards

EQO/EQS-: EQO/EQS approach introduced but unknown to what extent it is used

f=overflow frequency

V=volume of storage facility

A_{red}=reduced area of connected surface Q_p=peak DWF Q_m=mean DWF

*As a common result of the so-called Formula A (also used in Ireland)

**German ATV-128 requires 90% of the total load to be conveyed to the treatment plant

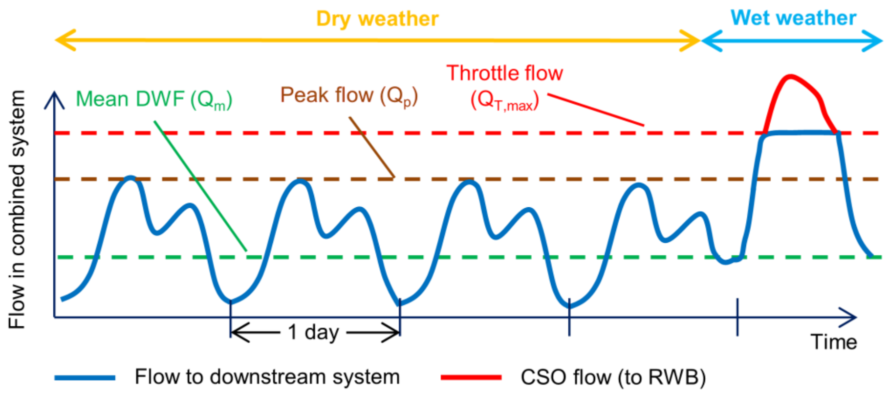


Figure 15. Schematic representation of Dry Weather Flow (DWF) parameters that are used in EU regulation to define the throttle flow for CSO structures.

The majority of the countries enforce regulation based on UES, with few countries solely implementing approaches based on EQS (e.g. United Kingdom). Interestingly, the EQS approaches are mostly inspired by the pioneering Danish guidelines, which were defined already in the mid-1980s (Spildevandskomitéen, 1985). A combination of the UES/EQS approaches can be found in several countries, as was the case for discharge regulation in Danish streams.

Table 10. Overview of the correlation between CSO indicators and typical CSO effects, as reported in Dirckx et al. (2011), simplified after Engelhard et al. (2008).

Impact type	Type of toxicity	Receiving water indicator	Fraction of overflow/total runoff volume	Frequency	Annual CSO volume	CSO peak flow
Morphology	-	Erosion frequency	Good	Bad	Good	Poor
Eutrophication	Chronic	Nitrogen load	Good	Bad	Good	Poor
Accumulation	Chronic	Copper load	Good	Bad	Good	Poor
Acute toxic	Acute	Ammonia	Poor	Bad	Bad	Bad
Oxygen depletion	Acute	Critical oxygen deficit	Bad	Bad	Bad	Poor

In the *vandplaner* valid until 2015, for example, a combined approach was used to regulate CSO discharges: a first flush (higher concentration in the initial phase of the event) was assumed (dilution), together with a specific annual volume (m^3 per reduced hectare) and an annual frequency (number of overflows per year). In some cases, the legislation also defines monitoring requirements. In France, for example, major CSO discharges (i.e. discharged with an estimated load greater than 1.2 kg BOD_5/day) should be monitored by automatic stations in order to report pollutant loads (*Arrêté du 21 juillet 2015* - JORF, 2015)

As pointed out by Dirckx et al. (2011), who summarized the simulation results from Engelhard et al. (2008) and Lau et al. (2002), CSO indicators cannot be used to directly assess acute impacts in the RWB (DO depletion, ammonia toxicity). The results from Engelhard et al. (2008) show that volume-based indicators can be used to estimate load-based impacts (i.e. long-term impacts), such as eutrophication and chronic toxicity (Table 10). The findings from Lau et al. (2002), on the other hand, show that overflow frequency can be used, within certain limitations, to evaluate DO depletion and ammonia intoxication. The use of this indicator can result in contrasting results when the entire integrated system is taken into consideration. In fact, if a decrease in CSO frequency positively affects oxygen levels in the river, this might result in an increase in toxicity due to ammonia peaks when the reduction in CSO events is obtained thanks to the addition of storage volume. An increase of the hydraulic load and resulting worsening of the WWTP removal performance can in fact then result in an increase of the ammonia concentrations released to the RWB (Lau et al., 2002; Rauch and Harremoës, 1998).

Overall, Dirckx et al. (2011) concluded that none of the available CSO indicators are capable of representing the entire range of impacts with an acceptable degree of certainty.
These considerations highlight how simple regulations, looking only at the discharge points, are not sufficient to grasp the complexity of the interactions between the elements of the considered system.

7.2 Freshwater quality criteria

7.2.1 Type of criteria

Freshwater quality criteria are based on *numerical limits* and/or *narrative statements*. For a specific water quality parameter, *numerical limits* are defined by a combination of three different aspects (US EPA, 2014):

- *Magnitude,* expressed as a concentration value. These values define the maximum allowable concentration in the RWB, and two definitions are usually adopted: a Maximum Allowable Concentration (MAC), to protect aquatic life from short-term (acute) effects; and a continuous concentration value (also defined as an Annual Average in the EU legislation – see section 3.1.1) to protect against long-term (chronic) effects. These thresholds are calculated based on toxicity tests performed on different time scales, depending on the analysed pollutant and aquatic species. Clearly, MACs are more relevant for the intermittent nature of wet weather discharges. For example, UK guidelines (Crabtree et al., 2012) define criteria for ammonia and dissolved oxygen, while the US handbook (US EPA, 2014) focuses on micropollutants and thereby mentions 48- and 96- hour lethality tests (which are commonly used in the ecotoxicity testing of chemicals).
- *Duration,* expressed as time. This value accounts for the need to average exposure of aquatic life to pollutants over specific time intervals in order to account for the variability and fluctuations in the RWB (e.g. flow, diffusion, dynamic nature of the pollutant source). This averaging is necessary to better evaluate the adverse effects caused by fluctuating exposures: generally, the shorter the exposure time, the higher is the capacity for aquatic life to minimize the negative impacts. Criteria for acute toxicity can e.g. be defined for average concentrations over a 1-hr, 6-hr, or 24-hr period, while criteria for chronic toxicity can be defined over longer time intervals. For example, US EPA (2014) recommends a 4 days average, while the EU legislation defines yearly average concentrations.
- *Frequency,* expressed as frequency of exceedance or return period. Since it is statistically impossible to assume that magnitude criteria will never be exceeded, it is necessary to specify the accepted frequency when a specific criterion (defined by magnitude and duration) is exceeded. This frequency should be defined by looking at the expected effects on the natural aquatic communities, the considered pollutant, and the intended environmental objective for the RWB. For example, the US EPA (2014) recommends a 3-year return period for exceedance of both short- and long-term criteria. This value is selected to ensure a sufficient recovery time for the natural environment when exposed to multiple stressors (i.e. exceedance of different pollutants). Conversely, UK guidelines (Crabtree et al., 2012) define quality criteria for different return periods (1-month, 3 months, and 1-year). Different values are defined based on the intended ability of the RWB to sustain fishery (e.g. suitable or marginal fishery ecosystem).

Figure 16 shows an example of the application of these three aspects to a hypothetical series of concentration data for a period of 12 days. Two different magnitude thresholds are set for two different durations (1 hr and 6 hrs). Based on these thresholds, the data shows that there are 4 exceedances for the short duration, while only 3 exceedances are observed for the longer duration. Based on these observations, it is then possible to calculate the frequency of exceedance and thereby their return period.

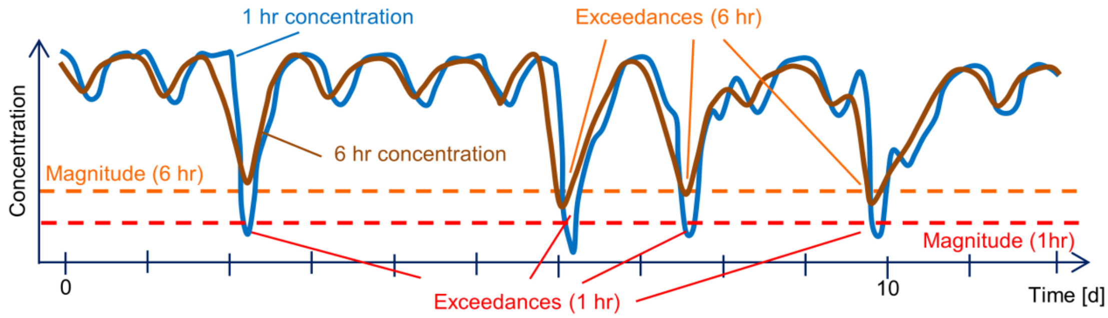


Figure 16. Example for evaluation of compliance with water quality criteria based on magnitude and different durations (in this example, 1 hr (blue line) and 6 hrs (brown line)).

Existing guidelines present a combination of these three aspects: Table 11 shows an example for ammonia guidelines for three different countries. The water quality criterion can be defined only in terms of magnitude (as by Canada) or using all three aspects (as by the UK). Also, limit values can be expressed as unionized ammonia (Canada, UK) or as Total Ammonia Nitrogen (TAN). The latter is defined according to temperature and pH, which affect the equilibrium between the ionized ammonium (NH_4^+) and the toxic unionized ammonia (NH_3). Canada also provides a conversion table between the water quality criterion expressed as unionized ammonia and the TAN values. The UK limits also distinguish between the intended environmental objectives for different RWBs, i.e. there are different magnitude thresholds for RWBs intended for sustainable salmon fishery (the most sensitive species), sustainable cyprinid fishery, and marginal cyprinid fishery (i.e. a RWB with the least ambitious environmental objectives). It can be seen that for DO, some of the quality criteria overlap, i.e. long duration criteria for highly sensitive rivers correspond to short duration criteria for less sensitive RWBs. Similarly, Danish criteria (Spildevandskomitéen, 1985) defined three environmental objectives based on the RWB classification: spawning and reproduction of salmon (i.e. Danish guidelines set stricter criteria than the UK), salmon fishery, and carp (cyprinid) fishery. A comparison between the UK and Danish guidelines (Figure 18 – see also Appendix D) shows how the latter are more conservative and they extend over long periods (i.e. higher return periods are defined).

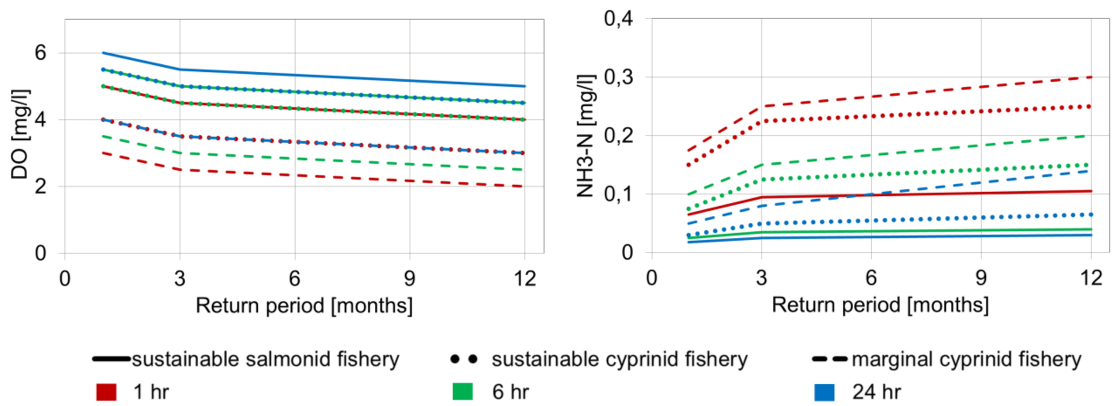


Figure 17. UK limits for Dissolved Oxygen (DO – left) and unionized ammonia (right) for different durations and typologies of RWBs.

Table 11. Comparison of freshwater quality criteria for unionised ammonia (NH_3-N) in three countries.

Country	Magnitude [mg/l]	Duration	Frequency/Return period	Note	Source
Canada	0.019			Guidelines include conversion table to total ammonia (dependant on temperature and pH)	Canadian Council of Ministers of the Environment (2010)
United Kingdom	0.065	1-hr	1 month	These values refer to ecosystems suitable for sustainable salmonid fishery. Other values are defined for ecosystems suitable for cyprinid fishery and for ecosystems with marginal cyprinid fishery (see Figure 17). A correction factors should be applied if oxygen levels are below 5 mg/l, pH <7, or T>5° C	Crabtree et al. (2012)
	0.095		3 months		
	0.105		1 year		
	0.025	6-hrs	1 month		
	0.035		3 months		
	0.040		1 year		
	0.018	24-hrs	1 month		
	0.025		3 months		
	0.03		1 year		
United States	17 (TAN) (pH 7, T 20° C)	1-hr average	Not to be exceeded once in three years on average		US Environmental Protection Agency (2013)
	1.9 (TAN) (pH 7, T 20° C)	30 days rolling average		Criteria based on 4-day averages are also defined	

TAN= Total Ammonia Nitrogen

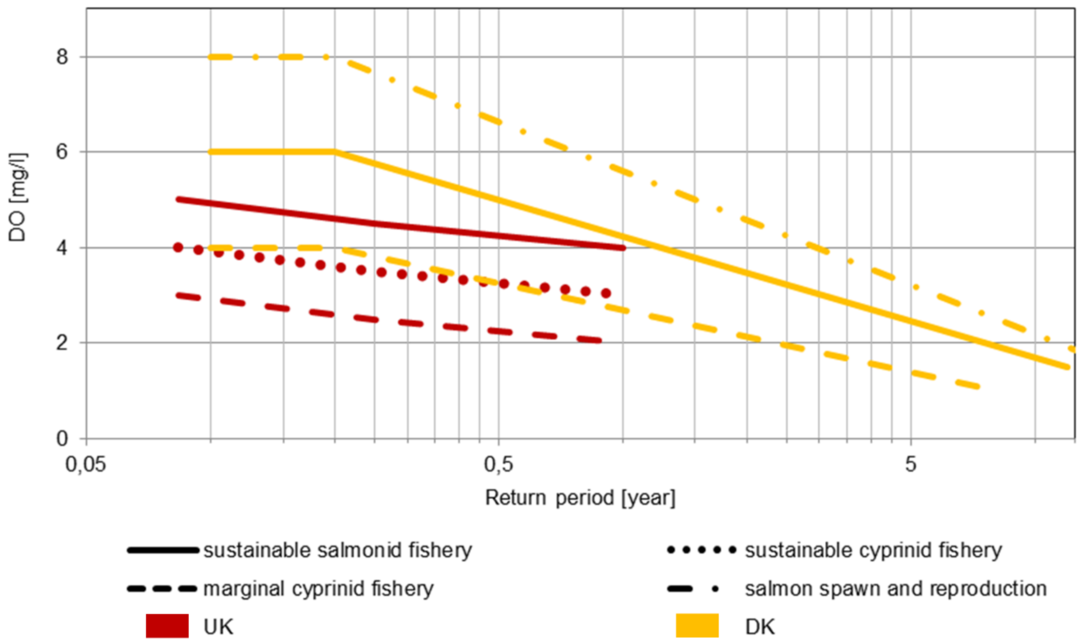


Figure 18. Comparison between the Danish and English 1-hr thresholds for Dissolved Oxygen (DO) for different RWB typologies.

Some countries also define *Water Quality Indices (WQI)*, which consider several water quality parameters in order to provide an overall overview of the status of the RWB. For example, Canada (Environment Canada, 2015) defined a WQI based on the combination of three factors: scope (percentage of parameters for which the limits are exceeded), frequency (percentage of samples not meeting quality guidelines), and amplitude (divergence of the measured values from the threshold value). This WQI is designed for long-term monitoring, i.e. to provide an overall evaluation of the quality of the RWB, and it is not intended for the evaluation of impacts from transient events (such as CSO discharges).

Narrative statements describe the desired water quality goal without using numerical values. An example for such criteria are provided by the US EPA (2014):
All waters, including those within the mixing zone, shall be free from substances attributable to wastewater discharge or other pollutant sources that:
1. Settle to form objectionable deposits;
2. Float as debris, scum, oil, or other matter forming nuisances;
3. Produce objectionable colour, odour, taste, or turbidity;
4. Cause injury to or are toxic to, or produce adverse physiological responses in humans, animals, or plants; or
5. Produce undesirable impacts or are a nuisance to aquatic life

7.2.2 Process for criteria formulation

The process for the formulation of water quality criteria involves several steps and decisions: the magnitude values are derived from available toxicology tests and from the expected impacts. To exemplify this process, the UK guidelines (whose derivation is described in Crabtree et al., 2012) are used as an example.

Data collection. Scientific literature is searched for results on toxicity tests regarding the specific pollutant of interest. Crabtree et al. (2012) listed ammonia toxicity values (expressed as LC_{50} and NOEC over different time intervals) for invertebrates (18 values), fish (12 values) and algae (1 value). These data enabled a statistical elaboration of the different toxicity values: for example, ratios between short-term (6 hrs) and long-term exposures (24 hrs) can be estimated for different categories of fish (salmonids and cyprinidis).

Definition of effect matrix. The likely ecological effects of different concentrations at different return periods are estimated. A good quality status is defined as a “slight deterioration from the reference condition”. For CSO discharges this “slight deterioration” could be a small change in the aquatic community, with focus on the taxonomic groups mostly affected by the investigated indicator (e.g. oxygen, unionized ammonia). When looking at ammonia and oxygen levels after CSO events, Crabtree et al. (2012) identifies additional effects than mortality, which are linked to the behaviour of different species. Based on these analyses and assumptions like those shown in Table 12, it was possible to quantify the “slight deterioration” as “a change in a given parameter (lethal or sublethal effects) […] less or equal to a small defined change (for example 10%)” (Crabtree et al., 2012). An example of the effect matrix for dissolved oxygen is shown in Figure 19: the effect (in this case, lethality) for different species and durations is shown as a function of time. Similar graphs are also provided for other effects such as growth rate and drift.

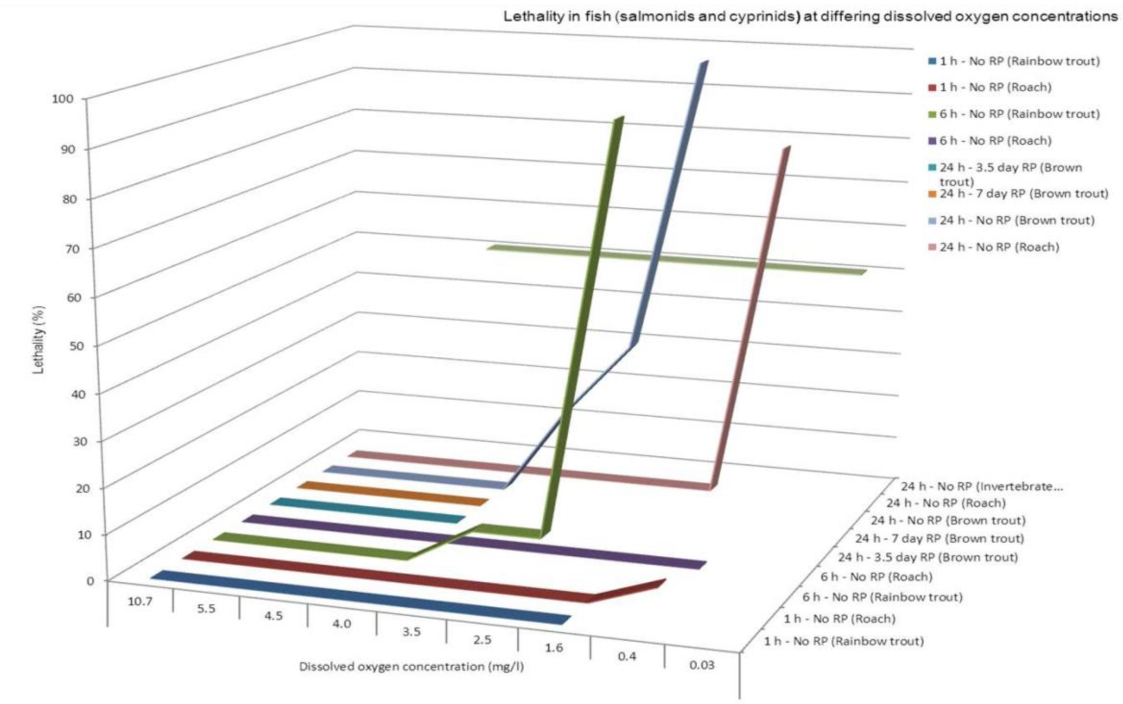


Figure 19. Effect matrix for dissolved oxygen (DO) from Crabtree et al. (2012): lethality is presented as a function of DO concentrations for different fish and durations.

Table 12. Examples of assumptions made in the definition of the effect matrix and threshold limits, as listed by Crabtree et al. (2012).

Assumption/decision	Dissolved oxygen	Unionized ammonia
Most sensitive taxa	Fish and macroinvertebrates (mainly due to drift rather than short-term mortality)	Fish and macroinvertebrates (mainly due to mortality of unionid mussels)
Most sensitive life-stage	Early life	Early life
Most important factor causing adverse effects after repeated short-term exposures	Magnitude and duration are more important than frequency	Toxic effect depends on all three factors (magnitude, duration, and frequency) High frequency becomes dominant
Other assumptions	- Fish recover rapidly after sub-lethal exposure, with little evidence of long-time effects - Low and high mortality concentrations depends on duration, but they are about 1 mg/l apart - Invertebrates can show large scale drifting after mild depletion, but populations recover after a few weeks	- Limits are based only on toxicity data on fish, assuming that they are the most sensitive organism

Estimation of threshold limits. Based on the collected data and the effect matrix, threshold concentrations can be defined. From the effect matrices for dissolved oxygen (including the one shown in Figure 19), it can be seen that no effect is observed for concentrations above 4 mg/l. This value is therefore defined as a threshold for salmonid river ecosystems for events with a long return period. For cyprinidis river ecosystems, where sensitive taxa commonly present in salmonid rivers are absent, a lower threshold of 3 mg/l can be fixed. These thresholds, combined with the assumptions shown in Table 12, lead to the definition of water quality standards (as those shown in Table 11 and Appendix D).

8. Modelling tools

8.1 Model goals

Mathematical models are useful tools that can be applied to (a) estimate CSO emissions and (b) assess the impact of CSO discharges on the RWB. In the first case, models can be used to calculate both pollutant concentrations and loads discharged from CSOs, and thereby can be applied to evaluated compliance with UES standards. In the latter case, the sewer network, the WWTP (if part of the considered system) and the RWB are included within the same model (the so-called *integrated models* - see Bach et al., 2014; Rauch et al., 2005). The integrated model can then be used to evaluate the effect of CSO discharges and WWTP overloading on the quality of the RWB. Therefore, compliance with EQS can be estimated.

Models can be used both for system understanding, planning, monitoring/surveillance, and operation of the integrated system:

- *System understanding*: models are used to estimate CSO discharges (both in terms of volumes, concentrations, and loads) and impacts on the RWB for different scenarios (e.g. statistics on water quality indicators in the RWB). The baseline scenario (i.e. the current situation) provides information such as: (a) discharges from a single overflow structure (for assessing compliance with UES), or (b) from the different CSOs across the analysed system (for prioritization of discharge points); and (c) current quality status of the RWB expressed by using the same water quality indicators defined by the existing regulation. This allows for analysing the different interactions between the different elements of the system, unveils cause-effect relationships, verifies hypotheses and assumptions and dismisses irrelevant factors. For example, models allow evaluating whether a specific CSO structure is complying with legislation, if it poses a risk to the status of the RWB, where the effect of CSO discharge(s) will be most detrimental, and what the impact of the CSO will be in comparison with the background status and WWTP discharges.
- *Planning*: Based on the results from the baseline scenario, it is possible to identify critical points, situations and to elaborate different strategies to achieve the desired environmental objectives (e.g. building of new infrastructure, installation of new treatment solutions, and implementation of real-time control strategies). These can be included in different scenarios, which are subsequently simulated and compared against the baseline scenario. The simulation results thus provide the basis for identifying and sizing the most cost-effective solution (Riechel et al., 2016; Langeveld et al., 2013a; Dirckx et al., 2011a).
- *Monitoring/surveillance*: dynamic models can be used to supplement additional information that integrates measurements. For example, hydraulic models can be used to estimate overflow volumes where rainfall data are not available (e.g. Leonhardt et al., 2012) or to assimilate censored data. An example of the latter can be found in Montserrat et al. (2016), who combined the data from temperature-based sensors (Montserrat et al., 2013) with a model to estimate CSO volumes. Dynamic models are also integrated into warning systems, with specific focus on health risks and threats to bathing water quality due to CSO discharges (Mälzer et al., 2016).

Operation: results from dynamic water quality models operating online can be used in combination with water-quality based control strategies to reduce impacts on the RWB. While current examples of these water-quality based control strategies rely on data from online sensors, future developments can lead to a combination with online models. In the example presented by Fricke et al. (2016) and Hoppe et al. (2011), flow from CSO structures is diverted according to online concentration measurements, with highly polluted flows sent to the WWTP and low-concentration flows discharged to the RWB. Löwe et al. (2016) applied a global optimization control strategy that used online prediction of overflow volumes to reduce the overall CSO risk. The same control strategy can operate based on water quality data (Vezzaro et al., 2013), making the implementation of water-based controls using online models only a matter of time.

8.2 Analytical models

In this report we define *analytical models* as all the modelling approaches that utilize analytical solutions to the equations used to describe the processes affecting water quality in the integrated urban water system. Analytical models are also deterministic models, i.e. they always provide the same results for a given set of parameters and forcing function (as they are based on the same set(s) of assumptions). Given the high natural variability of the processes linked to CSO discharges, it is therefore necessary to predefine all the settings and conditions that are needed to apply these models and compare their results. These are usually set in the guidelines which help consultants, operators and regulators in addressing all the issues linked to CSO discharges. The German guidelines elaborated by the German Association for Water Management, Wastewater and Waste (DWA, 2016) are hereby used to exemplify the use of these model typologies. The DWA guidelines utilize an immission-emission combined approach, i.e. a combination of UES and EQS (see section 6.1). The DWA approach can be schematized in different steps (also summarized in Appendix E):

1. *Catchment characterization*
2. *Calculation of expected flows*
3. *Definition of expected pollution levels*
4. *Calculation of expected pollutant fluxes at CSO*
5. *Calculation of expected CSO concentrations*:
6. *Calculation of pollutant fluxes in RWB*
7. *Calculation of water quality indicators*

The German example shows how analytical models can be applied for a limited amount of pollutants and processes. In fact, the DWA guideline focuses only on ammonia/nitrogen and oxygen depletion caused by the discharge of organic matter, and all the necessary steps require simple calculations that can be made in a spreadsheet. When a more complex description of the system is needed, probabilistic or numerical dynamic models are needed (see the following sections).

8.3 Probabilistic models

While analytical models rely on a series of assumptions, such as choice of average concentration values, worst case scenarios, etc., the categories including statistical and probabilistic models recognize the intrinsic natural variability of the processes behind CSO events (rainfall and pollutant generation and transport processes). Probabilistic models are based on the estimation of probability distributions for the (key) model parameters (e.g. distributions of CSO loads and/or concentrations).

The output from *probabilistic models* cannot therefore be described in term of a single value (as for deterministic models), but instead using statistical terms (e.g. average, standard deviation, quantiles and percentiles).

The parameter distributions behind probabilistic models are calculated by using data from sufficiently large datasets. The analysis from measurement campaigns carried out in the past decades showed how the distributions can be described by using log-normal distributions (e.g. Maestre et al., 2005; VanBuren et al., 1997). There are several attempts to link discharged concentrations to other factors, such as rainfall intensity or flow (e.g. Daly et al., 2014; Bach et al., 2010). However, as pointed out by Bertrand-Krajewski et al. (1998), the complexity of the involved processes, affected by a multitude of different factors, rarely reduces the uncertainty even at individual sites. The transferability to other locations is low, which means that the overall uncertainty is not reduced by the use of such models. When applied to specific sites, additional measurements are needed to reduce the parameter uncertainty and to take into account the specific site characteristics (as suggested by e.g. Rossi et al., 2005).

Probabilistic models can differ in their structure: they can disregard the processes taking place in the upstream catchment by e.g. including only a description of concentrations/loads at the discharge point (as in Harremoes, 1988), they can include several sub-models describing different processes. For example, the TSS model proposed by Rossi et al. (2005) includes distributions to describe TSS contribution from (i) stormwater, (ii) wastewater, and (iii) sediments; and it accounts for “first flush” processes and potential treatment options.

The complexity in the interactions between CSO discharges and water quality in the RWB, along with a general lack of data necessary to establish cause-effect relationships, limits the possibility to create probabilistic integrated models. For example, Schaarup-Jensens and Hvitved-Jacobsen (1994) demonstrated the feasibility of a probabilistic model to evaluate DO levels after CSO discharges, but their findings are based on results from a water quality model combined with a Monte-Carlo approach.

The results of analytical models can be compared against water quality criteria only in terms of magnitude (e.g. exceedance of a specific concentration threshold). Conversely, results from probabilistic models provide information also in the frequency domain. In the examples provided by Rossi et al. (2006, 2009), the probabilistic models represent one of the essential elements in the definition of TSS water quality criteria.

8.4 Dynamic models

Dynamic models describe all the major processes affecting water quality at CSOs and in the RWB as a function of time, where the majority of the differential equations used to describe these processes cannot be solved using analytical solutions (i.e. by analytical models – see section 8.2). An overview of some of the available software packages for sewer and river quality simulation can be found in e.g. Obropta and Kardos (2007) and Sharma and Kansal (2013), but several other modelling examples can be found in literature (e.g. Saagi et al., 2017).

In dynamic models of the integrated urban system (as sketched in Figure 2), rainfall represents the main forcing function since it affects both the quantity and the quality of the wet weather flows across the system. Catchment sub-models simulate rainfall-runoff processes, waste- and stormwater routing along the combined sewer network, and overflows at CSO structures. The approaches utilized to simulate water quantity in catchments range from conceptual (e.g. linear reservoir cascade) to detailed hydrodynamic models (based on the de-Saint-Venant equation). While the complexity for hydraulic models can be quite high, model structures for catchment water quality models remain simple. This is due to a combination of several factors (see also the discussion in Bertrand-Krajewski, 2007): lack in process understanding (e.g. there are no models capable of satisfactorily describing TSS behaviour in sewers for all events), scarcity of representative data (e.g. water quality data are collected only at the catchment outlet and they are the result of processes taking place in a complex network of drainage pipes), and measurement uncertainty (due to the intrinsic difficulties in measuring sewer water quality).

As discussed in Sharma and Kansal (2013), there exists a wide range of models available to simulate the RWB, which differ in terms of model structure, assumptions, simulated water quality parameters and processes. The selection of the modelling tools should therefore be based on specific considerations about the relevant processes and water quality parameters. This procedure is exemplified by the suggestions provided by the authors of the River Water Quality Model (RWQM) no. 1 (Shanahan et al., 2001): while presenting a detailed model that includes 24 water quality parameters and 23 processes (Reichert et al., 2001), the authors also provided a methodology to simplify the RWQM model and to adapt it for specific case studies (Vanrolleghem et al., 2001). In this example, it is shown how the RWQM1 can be simplified down to the structure of the Streeter-Phelps DO model (1925).

Dynamic models can be used to generate long-term simulations and thereby enable the evaluation of water quality criteria both in terms of magnitude, frequency and duration (Fu and Butler, 2012; Johansen et al., 1984). The vast majority of the available models focus on dissolved oxygen (thereby including the simulation of organic matter) and ammonia, with some examples including phosphorus (Holguin-Gonzalez et al., 2014). Recently Vezzaro et al. (2014) presented a library to simulate micropollutant fluxes across the integrated urban water system. Holguin-Gonzalez et al. (2014) utilized an integrated model to simulate chemical indicators that were subsequently converted into ecological indicators, enabling the evaluation of different control strategies in terms of ecological status.

The benefits in using integrated models for the perspective of fulfilling the objectives of the WFD have been shown in several simulation studies (e.g. Blumensaat et al., 2009; Even et al., 2007; Butler and Schutze, 2005; Vanrolleghem et al., 2005; Rauch et al., 2002). The KALLISTO project (Benedetti et al., 2013; Weijers, 2012), which was carried out to fulfill the WFD goals for the Dommel River (The Netherlands), represents one of the latest full-scale examples for the application of integrated dynamic models. A detailed hydrodynamic model was combined with a WWTP and a river model to evaluate the RWB quality in terms of oxygen and ammonia peaks. Specifically, the model results presented by Langeveld et al. (2013a) showed how strategies aiming at reducing DO depletion (mainly caused by CSO discharges) were increasing problems linked to ammonia peaks (mainly due to WWTP overloading). This example shows the utility of these model typologies for fully describing the interactions inherent between the elements of the integrated urban water system.

8.5 Considerations for the application of modelling tools

The examples provided in the previous sections highlight how models can be useful tools in supporting the achievement of good ecological status. However, these models rely on a large amount of data, which are essential in defining the quality of the simulation results. Long measurement time series with high time resolution are necessary to estimate the parameters found in the complex dynamic models described in Section 8.4. However, as discussed in Langeveld et al. (2013b), such data are seldom available.

Hybrid approaches, combining different models with different characteristics, can be applied to overcome some of these difficulties. For example, Langeveld et al. (2013a) recognized the poorness of existing catchment water quality models and thereby combined a detailed hydrodynamic model (to estimate CSO volumes) with a stochastic quality model (to estimate the CSO load). Similarly, Andrés-Doménech et al. (2010) combined two models using different temporal scales: an event-based model to simulate CSO discharges and a continuous river model to simulate the effect on the RWB over a long time interval.

Generally modellers are forced to find a compromise between the available knowledge and the model objectives (Harremoës and Madsen, 1999). Table 13 summarizes the model features listed in the previous sections: while dynamic models are capable of generating outputs that can be used to compute water quality indicators, they are hampered by high data requirements which limits their parameters' identifiability (Reichert and Vanrolleghem, 2001). On the other hand, analytical models have low data requirements (they can be applied by using literature data, as in the DWA guidelines) but they require a strict set of assumptions (e.g. *worst case scenario* – dissolved oxygen should be evaluated for low river flow and high temperature conditions).

Acknowledging uncertainty in the modelling results is also an essential step in the application of (any of) these tools. The procedures illustrated in Benedetti et al. (2013) and Schellart et al. (Schellart et al., 2010) provide examples for how the inclusion of uncertainty analyses can improve the reliability and applicability of the modelling results.

Table 13. Schematization of minimum data requirement and main outputs in terms of water quality criteria.

Model typology	Minimum data requirement		Water Quality criteria		
	From literature	Site specific	Magnitude	Frequency	Duration
Analytical	Can be sufficient	Average values	X		
Probabilistic	Yes, can be sufficient	Event-based time series	X	X	
Dynamic	Can integrate missing data	Time series	X	X	X

9. Conclusions and recommendation

The overview provided in the previous sections highlights how:

- Wet weather discharges from urban areas are characterized by an intrinsic natural variability (both in terms of volumes and pollutant concentrations). This, in combination with the intermittent nature of wet weather discharges, hinders the direct application of Emission Level Value regulations.
- The available measurements show how pollutant concentrations in CSO discharges can exceed the Environmental Quality Standards (EQS) defined by existing Danish legislation. Since EQS are defined for the Receiving Water Body, processes such as dilution, transportation, and chemical transformation should be taken into consideration.
- For many chemicals that potentially act as stressors, no measurements are available, hampering a complete assessment of the CSO impacts. The lack of measurements for a large fraction of priority pollutants is one of the factors that inhibit the possibility to establish a simple causal relationship between emissions and impacts on chemical and ecological status.
- The status of headwater streams is relevant for predicting/determining the potential for CSOs to negatively impact ecological conditions, where it has been shown that upstream catchments with high ecological quality may mask some of the negative effects expected from chemical and hydrological disturbances associated with urban water discharges (e.g. through a higher recolonization/dispersal potential). The environmental context (i.e. hydromorphological, chemical and ecological conditions characterizing upstream sections) will in fact influence the ecological quality of the RWB at downstream sites, and it will additionally influence the ecological response to urban water discharges in the RWB.
- Current knowledge may not allow for a differentiation or ranking of individual stressors in a multi-stressor context, indicating that mitigation measures focusing on individual stressors (chemicals) may not be effective in reducing ecological risks.
- Combined Sewer Overflows usually represent a stressor that prevents good chemical and/or ecological status in the RWB. However, depending on site-specific conditions (e.g. rare discharges that are sufficiently diluted in sufficiently clean (upstream) water), the CSO role as a stressor might be reduced, not significantly hindering good chemical or ecological status.
- Combined Sewer Overflows can also act in combination with other stressors, contributing to the deterioration of the chemical and ecological status. There is very limited knowledge on how to assess the relative importance of stressors for a given water body and no Danish studies have been reported in the scientific literature focussed on this aspect.
- Wet weather discharges from separate systems and WWTPs can also affect the chemical and ecological status of the RWB. For separate systems, the major sources of impacts are priority pollutants, suggesting a potential for chronic toxicity. However, the difficulties linked to monitoring these pollutants require the application of innovative monitoring approaches. For discharges from WWTPs the data are limited, but they are also expected to threaten the RWB quality status. However, these discharges typically fall within legislation dealing with dry weather discharges (i.e. WWTP discharge permits).

- Collection of representative data is challenged by several factors such as the variability of the monitored processes, the practical difficulties in collecting good quality measurements at high temporal resolution, and the choice of representative monitoring locations. Modelling can be used to integrate the information provided by the available measurements.
- Studies highlight that ammonia and/or oxygen depletions can be useful indicators for assessing the ecological consequences of combined sewer overflows under the assumption that none of the possibly toxic anthropogenic chemicals and heavy metals will exert a severe negative influence. These indicators can be integrated with bioavailable heavy metal and PAHs concentrations which are, however, more difficult to analyse at a time-resolution that is representative for wet-weather discharges. In this scenario, it is possible to make reasonable predictions for effects on fish and macroinvertebrate communities. However, possible relationships between CSOs and ecological quality have not been established/verified. For both ammonia and DO, it is possible to establish simple mathematical models to verify compliance with water quality criteria given a sufficient number of available measurements.
- When results from measurement campaigns show that the above-mentioned indicators comply with water quality standards, it is reasonable to assume that CSOs are not the main contributors affecting the RWB status.

These considerations suggest that CSO regulations cannot utilize a “one size fits all” solution, such as ELV or other indicators related to sewer system criteria, in order to ensure good chemical and ecological status. This requires site-specific regulations that consider the interactions between the sewer system and the receiving water body. Ideally, this regulation should build upon an extensive data background, focusing on various water quality indicators and aiming at better describing the cause-effect relationships between CSO discharges and the RWB quality status. In this context, mathematical models can be used to integrate information from monitoring networks, thus supporting the assessment of the current quality status and the development of strategies for impact reduction.

However, this approach is not feasible for the vast majority of the cases due to limitations in monitoring resources. Therefore, a minimum water regulation focusing on a reduced number of indicators (initially hydraulic parameters, followed by ammonia and DO) is suggested. This basic regulation can subsequently be extended to include additional indicators whenever this is needed by the specific characteristics of the RWB (e.g. where poor quality status is mainly caused by other stressors than acute NH_3 toxicity and DO depletion). Water quality regulations should be framed around the concepts described in Section 7.2, i.e. based on the definition of allowed magnitude, duration, and frequency.

A practical stepwise approach for the implementation of CSO regulation is also proposed (Figure 20). This considers well-established monitoring technologies and it proposes practical solutions that can easily be implemented in a Danish context. Acknowledging the practical difficulties in collecting water quality data at CSO discharge points, the recommendations focus on indicators that can easily be measured at the discharge points or in the receiving water body. The considerations are summarized in Table 14, which provides a relative comparison of the different steps based on a qualitative assessment.

The comparison focuses on measurements (considering difficulties in the collection of good quality data, and their information content for minimizing impacts from CSO discharges), resource requirements (investments in terms of sensors, maintenance and the operation of monitoring networks), and effectiveness of the collected data in describing the CSO-RWB interactions (where the uncertainty is high, higher safety factors should be applied and more conservative assumptions need to be made).

- *Assessment based on hydraulic parameters*: once no compliance of the RWB with good status is defined, an initial assessment based on hydraulic variables provides the basic information to evaluate the potential for CSOs to impact the RWB status. This stage is linked to a screening/planning phase, aiming at evaluating the importance of CSO discharges as a major contributor to the RWB. This assessment should link the hydraulic information on CSO discharges (maximum flows, volumes, frequency of overflows) to the RWB status (base-flow). This allows for the consideration of physical impacts (e.g. erosion), aesthetic impacts (based on e.g. frequency), and chemical impacts (after conservative assumptions on CSO pollution levels).

  If the measurements of these hydraulic parameters show that CSO discharges are not significant compared to the river base-flow (e.g. events with a low frequency, high dilution factor), these are sufficient to regulate the discharge point. In fact, these measurements allow an estimation of nutrient loads in order to assess long-term effects (eutrophication). Furthermore, the calculation of expected dilution rates can provide a rough assessment of CSO effects with respect to chemical indicators (EQS values). The uncertainty in the results obtained is high, and a conservative approach is needed (*worst case*). For example, the needed assumptions require high-range CSO pollution levels, low RWB base-flow, and low pollution levels in the RWB upstream of the discharge point, and can be verified with simple modelling approaches (e.g. those described in Section 8.2).

- *Short term (event-based) water quality monitoring:* when the measurement of hydraulic variables show a potential for CSO discharges to affect the RWB status, short monitoring campaigns can be established to collect relevant information on an event-basis. This stage is also linked to a screening/planning phase, aiming at better evaluating the importance of CSO discharges as a major contributor to the RWB based on water quality indicators. The collected water quality data provide for an estimation of the magnitude of the CSO impacts at the monitoring site. The number of monitored events should be sufficient to enable the parameter estimation of simple models (analytical and probabilistic) and thereby allow a conservative assessment of short-term impacts, such as oxygen depletion and ammonia-related toxicity. Also, these data can reduce the uncertainty linked to the estimation of pollution loads. Data should be collected at representative points along the RWB (e.g. upstream and downstream of discharge points).

- *High time resolution monitoring of basic water quality indicators.* Once the impact of CSO discharges is unveiled, high time resolution measurements are essential to grasp the high variability of CSO discharges and of their negative effects. These data will support the implementation of the suggested basic level of water quality regulation, following the concepts described in Section 7.2. The available measuring techniques only allow measurements for basic water quality parameters such as dissolved oxygen, ammonia/ammonium, and turbidity (converted to Total Suspended Solids). The first two chemical indicators can be directly linked to water quality criteria, expressed as magnitude, frequency and duration.

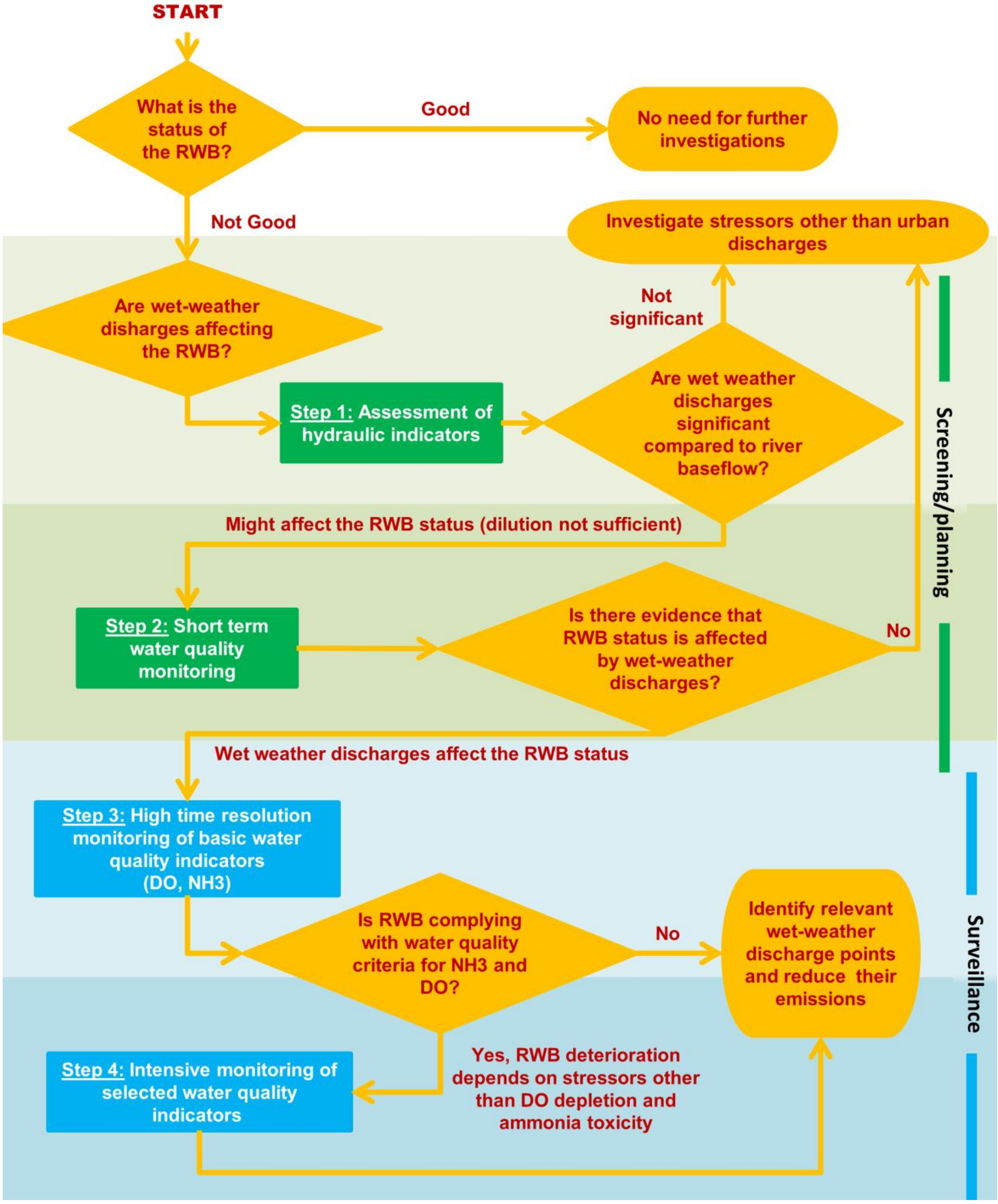


Figure 20. Suggestion for a decision process for the evaluation and regulation of the negative effects of CSO discharges. Note that step 1 can also be applied for surveillance

Particle concentrations can be used as a proxy for other micropollutants, but a series of assumptions on e.g. pollution levels at discharge points, partitioning, and particle size needs to be made. The high-time resolution data can be used to calibrate complex dynamic models in order to more accurately simulate the integrated urban water system. Data should be collected at representative points along the RWB.

- *Intensive monitoring of selected water quality indicators.* Since compliance with basic water quality criteria (DO and NH3) may not be sufficient to ensure the achievement of good ecological status, supplementary data should be collected to expand the overview of the integrated urban water system. The measurements of selected water quality indicators will enable a more thorough assessment of the CSO-related impacts in the RWB, although limited to individual chemical indicators. Considering the CSO pollution levels (i.e. Section 3.3) and the available monitoring techniques, the suggested indicators to be monitored include (in order of suggested prioritization): heavy metals (e.g. copper, zinc) and polycyclic aromatic hydrocarbons (PAH). Since high time resolution measurements are currently not possible/feasible, measurement campaigns can employ traditional event-based monitoring approaches (with high temporal inter-event resolution) or a combination of innovative approaches (e.g. passive samplers in combination with modelling tools – see Section 6.2). When coupled with high time resolution measurements (turbidity), possible correlations can be built and used to extrapolate the values of selected indicators over longer time intervals. Moreover, these measurements can be coupled with models to supplement additional information/understanding of the system.

The choice of the site-specific monitoring and regulation approach should be based on different site-specific considerations, which include among others: the sensitivity of the RWB, the number of CSO structures, and the available resources for establishing and carrying out monitoring campaigns.

Table 14. Relative comparison of the recommended steps for CSO regulation.

Step	Type of investigated impacts						Data					Resource requirements	Effectiveness in achieving environmental targets	
							Type of measurements				Difficulty in collection of good quality data			
								Water Quality chemical indicators						
	Physical modifications	Aesthetical pollution	Eutrophication	Human health	Acute effects (DO depletion, NH3 toxicity)	Priority pollutants (acute and chronic)	Hydraulic (flows, high time resolution)	event based (automatic samplers)	on line sensors (high time resolution))	Passive samplers			Uncertainty in the estimation of compliance	Needed safety factor
Assessment of hydraulic parameters	X	A	X	A	A	A	X				Low	Low	High	High
Short term water quality monitoring		X	X	X	X	X	X	X		X	Low/medium	Low/medium	High/Medium	Medium
High time resolution monitoring of basic water quality indicators			X		X	A	X		X		Medium/high	Medium/high	Medium/low	Medium/low
Intensive monitoring of selected water quality indicators			X	X	X	X	X	X	X	X	High	High	Low	Low

X: Directly measurable; A: requires assumptions (e.g. solid/water partition of priority pollutants, pollutant concentrations in CSO discharges)

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Appendix A Measured concentrations in wet weather discharges

This appendix provides all the available measurements of pollutant concentrations measured in Combined Sewer Overflows and in discharges from separate systems. Wet weather discharges from Wastewater Treatment Plants are not included due to the limited number of available studies (see Section 3.5). The critical pollutants are identified based on the methodology described in Section 3.1.

The measured pollutant concentrations are compared against the Environmental Quality Standards defined in the current Danish legislation (BEK 439 19/05/2016 – see Table A-1. The utilized data sources are listed in Table A-4.

Table A-1. List of substances listed in the Danish legislation for freshwater quality (BEK 439 19/05/2016), along with data availability in existing literature. Substances with light blue background are classified as "priority hazardous pollutants"

CAS number[1]	Name of substance	Identified as priority hazardous substance	Inland freshwater Environmental Quality Standard		Measurement available	
			Annual Average[2] [µg/l]	Maximum Allowable Concentration [µg/l]	Combined	Separate
National Enviromental Quality Standards for water						
75-05-8	Acetonitrile		2000	191000	X	
83-32-9	Acenaphthene (PAH)		3,8	3,8	X	X
208-96-8	Acenaphthylene (PAH)		1,3	3,6	X	X
107-02-8	Acrolein (Acraldehyde)		0,1	1		X
393085-45-5	2-Amino-4-(methylsulfonyl)benzoic acid, AMBA		77	140		
41668-11-5	6-Amino-5-chloronicotinic acid		95	949		
26787-78-0	Amoxcillin		0,078	0,37		
118-92-3	Anthranilic acid		19,4	194		
7440-36-0	Antimony		113	177	X	X
7440-38-2	Arsenic		4,3[3]	43	X	X
7440-39-3	Barium		194[3]	145	X	X
25057-89-0	Bentazon		45	450		X
56-55-3	Benzo(a)anthracene (PAH)		0,012	0,018	X	
94-09-7	Benzocaine		7,2	72		

[1] CAS: Chemical Abstracts Service.
[2] Expressed as yearly concentration. The value refers to all the sum concentration of all the isomers unless differently specified.
[3] EQS is expressed as value summed to the natural background concentration.

CAS number[1]	Name of substance	Identified as priority hazardous substance	Inland freshwater Environmental Quality Standard		Measurement available	
			Annual Average[2] [µg/l]	Maximum Allowable Concentration [µg/l]	Combined	Separate
65-85-0	Benzoic acid		90	900		
100-51-6	Benzyl alcohol		360	3600		
98-87-3	Benzal chloride (alfa, alfa-dichlorotoluene)		0,21	2,1		
50-28-2	Estradiol-17-beta		0,0001	4,6		
80-05-7	Bisphenol A 2,2-bis(4-hydroxyphenyl)propane		0,1	10	X	X
7440-42-8	Boron		94[3] 20000[4]	2080[3]		
3844-45-9	Brilliant Blue		96	960		
7722-84-1	Hydrogen peroxide		10[4]	100		
85-68-7	Butyl benzyl phthalate (BBP)		7,5	15	X	X
79456-26-1	3-Chloro-5-(trifluoromethyl)pyridin-2-amine		0,08	160		
29091-09-6	2,4-dichloro-3,5-dinitro-benzotrifluoride		0,0006	0,06		
97-00-7	1-chloro-2,4-dinitrobenzene (DNCB)		5	37		
90-13-1 91-58-7	1-chloronaphtalene 2- chloronaphtalene		Σ = 2,7	Σ = 3,7		
89-63-4	4-chloro-2-nitroaniline		1	10		
59-50-7	4-chlor-3-methylphenol (PCMC)		9	90		X
95-74-9	3-chloro-p-toluidine		0,62	62		

[4] EQS valid for total concentration, irrespective of the total natural background concentration

<table>
<tr><th rowspan="2">CAS number[1]</th><th rowspan="2" colspan="2">Name of substance</th><th rowspan="2">Identified as priority hazardous substance</th><th colspan="2">Inland freshwater Environmental Quality Standard</th><th colspan="2">Measurement available</th></tr>
<tr><th>Annual Average[2] [µg/l]</th><th>Maximum Allowable Concentration [µg/l]</th><th>Combined</th><th>Separate</th></tr>
<tr><td>130-16-5</td><td colspan="2">Clioquinol</td><td></td><td>0,027</td><td>0,27</td><td></td><td></td></tr>
<tr><td>88349-88-6</td><td colspan="2">Cloquintocet</td><td></td><td>30</td><td>300</td><td></td><td></td></tr>
<tr><td>57-15-8
1320-66-7</td><td colspan="2">Chloretone
Butylene chlorohydrin</td><td></td><td>135</td><td>1350</td><td></td><td></td></tr>
<tr><td>79-11-8</td><td colspan="2">Chloro acetic acid (MCAA)</td><td></td><td>0,58</td><td>3,3</td><td></td><td></td></tr>
<tr><td>126-99-8</td><td colspan="2">chlorprene (2-chloro-1,3 butadiene)</td><td></td><td>32</td><td>2000</td><td></td><td></td></tr>
<tr><td>615-65-6</td><td colspan="2">2-chloro-p-toluidine</td><td></td><td>0,62</td><td>62</td><td></td><td></td></tr>
<tr><td>89402-40-4</td><td colspan="2">Phenol, 4-[(5-chloro-3-fluoro-2-pyridinyl)oxy]-</td><td></td><td>2,4</td><td>24</td><td></td><td></td></tr>
<tr><td>114420-56-3</td><td colspan="2">Clodinafop</td><td></td><td>3,2</td><td>450</td><td></td><td></td></tr>
<tr><td>105512-06-9</td><td colspan="2">Clodinafop-propargyl</td><td></td><td>10</td><td>21</td><td></td><td></td></tr>
<tr><td>56-72-4</td><td colspan="2">Coumaphos</td><td></td><td>0,0007</td><td>0,007</td><td></td><td></td></tr>
<tr><td rowspan="2">7440-47-3</td><td rowspan="2">Chromium</td><td>Cr VI</td><td></td><td>3,4</td><td>17</td><td rowspan="2">X</td><td rowspan="2">X</td></tr>
<tr><td>Cr III</td><td></td><td>4,9</td><td>124</td></tr>
<tr><td>218-01-9</td><td colspan="2">Chrysene</td><td></td><td>0,014</td><td>0,014</td><td>X</td><td>X</td></tr>
<tr><td>7440-48-4</td><td colspan="2">Cobalt</td><td></td><td>0,28[3]</td><td>18</td><td>X</td><td>X</td></tr>
<tr><td>108-39-4
95-48-7
106-44-5</td><td colspan="2">m-cresol
o-cresol
p-cresol</td><td></td><td>Σ = 100</td><td>Σ = 1000</td><td></td><td>X</td></tr>
</table>

CAS number[1]	Name of substance	Identified as priority hazardous substance	Inland freshwater Environmental Quality Standard		Measurement available	
			Annual Average[2] [µg/l]	Maximum Allowable Concentration [µg/l]	Combined	Separate
504-02-9	1,3-Cyclohexanedione (1,3 CHD)		24	240		
913545-19-4 1156459-77-6	2-cyclohexen-1-one,3hydroxy-2-(6-(methylsulfonyl)-2,1-benzisoxazol-3-yl), M4[5]		47,6	476		
103-23-1	Bis(2-ethylhexyl) adipate (DEHA)		0,7	6,6	X	X
53-70-3	Dibenzo(a,h)anthracene (PAH)		0,0014	0,018	X	X
106-93-4	Ethylene dibromide (1,2-dibromethane)		0,002	0,02		
84-74-2	Dibutyl phthalate (DBP)		2,3	35	X	X
69045-84-7	2,3-dichloro-5-(trifluoromethyl)pyridine		0,53	30		
2008-58-4	2,6-dichlorobenzamide (BAM)		78	780		X
91-94-1	Dichlorobenzidine (3,3'-dichlorbenzidin), (DCB)		0,001	0,01		
75-34-3	1,1-dichlorethane		10			
540-59-0 75-35-4	1,2-dichlorethylene 1,1-dichlorethylene		6,8	68		
120-83-2	2,4-dichlorophenol		0,2	20		
87-65-0	2,6-dichlorophenol		3,4	34		
15165-67-0 120-36-5	Dichlorprop-P (Dichlorprop)		41	41		
342-25-6	2,4'-Difluorobenzophenone		0,082	8,2		

[5] Danish name

CAS number[1]	Name of substance	Identified as priority hazardous substance	Inland freshwater Environmental Quality Standard		Measurement available	
			Annual Average[2] [µg/l]	Maximum Allowable Concentration [µg/l]	Combined	Separate
887502-60-5	3,4-dihydro-6-(methylsulphonyl)-1H-xanthene-1,9(2H)-dion, Xanth[5]		83	830		
68-12-2	N,N-Dimethylformamide		22800	22800		
576-26-1 105-67-9 108-68-9 95-65-8 526-75-0 95-87-4 1300-71-6	Dimethylphenol (6 isomersr af dimethylphenol)		Σ = 13,1	Σ = 132		
75-18-3	Methyl sulfide		15	230		
13472-45-2	Sodium tungstate		33	330		
383412-05-3	1-methylhexyl chloroacetate		0,036	0,36		
99607-70-2	Cloquintocet-mexyl		0,02	5,3		
57-63-6	Ethinylestradiol		0,000075	0,00075		
110-76-9	2-Ethoxyethylamine		152	1520		
100-41-4	Ethylbenzene		20	180	X	X
76639-94-6	Florfenicol		7	21		
79622-59-6	Fluazinam		0,29	0,36		
462-06-6	Fluorobenzene		7,4	74		
445-29-4	2-Fluorobenzoic acid		900	9000		
86-73-7	Fluorine		2,3	21,2	X	X

CAS number[1]	Name of substance	Identified as priority hazardous substance	Inland freshwater Environmental Quality Standard		Measurement available	
			Annual Average[2] [µg/l]	Maximum Allowable Concentration [µg/l]	Combined	Separate
88374-05-04	Fluorphenyl epoxy ethan (FOX)		0,048	4,8		
76674-21-0	flutriafol		31	31		
54041-17-7	N-(4-fluorophenyl)-2-hydroxy-N-(1-methylethyl)acetamide		23	230		
201668-31-7	[(4-fluorophenyl)(1-methylethyl)amino](oxo)acetic acid		4750	47500		
201668-32-8	Flufenacetsulfonic acid		760	980		
50-00-0	Formaldehyde		9,2 5)	46		
16872-11-0	Fluoroboric acid		830	8300		
94050-90-5	HPPA		35	350		
514797-96-7	2(1H)-Pyridinone, 5-chloro-3-fluoro- (FCHP)		100	1000		
611-70-1	Isobutyrophenone		13,2	132		
98-82-8	Isopropylbenzene (cumene)		22	22		
7553-56-2	Iodine		10[3]	10[3]		
562-54-9	Potassium methyl sulphate		1000	10000		
7722-64-7	Potassium permanganate		0,84	8,4		
127-65-1	Chloramine (T)		5,8	5,8		
7440-50-8	Copper		1[3,6] 4,9[4]	2[3] 4,9[4]	X	X
68411-30-3	Sodium alkylbenzene sulfonate		54	160	X	

[6] EQS valid for bioavailable concentration.

CAS number[1]	Name of substance	Identified as priority hazardous substance	Inland freshwater Environmental Quality Standard		Measurement available	
			Annual Average[2] [µg/l]	Maximum Allowable Concentration [µg/l]	Combined	Separate
7439-96-5	Manganese		150[3]	420[3]	X	
16484-77-8 93-65-2	Mecoprop-p (Mecoprop)		18	187	X	X
104206-82-8	mesotrione		0,2	0,77		
 90-12-0 91-57-6 28804-88-8 28652-77-9	Methylnaphtalene (PAH), including: 1-methylnaphtalene 2- methylnaphtalene Dimethylnaphthalene, mixture of isomers methylnaphtalene		Σ = 0,12	Σ = 2	X X X	X X X
121-44-8	Triethylamine		110	800		
104-96-1	4-Amino thioanisole		1,5	15		
1671-49-4	4-Methylsulfonyl-2-nitrotoluene, NMST		1000	5900		
1671-48-3	2-Methyl-5-(methylsulfonyl)aniline, AMST		65	650		
110964-79-9	4-Methylsulfonyl-2-nitrobenzoic acid		1000	1300		
1634-04-4	Tert-butyl methyl ether (MTBE)		10	90		X
7439-98-7	Molybdenum		67	587	X	
110-71-4	Monoglyme		500	5000		
81-15-2	Musk xylene		0,11	0,68		X
917-61-3	Potassium cyanate		1	47		
14698-29-4	Oxolinic acid		15	18		
79-57-2	Oxytetracycline		10	21		
106700-29-2	Pethoxamid		0,12	0,12		

CAS number[1]	Name of substance	Identified as priority hazardous substance	Inland freshwater Environmental Quality Standard		Measurement available	
			Annual Average[2] [µg/l]	Maximum Allowable Concentration [µg/l]	Combined	Separate
85-01-8	Phenanthrene (PAH)		1,3	4,1	X	X
108-95-2	Phenol		7,7	310	X	
129-00-0	Pyrene		0,0046	0,023	X	X
69-72-7	Salicylic acid		171	390		
7782-49-2	Selenium		0,1[3]	31[3]		X
124774-27-2	Flutriafol IMpurity A		25	250		
7440-24-6	Strontium		2100	5530[3]		X
68-35-9	Sulfadiazine		4,6	14		
7440-22-4	Silver		0,017[3]	0,36[3]		X
79-34-5	Tetrachloroethane		70	93		
13674-84-5	Tris(1-chloro-2-propyl) phosphate (TCPP)		640	640	X	
7440-28-0	Thallium		0,48[3]	1,2[3]		X
7440-31-5	Tin		2	20		
108-88-3	Toluene		74	380	X	X
288-88-0	1,2,4-triazol		64	225		
71-55-6	1,1,1-trichlorethane		21	54		X
88-06-2	2,4,6-trichlorophenol		1	160		X
112-27-6	Triethylene glycol		120000	390000		
126-73-8	Tributyl phosphate		82	170		X
738-70-5	Trimethoprim		100	160		

CAS number[1]	Name of substance	Identified as priority hazardous substance	Inland freshwater Environmental Quality Standard		Measurement available	
			Annual Average[2] [µg/l]	Maximum Allowable Concentration [µg/l]	Combined	Separate
115-86-6	Triphenyl phosphate (TPP)		0,74	1,8	X	X
7440-61-1	Uranium		0,015[3]	2,3[3]		
7440-62-2	Vanadium		4,1[3]	57,8	X	X
75-01-4	Vinyl chloride		0,05	0,5		
1330-20-71	Xylenes (o-, p- og m-xylene)		Σ = 10	Σ = 100	X	X
7440-66-6	Zinc		7,8[3,6] 3,1[3,7]	8,4[3]	X	X
Environmental Quality standards for priority hazardous substances and other pollutants						
15972-60-8	Alachlor		0,3	0,7		X
120-12-7	Antracene	X	0,1	0,1	X	X
1912-24-9	Atrazine		0,6	2,0	X	X
71-43-2	Benzene		10	50	X	X
32534-81-9	Pentabromodiphenyl ether[8]	X		0,14		
7440-43-9	Cadmium and cadmium compounds (depending on the water hardness)[9]	X	≤ 0,08 (class 1) 0,08 (class 2) 0,09 (class 3) 0,15 (class 4) 0,25 (class 5)	≤ 0,45 (class 1) 0,45 (class 2) 0,6 (class 3) 0,9 (class 4) 1,5 (class 5)	X	X

[7] EQS valid for soft water (H<24 mg CaCO3/l)
[8] For this group of substances the EQS is valid for the sum of isomers 28, 47, 99, 100, 153 and 1
[9] For cadmium and cadmium and its compound the EQS depends on the water hardness, which is subdivided into five categories Category 1: < 40 mg CaCO3/l, Category 2: from 40 to < 50 mg CaCO3/l, category 3: from 50 to < 100 mg CaCO3/l, category 4: from 100 to < 200 mg CaCO3/l and category 5: ≥ 200 mg CaCO3/l)..

CAS number[1]	Name of substance	Identified as priority hazardous substance	Inland freshwater Environmental Quality Standard		Measurement available	
			Annual Average[2] [µg/l]	Maximum Allowable Concentration [µg/l]	Combined	Separate
56-23-5	Tetrachlormethan		12	Not applied		
85535-84-8	Alkanes, C10-13, chloro[10]	X	0,4	1,4	X	
470-90-6	Chlorfenvinphos		0,1	0,3		X
2921-88-2	Chlorpyrifos		0,03	0,1		X
	Organochloride pesticides		Σ = 0,01	not applied		
309-00-2	aldrin				X	X
60-57-1	dieldrin				X	X
72-20-8	endrin					X
465-73-6	isoendrin					
not applied	Total DDT[11]		0,025	not applied		X
50-29-3	para-para-DDT (clofenotane)		0,01	not applied		
107-06-2	1,2-dichlorethane		10	not applied		X
75-09-2	Dichlormethane		20	not applied		X
117-81-7	Bis(2-ethylhexyl) phthalate (DEHP)	X	1,3	not applied	X	X
330-54-1	Diuron		0,2	1,8	X	X
115-29-7	Endosulfan	X	0,005	0,01		X
206-44-0	Fluoranthene		0,0063	0,12	X	X
118-74-1	Hexachlorobenzene	X		0,05		X

[10] There is no indicator parameter for these substances. The indicator parameter is defined based on the analysis methodology.
[11] Total DDT is calculated as the sum of the isomers 1,1,1-trichlor-2,2-bis(p-chlorphenyl)ethan (CAS-number 50-29-3; EU-number 200-024-3); 1,1,1-trichlor-2-(o-chlorphenyl)-2-(p-chlorphenyl)ethan (CAS-number 789-02-6; EU-number 212-332-5); 1,1-dichlor-2,2-bis(p-chlorphenyl)ethylen (CAS-number 72-55-9; EU-number 200-784-6) og 1,1-dichlor-2,2-bis(p-chlorphenyl)ethan (CAS-number 72-54-8; EU-number 200-783-0).

CAS number[1]	Name of substance	Identified as priority hazardous substance	Inland freshwater Environmental Quality Standard		Measurement available	
			Annual Average[2] [µg/l]	Maximum Allowable Concentration [µg/l]	Combined	Separate
87-68-3	Hexachlorobutadiene	X		0,6		
608-73-1	Benzene hexachlorid	X	0,02	0,04		
34123-59-6	Isoproturon		0,3	1,0	X	X
7439-92-1	Lead and lead compounds		1,2 [6]	14	X	X
7439-97-6	Mercury and mercury compounds	X		0,07	X	X
91-20-3	Naphthalene		2	130	X	X
7440-02-0	Nickel and nickel compounds		4 [6]	34	X	X
84852-15-3	Nonylphenols (4-nonylphenol)		0,3	2,0	X	X
140-66-9	Octylphenols (4-(1,1',3,3'-tetramethylbutyl)-phenol)	X	0,1	not applied	X	
608-93-5	Pentachlorobenzene	X	0,007	not applied		X
87-86-5	Pentachlorophenol		0,4	1		X
not applied	Polycyclic Aromatic Hydrocarbons (PAH)[12]	X	not applied	not applied		
50-32-8	Benzo(a)pyrene		$1{,}7 \times 10^{-4}$	0,27	X	X
205-99-2	Benzo(b)fluoranthene		[12]	0,017	X	X
207-08-9	Benzo(k)fluoranthene		[12]	0,017	X	X
191-24-2	Benzo(g,h,i)perylene		[12]	8,2 × 10-3	X	X

[12] For this group of priority hazardous substance is valid the EQS for biota and the general water EQS for benzo(a)pyrene, which is used to estimate the biota toxitcity, Benzo(a)pyrene can be used as indicator for the whole PAH group, and therefore only benzo(a)pyrene needs to be monitored to assess compliance with EQS in freshwater.

CAS number[1]	Name of substance	Identified as priority hazardous substance	Inland freshwater Environmental Quality Standard		Measurement available	
			Annual Average[2] [µg/l]	Maximum Allowable Concentration [µg/l]	Combined	Separate
193-39-5	Indeno(1,2,3-cd)-pyrene		[12]	not applied	X	X
122-34-9	Simazine		1	4		X
127-18-4	Tetrachloroethylene		10	not applied	X	X
79-01-6	Trichloroethylene		10	not applied	X	X
36643-28-4	Tributyl compounds	X	0,0002	0,0015	X	X
12002-48-1	Trichlorobenzens		0,4	not applied		
67-66-3	Trichloromethane		2,5	not applied		X
1582-09-8	Trifluralin	X	0,03	not applied		
115-32-2	Dicofol	X	1,3 × 10-3	not applied[13]		
1763-23-1	Perfluorooctanesulfonic acid and related compounds (PFOS)	X	6,5 × 10-4	36		X
124495-18-7	Quinoxyfen	X	0,15	2,7		
[14]	Dioxins and similar compounds	X		not applied	X	X
74070-46-5	Aclonifen		0,12	0,12		

[13] There are not sufficient data to define a maximum concentration for this substance
[14] This is valid for the following substances
– 7 polychlorerede dibenzo-p-dioxiner (PCDD): 2,3,7,8-T4CDD (CAS 1746-01-6), 1,2,3,7,8-P5CDD (CAS 40321-76-4), 1,2,3,4,7,8-H6CDD (CAS 39227-28-6), 1,2,3,6,7,8-H6CDD (CAS 57653-85-7), 1,2,3,7,8,9-H6CDD (CAS 19408-74-3), 1,2,3,4,6,7,8-H7CDD (CAS 35822-46-9) og 1,2,3,4,6,7,8,9-O8CDD (CAS 3268-87-9)
– 10 polychlorerede dibenzofurans (PCDF): 2,3,7,8-T4CDF (CAS 51207-31-9), 1,2,3,7,8-P5CDF (CAS 57117-41-6), 2,3,4,7,8-P5CDF (CAS 57117-31-4), 1,2,3,4,7,8-H6CDF (CAS 70648-26-9), 1,2,3,6,7,8-H6CDF (CAS 57117-44-9), 1,2,3,7,8,9-H6CDF (CAS 72918-21-9), 2,3,4,6,7,8-H6CDF (CAS 60851-34-5), 1,2,3,4,6,7,8-H7CDF (CAS 67562-39-4), 1,2,3,4,7,8,9-H7CDF (CAS 55673-89-7), 1,2,3,4,6,7,8,9-O8CDF (CAS 39001-02-0)
– 12 dioxi-similar polychlorerede biphenyler (DL-PCB): 3,3,4,4-T4CB (PCB 77, CAS 32598-13-3), 3,3,4,5-T4CB (PCB 81, CAS 70362-50-4), 2,3,3,4,4-P5CB (PCB 105, CAS 32598-14-4), 2,3,4,4,5-P5CB (PCB 114, CAS 74472-37-0), 2,3,4,4,5-P5CB (PCB 118, CAS 31508-00-6), 2,3,4,4,5-P5CB (PCB 123, CAS 65510-44-3), 3,3,4,4,5-P5CB (PCB 126, CAS 57465-28-8), 2,3,3,4,4,5-H6CB (PCB 156, CAS 38380-08-4), 2,3,3,4,4,5-H6CB (PCB 157, CAS 69782-90-7), 2,3,4,4,5,5-H6CB (PCB 167, CAS 52663-72-6), 3,3,4,4,5,5-H6CB (PCB 169, CAS 32774-16-6) og 2,3,3,4,4,5,5-H7CB (PCB 189, CAS 39635-31-9).

CAS number[1]	Name of substance	Identified as priority hazardous substance	Inland freshwater Environmental Quality Standard		Measurement available	
			Annual Average[2] [µg/l]	Maximum Allowable Concentration [µg/l]	Combined	Separate
42576-02-3	Bifenox		0,012	0,04		
28159-98-0	Cybutryn		0,0025	0,016		X
52315-07-8	Cypermethrin		8 × 10-5	6 × 10-4		
62-73-7	Dichlorvos		6 × 10-4	7 × 10-4		
[15]	Hexabromocyclododecanes (HBCDD)	X	0,0016	0,5		
76-44-8/1024-57-3	Heptachloro og heptachlor epoxide	X	2 × 10-7	3 × 10-4		
886-50-0	Terbutryn		0,065	0,34	X	X

[15] This is valid for 1,3,5,7,9,11-hexabromcyclododecan (CAS 25637-99-4), 1,2,5,6,9,10- hexabromcyclododecan (CAS 3194-55-6), α-hexabromcyclododecan (CAS 134237-50-6), β-hexabromcyclododecan (CAS 134237-51-7) og γ-hexabromcyclododecan (CAS 134237-52-8)

Table A-2. Measured concentrations for discharges from Combined Sewer Overflows, Environmental Quality Standards (as defined in BEK 439 19/05/2016), estimated threat to the RWB chemical status and number of available measurements.

CAS Number [1]	Name of substance	Annual Average EQS[2] [µg/l]	Maximum Allowable Concentration EQS [µg/l]	Measured ranges [min-max][3]		Threat to good chemical status	Available measurements [events]
				All available data	Danish data		
National Environmental Quality Standards for water							
83-32-9	Acenaphthene (PAH)	3,8	3,8	0,009-1	0,01-1		>15
208-96-8	Acenaphthylene (PAH)	1,3	3,6	0,002-0,029			5-15
7440-36-0	Antimony	113	177	0,3-1,5	0,3-1,5		>15
7440-38-2	Arsenic	4,3[4]	43	0,54-30,6	0,80-30,6		>15
7440-39-3	Barium	19[4]	145	1-316	1-316		>15
56-55-3	Benzo(a)anthracene (PAH)	0,012	0,018	0,01-0,22	0,01-0,06		>15
80-05-7	Bisphenol A 2,2-bis(4-hydroxyphenyl)propane	0,1	10	0,10-0,56	0,10-0,56		>15
7440-42-8	Boron	94[4]	2080	10-86	10-86		>15
85-68-7	Butyl benzyl phthalate (BBP)	7,5	15	0,1-5	0,1-5		>15
7440-47-3	Chromium Cr VI	3,4	17	0,29-65,2	0,29-65,2		>15
	Cr III	4,9	124				

[1] CAS: Chemical Abstracts Service.
[2] Expressed as yearly concentration. The value refers to all the sum concentration of all the isomers unless differently specified.
[3] Dissolved concentrations (if available) are listed in brackets
[4] EQS is expressed as value summed to the natural background concentration.

CAS Number [1]	Name of substance	Annual Average EQS[2] [µg/l]	Maximum Allowable Concentration EQS [µg/l]	Measured ranges [min-max][3]		Threat to good chemical status	Available measurements [events]
				All available data	Danish data		
218-01-9	Chrysene	0,014	0,014	0,049-0,273			5-15
7440-48-4	Cobalt	0,28[4]	18	0,24-2,10	0,24-2,10		5-15
103-23-1	Bis(2-ethylhexyl) adipate (DEHA)	0,7	66	0,1-0,62	0,1-0,62		>15
53-70-3	Dibenzo(a,h)anthracene (PAH)	0,0014	0,018	0,007-0,91			5-15
84-74-2	Dibutyl phthalate (DBP)	2,3	35	0,1-10	0,1-10		>15
100-41-4	Ethylbenzene	20	180	0,02-0,6	0,02-0,18		>15
86-73-7	Fluorine	2,3	21,2	0,006-1	0,01-1		>15
7440-50-8	Copper	1[4,5] 4,9[6]	2[4] 4,9[6]	4-230 (2,17-23)	4-230 (2,17-23)		>15
68411-30-3	Sodium alkylbenzene sulfonate	54	160	630-1800	630-1800		>15
7439-96-5	Manganese	150[4]	420[7]	135-191 (14-492)	- (14-492)		>15
16484-77-8 93-65-2	Mecoprop-p (Mecoprop)	18	187	0,1-0,378	0,1-0,378		<5

[5] EQS applies to bioavailable concentration.
[6] EQS applies to total concentration, irrespective of the total natural background concentration
[7] EQS is expressed as value summed to the natural background concentration.

CAS Number [1]	Name of substance	Annual Average EQS[2] [µg/l]	Maximum Allowable Concentration EQS [µg/l]	Measured ranges [min-max][3]		Threat to good chemical status	Available measurements [events]
				All available data	Danish data		
90-12-0 91-57-6 28804-88-8 28652-77-9	Methylnaphtalene (PAH), including: 1-methylnaphtalene 2- methylnaphtalene Dimethylnaphthalene, mixture of isomers methylnaphtalene	Methylnaphtalene (PAH), including:	Σ = 2	0,1-0,5 0,01-0,1 0,01-10	0,1-0,5 0,01-0,1 0,01-10		>15
7439-98-6	Molybdenum	67	587	0,44-7,28	0,44-7,28		5-15
85-01-8	Phenanthrene (PAH)	1,3	4,1	0,01-0,5	0,01-0,5		>15
108-95-2	Phenol	7,7	310	0,3-2,8	0,3-2,8		>15
129-00-0	Pyrene	0,0046	0,023	0,01-0,41	0,01-0,24		>15
13674-84-5	Tris(1-chloro-2-propyl) phosphate (TCPP)	640	640	0,22-1,5	0,22-1,5		>15
108-88-3	Toluene	74	380	0,16-7,4	0,16-7,4		>15
115-86-6	Triphenyl phosphate (TPP)	0,74	1,8	0,02-0,280	0,02-0,14		>15
7440-62-2	Vanadium	4,1[4]	57,8	0,36-10,8	0,36-10,8		>15
1330-20-71	Xylenes (o-, p- og m-xylene)	Σ = 10	Σ = 100	0,02-1,2	0,02-0,19		>15
7440-66-6	zinc	7,8[4,5] 3,1[4,8]	8,4[4]	15-1177 (3,03-128)	25,6-962 (3,03-128)		>15

[8] EQS applies to soft water (H<24 mg CaCO3/l)

CAS Number [1]	Name of substance	Annual Average EQS[2] [µg/l]	Maximum Allowable Concentration EQS [µg/l]	Measured ranges [min-max][3]		Threat to good chemical status	Available measurements [events]
				All available data	Danish data		
Environmental Quality standards for priority hazardous substances and other pollutants							
120-12-7	Antracene	0,1	0,1	0,008-0,067	0,01-0,06		>15
1912-24-9	Atrazin	0,6	2,0	0,03			<5
71-43-2	Benzene	10	50	0,02-0,18	0,02-0,18		>15
7440-43-9	Cadmium and cadmium compounds (depending on the water hardness)[9]	≤ 0,08 (class 1) 0,08 (class 2) 0,09 (class 3) 0,15 (class 4) 0,25 (class 5)	≤ 0,45 (class 1) 0,45 (class 2) 0,6 (class 3) 0,9 (class 4) 1,5 (class 5)	0,004-1,5	0,004-1,5		>15
85535-84-8	Alkanes, C10-13, chloro[10]	0,4	1,4	15-50			<5
 309-00-2 60-57-1 72-20-8 465-73-6	Organochloride pesticides Aldrin Dieldrin Endrin Isoendrin	Σ = 0,01	not applied	 0,27-0,574 0,204-0,98			<5
117-81-7	Bis(2-ethylhexyl) phthalate (DEHP)	1,3	not applied	0,7-25	1-25		>15
330-54-1	Diuron	0,2	1,8	0,05-0,618			5-15

[9] For cadmium and cadmium and its compound the EQS dependes on the water hardness, which is subdivided into five categories Category 1: < 40 mg CaCO3/l, Category 2: from 40 to < 50 mg CaCO3/l, category 3: from 50 to < 100 mg CaCO3/l, category 4: from 100 to < 200 mg CaCO3/l and category 5: ≥ 200 mg CaCO3/l).
[10] There is no indicator parameter for these substances. The indicator parameter is defined based on the analysis methodology.

CAS Number [1]	Name of substance	Annual Average EQS[2] [µg/l]	Maximum Allowable Concentration EQS [µg/l]	Measured ranges [min-max][3]		Threat to good chemical status	Available measurements [events]
				All available data	Danish data		
206-44-0	Fluoranthene	0,0063	0,12	0,01-0,373	0,01-0,23		>15
34123-59-6	Isoproturon	0,3	1,0	0,020-0,180			5-15
7439-92-1	Lead and lead compounds	1,2[4]	14	0,023-650	0,023-650		>15
7439-97-6	Mercury and mercury compounds		0,07	0,03-0,36	0,02-0,2		>15
91-20-3	Naphthalene	2	130	0,04-5	0,04-5		>15
7440-02-0	Nickel and nickel compounds	4[4]	34	1,44-50,9 (1,02-17,2)	1,44-50,9 (1,02-17,2)		>15
84852-15-3	Nonylphenols (4-nonylphenol)	0,3	2,0	0,1-16 (0,086-0,63)	0,1-16		>15
140-66-9	Octylphenols (4-(1,1',3,3'-tetramethylbutyl)-phenol)	0,1	not applied	0,645-2,19			<5
50-32-8	Benzo(a)pyrene	1,7 × 10-4	0,27	0,01-0,5	0,01-0,5		>15
205-99-2	Benzo(b)fluoranthene	[11]	0,017	0,01-0,5	0,01-0,5		5-15
207-08-9	Benzo(k)fluoranthene	[11]	0,017	0,025-0,371			5-15
191-24-2	Benz(g,h,i)perylene	[11]	8,2 × 10-3	0,01-0,259	0,01-0,15		>15
193-39-5	Indeno(1,2,3-cd)-pyrene	[11]	not applied	0,02-0,5	0,02-0,5		>15

[11] For this group of priority substance, polyaromatic aromatic hydrocarbons (PAH), the EQS for biota and the corresponding EQS for concentration of benzo(a)pyrene are applied. Benzo(a)pyrene can be used as marker for the whole PAH group, and therefor only benzo(a)pyrene needs to be monitored when looking at EQS for biota and corresponding EQS for water.

CAS Number [1]	Name of substance	Annual Average EQS[2] [µg/l]	Maximum Allowable Concentration EQS [µg/l]	Measured ranges [min-max][3]		Threat to good chemical status	Available measurements [events]
				All available data	Danish data		
127-18-4	Tetrachloroethylene	10	not applied	2,6-9			<5
79-01-6	Trichloroethylene	10	not applied	1,3-1,7			<5
36643-28-4	Tributyl compounds	0,0002	0,0015	0,029-0,105			<5
[12]	Dioxins and similar compounds		not applied	0,003-0,01			<5
886-50-0	Terbutryn	0,065	0,34	0,055-0,122			<5

[12]This is valid for the following substances
– 7 polychlorerede dibenzo-p-dioxiner (PCDD): 2,3,7,8-T4CDD (CAS 1746-01-6), 1,2,3,7,8-P5CDD (CAS 40321-76-4), 1,2,3,4,7,8-H6CDD (CAS 39227-28-6), 1,2,3,6,7,8-H6CDD (CAS 57653-85-7), 1,2,3,7,8,9-H6CDD (CAS 19408-74-3), 1,2,3,4,6,7,8-H7CDD (CAS 35822-46-9) og 1,2,3,4,6,7,8,9-O8CDD (CAS 3268-87-9)
– 10 polychlorerede dibenzofurans (PCDF): 2,3,7,8-T4CDF (CAS 51207-31-9), 1,2,3,7,8-P5CDF (CAS 57117-41-6), 2,3,4,7,8-P5CDF (CAS 57117-31-4), 1,2,3,4,7,8-H6CDF (CAS 70648-26-9), 1,2,3,6,7,8-H6CDF (CAS 57117-44-9), 1,2,3,7,8,9-H6CDF (CAS 72918-21-9), 2,3,4,6,7,8-H6CDF (CAS 60851-34-5), 1,2,3,4,6,7,8-H7CDF (CAS 67562-39-4), 1,2,3,4,7,8,9-H7CDF (CAS 55673-89-7), 1,2,3,4,6,7,8,9-O8CDF (CAS 39001-02-0)
– 12 dioxi-similar polychlorerede biphenyler (DL-PCB): 3,3,4,4-T4CB (PCB 77, CAS 32598-13-3), 3,3,4,5-T4CB (PCB 81, CAS 70362-50-4), 2,3,3,4,4-P5CB (PCB 105, CAS 32598-14-4), 2,3,4,4,5-P5CB (PCB 114, CAS 74472-37-0), 2,3,4,4,5-P5CB (PCB 118, CAS 31508-00-6), 2,3,4,4,5-P5CB (PCB 123, CAS 65510-44-3), 3,3,4,4,5-P5CB (PCB 126, CAS 57465-28-8), 2,3,3,4,4,5-H6CB (PCB 156, CAS 38380-08-4), 2,3,3,4,4,5-H6CB (PCB 157, CAS 69782-90-7), 2,3,4,4,5,5-H6CB (PCB 167, CAS 52663-72-6), 3,3,4,4,5,5-H6CB (PCB 169, CAS 32774-16-6) og 2,3,3,4,4,5,5-H7CB (PCB 189, CAS 39635-31-9).

Table A-3. Measured concentrations for discharges from separate sewer systems, Environmental Quality Standards (as defined in BEK 439 19/05/2016), estimated threat to the RWB chemical status and number of available measurements.

CAS Number [1]	Name of substance	Annual Average EQS[2] [µg/l]	Maximum Allowable Concentration EQS [µg/l]	Measured ranges [min-max][3]	Threat to good chemical status	Available measurements [monitoring campaigns]
Nationalt fastsatte miljøkvalitetskrav for vand						
83-32-9	Acenaphthene (PAH)	3,8	3,8	0,005-0.27		>15
208-96-8	Acenaphthylene (PAH)	1,3	3,6	0,004-0.13		>15
107-02-8	Acrolein (Acraldehyde)	0,1	1	240		<5
7440-36-0	Antimony	113	177	0,62-100		5-15
7440-38-2	Arsenic	4,3[4]	43	0,38-310		5-15
7440-39-3	Barium	19[4]	145	2-1500[5]		5-15
25057-89-0	Bentazon	45	450	0,01-0,05		<5
56-55-3	Benzo(a)anthracene (PAH)	0,012	0,018	0,005-0.3		5-15
80-05-7	Bisphenol A 2,2-bis(4-hydroxyphenyl)propane	0,1	10	0,09-0,62		5-15
85-68-7	Butyl benzyl phthalate (BBP)	7,5	15	0,12-0,41		5-15
59-50-7	4-chlor-3-methylphenol (PCMC)	9	90	<0,01-1,5		<5
7440-47-3	Chromium Cr VI	3,4	17	0,023-560		>15

[1] CAS: Chemical Abstracts Service.
[2] Expressed as yearly concentration. The value refers to all the sum concentration of all the isomers unless differently specified.
[3] Dissolved concentrations (if available) are listed in brackets
[4] EQS is expressed as value summed to the natural background concentration.

CAS Number [1]	**Name of substance**	**Annual Average EQS[2] [µg/l]**	**Maximum Allowable Concentration EQS [µg/l]**	**Measured ranges [min-max][3]**	**Threat to good chemical status**	**Available measurements [monitoring campaigns]**
	Cr III	4,9	124			
218-01-9	Chrysene	0,014	0,014	0,005-0.66		>15
7440-48-4	Cobalt	0,28[4]	18	0,01-4		<5
108-39-4 95-48-7 106-44-5	m-cresol o-cresol p-cresol	Σ = 100	Σ = 1000	0,11-0,3 0,06-1,2		<5
103-23-1	Bis(2-ethylhexyl) adipate (DEHA)	0,7	6,6	0,58-1,3		5-15
53-70-3	Dibenzo(a,h)anthracene (PAH)	0,0014	0,018	0,005-0,11		>15
84-74-2	Dibutyl phthalate (DBP)	2,3	35	0,18-1.3		>15
2008-58-4	2,6-dichlorobenzamide (BAM)	78	780	0,13-0,22		5-15
100-41-4	Ethylbenzene	20	180	0,025-1		5-15
86-73-7	Fluorene	2,3	21,2	0,005-0,11		>15
7440-50-8	Copper	1[4,5] 4,9[Error! Bookmark not efined.]	2 4,9	0,05-220 ($5,5\ 10^{-5}$ – 6800)		>15
16484-77-8 93-65-2	Mecoprop-p (Mecoprop)	18	187	$3,0\ 10^{-4}$-1		5-15

[5] EQS valid for bioavailable concentration.

CAS Number [1]	Name of substance	Annual Average EQS[2] [µg/l]	Maximum Allowable Concentration EQS [µg/l]	Measured ranges [min-max][3]	Threat to good chemical status	Available measurements [monitoring campaigns]
90-12-0 91-57-6 28804-88-8 28652-77-9	Methylnaphtalene (PAH), including: 1-methylnaphtalene 2- methylnaphtalene Dimethylnaphthalene, mixture of isomers methylnaphtalene	Σ = 0,12	Σ = 2	0,15 0,021-0,04 0,95		<5
1634-04-4	Tert-butyl methyl ether (MTBE)	10	90	0,03-37		5-15
81-15-2	Musk xylene	0,11	0,68	0,1		<5
85-01-8	Phenanthrene (PAH)	1,3	4,1	0,005-0,73		>15
129-00-0	Pyrene	0,0046	0,023	0,005-3,3		>15
7782-49-2	Selenium	0,1[4]	31	0,09-54		<5
7440-24-6	Strontium	2100	5530	37-840		<5
7440-22-4	Silver	0,017[4]	0,36	0,0012-170		<5
7440-28-2	Thallium	0,48[4]	1,2	0,0073-51		<5
108-88-3	Toluene	74	380	0,05-1		5-15
71-55-6	1,1,1-trichlorethane	21	54	0,032-0,34		<5
88-06-2	2,4,6-trichlorophenol	1	160	0,014-0,015		<5
126-73-8	Tributyl phosphate	82	170	0,06-0,14		5-15
115-86-6	Triphenyl phosphate (TPP)	0,74	1,8	0,05-0,5		5-15
7440-62-2	Vanadium	4,1[4]	57,8	2,1-32		5-15
1330-20-71	Xylenes (o-, p- og m-xylene)	Σ = 10	Σ = 100	0,16-6,8		<5

CAS Number [1]	Name of substance	Annual Average EQS[2] [µg/l]	Maximum Allowable Concentration EQS [µg/l]	Measured ranges [min-max][3]	Threat to good chemical status	Available measurements [monitoring campaigns]
7440-66-6	Zinc	7,8[4,5] 3,1[4,6]	8,4	0,2-3000[6] 0,03-23000		>15
Environmental Quality standards for priority hazardous substances and other pollutants						
15972-60-8	Alachlor	0,3	0,7	0,019		<5
120-12-7	Antracene	0,1	0,1	0,004 -0,1		>15
1912-24-9	Atrazine	0,6	2	0,002-0,015		<5
71-43-2	Benzene	10	50	0,057-0,1		5-15
7440-43-9	Cadmium and cadmium compounds (depending on the water hardness)[7]	≤ 0,08 (class 1) 0,08 (class 2) 0,09 (class 3) 0,15 (class 4) 0,25 (class 5)	≤ 0,45 (class 1) 0,45 (class 2) 0,6 (class 3) 0,9 (class 4) 1,5 (class 5)	$5\ 10^{-4}$-400		>15
470-90-6	Chlorfenvinphos	0,1	0,3	$5\ 10^{-4}$-0,12		<5
2921-88-2	Chlorpyrifos	0,03	0,1	0,003		<5
 309-00-2 60-57-1 72-20-8 465-73-6	Organochloride pesticides aldrin dieldrin endrin isoendrin	Σ = 0,01	not applied	 0,04 0,015 0,41		 <5 <5 <5

[6] EQS valid for soft water (H<24 mg CaCO3/l)
[7] For cadmium and cadmium and its compound the EQS depends on the water hardness, which is subdivided into five categories Category 1: < 40 mg CaCO3/l, Category 2: from 40 to < 50 mg CaCO3/l, category 3: from 50 to < 100 mg CaCO3/l, category 4: from 100 to < 200 mg CaCO3/l and category 5: ≥ 200 mg CaCO3/l)..

CAS Number [1]	Name of substance	Annual Average EQS[2] [µg/l]	Maximum Allowable Concentration EQS [µg/l]	Measured ranges [min-max][3]	Threat to good chemical status	Available measurements [monitoring campaigns]
not applied	Total DDT[8]	0,025	not applied	0,00032-1		<5
107-06-2	1,2-dichlorethane	10	not applied	1,5-3		<5
75-09-2	Dichlormethane	20	not applied	0,2-0,51		<5
117-81-7	Bis(2-ethylhexyl) phthalate (DEHP)	1,3	not applied	8,5-28		>15
330-54-1	Diuron	0,2	1,8	0,03-1,8		5-15
115-29-7	Endosulfan	0,005	0,01	3,67		<5
206-44-0	Fluoranthene	0,0063	0,12	0,005-0,95		>15
118-74-1	Hexachlorobenzene		0,05	0,01		<5
34123-59-6	Isoproturon	0,3	1	0,001-0,14		5-15
7439-92-1	Lead and lead compounds	1,2 [5]	14	0,0032-130		>15
7439-97-6	Mercury and mercury compounds		0,07	0,01-160		5-15
91-20-3	Naphthalene	2	130	0,005-6.5		>15
7440-02-0	Nickel and nickel compounds	4 [5]	34	0,012-17		>15
84852-15-3	Nonylphenols (4-nonylphenol)	0,3	2	0,02-9,2		5-15
608-93-5	Pentachlorobenzene	0,007	not applied	0,0087		<5
87-86-5	Pentachlorophenol	0,4	1	0,031-0,045		<5

[8] Total DDT is calculated as the sum of the isomers 1,1,1-trichlor-2,2-bis(p-chlorphenyl)ethan (CAS-number 50-29-3; EU-number 200-024-3); 1,1,1-trichlor-2-(o-chlorphenyl)-2-(p-chlorphenyl)ethan (CAS-number 789-02-6; EU-number 212-332-5); 1,1-dichlor-2,2-bis(p-chlorphenyl)ethylen (CAS-number 72-55-9; EU-number 200-784-6) og 1,1-dichlor-2,2-bis(p-chlorphenyl)ethan (CAS-number 72-54-8; EU-number 200-783-0).

CAS Number [1]	Name of substance	Annual Average EQS[2] [µg/l]	Maximum Allowable Concentration EQS [µg/l]	Measured ranges [min-max][3]	Threat to good chemical status	Available measurements [monitoring campaigns]
50-32-8	Benzo(a)pyrene	$1{,}7 \times 10^{-4}$	0,27	0,005-0,32		>15
205-99-2	Benzo(b)fluoranthene		0,017	0,06-0.66		5-15
207-08-9	Benz(k)fluoranthene	[9]	0,017	0,016-0,23		5-15
191-24-2	Benzo(g,h,i)perylene	[9]	$8{,}2 \times 10^{-3}$	0,005-0,57		>15
193-39-5	Indeno(1,2,3-cd)-pyrene	[9]	$1{,}7 \times 10^{-4}$	0,005-0,39		>15
122-34-9	Simazine	1	4	0,003-0,15		5-15
127-18-4	Tetrachloroethylene	10	not applied	0,82-1,3		5-15
79-01-6	Trichloroethylene	10	not applied	0,18		5-15
36643-28-4	Tributyl compounds	0,0002	0,0015	0,078		<5
67-66-3	Trichloromethane	2,5	not applied	0,02-0,034		<5
1763-23-1	Perfluorooctanesulfonic acid and related compounds (PFOS)	6,5 × 10-4	36	0,007-0,03		5-15
[10]	Dioxins and similar compounds		not applied	$1{,}3\ 10^{-5}$-$7{,}3\ 10^{-1}$		>15

[9] For this group of priority hazardous substance is valid the EQS for biota and the general water EQS for benzo(a)pyrene, which is used to estimate the biota toxitcity, Benzo(a)pyrene can be used as indicator for the whole PAH group, and therefore only benzo(a)pyrene needs to be monitored to assess compliance with EQS in freshwater.

[10] This is valid for the following substances

– 7 polychlorerede dibenzo-p-dioxiner (PCDD): 2,3,7,8-T4CDD (CAS 1746-01-6), 1,2,3,7,8-P5CDD (CAS 40321-76-4), 1,2,3,4,7,8-H6CDD (CAS 39227-28-6), 1,2,3,6,7,8-H6CDD (CAS 57653-85-7), 1,2,3,7,8,9-H6CDD (CAS 19408-74-3), 1,2,3,4,6,7,8-H7CDD (CAS 35822-46-9) og 1,2,3,4,6,7,8,9-O8CDD (CAS 3268-87-9)

– 10 polychlorerede dibenzofurans (PCDF): 2,3,7,8-T4CDF (CAS 51207-31-9), 1,2,3,7,8-P5CDF (CAS 57117-41-6), 2,3,4,7,8-P5CDF (CAS 57117-31-4), 1,2,3,4,7,8-H6CDF (CAS 70648-26-9), 1,2,3,6,7,8-H6CDF (CAS 57117-44-9), 1,2,3,7,8,9-H6CDF (CAS 72918-21-9), 2,3,4,6,7,8-H6CDF (CAS 60851-34-5), 1,2,3,4,6,7,8-H7CDF (CAS 67562-39-4), 1,2,3,4,7,8,9-H7CDF (CAS 55673-89-7), 1,2,3,4,6,7,8,9-O8CDF (CAS 39001-02-0)

– 12 dioxi-similar polychlorerede biphenyler (DL-PCB): 3,3,4,4-T4CB (PCB 77, CAS 32598-13-3), 3,3,4,5-T4CB (PCB 81, CAS 70362-50-4), 2,3,3,4,4-P5CB (PCB 105, CAS 32598-14-4), 2,3,4,4,5-P5CB (PCB 114, CAS 74472-37-0), 2,3,4,4,5-P5CB (PCB 118, CAS 31508-00-6), 2,3,4,4,5-P5CB (PCB 123, CAS 65510-44-3), 3,3,4,4,5-P5CB (PCB 126, CAS 57465-28-8), 2,3,3,4,4,5-H6CB (PCB 156, CAS 38380-08-4), 2,3,3,4,4,5-H6CB (PCB 157, CAS 69782-90-7), 2,3,4,4,5,5-H6CB (PCB 167, CAS 52663-72-6), 3,3,4,4,5,5-H6CB (PCB 169, CAS 32774-16-6) og 2,3,3,4,4,5,5-H7CB (PCB 189, CAS 39635-31-9).

CAS Number [1]	Name of substance	Annual Average EQS[2] [µg/l]	Maximum Allowable Concentration EQS [µg/l]	Measured ranges [min-max][3]	Threat to good chemical status	Available measurements [monitoring campaigns]
28159-98-0	Cybutryn	0,0025	0,016	0,01		5-15
886-50-0	Terbutryn	0,065	0,34	0,010-0,1		5-15

Table A-4. Sources of measured concentrations from wet weather discharges from urban areas.

Combined systems		Separate systems	
Reference	**Typology**	**Reference**	**Typology**
Arnbjerg-Nielsen et al. (2003)	Analysis of data from database	Arnbjerg-Nielsen et al. (2002)	Analysis of data from database
Arnbjerg-Nielsen et al. (2000)	Literature review	Becouze-Lareure et al. (2016)	Monitoring campaign
Aarhus Vand (2015)	Monitoring campaign	Birch et al. (2011)	Monitoring campaign
Boutrup et al. (2015)	Analysis of data from database	Clara et al. (2010)	Monitoring campaign
Brzezińska et al. (2016)	Monitoring campaign	DHI (2015)	Database
Drozdova et al. (2015)	Monitoring campaign	Eriksson et al (2007)	Literature review
Gasperi et al. (2012)	Monitoring campaign	Gasperi et al. (2014)	Monitoring campaign
Gooré Bi et al. (2015)	Monitoring campaign	Ingvertsen et al. (2011)	Literature review
Kay et al. (2017)	Monitoring campaign	Kayhanian et al. (2007)	Analysis of data from database
Kwon et al. (2015)	Monitoring campaign	Kjølholt et al. (1997)	Literature review and monitoring campaign
Launay et al. (2016)	Monitoring campaign	Kjølholt et al. (2001)	Monitoring campaign
Masi et al. (2017)	Monitoring campaign	Kjølholt et al. (2007)	Literature review
Yin et al. (2017)	Monitoring campaign	Københavns Kommune (2009) (cited in Larsen et al., 2012)	Monitoring campaign
		Lützhøft et al. (2011)	Literature review
		Lützhøft et al. (2012)	Literature review
		Madsen and Nielsen (2008)	Monitoring campaign
		Miljøstyrelsen (2006)	Monitoring campaign
		Miljøstyrelsen (2016)	Database of measurement campaigns
		Pedersen et al. (2009)	Monitoring campaign
		Pedersen (2013)	Literature review
		Polmit (2002)	Monitoring campaign
		Näf et al. (1990)	Monitoring campaign
		Sebastian (2013)	Monitoring campaign
		US EPA (2015)	Database of measurement campaigns
		Wenning et al. (1999)	Monitoring campaign
		Wicke et al. (2016)	Monitoring campaign
		Zgheib et al. (2012)	Monitoring campaign

Appendix B Literature review on effect-based studies using fish or macroinvertebrates as indicator organisms.

This appendix presents the list of all the studies investigating the effect of discharges from urban areas on the ecological status of Receiving Water Bodies. These studies provided the basis for the results presented in Chapter 4.

Table 9. Content overview of the reviewed literature containing effect-based studies using fish or macroinvertebrates as indicator organisms. Study information, in terms of spatiotemporal resolution of ecological and supporting chemical, physical and hydromorphological parameters are mentioned.

Reference	Study period	Urban discharge type	Number of sites	Temporal resolution of urban discharge data	Measured chemical constituents and habitat characteristics	Biological endpoint	Study design	Ecological quality index responses included	Ecological effects	Attempted quantification of threshold for effects
Hall et al. (1998)	1993-1996	CSO	52	Daily average	None (modelled based on 7 case studies)	Macroinvertebrates	Downstream only, no control	No	Community changes with highest modelled toxic load in RWB.	No
Kosmala et al. (1999)	1995-1996	WWTP	1	Monthly grab samples	BOD, nutrients, heavy metals, Chlorinated solvents	Macroinvertebrates	Upstream-downstream	IBG[1]	Lower IBG values downstream in summer. Significance tests lacking.	No
Lydy et al. (2000)	1981-1987	WWTP	3	None	None	Macroinvertebrates	BACI[2]	HI[3] ASPT[4]	Temporal improvement in HI after initiated waste water treatment. No change in ASPT. Significance lacking	No
Reiss et al. (2002)	1	WWTP	Extrapolative modelling	None	None (triclosan modelled based on 4 case studies)	Macroinvertebrates, fish	N/A	None	Risk assessment based on concentrations derived from models showed no exceedance of acute or chronic LC50 for daphnia or fish.	

[1] Global Biological Index, targeting pollution with easily degradable organic material
[2] BACI = Before-After, Control-Impact (i.e. upstream-downstream)
[3] Hilsenhoff's Index, targeting pollution with easily degradable organic material
[4] Average Score Per Taxon (Sister index to DSFI), targeting pollution with easily degradable organic material

Reference	Study period	Urban discharge type	Number of sites	Temporal resolution of urban discharge data	Measured chemical constituents and habitat characteristics	Biological endpoint	Study design	Ecological quality index responses included	Ecological effects	Attempted quantification of threshold for effects
Gücker et al. (2006)	2002	WWTP	2	Daily average for water quantity. Grab samples for chemicals.	BOD, nutrients	Macroinvertebrates	Upstream-downstream	SI[5]	None. Explained by the highly deteriorated upstream catchments.	No
Lewis et al. (2007)	2003	WWTP Diffuse urban pollution	23	1-6 grab samples for water chemistry. Urban water discharge quantity not measured.	N, P, micronutrient cations and anions.	Fish	Spatial extent secures gradient for multivariate analysis	None	None. Explained by the overall deterioration of the stream system.	No
Canobbio, et al. (2009)	2001-2006	WWTP, CSO	11, all in same river system	Monthly grab samples for water quality. Mike 11 model for water quantity	N, P, DO	Macroinvertebrates (only sampled at 4 sites)	Each site representative for specific urban water discharge type	EBI[6]	Lowest EBI scores at sites most influenced by WWTP and CSO effluents – coupled with both large variations in flow regimes and in nutrient and oxygen conditions.	No

[5] Saprobic Index, used in German speaking countries and in Eastern Europe, targeting pollution with easily degradable organic material
[6] Extended Biotic Index, targeting pollution with easily degradable organic material

Reference	Study period	Urban discharge type	Number of sites	Temporal resolution of urban discharge data	Measured chemical constituents and habitat characteristics	Biological endpoint	Study design	Ecological quality index responses included	Ecological effects	Attempted quantification of threshold for effects
Wright and Burgin (2009)	2003	WWTP (organic pollution), mine drainage (inorganic pollution)	10, all within same river system	Three grab samples with monthly intervals for water chemistry. Water quantity not measured.	Heavy metals, N, P	Macroinvertebrates	Upstream, impact, downstream	EPT[7] abundance	Differences in community response to the two stressors. EPT abundance reduced in presence of both stressors. Upstream sites were pristine.	No
Munoz et al. (2009)	2005-2006	Textile and paper industrial effluents, WWTP	7, all within the same river system	Three grab samples with 6 month intervals for water chemistry. Water quantity not measured.	Pharmaceuticals, DO, N, P	Macroinvertebrates	Sites represent a gradient in pollution pressure	No	The abundance of *Chironomus* sp. and *Tubifex tubifex* were negatively correlated with concentrations of ß-blockers and anti-inflammatories.	No
Slye et al. (2011)	2005	WWTP, industrial effluents	10, all within the same river system	1 grab sample for chemical analysis.	Surfactants, Toxic Units (surfactants), N, P, DO, BOD Habitat quality mapped.	Macroinvertebrates	Sites represent a gradient in pollution pressure	No	Community structure changed as a function of Toxic Units (surfactants), habitat quality, and BOD.	No

[7] Ephemeroptera (mayflies), Plecoptera (stoneflies), Trichoptera (caddisflies)

Reference	Study period	Urban discharge type	Number of sites	Temporal resolution of urban discharge data	Measured chemical constituents and habitat characteristics	Biological endpoint	Study design	Ecological quality index responses included	Ecological effects	Attempted quantification of threshold for effects
Brown et al. (2011)	2008	WWTP	9, all within the same river system	None	Habitat quality mapped	Fish	Sites represent a gradient in expected pollution pressure	No	Rainbow darter (*Etheostoma caeruleum*) increased in abundance downstream of WWTPs, and Greenside Darter (*E. blennioides*) decreased in abundance.	No
Vaughan and Ormerod (2012)	1990-2008	WWTP, diffuse urban pollution	1,500	Monthly grab samples for water chemistry.	N, P, BOD, Habitat quality mapped	Macroinvertebrates	Sites represent a gradient in pollution pressure and integrate the time from implementation of wastewater treatment.	No	Overall, family richness increased with time, and this increase was most pronounced in urban catchments, probably due to improved waste water treatment.	No
Englert et al. (2013)	2010-2011	WWTP	1	Weekly grab samples for water chemistry. Water quantity measured.	N, P, DO	Macroinvertebrates	Upstream-downstream	No	Community structure different between upstream and downstream (<500 m). 1,000 m downstream of the WWTP, no effects were visible.	No
Tetreault et al. (2013)	2007-2008	WWTP	2	None	None	Fish	Upstream-downstream	No	Fish community structure was increasingly dominated by pollution tolerant taxa at downstream sites.	No

Reference	Study period	Urban discharge type	Number of sites	Temporal resolution of urban discharge data	Measured chemical constituents and habitat characteristics	Biological endpoint	Study design	Ecological quality index responses included	Ecological effects	Attempted quantification of threshold for effects
Bunzel et al. (2013)	2005-2006	WWTP	328	None	None	Macroinvertebrates	Presence or absence of WWTPs upstream of sampling site	SPEAR[8][9], SI[5]	SPEAR and SI were both significantly reduced at sites with WWTP influence compared to sites without WWTP.	No
Gonzalo and Camargo (2013)	2007-2008	Industrial effluent	1	Monthly grab samples for water chemistry analysis.	N, P, DO	Macroinvertebrates	Upstream-downstream	BMWQ[9]	Lower BMWQ values at downstream site compared to upstream.	No
De Castro-Catala et al. (2015)	2010-2011	WWTP, Industrial effluents, CSO	20	One grab sample per site for chemical analysis.	N, P, Dissolved Organic Carbon, Pesticides, pharmaceuticals, perflourinated compounds, endocrine disrupters	Macroinvertebrates	Sites represent gradients in pollution from different sources	No	Macroinvertebrate community changes most strongly related to endocrine disrupters and pharmaceuticals.	No

[8] SPEcies At Risk index, targeting effects of pesticide pollution, mainly insecticides
[9] Biological Monitoring Water Quality index, targeting pollution with easily degradable organic material

Reference	Study period	Urban discharge type	Number of sites	Temporal resolution of urban discharge data	Measured chemical constituents and habitat characteristics	Biological endpoint	Study design	Ecological quality index responses included	Ecological effects	Attempted quantification of threshold for effects
Arnon et al. (2015)	2010-2012	WWTP	2, within the same river system	One grab sample per site for chemical analysis	N, P	Macroinvertebrates	Upstream-downstream	No	Macroinvertebrate community structure not different between upstream and downstream sites due to overall degraded hydromorphological conditions in the river system.	No
Sabater et al. (2016)	2010-2011	WWTP, industrial effluents	19	One grab sample per site	N, P, Dissolved Organic Carbon, Pharmaceuticals, pesticides, perflourinated compounds, endocrine disrupters	Macroinvertebrates	Sites represent gradients in pollution from different sources	No	Community changes were significantly correlated with anthropogenic chemicals, but multivariate partitioning showed that no single group of contaminants could be pinpointed as primary cause of community change.	No

Reference	**Study period**	**Urban discharge type**	**Number of sites**	**Temporal resolution of urban discharge data**	**Measured chemical constituents and habitat characteristics**	**Biological endpoint**	**Study design**	**Ecological quality index responses included**	**Ecological effects**	**Attempted quantification of threshold for effects**
Parker et al. (2016)	1983-2010	WWTP	15	2-12 grab samples per year for water chemistry analysis	N, P, DO, BOD, Heavy metals	Fish	Sites represent gradients in pollution, and the temporal aspect represents the potential recovery time after implemented waste water treatment	No	DO and unionized ammonia were most important parameters driving species richness and abundance and biomass of native fish species.	No
Burdon et al. (2016)	2013-2014	WWTP	12	Monthly grab samples collected in stream water and WWTP effluent water for water chemistry analysis	N, P, macronutrients, habitat quality	Macroinvertebrates	Sites represent a gradient in WWTP influence in terms of effluent water quantity.	SPEAR[8], EPT[7], SI[5]	Effects of WWTP effluents on SI was context dependent and was mostly related to overall catchment characteristics (i.e. degraded upstream sites always lead to low SI scores at downstream sites). SPEAR responded negatively to the proportional contribution of WWTP effluents to the total stream flow indicating effects of pesticides.	No

Reference	Study period	Urban discharge type	Number of sites	Temporal resolution of urban discharge data	Measured chemical constituents and habitat characteristics	Biological endpoint	Study design	Ecological quality index responses included	Ecological effects	Attempted quantification of threshold for effects
Penczak et al. (2017)	2000-2012	WWTP, Industrial effluents, CSO	14, all within the same river system	None	None	Fish	Sites represent gradients in pollution, and the temporal aspect represents the potential recovery time after implemented waste water treatment	No	Species richness, especially related to native species, increased with the introduction of waste water treatment and reduction of industrial effluents. The most upstream and unimpacted sites still have more species which is ascribed to storm water discharges of untreated urban water.	No
Münze et al. (2017)	2013	WWTP	7	Time integrated passive samplers	Pesticides, pharmaceuticals	Macroinvertebrates	Upstream-downstream	SPEAR[8]	SPEAR reduced by approximately 40% at downstream sites mainly due to neonicotinoid insecticides	No

Appendix C Literature review indicating state-of-the-art with respect to the risk assessment of mixed land use stream systems

This appendix presents the list of all the studies performing a risk assessment in Receiving Water Bodies affected by multiple stressors. These studies provided the basis for the results presented in Chapter 5.

Table 5: Literature review indicating state-of-the-art with respect to the risk assessment of mixed land use stream systems (Sonne et al., 2017).

Reference	Compartment	Contaminant Group	Ecological quality	Toxic potential	Factor relationship	Investigated sources	Findings
One compound group in one stream compartment							
Wittmer et al. (2010)	SW	Pesticides	-	-	Time cross-correlated conc. with location and events	Identified associated point sources (wastewater discharge from urban drainage system), diffuse agricultural sources	Equally important sources
Yu et al. (2014)	SW, rain, storm water	Metals	-	-	Multivariate statistical analyses: (long-term investigations) conc. vs. land use, events	Impact of diffuse land use	Metals: Farmland constant source, urban runoff periodic source (vehicle traffic)
Ding et al. (2016)	SW	General water chemistry	Algae growth (Chl-α, eutrophication indicator)	-	Multivariate statistical analyses and model: conc. vs. Chl-α, land use and geomorphic regions (scale-effect)	Impact of diffuse land use	Poor water quality: cropland, orchards, grassland in mountain catchments and urban land use in plain catchments Best estimate of the variation: land use on a catchment scale
Multiple compound groups							
Höss et al. (2011)	BS	Organic xenobiotics (e.g. pesticides, polyaromatic hydrocarbons), metals	Meio (nematodes) community	TU(PW) (macro)	Multivariate statistical analyses: ecological and toxicological descriptors, BS properties	Not source oriented	Development of two nematode indices (meioinvertebrate) sensitive to metal and organic xenobiotic BS contamination: NemaSPEAR (organic, metals)

Reference	Compartment	Contaminant Group	Ecological quality	Toxic potential	Factor relationship	Investigated sources	Findings
Malaj et al. (2014)	SW	Organic xenobiotics (e.g. pesticides, brominated flame retardants)	Diatoms, macro and fish communities	Acute(Cmax/10) & chronic (1/1000, 1/100, 1/50) threshold selection using LC_{50} values (algae, macro, fish)	Multivariate statistical analyses: land use, ecological and toxicological descriptors	Impact from diffuse land use (natural vegetation, agricultural & urban practices)	Organic chemicals are an environmental problem on a continental scale
Sabater et al. (2016)	SW	Organic xenobiotics (e.g. herbicides, antibiotics, hormones)	Diatoms (in the biofilm), invertebrate community	-	Multivariate statistical analyses: ecological descriptors vs. land use, conc., BS properties, hydrological characteristics	Impact of diffuse land use	Ecological degradation from increasing agricultural and urban-industrial activities, high water conductivity, dissolved organic carbon and inorganic N and high conc. pharmaceutical & industrial compounds
Kuzmanovic et al. (2016)	SW	Organic xenobiotics (e.g. pesticides, pharmaceuticals), metals	Macro community $SPEAR_{organic}$ $SPEAR_{pesticides}$	TU(SW) (algae, macro, fish)	Multivariate statistical analyses: land use, ecological and toxicological descriptors	Not source oriented	SW: Metals posed acute risk at 44% of the sites, organic chemicals (mainly pesticides) 42%. Several emerging contaminants pose chronic effects risk
Castro-Catalá et al. (2016)	BS	Organic xenobiotics (e.g. endocrine disrupting compounds, pharmaceutical active compounds), metals	Macro community	TU(PW)(algae, macro), acute porewater & whole-sediment exposure tests	Multivariate statistical analyses: ecological and toxicological descriptors, toxicity tests, BS properties	Not source oriented	Organophosphate insecticides and metals main stressors to BS toxicity
Berger et al. (2016)	SW	Organic xenobiotics (e.g. pesticides,	Macro community (over	Threshold Indicator Taxa	Multivariate statistical analyses:	Impact of diffuse land use, source associated	WWTP: Strong effects to wastewater-associated

Reference	Compartment	Contaminant Group	Ecological quality	Toxic potential	Factor relationship	Investigated sources	Findings
		pharmaceuticals, plasticisers, flame retardants)	time) using	Analysis (TITAN), EQS, PNEC	change points in taxon and conc., conc. vs. land use, catchment size	compounds	compounds. Observed ecological effects at conc.<EQS, PNECs at change points
Multiple stream compartments							
Moon et al. (1994)	SW, BS	Metals (Cu, Pb, Zn)	-	-	Time cross-correlated conc. (SW and BS), land use, SB properties	Impact from diffuse land use, identified associated point sources (domestic effluents)	Cu, Pb, Zn domestic effluents (urban) >>rural land use during dry periods
Stutter et al. (2007)	SW, SPM, BS	General water chemistry, P, N, C	Algae growth (Chl-α), macro community, trait-specific changes	Recommended threshold criteria in SW (Scottish EPA)	Multivariate statistical analyses: conc. (SS, BS), land use, catchment size, ecological descriptors, physical stream parameters	Diffuse land use sources	Biologically available P: Greatest pressure from agricultural land use was seen in SPM > BS (in organic C). Chl-α increase correlated with increase in P-contaminated SPM
Multiple compound groups and stream compartments							
Rasmussen et al. (2013a)	SW, SS	General water chemistry, Organic xenobiotics (e.g. pesticides, CAHs, petroleum hydrocarbons)	Macro community DSFI, $SPEAR_{pesticides}$	TU(SW, SS) (macro)	Multivariate statistical analyses: ecological and toxicological descriptors, physical stream parameters	Diffuse land use, contaminated sites, low base-flow due to water abstraction, hydromorphological quality	Identified numerous chemical and hydromorphological impacts. Not able to rank the sources based on the major ecological impairments. $SPEAR_{pesticides}$ indicates insecticides were an essential contributor
Nazeer et al. (2014)	SW, SS, BS	Heavy metals, general water chemistry, nutrients	Bacteria	Water quality index (WQI) based on presence bacteria, metals,	Time cross-correlated conc. (SW, SS, BS), WQI, with location and events	Not source oriented	SW: Nutrient load high during pre-monsoon season, metals high during post-monsoon. Metals: SS>BS from both natural processes

Reference	Compartment	Contaminant Group	Ecological quality	Toxic potential	Factor relationship	Investigated sources	Findings
				nutrients, pesticides			and anthropogenic activities. Cd, Zn, Pb threats to aquatic ecosystems
Fairbairn et al. (2015)	SW, BS	Organic xenobiotics (e.g. personal care products, pesticides, human and veterinary medications)	-	-	Time cross-correlated conc. (SW, BS) with location and events	Diffuse land use	Spatial and temporal analysis: pharmaceuticals & personal care products highest in SW+BS with population density (>100 people/km^2) and %developed land use (>8% of the sub-watershed area). Pesticides in agricultural land use. Measured more in BS than predicted. Seasonal in SW not in BS

Appendix D UK and Danish water quality criteria

This appendix lists the various water quality criteria defined in the UK guidelines (as listed in Crabtree et al., 2012) and, when those are available, with the corresponding criteria from the Danish guidelines (Spildevandskomitéen, 1985).

Table D-1. UK freshwater quality criteria for unionised ammonia (NH_3-N) for the different RWB typologies.

Duration [hrs]	Frequency/Return period	Magnitude [mg/l]		
		Sustainable salmon fishery	Sustainable cyprinid fishery	Marginal cyprinid fishery
1	1 month	0.065	0,150	0,175
	3 months	0.095	0,225	0,250
	1 year	0.105	0,250	0,300
6	1 month	0.025	0,075	0,100
	3 months	0.035	0,125	0,150
	1 year	0.040	0,150	0,200
24	1 month	0.018	0,030	0,050
	3 months	0.025	0,050	0,080
	1 year	0.030	0,065	0,140

Table D-2. Comparison between Danish and UK freshwater quality criteria for dissolved oxygen (DO) for the different RWB typologies.

Duration [hrs]	Frequency/ Return period	Magnitude [mg/l]							
		Salmon spawning and reproduction		Sustainable salmon fishery		Sustainable cyprinid fishery		Marginal cyprinid fishery	
		DK	UK	DK	UK	DK	UK	DK	UK
1	1 month				5,0		5,5		6,0
	≤0,1 years (1,2 months)	8,0		6,0		4,0			
	3 months				4,5		5,0		5,5
	1 year				4		4,5		5,0
	≥8 years	1,5 (16 yrs)		1,5 (12 yrs)		1,0 (8 yrs)			
6	1 month				4,0		5,0		5,5
	3 months				3,5		4,5		5,0
	1 year				3,0		4,0		4,5
12	≤0,1 years (1,2 months)	9,0		7,0		5,0			
	≥8 years	2,0 (16 yrs)		2,0 (12 yrs)		4,0 (8 yrs)			
24	1 month				3,0		3,5		4,0
	3 months				2,5		3,0		3,5
	1 year				2,0		2,5		3,0

Appendix E Analytical model from DWA

This appendix provides a detailed description of the guidelines for CSO design and the analytical model proposed by the German Association for Water Management, Wastewater and Waste (DWA, 2016). The guidelines are inspired by a similar Danish work (Spildevandskomitéen, 1985), with additional details about the modelling procedure and the parameters to be employed in the design phase. Overall, the DWA guidelines represent an important example on how analytical models can be used for CSO design and regulation.

E 1 Modelling steps

The DWA approach can be schematized in different steps:

1. *Catchment characterization*: the main characteristics of the upstream urban area are defined in terms of total area, runoff coefficient (i.e. area contributing to runoff generation), transport time (i.e. maximum length of the drainage network)
2. *Calculation of expected flows*: classical formulas for design of drainage systems (e.g. rational method) are used to estimate the expected flow at the CSO structure. This step also requires rainfall statistics for the specific area.
3. *Definition of expected pollution levels*: the expected concentrations for the different flow (wastewater, stormwater, and infiltration water) are defined based on the statistical elaboration of available measurements
4. *Calculation of expected pollutant fluxes at CSO*: based on the results from the previous steps, it is possible to calculate the pollutant loads from different sources (e.g. wastewater, stormwater, sediment resuspension) during an overflow event
5. *Calculation of expected CSO concentration*: a simple dilution model is used to calculate concentration at the overflow structure
6. *Calculation of pollutant fluxes in RWB:* simple water and mass balances are used to calculate pollutant concentrations in the river. These calculations are based on worst-case scenarios (i.e. the river is assumed to be at the seasonal minimum for flow) and require the availability of data on the upstream/background pollution level
7. *Calculation of water quality indicators:* advection is assumed in the RWB, and concentrations of relevant pollutant are calculated based on this assumption. Dissolved Oxygen is calculated by using a well-established analytical model.

E 2 Catchment model

Overflow volumes and concentrations can be calculated by using simple equations.
The maximum flow from an urban catchment connected to a CSO can be calculated by using the rational method. For a specific return period, a simple formula can be applied:

$$Q_{\max} = A\theta P + Q_{DWF} \tag{1}$$

Where A [L^2] is the catchment area, θ [-] is the runoff coefficient, P [L/T] is the rainfall intensity for the desired frequency and the duration equal to the transport time across the catchment, and Q_{DWF} is the mean Dry Weather Flow. This simple formulation can be modified to account for other factors such as groundwater infiltration, water storage in detention basins, and presence of other stormwater control measures (which are usually accounted for by modifying the runoff

coefficient θ). The transport time across the catchment is calculated by using the Manning's equation, assuming average slopes and velocity in the drainage network.
The CSO flow (Q_{CSO}) is calculated by assuming a throttle regulation at the CSO structure (Q_{thr}), which depends on design guidelines. The difference between Q_{max} and the throttled flow gives the expected CSO flow.

$$Q_{CSO} = Q_{\max} - Q_{thr} \tag{2}$$

The water quality is defined according to tabular values, which are based on long term monitoring campaigns. For example, the values listed in Table E-1 are derived from the 75% percentiles of the measurements collected in the period 1975-2000 (DWA, 2016).

Table E-1. Standard water quality parameters for a catchment with an average rainfall depth of 800 mm/yr and a runoff coefficient of 0.7 (DWA, 2016)**.**

Typical concentrations			
	BOD_5	Ntot	pH
Stormwater	20 mg/l	5 mg/l	<7.4
Wastewater	500 mg/l	90 mg/l (nitrate and nitrite are assumed negligible)	<7.4
Typical loads			
	60 g/inhabitant/day	11 g/inhabitant/day (of which 2 g/inhabitant/day inert nitrogen)	

The concentrations at the CSO discharge points can then be calculated based on a simple mass balance, where the different components are taken into account. For example, the mass flux for a generic pollutant can be expressed as:

$$F_{tot} = Q_{DWF} C_{DWF} + F_{sed} + Q_{runoff} C_{runoff} \tag{3}$$

Where C_{DWF} [M/L^3] is the average concentration in Dry Weather Flow (e.g. Table E-1), F_{sed} [M/T] is the flux deriving sediment resuspension (which can be expressed as function of the flow), Q_{runoff} [L^3/T] is the runoff flow (first term in eq. 1) and C_{runoff} [M/L^3] is the average concentration in stormwater (e.g. Table E-1). The DWA guidelines list a number of detailed equations to estimate the different terms of eq. 3, accounting e.g. for regional variations in the rainfall depth, pollutant reduction in treatment and/or storage facilities.
The concentration in the overflow water (C_{CSO}) and the CSO flux (F_{DWF}) are then calculated by assuming complete mixing:

$$C_{CSO} = \frac{F_{tot}}{Q_{\max}} \tag{4}$$

$$F_{CSO} = C_{CSO} Q_{CSO} \tag{5}$$

E 3 Receiving water body model

The estimation of the CSO impact on the RWB is based on a worst-case scenario, i.e. the CSO is assumed to take place when the flow in the RWB is at its lowest level.
The water balance in the RWB, after the CSO, is calculated as:

$$Q_{river} = Q_{low,mean} + Q_{CSO} \tag{6}$$

Where $Q_{low,mean}$ [L^3/T] is the average minimum flow in the RWB.
For nitrogen, a simple balance is used to calculate the flux in the river:

$$F_{river} = F_{river} + F_{CSO} \tag{7}$$

Where F_{river} [M/T] is the background nitrogen flux in the RWB, which depends on the sources upstream of the discharge points (point sources other than CSOs, or diffuse sources).
The Dissolved Oxygen (DO) concentration in the river is calculated by using the Streeter-Phelps model (Streeter and Phelps, 1925), which allows both the estimation of the lowest DO deficit (Dc), as well as the critical time when the minimum DO will be reached (t_c):

$$D_c = \frac{k_1}{k_2} C_{BOD} e^{(-k_1 t_c)} \tag{8}$$

Where k_1 [1/T] is the deoxygenation rate, linked to the degradation of organic matter, k_2 [1/T] is the reareation rate, C_{BOD} [M/L^3] is the initial concentration of organic matter (obtained from the combination of eq. 6 and eq. 7). The critical time t_c is calculated as:

$$t_c = \frac{1}{k_2 - k_1} \ln\left[\frac{k_2}{k_1}\left(1 - \frac{D_0(k_2 - k_1)}{k_1 C_{BOD}}\right)\right] \tag{9}$$

Where D_0 [M/L^3] is the initial DO deficit in the RWB. The DWA guidelines provide a long and detailed description of the equations that should be used to calculate the different parameters of the Streeter-Phelps model: reareation rate, deoxygation rate, temperature dependencies, level of initial DO deficits based on the RWB characteristics, etc. Also, other analytical models have been proposed to address specific issues, such as oxygen demand dominated by river sediments (Waterman et al., 2016). Nevertheless, all the necessary calculations can be performed in a simple spreadsheet.

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