



**Ministry of Environment  
and Food of Denmark**  
Environmental  
Protection Agency

# **Investigating stream water quality under conditions of multiple stress**

**A decision support tool for  
assessing contaminated  
sites in relation to other  
potential sources impacting  
the stream**

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Sources must be acknowledged.

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# Executive summary

The protection of freshwater and groundwater systems is a key element of the European Water Framework Directive. Addressing contamination sources and preventing the deterioration of water quality and ecosystem health is necessary in order to meet the EU requirements stated therein. Contaminated sites are among one of the major environmental problems in Denmark, contaminating soil, groundwater and surface water bodies located nearby. Recently, screening tools and risk assessment methods have been developed to support the Danish Regions in evaluating the impact contaminated groundwater originating from these sites may have on Danish streams (Miljøstyrelsen, 2016a; 2014). However, investigations related to stream water affected by contaminated sites have to-date only covered single sources of contaminants. The presence of multiple sources of chemical stressors in the same watercourse can complicate the identification and separation of the distinct effects of individual compounds. This may lead to a poor understanding of the impacts on the stream system and possibly even to the failure of river restoration projects.

Therefore, with the initial condition of the presence of a contaminated site impacting a nearby stream, this report aims to provide a decision support tool for assessing the importance of contaminated sites in relation to other potential sources impacting the streams, with the aim of identifying the impact drivers in a multiple stressor context. For this study, only sites contaminating streams impacted by chlorinated compounds were assessed, referring to the same administrative stretches (or *vandområder*) as defined in the Vandområdeplaner (2015-2021). Attention was given strictly to the stream water compartment, focusing on the contamination related to xenobiotic organic compounds (XOCs) and heavy metals.

The proposed integrated decision support tool is divided into three main steps: Desktop Screening, Impact Assessment and Assessment Support (see detailed description of the method in Chapter 5). The Desktop Screening helps to obtain and collate information regarding the contaminated sites and any additional sources potentially impacting a nearby stream section. The information has been collected from a variety of sources including national databases providing environmental data (e.g. MiljøGIS and MiljøPortalen), from existing site-specific past investigations or by directly acquiring new data through field measurements.

The Impact Assessment refines the desktop screening through a three-step assessment approach that has been applied to each chemical detected in the stream:

1. Impact Screening (IS). Collects information regarding Environmental Quality Standards (EQS), ecotoxicity and bioaccumulation of the detected chemicals in freshwater systems;
2. Impact Characterization (IC). Characterizes the impact by comparing the values of the chemical concentrations detected in the stream and the respective EQS values. In cases where EQS values are not defined, the chemical is assessed via the ecotoxicity and bioaccumulation data. The IC divides the chemicals into four classes: *Impact to the watercourse even with high dilution*, *impact to the watercourse during low flow conditions*, *potential impact to the watercourse*, and *no expected impact*.
3. Spatial (S) and Temporal (T) distribution. The occurrence of the chemicals is addressed both spatially and temporally. The S distribution is evaluated and sorted into three groups: *widespread contamination*, *semi-widespread contamination* and *limited contamination*. The T distribution characterizes the temporal variation of the pollutants through three classes: *continuous contamination*, *semi-continuous contamination* and *pulse contamination*. In the case of a *continuous contamination*, the contaminant mass discharge (CMD, kg/year) can be calculated and classified into three magnitude categories: *Mag 1* (CMD < 1kg/year), *Mag 2* (1 < CMD < 10 kg/year), *Mag 3* (CMD > 10kg/year).

The Assessment Support helps the regulator to determine which pollutant category may be driving the contamination of the stream stretch of interest. The information obtained in the Impact Assessment is processed and the expected or known source(s) are reported. Once the sources driving the contamination are revealed, the information can be passed to a final decision phase encompassing the final assessment and/or plans for remediation. The final prioritization of remedial actions is outside the scope of this project, as it may depend on a number of external factors related to the national strategy for managing surface water contamination.

After a preliminary assessment of potential contaminant sources in addition to the contaminated site(s) located in eight streams impacted by chlorinated solvents, three cases were chosen to serve as site-specific examples: Køge Å, Skensved Å and Kirke Å. The application of the approach to the three study cases is reported in Chapter 9.

## Køge Å

### **Desktop Screening**

In addition to four contaminated sites, agricultural fields nearby the stream, combined sewer overflow (CSO) and separate stormwater system pipe outlets were identified as the additional potential sources of pollution. A site-specific evaluation along Køge Å revealed the presence of three chlorinated ethenes, including PCE and the degradation products cis-DCE and VC, five pesticides and metabolites (glyphosate, AMPA, desphenyl-chloridazon, MCPA, propyazamide), and high concentrations of cadmium (Cd) in one sampling point (K3).

### **Impact Assessment and Assessment Support**

The detected chlorinated compounds are known to originate from nearby contaminated sites located in Køge. According to the IC analysis, VC has a documented *impact to the watercourse during low flow conditions*, while PCE and cis-DCE have *no expected impact* to the watercourse. The S analysis revealed that all detected chlorinated ethenes could be categorized as *limited contamination*, as they were detected in less than 10% of the vandområde of interest. Regarding the T distribution, chlorinated ethenes discharge without interruption into the watercourse, producing a *continuous contamination*. CMD estimates for PCE, cis-DCE and VC all fell into the *Mag 2* category, as the calculated CMDs were between 1 and 10 kg/year.

The expected sources for the pesticides detected in Køge Å are the agricultural fields located close to the stream. Results of the IC analysis for glyphosate, desphenyl-chloridazon, MCPA and propyazamide indicated a *potential impact to the watercourse*, while AMPA had *no expected impact*. The S analysis revealed that glyphosate, AMPA and propyazamide result in *widespread contamination* (present in more than 50% of the stretch of interest), while desphenyl-chloridazon and MCPA produced a *semi-widespread contamination* (present in a portion between 10 and 50% of the stream stretch of interest). The pesticides found in the stream were classified as *semi-continuous contaminants* according to their T distribution, due to their release during and/or after the spraying season (further investigations are needed to confirm this hypothesis).

Among the investigated heavy metals, Cd was classified as having an *impact to the watercourse during low flow conditions*. The S analysis defined the distribution of Cd as *semi-widespread*. The T distribution resulted in a double classification for Cd as both a *pulse* and a *continuous contamination*, as its presence could be related to both types of stormwater systems (CSOs/separate rainwater) linked to urban and traffic systems, or to agricultural fields fertilized with manure containing heavy metals – both of which could result in a *pulse contamination* scenario – but at the same time, it could be originating from geogenic sources thus resulting in a *continuous contamination*.

## Skensved Å

### Desktop Screening

In addition to one contaminated site, agricultural fields nearby the stream, as well as pipe outlets associated with CSOs, separate stormwater, private wastewater and one industrial discharge location were identified as the additional potential sources of pollution. Previous investigations and the field campaign performed after the desktop study revealed the presence of numerous categories of pollutants along Skensved Å: three chlorinated ethenes and degradation products (TCE, 1,1-DCE and cis-DCE), four pesticides and metabolites (glyphosate, AMPA, bentazone and desphenyl-chloridazon), fifteen PAHs (naphthalene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b+j+k)fluoranthene, benz(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, benzo(ghi)perylene, benzo(e)pyrene) and three heavy metals (copper (Cu), zinc (Zn) and lead (Pb)).

### Impact Assessment and Assessment Support

Chlorinated compounds are known to be related to the contaminated site located in Lille Skensved. However, the presence of 1,1-DCE in the stream is unusual because: 1) it was found far from the expected and well-investigated discharge location of the contaminated groundwater, and 2) it is the least prevalent metabolite in the reductive dechlorination of PCE/TCE. This analysis suggests the existence of another source located downstream from the known contaminated site located directly within the town of Lille Skensved. The IC analysis indicated that all detected compounds fell into the *no expected impact* category. According to the S analysis, the presence of the chlorinated compounds creates a *semi-widespread contamination*; regarding the T distribution, the CMD was calculated for the chlorinated solvents, due to their *continuous contamination*. CMD for TCE can be classified as *Mag1-Mag2*, while both 1,1-DCE and cis-DCE fell into the *Mag 1* class.

The expected sources related to pesticide contamination of Skensved Å are the agricultural fields close to the stream, identified as diffuse sources of pollution. Glyphosate and desphenyl-chloridazon result in *potential impact to the watercourse*, while bentazone and AMPA have *no expected impact*. However, the S distribution analysis revealed that glyphosate, AMPA and desphenyl-chloridazon are present in more than 50% of the vandmråde of interest (*widespread contamination*) while bentazone produces a *limited contamination*. Former investigations in Skensved Å related to pesticides documented the potential for seasonal variations in concentrations entering the stream (Mcknight et al., 2012); therefore the contamination has been classified as *semi-continuous*.

PAHs are directly linked to point source discharges such as stormwater separate system and CSO outlets. According to the IC classification, seven PAHs (fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b+j+k)fluoranthene, dibenzo(a,h)anthracene and benzo(ghi)perylene) were classified as having *impact to the watercourse even with high dilution*, two cause *impact to the watercourse during low flow conditions* and one (benzo(e)pyrene) was classified as *potential impact to the watercourse*. The S analysis showed that five PAHs (phenanthrene, fluoranthene, pyrene, benzo(ghi)perylene and benzo(e)pyrene) result in *widespread contamination*, while all the other detected PAHs revealed a *semi-widespread contamination*. The T analysis for all detected PAHs resulted in the classification of *pulse contamination*, most likely entering the stream intermittently through stormwater and CSO discharges after rain events.

The heavy metals could be related to geogenic, diffuse (agricultural fields) and point (stormwater and CSO outlets) sources. The IC analysis indicated that Zn causes *impact to the watercourse even with high dilution* while Pb results in *impact to the watercourse during low flow conditions*. Cu had *no expected impact* to the watercourse. According to the S analysis, Zn is

classified as *widespread contamination*, while Pb and Cu as *limited contamination*. Regarding the T classification, Cu, Zn and Pb all fell into the category of *continuous and/or pulse contamination*, for the same reasons discussed for the previous site.

## Kirke Å

### **Desktop Screening**

In addition to one contaminated site, agricultural fields nearby the stream, as well as pipe outlets associated with CSO and separate stormwater systems were identified as additional potential sources of pollution within the vandområde of interest. Due to budget and time constraints, site-specific field investigations of the additional sources could not be conducted.

### **Impact Assessment and Assessment Support**

Due to the absence of input data regarding the additional potential sources of contamination, the Impact Assessment and Assessment Support could not be performed on this study case. It was determined that further site-specific measurements would be required to support any evaluation of the potential contribution of additional pollutants to the stream.

## **Conclusions**

- This project confirmed the relevance of studying the anthropogenic impact to surface waters through an integrated and comprehensive approach.
- The method was able to support the assessment of water quality and facilitate the link between sources and receptors: the sources initially screened in the Desktop Screening could in most cases be linked to the pollutants found in the stream during the site-specific field investigations.
- Including the environmental fate and toxicity of chemicals not regulated by EQS enables a more comprehensive assessment of the potential risk for non-regulated (e.g. emerging) pollutants for which monitoring data in the aquatic environment are still needed.
- Spatial and temporal occurrence of chemicals entering streams are useful parameters that could be of further assistance in the planning and optimization of future water quality monitoring campaigns, including evaluating the placement of existing (macro-, micro- and representative) monitoring locations with the aim of delineating “worst-case” scenario conditions.
- The method provides decision support to the regulator regarding which category of pollutant (and source) may be driving stream’s contamination, as well as serves as a gap analysis, to guide future data acquisition campaigns where linkages could not be made.

## **Future perspectives**

- With such a variety of potential sources and chemicals, and the necessity of looking at a larger scale (compared to the impact from a single contaminated site impacting surface water), it is difficult to predict and evaluate the major pollutant drivers from a single investigation. The resulting “snapshot” of the status of the receiving water body may in reality not be enough to uniquely identify the real pollution drivers, or may miss that these drivers can shift according to e.g. season. Spatial and temporal variations in pollutant loads and dilution conditions therefore need to be more accurately assessed through site-specific representative data collection and modelling.
- Furthermore, investigations encompassing only the stream water compartment were not conclusive enough to definitively pinpoint pollution drivers, complicating efforts to link sources and contaminants in streams. Moreover, this study neglected potential cumulative effects (joint toxicity) of chemicals, which could also be a limiting factor.
- It is therefore recommended to: 1) test this approach on other streams potentially impacted by contaminated sites polluting the receiving water bodies with chemicals other than chlorinated compounds; 2) determine the timing, monitoring locations and sampling methods applied in the field investigations depending on the characteristics of the investigated sources; 3) integrate the approach proposed by Vezzaro et al. (2017) into the current method to bet-



ter address the negative impacts coming from stormwater (CSOs/separate rainwater systems); 4) perform a multiple-compartment assessment for Køge Å, Skensved Å and Kirke Å to compare with current results and demonstrate the potential for enabling a better source-pathway-receptor linkage which may lead to more cost-effective solutions for some source types.

# 1. Introduction

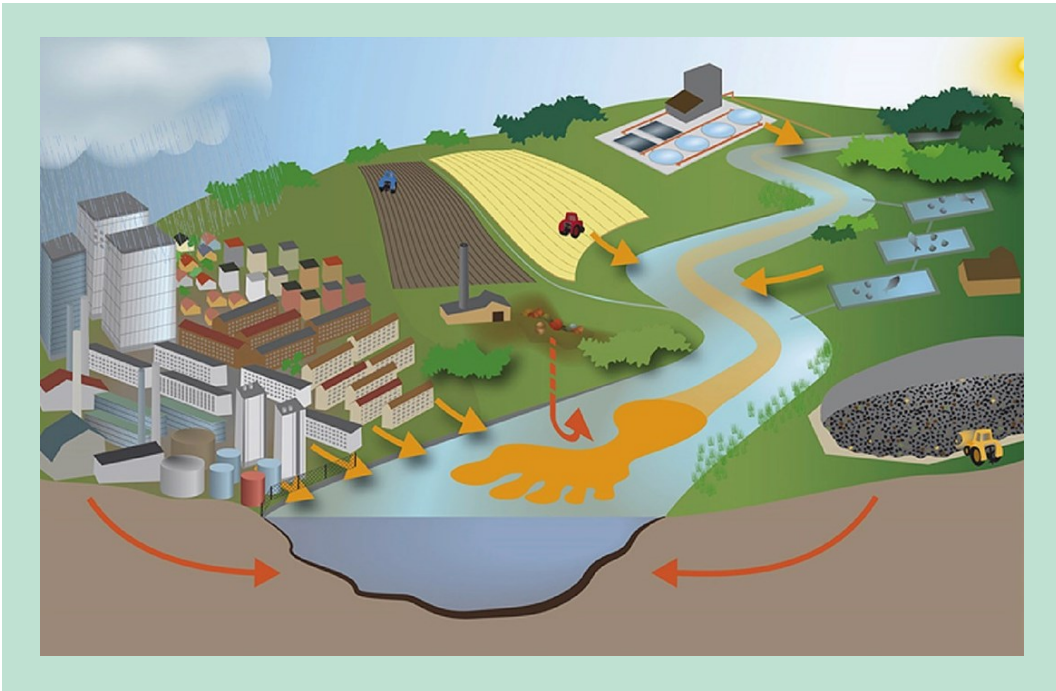
## 1.1 Motivation of the study

Land use changes and economic growth largely contribute to the deterioration of stream water and groundwater resources, including habitat degradation, hydrological alterations, water pollution and biological invasions (McKnight et al., 2015, 2010; Rasmussen et al., 2013; Schinegger et al., 2012; Schäfer et al., 2016; Sonne et al., 2017; Yu et al., 2014). More attention in the last years has been given to the characterization of anthropogenic contamination potentially impacting freshwater ecosystems, as the European Water Framework Directive (WFD) requires all Member States to ensure good ecological and chemical status of their surface waters.

Contaminated sites are posing a major problem in Denmark. In total, more than 35,000 sites are contaminating or potentially contaminating soil and groundwater (Miljøstyrelsen, 2016b) whereby some contaminated sites, particularly those located close to a stream, may additionally threaten the state of the natural ecosystem and the chemical quality of the water (Miljøstyrelsen, 2016a, 2014; Sonne et al., 2017). When the Danish Soil Act was adapted to include contaminated sites as a source of pollutants impacting stream systems (BEK nr. 1552 of 17/12/2013), the regions began mapping contaminated sites that could threaten nearby watercourses through groundwater contamination. To date, studies have started using a screening tool which could assist to select the contaminated sites posing a risk to streams (Miljøstyrelsen, 2016a, 2014). As initial step, this tool estimates the concentrations in the stream during low flow conditions based on the median minimum water flow.

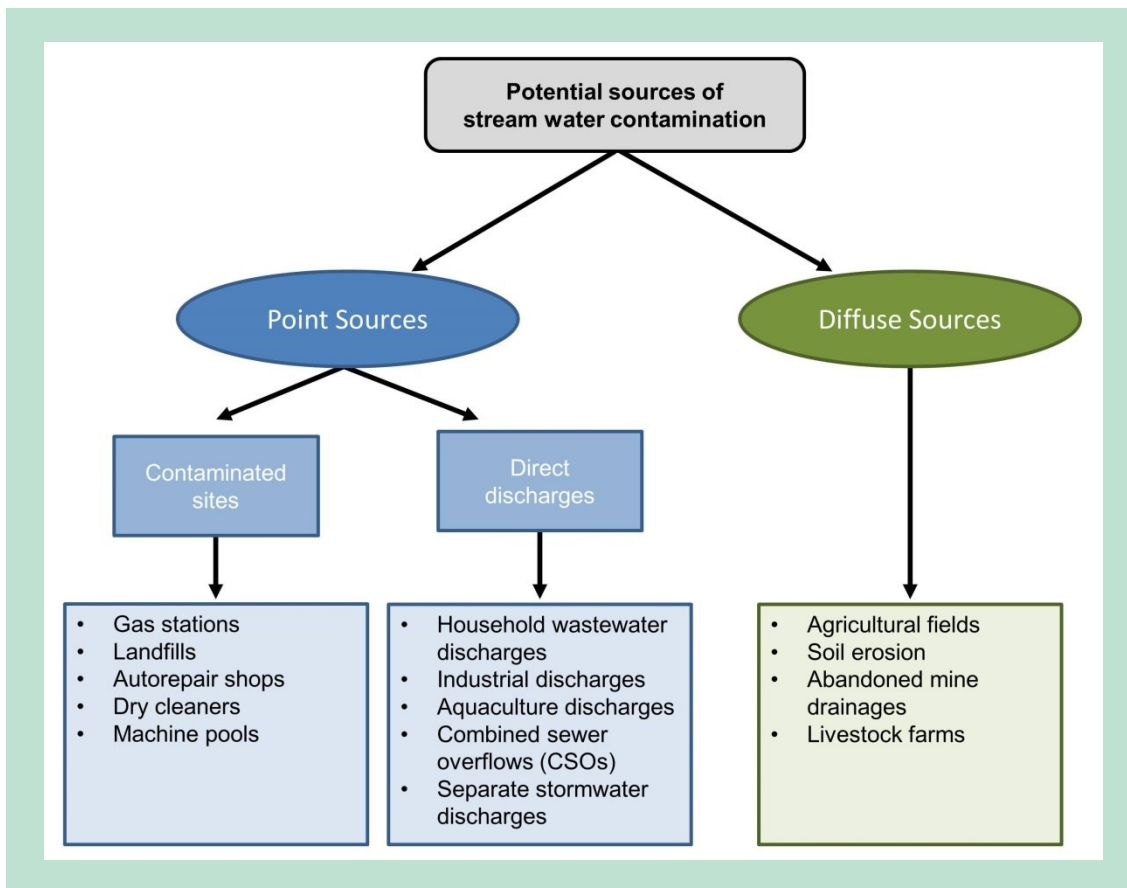
Attention has been given especially to chlorinated aliphatic hydrocarbons (CAHs) due to their widespread use in industrial processes and their chemical properties. In case of leakage, CAHs such as perchlorethylene (PCE) and trichloroethylene (TCE) can dissolve easily below the groundwater table forming troublesome contaminated plumes that last decades (Ellis and Rivett, 2007; Matteucci et al., 2015). Anaerobic conditions in the aquifer often result in the formation of vinyl chloride (VC), a highly mobile and carcinogenic degradation product (Smits et al., 2011). Moreover, chlorinated solvents and degradation products have a large potential to discharge in surface waters due to their high mobility and persistence (Ellis and Rivett, 2007). However, other contaminated sites such as dry cleaners, former gasoline stations or old landfills may also pose a risk to surface water (Miljøstyrelsen, 2016a, 2014).

To date, investigations related to stream water affected by contaminated sites have only considered single sources of contaminants, disregarding other potential sources close to the site. However, streams can be impacted by other contaminant sources than contaminated sites, especially in peri-urban (mixed land-use) stream corridors as illustrated in Figure 1. This includes discharge to streams of fertilizers and pesticides applied on agricultural fields, wastewater discharges containing nutrients and xenobiotic organic compounds (XOCs) and stormwater discharges with heavy metals and polyaromatic hydrocarbons (Bollmann et al., 2014; Eriksson et al., 2007; Matthaei et al., 2010; Sonne et al., 2017).



**FIGURE 1. Conceptual sketch of the multiple sources affecting stream water chemical and ecological status (Sonne et al., 2017). The pathways of the sources to the receiving water body are shown with the arrows (underground and surface pathways represented with red and orange arrows, respectively).**

The contaminant sources are typically divided into point and diffuse sources as illustrated in Figure 2. The pollutants can enter streams through different pathways such as groundwater discharge, surface runoff or simply direct discharge (e.g. sewage effluent and drainage systems). This depends mostly on the land use and the type of source, as well as its proximity to the stream.



**FIGURE 2. Potential sources causing stream water pollution and their division into point and diffuse sources. For each category, examples for some of the sources are given. The figure is developed based on the literature survey in this report. Further details and more concrete examples of contaminant sources are reported in Chapters 2 and 4.**

The resulting contaminations can spread continuously, acting as constant sources of pollution, or be characterized by periodic peaks depending on the season and/or on rainfall intensities. These combined chemical stressors, acting in the same area, could mask or contribute to the impairing effects, making the identification of sources and pathways harder. This could lead to uncertainties and poor understanding of the main impacts on the stream system, as a holistic understanding of the entire system is lacking especially in mixed land-use stream corridors.

Consequently, mitigation measures focusing on individual contaminated sites may not necessarily be able to ensure good ecological and chemical status in the stream, as the impairment could be driven by more than one source of contamination. This is supported by a number of studies confirming this supposition. For example, Schäfer et al. (2016) and Schinegger et al. (2012) reported that the majority of streams and rivers in Europe are affected by at least two different stressors, implicating that to improve ecological conditions it is important to adopt a multiple stressor context that could avoid the failure of river restoration projects or remedial actions. Therefore, multiple source assessments are also becoming more common, with recent studies typically reporting more than one stressor and/or pathway affecting stream water quality (Barber et al., 2006; Bigi, 2017; Kuzmanović et al., 2016; McKnight et al., 2012; Sonne et al., 2017).

Thus, management of contaminated sites requires a methodology for assessing whether the identified sites affecting stream water quality are the only source impairing the stream, and otherwise provide an approach for classifying the sources and related impacts of pollution in

order to facilitate decisions of further actions. To do this, a more holistic source-pathway-receptor methodological approach to water management is needed, linking the sources to the pathways and finally the affected surface waters. This concept is also one of the key principles set by the WFD, requiring that the stressors and their sources are studied together, improving the understanding of the governing processes, the source composition and origin (EA, 2005).

## 1.2 Aim of the project

The purpose of this project is to develop a methodology for assessing the importance of individual contaminated sites in relation to other potential sources of chemical stressors impacting streams, enabling pollution driver identification (comparing source importance) in order to support the prioritization of remediation strategies for only those sources truly driving impact in stream systems. This project will improve the overall understanding of the major sources impacting surface water, expanding the screening process to more compounds and potentially a larger scale thereby providing a more comprehensive approach to surface water pollution.

The methodological approach will help to:

- Screen potential sources of multiple stressors;
- Support the assessment of water quality and thus chemical status;
- Help identifying the dominant sources driving the pollution of the stream;
- Link specific contaminants to their respective sources.

## 1.3 Project content

The project consists of 5 main activities:

1. Review and description of both sources and pollutants of concern typically found in mixed land use stream systems/corridors. This also includes a brief description of Danish streams, and water quality and assessment methods specific for Denmark.
2. Description and concretization of the proposed methodological approach.
3. Review of a subset of identified contaminated sites in Denmark found to pose a risk to nearby streams, where sites were chosen such that stream corridors representing different types of land use and hence chemical stressor sources are covered. After an initial general screening, three specific streams are described in more detail and assessed as study cases: Køge Å, Skensved Å and Kirke Å.
4. Additional field investigations conducted to supplement existing data and/or fill data gaps to permit a first quantification of the contribution of each source. Only Køge Å and Skensved Å have been investigated due to budget and time constraints.
5. Application of the developed approach for the three study cases, and a final discussion of limitations and further perspectives.

## 1.4 Focus and boundaries of the study

For this study, only sites contaminating streams impacted by chlorinated compounds will be assessed. Landfills, pesticide point sources or other types of contaminated sites were not considered in order to delineate the study boundaries and spend more resources on one type of contaminated site. In addition to this:

- Contamination by chlorinated compounds remains one of the main focal points for the Danish Environmental Protection Agency (EPA) and Danish Regions;

- Contamination related to chlorinated compounds is specifically related to well-known compounds (chlorinated solvents and degradation products);
- This study can build on existing field studies, i.e. the Danish EPA in collaboration with Danish Regions have already identified a number of contaminated sites posing a risk to nearby streams due to contamination by chlorinated solvents (Miljøstyrelsen, 2016a).

This study will assess the streams following the Vandområdeplaner (2015-2021), which specifically defines which stream sections (according to typology and hydromorphology) have to be monitored and remediated to improve the Danish aquatic environment. The current investigation will thus assess multiple sources referring to the same administrative stream stretches (or *vandområder*) as defined by the Ministry of Environment and Food.

Attention will be given strictly to the stream water compartment. Therefore, the current project will not cover contamination of the immediate groundwater, sediment and hyporheic zone compartments, thereby excluding the screening of sediment-bound or groundwater contaminants not present in stream water.

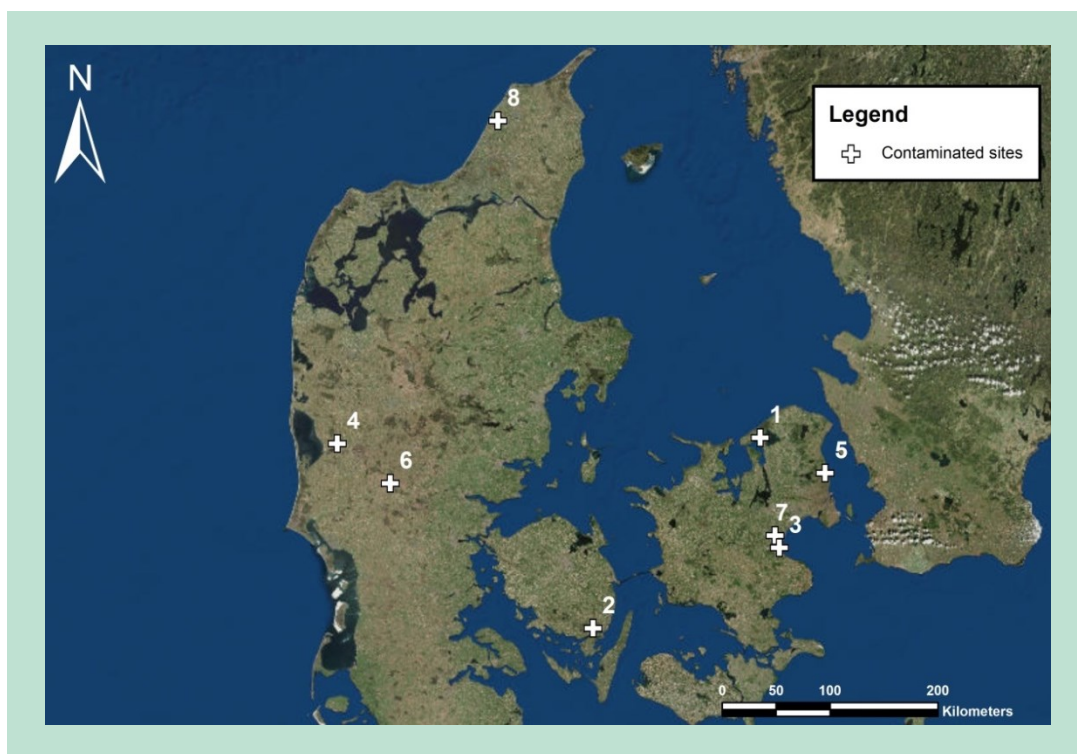
Regarding the other sources that will be described in this study, a general overview of the contaminants related to each type of source will be given. However, the focus of this project will be on XOCs and heavy metals.

## 2. Examples of contaminated sites in a multiple stressor context

### 2.1 Identification and characteristics of existing contaminated sites

The starting point for this analysis is the presence of a contaminated site impacting a nearby watercourse. Therefore, the first phase consisted of clarifying whether the contaminated site is relevant or not in a multiple stressor context. To this end, a review of concrete examples of sites contaminating stream water with chlorinated solvents was performed. Available information from previous screenings of contaminated sites was used to select potential study cases where, besides the contaminated site, other sources may adversely affect the chemical water status. In addition to reviewing Miljøprojekt nr.1846 (Miljøstyrelsen, 2016a), other known investigations related to sites contaminated with chlorinated compounds have been assessed.

Overall, eight contaminated sites distributed around Denmark have been taken as examples of cases causing stream impairment. All the selected cases are characterized by chlorinated solvent contamination; however, they differ in land use characteristics and geographical location. Figure 3 shows the location of the sites.



**FIGURE 3.** Location of the selected contaminated sites impacting nearby streams. These contaminated sites were selected for a more refined study.

Table 1 presents the selected contaminated sites and related watercourses known to be impacted by chlorinated compounds, together with the length of the stream water section that will need to be investigated, the current ecological status and ecological objective reported in the

Vandområdeplaner 2015-2021. The stream typology and hydromorphological characteristics are included in Table 1, as the typology affects which biological elements are used in determining ecological status in Denmark. It is well-known that poor hydromorphological conditions can mask other stressor effects in a stream, making it hard to distinguish whether the modification of ecological communities is driven by source pollution or hydromorphological alterations of the river (Buffagni et al., 2016; Rasmussen et al., 2011). The sites were furthermore divided based on the surrounding land use characteristics, as the types of contaminants and sources present will be closely related to the land use practices. The criteria for how the typology, ecological status and ecological objective of a stream are further described in Chapter 3.

None of the selected stream stretches except for Kobberbæk are characterized by *good* ecological status. The longest stream stretch considered is for Skensved Å, encompassing 9.3 km; the shortest is 1.5 km (Grindsted Å). Regarding the hydromorphological conditions of the stream stretches of interest, two are classified as highly modified, while the others are characterized by a natural profile and therefore did not undergo processes of channelization or high modification during the past decades.

**TABLE 1. Selected stream stretches contaminated by chlorinated compounds, their relative stream typology, hydromorphological characteristics, current ecological status (according to the WFD 5 water quality class system), and ecological objectives.**

	Stream	Region	Contaminated site location	Stream stretch length (km)	Stream typology	Hydromorphological characteristics	Current ecological status	Ecological objectives
<b>Urban areas</b>								
1	Arresø Kanal	Region Hovedstaden	Frederiks-kværk	2,3	2	Highly modified	<b>Moderate</b> ecological potential	Good ecological <b>po-tential</b>
2	Kobberbæk	Region Syddan-mark	Svendborg, Kobber-bæksvej 75	5,5	1	Not highly modi-fied	<b>Good</b> ecologi-cal status	Good ecologi-cal <b>sta-tus</b>
<b>Mixed land use</b>								
3	Køge Å	Region Sjælland	Køge, Torvet 20	7,6	2	Not highly modi-fied	<b>Poor</b> ecologi-cal status	Good ecologi-cal <b>sta-tus</b>
4	Kirke Å	Region Midtjylland	Bredgade 1-9, Skjern	8,5	2	Not highly modi-fied	<b>Bad</b> ecologi-cal status	Good ecologi-cal <b>sta-tus</b>
5	Mølleåen	Region Hovedstaden	Raadvad Knivfabrik	1,7	3	Highly modified	<b>Moderate</b> ecological potential	Good ecologi-cal <b>po-tential</b>
6	Grindsted Å	Region Syddan-mark	Grindsted	1,5	2	Not highly modi-fied	<b>Moderate to good</b> ecologi-cal status	Good ecologi-cal <b>sta-tus</b>
<b>Rural areas</b>								
7	Skensved Å	Region Sjælland	Lille Skensved	9,3	2	Not highly modi-fied	<b>Poor</b> ecologi-cal status	Good ecologi-cal <b>sta-tus</b>



8	Hundelev Å	Region Nordjylland	Løkkensvej 690, Hundelelev	3,0	1	Not highly modified	Poor ecological status	Good ecological status
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## 2.2 Initial screening for additional contaminant sources

A possible list of additional contaminant sources were identified in a literature review about the common sources threatening streams in mixed land use catchments (Figure 2). A more detailed description of the single sources and their respective pollutants can be found in Chapter 4. The two online databases MiljøGIS and MiljøPortalen were used to collect information on these sources and existing environmental data regarding the streams in the water courses of interest (Table 1).

Table 2 shows that all the streams are characterized by at least one (or more) contaminated sites threatening or potentially threatening the water quality. Besides the contaminated sites, all sites include multiple other sources of different natures. Combined sewer overflows (CSOs) and urban stormwater discharges are the most frequently observed point sources. CSOs and stormwater drains could potentially pollute the stream with wastewater or urban water in every stream listed in Table 2 except for Hundelev Å. Pesticides could impact Køge Å, Grindsted Å, Skensved Å and Hundelev Å due to the presence of nearby agricultural fields.

Thus, this initial screening highlights the need for a holistic approach, where not only contaminated sites are assessed, but also other relevant contaminant sources along the watercourse.

**TABLE 2. List of potential sources within the stream section of interest and located within close proximity to the contaminated site.**

		Contaminated site	Wastewater discharges	Industrial discharges	Fish farms	Close Agricultural fields	CSO drains	Urban Stormwater drains
<b>Urban areas</b>								
1	Arresø Kanal	X					X	X
2	Kobberbaek	X					X	X
<b>Mixed Land Use</b>								
3	Køge Å	X				X	X	X
4	Kirke Å	X	(X) downstream from the section of interest	(X) downstream from the section of interest			X	X
5	Mølleåen	X	(X) upstream of the section of interest				X	X
6	Grindsted Å	X	X	X	X	X	X	X
<b>Rural Areas</b>								
7	Skensved Å	X	X	X		X	X	X
8	Hundelev Å	X				X		

# 3. Chemical and ecological stream water quality

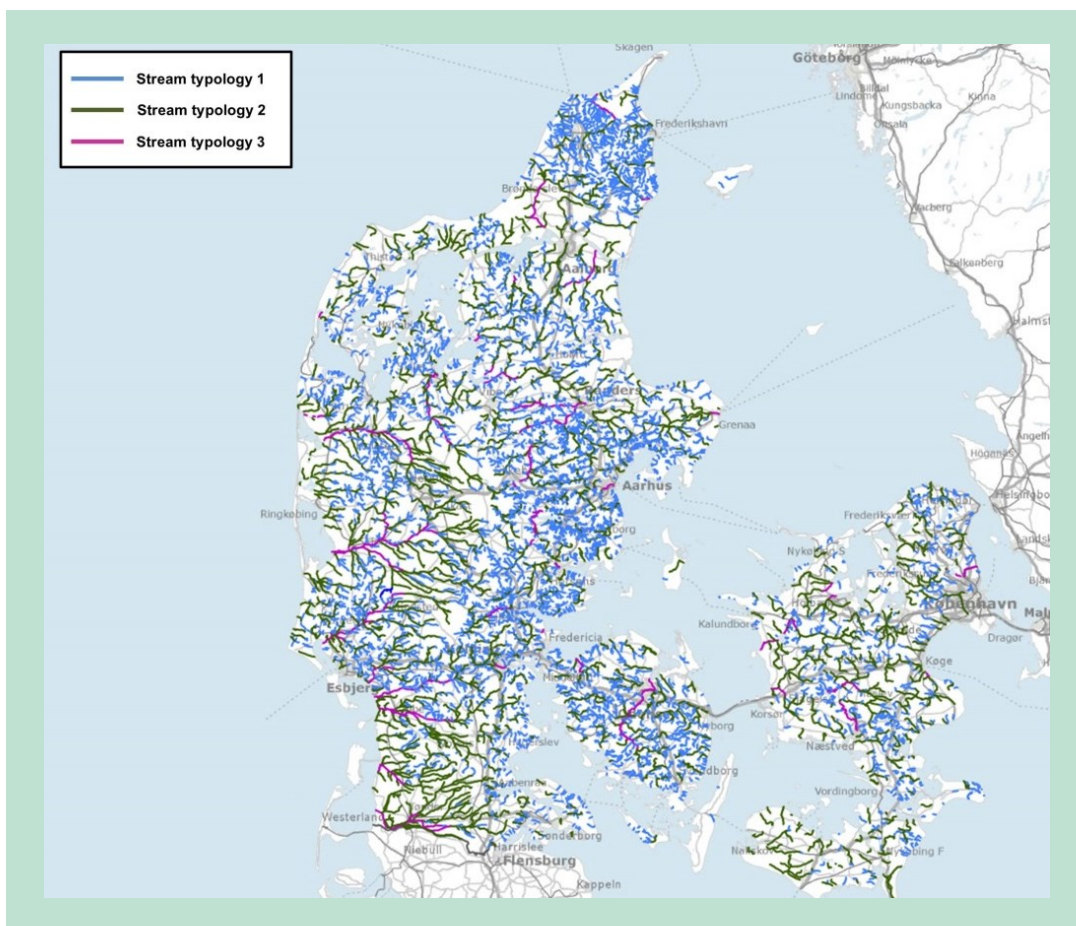
## 3.1 Stream classification

The Danish National Water Plans for 2015-2021 characterize the streams physically according to typologies. This helps to determine stream type-specific conditions and enable comparisons to other water bodies of the same type. Three different typologies are used to characterize the stream according to the width of the watercourse, the extent of the river basin and the distance from the stream origin. Table 3 presents an overview of the characteristics for each typology. A watercourse will be classified according to the type in which most properties fall (Vandområdeplaner, 2014).

**TABLE 3. Characteristics of the different stream types as defined in the Water Plans 2015-2021.**

Type	1	2	3
Width of the watercourse (m)	<2	2-10	>10
Scale of the basin (km <sup>2</sup> )	<10	10-100	>100
Distance from the stream origin (km)	<2	2 - 40	>40

According to the classification described in Table 3, the majority of Danish streams is classified as type 1. Figure 4 shows the Danish streams classified with different colors according to the stream typology (1, 2 or 3). The presence of larger streams is more common in Regions Midtjylland and Syddanmark, while Regions Sjælland, Hovedstaden and Nordjylland are predominantly characterized by streams within typology 1 and 2.



**FIGURE 4. Map showing the Danish streams divided according to typology (source: MiljøGIS 2018).**

Watercourses are also classified depending on the hydromorphology. The division is between natural watercourses (or not highly modified) and highly modified or artificial watercourses. The latter case designates streams that have been created by human activities (e.g. channels) or heavily modified for human purposes (e.g. drainage, irrigation, water navigation) thus heavily adapting the physical morphology of the course and the banks (e.g. channel straightening, dredging). For these kinds of artificial streams, it is sufficient to reach good chemical status and good ecological *potential* under the WFD, as the remediation actions needed to reach good ecological status would have a negative effect on human activities (such as recreational water activities) and high costs of restoration for the municipality (Vandområdeplaner, 2014). Denmark has ca. 60,000 km of watercourses with around two thirds defined as artificial or highly modified (Vezzaro et al., 2017).

### 3.2 Chemical status in streams

The WFD requires that good chemical status is reached in all running waters. The chemical status is determined by comparing the concentrations of a range of priority pollutants with their respective Environmental Quality Standards (EQS). Good chemical status is reached if all detected chemicals comply with their EQS values. The watercourse will not meet the target if only one of the measured hazardous pollutants exceeds its related water quality criterion (Vandområdeplaner, 2014). The list of substances that pose a risk to the aquatic environment were selected by the European Commission (Priority Pollutants EU Directive 2000/60/EC, 2008/105/EC, 2013/39/EU) and then extended by the Danish Ministry of Environment and Food (BEK 439 19/05/2016). The European commission selected 45 priority pollutants and defined specific EQS to evaluate the chemical status of the streams. The Danish authorities monitor an additional 134 compounds with supplementary national quality standards.

The existing EU regulation sets two guidelines: the Annual Average (AA) and the Maximum Allowable Concentration (MAC), which are translated as *Generelt kvalitetskrav* and *Maksimumkoncentration*, respectively, for the Danish National regulation. For simplicity, the acronyms AA and MAC will be used in this report to refer both to the National and EU guidelines. The purpose of the AA guideline of a substance is to ensure protection against long-term exposure; therefore, it has to be compared to the average concentration measured over a one-year period. The purpose of the MAC guideline is to ensure protection against short-term pollution peaks where it has to be compared with the maximum concentration detected. The complete list of compounds regulated by the EU and/or the Danish EPA together with their respective AA and MAC EQS values can be found in the directive BEK 1625 19/12/2017.

In Denmark, only a small fraction of the streams have been monitored to address the chemical status. Counting the ca. 20,000 km of natural streams present, 205 km have been investigated with respect to hazardous water pollutants (Vandområdeplaner, 2014), resulting in that only 1% can be fully assessed. The limited number of available data is represented in Figure 5, showing the streams where data regarding the chemical status are available. The map includes the highly modified streams. It should be noted that some information and data from recent investigations e.g. conducted by universities or private companies may not be included in the map. Collecting environmental data from different sources is essential to obtain a reliable and consistent database that is more representative of the current monitoring extent.

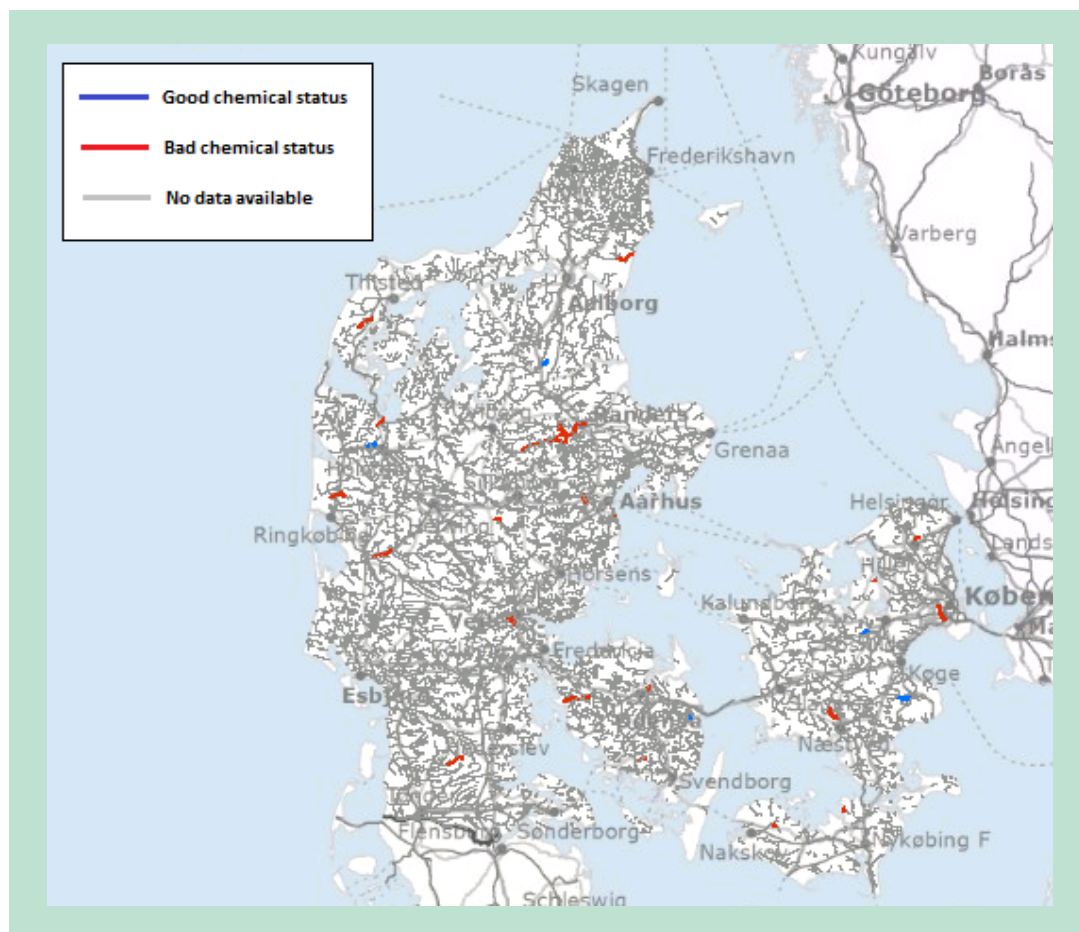


FIGURE 5. Map showing the chemical status of Danish streams (source: MiljøGIS 2018).

### 3.3 Ecological indicators of streams and rivers

According to the WFD and the Danish Water Plans for 2015-2021, the ecological status of streams should be defined by four biological indicators: benthic macroinvertebrates, freshwa-

ter plants (macrophytes), fish and benthic algae. Each indicator has six classes indicating their status: Excellent, Good, Moderate, Poor, Bad or unknown. In Denmark, only fish, benthic macroinvertebrates and freshwater plants have been used for assessing the ecological status so far, as the benthic algae index has not yet been completed. However, the aim is to finalize it for inclusion in the biological assessment scheme by 2021 (Vezzaro et al., 2017).

The macroinvertebrate community is classified according to the Danish Stream Fauna Index (DSFI), a method used to quantify the status of oxygen sensitive species in streams. Since oxygen levels are affected by a number of contaminants, e.g. increased 5-day biological oxygen demand (BOD5) or high nutrient levels, the index can also provide some indication of the chemical status of a stream (McKnight et al., 2012; Vezzaro et al., 2017). The DSFI is comprised of seven values that represent a specific class from the WFD (Table 4), and has been intercalibrated with European standards (Vezzaro et al., 2017).

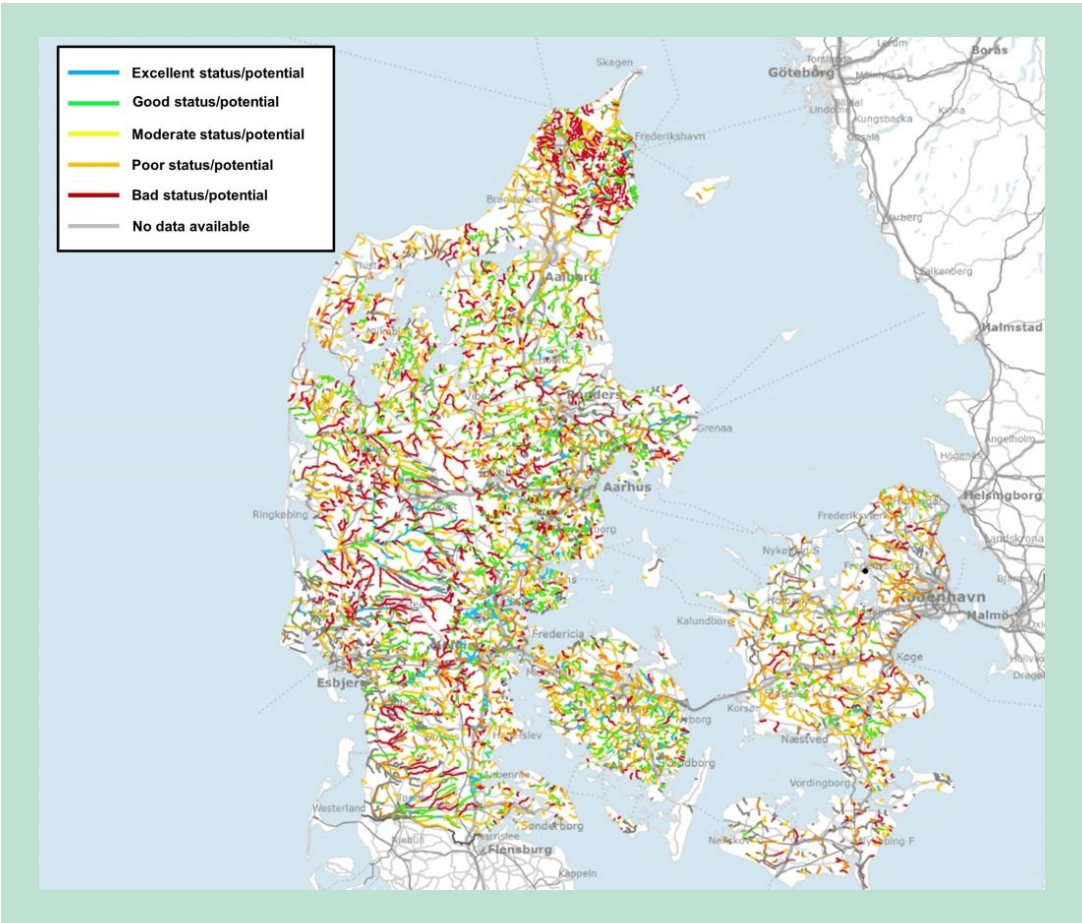
**TABLE 4. DSFI classes representing the status of the benthic macroinvertebrate community in conjunction with the WFD classification system.**

WFD Status	DK DSFI
Excellent	7
Good	5-6
Moderate	4
Poor	3
Bad	1-2
Unknown	0

The plant status is based on the Danish Stream Plant Index (DSPI). This type of index aims to provide information regarding the nutrient levels and the hydromorphological changes of the stream related to human activities (e.g. dredging). However, the DSPI is applied only for larger streams falling into the typology categories 2 or 3 (Vandområdeplaner, 2014) which somewhat restricts its use in Denmark as the majority of streams are characterized by typology class 1. Regarding the fish bioindicator, the Danish Fish Index for Streams (DFIS) is used to assess the species richness and diversity. This index can also be used for larger streams (types 2 and 3) where it is more common to detect three or more species of fish. However, streams characterized by typology class 1 are expected to be poor in their number of representative fish species. For this reason, the DFIS was split into two new national indices, which still need to be intercalibrated at the EU level (Vezzaro et al., 2017): the DFIS<sub>a</sub> and the DFIS<sub>ø</sub>, where *a* stands for *art* (referring to taxonomic composition, and used in larger streams) and *ø* stands for *ørred* (referring to e.g. trout species found in the smaller type 1 streams) (Kristensen et al., 2014). To sum up, streams within typology 2 and 3 are evaluated through a combination of DSFI, DFIS and DSPI. For smaller streams (typology 1), the biological status is only based on the DSFI and the DFIS<sub>ø</sub>. The overall surface water status is then determined by the lowest ecological status between the different indices used in the evaluation; i.e. with a “one out, all out” standpoint.

Notably, many more investigations of the ecological status of Danish streams have been carried out in recent years compared to the investigations of chemical status, as shown in Figure 6. In case of highly modified streams, the ecological status is reported as “potential”, as the goal of good ecological status doesn’t have to be reached due to the modified hydromorphological conditions of these streams. It can be seen that only part of the streams are characterized by excellent/good ecological status/potential (indicated in light blue/green, respectively), while most of them are in moderate/poor/bad condition (yellow, orange, red, respectively), especially in Region Nordjylland and Region Sjælland. This could be attributed in part to the fact that

chemical stressors have only relatively recently been recognized as a stressor of major concern (in addition to e.g. habitat alteration; invasive species) (e.g. Malaj et al., 2014; Schäfer et al., 2016; Sonne et al., 2017), whereby the study of multiple stressor systems is still somewhat in its infancy due in part to issues complicating experimental conditions for studies with greater than two-stressor interactions (Schäfer and Piggott, 2018).



**FIGURE 6.** Map showing the overall ecological status/potential of Danish watercourses (source: MiljøGIS 2018).

# 4. Identification and description of sources and pollutants

The quality of numerous streams frequently does not meet the ecological standards and most of the Danish streams lack data regarding the presence of environmental hazardous pollutants. Stream water contaminants include a wide range of organic and inorganic chemicals, pathogens and nutrients which alter the water chemical properties besides affecting the natural biological communities.

This chapter will focus on describing the main stream water pollution source categories, in addition to characterizing the pollutants that could be present and simultaneously cause water impairment and degradation.

## 4.1 Water pollution source categories and pathways

As previously outlined in Chapters 1 and 2 (Figures 1 and 2), there are many sources potentially affecting water quality. Table 5 presents the two general source categories (point and diffuse) together with their key characteristics.

**TABLE 5. List of the main water pollution sources together with their primary attributes.**

Point sources		Characteristics
Contaminated sites	<ul style="list-style-type: none"> <li>- Gas stations</li> <li>- Landfills</li> <li>- Auto repair shops</li> <li>- Dry cleaners</li> <li>- Machine pools</li> </ul>	<ul style="list-style-type: none"> <li>- Continuous sources of pollution</li> <li>- Contamination mainly introduced in the stream due to groundwater discharge</li> <li>- Discharge location typically identifiable despite spatial and temporal variations</li> <li>- Impact from these sources increases during low flow conditions</li> </ul>
Direct discharges	<ul style="list-style-type: none"> <li>- Household wastewater discharges</li> <li>- Industrial discharges</li> <li>- Aquaculture discharges</li> </ul>	<ul style="list-style-type: none"> <li>- Single identifiable source that can be distinguished from other pollution sources</li> <li>- Contaminants introduced directly into the aquatic environment at a single location: emission limit values can be set to regulate pollution loads</li> <li>- Impact from these sources increases during low flow conditions</li> </ul>
	<ul style="list-style-type: none"> <li>- Combined sewer overflows (CSOs)</li> <li>- Separate stormwater discharges</li> </ul>	<ul style="list-style-type: none"> <li>- Single identifiable source that can be distinguished from other pollution sources</li> <li>- Contaminants introduced directly into the aquatic environment at a single location: emission limit values can be set to regulate pollution loads</li> <li>- Impact of these sources most often increases as discharged flow increases during rain events</li> </ul>
<b>Diffuse sources</b>		
	<ul style="list-style-type: none"> <li>- Agricultural fields*</li> <li>- Abandoned mine drainage</li> <li>- Soil erosion</li> <li>- Livestock farms</li> </ul>	<ul style="list-style-type: none"> <li>- Difficult to identify the discharge location due to spatial and temporal variations</li> <li>- Impact of these sources increases as flow increases during rain events</li> </ul>

\* Runoff and discharge to streams from agricultural fields can be conveyed either as direct surface runoff, or enter via tile drains or groundwater. Tile drains could be viewed as a direct point discharge, but the purpose of tile drains is to drain the agricultural fields, and often there are more than one along a stretch of interest. Thus, the water in the drains represents the water leaching out of the field, and is thus considered a diffuse source in this report.

Contaminated sites, household wastewater, industrial and fish farm discharges are all categorized as point sources of pollution, releasing chemicals from discrete stationary conveyances; however, they are of a very different nature. Contaminant plumes from contaminated sites usually discharge into streams via groundwater in areas with presence of groundwater-stream water contact zones. The plumes can vary in width from a few meters up to wide plumes from landfills or even large plumes, especially from former industrial facilities. Sewage treatment plants and fish farms typically have discharging pipes or ditches connecting the source to the stream and limits are often set to regulate the pollution load flowing into the running waters. Point sources are usually more relevant in terms of concentration during low streamflow conditions, as the dilution factor is lower compared to the winter season, increasing the pollutants' concentrations in the river (Eriksson et al., 2007; Rasmussen et al., 2013).

On the other hand, there are point sources of pollution typical for urban areas, such as CSOs and separate stormwater discharges (Eriksson et al., 2006; Vezzano et al., 2017; Wicke et al., 2014). The combined sewers collect the water from waste- and stormwater before conveying everything to the wastewater treatment plant. CSOs may discharge into surface waters when the capacity of the drainage network is exceeded. The separate stormwater systems are separate drainage systems built to collect water from roofs, streets and highways, with the intention of discharging it into a stream after some retention (smoothing of the peak flows) and perhaps pollutant removal, depending on the regulations given by the municipality. This helps to reduce the amount of water going to the treatment plant during wet weather periods as well as reduce the volumes discharged via CSOs. Sometimes retention basins are also built to reduce the CSO volumes. They store the mixture of sewage and stormwater before sending it to a wastewater treatment plant.

Nonpoint (diffuse) sources generally refer to pollutants coming from a variety of activities and not a unique and identifiable pipe (as with wastewater discharges, CSOs or stormwater outflows) or hotspot (contaminated sites). Agricultural lands, livestock farms, soil erosion and mine drainages are typically placed in this category. Diffuse sources release contaminants with high spatial and temporal variations, depending for example on the pesticides spraying season or heavy rainfall periods. Typical pathways connecting diffuse sources to streams are groundwater-surface water contact zones, surface runoff and superficial or underground drains collecting the water and discharging it to the stream.

These different types of sources can interact together, making it difficult to distinguish the sources of contaminants detected in streams and thus to predict the effects of multiple stress- or contamination (Matthaei et al., 2010; Rasmussen et al., 2013). For this reason, implementing the right remediation strategy to reduce or eliminate the contamination may be difficult.

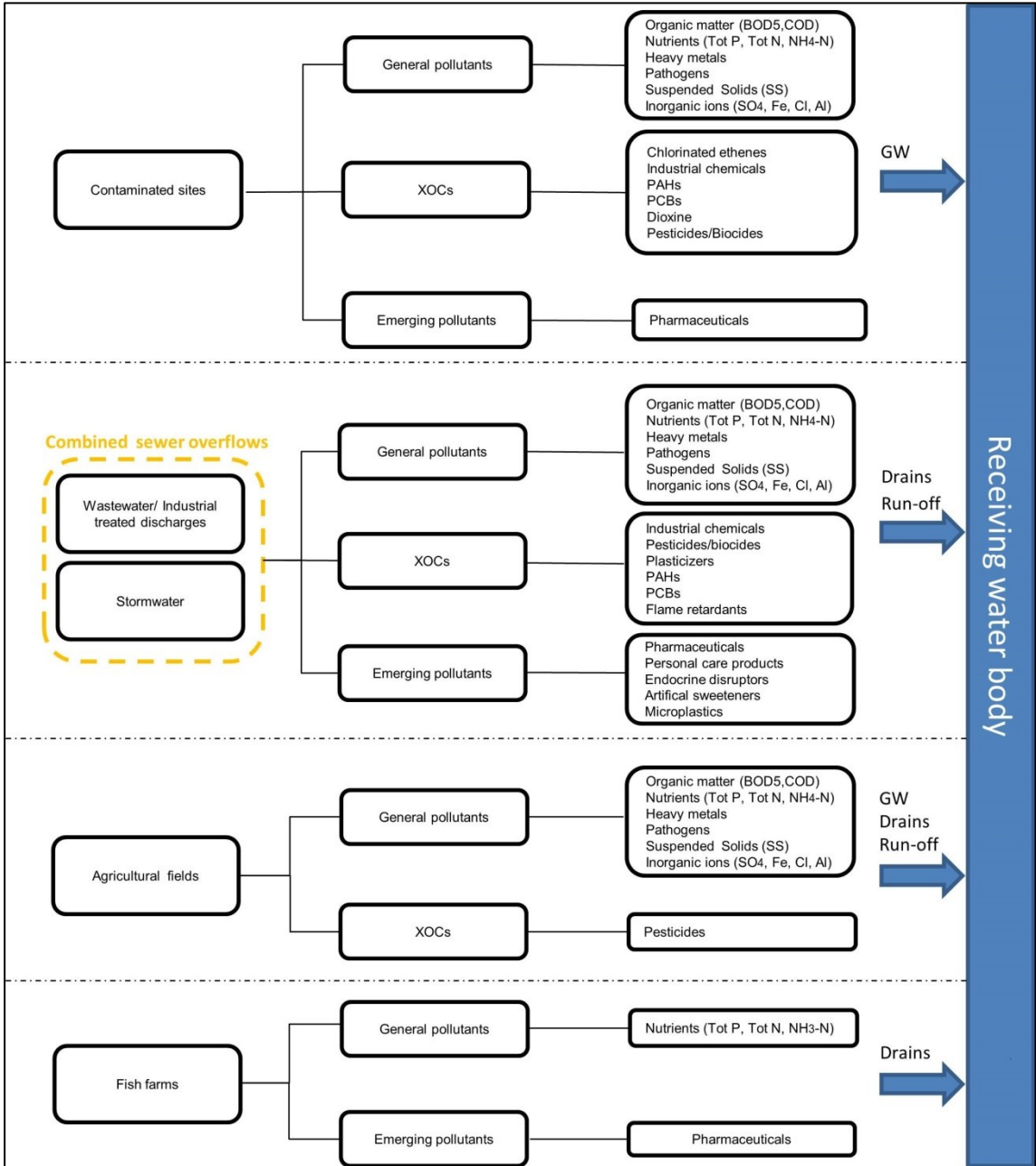
## 4.2 Contaminants

Depending on the type of source, different contaminants could impact the receiving water body. Based on available information regarding pollutants found in past investigations and a literature review, it was possible to divide the categories of expected contaminants relative to each type of source. The pollutants could be subdivided into general pollutants, XOCs and emerging pollutants.

General pollutants include traditional chemical parameters typically analyzed to give an overview of the general chemical status of a river such as organic matter, nutrients and inorganic macro-ions, but also pathogens, heavy metals and suspended solids (SS). XOCs represent the list of toxic chemical pollutants not naturally found in the environment and commonly present in low concentration ranges ( $\mu\text{g/l}$  or below). The XOCs include for example dioxins, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and pesticides. Emerging pollutants are described as contaminants not commonly monitored which have the potential to enter the environment and harm ecological and human health. The overall



knowledge of this category of pollutants is relatively sparse, meaning that maximum allowed concentrations in the environment are not regulated or sampling methods are not yet harmonized. For this reason, the EU created through the directive 2013/39/EU a Watch List, including a number of emerging pollutants for which monitoring data in the aquatic environment are needed to provide information regarding concentrations of new pollutants potentially posing a risk to the environment and human health (Carvalho et al., 2015). The emerging pollutants include pharmaceuticals, personal care products, artificial sweeteners and endocrine disruptors (Fairbairn et al., 2015; Vezzano et al., 2017). Figure 7 gives an overview of the types of pollutants potentially coming from a specific source. The main pathways of pollutants from the source to the receiving water body are also included.



**FIGURE 7. Schematic representation of sources, pathways and related pollutants contaminating the water courses in Denmark. Abbreviations: BOD5= 5-day biological oxygen demand, COD=chemical oxygen demand, GW=groundwater, XOCs=xenobiotic organic compounds, PAHs=polycyclic aromatic hydrocarbons, PCBs=polychlorinated biphenyls.**

### 4.2.1 Contaminated sites

There are many pollutants related to contaminated sites: in Denmark there are more than 35,000 documented contaminated sites, which taken together comprise a very large number of different chemical compounds and their metabolites. The contaminants found at the sites will of course depend on the specific contaminated site.

Landfills for example, have a very heterogeneous contamination, from general pollutants such as inorganic ions, non-volatile organic carbon (NVOC) and ammonium (NH<sub>4</sub><sup>+</sup>) to xenobiotic organic compounds and emerging pollutants such as pesticides, dioxins and pharmaceuticals (Miljøstyrelsen, 2014; Milosevic et al., 2012; Sonne et al., 2017; Thomsen et al., 2012). Landfills are the second major cause of soil and groundwater pollution in Denmark, accounting for approximately 2150 sites where the guideline value for at least one compound has been exceeded and therefore the site was listed at knowledge level 2 (established contamination) (Miljøstyrelsen, 2014).

On the other hand, contaminated sites such as gasoline stations or dry cleaner facilities comprise another major category of specific pollutants, respectively BTEXs and chlorinated solvents. Overall, there are 2491 documented gasoline stations and 917 dry cleaning facilities causing soil and groundwater contamination in Denmark (DKJORD, 2012).

Pesticide point sources are also receiving more attention in recent years. Herbicides such as phenoxy acids, chloridazon and their degradation products were found contaminating soil and groundwater due to the presence of leaching machine pools, market gardens or tanks containing elevated concentrations of pesticides (Miljøstyrelsen, 2013; Reitzel et al., 2004). In Syddanmark, machine pools were among various point sources suggested as the most pronounced point source for chloridazon and its degradation products (Miljø og Ressourcer, 2016).

In this project, only sites contaminated by chlorinated compounds have been investigated, recognizing that this is just a small part of the great number of sites potentially able to contaminate nearby streams through groundwater discharge.

### 4.2.2 Combined sewer overflows, separate stormwater systems and wastewater effluents

Combined sewer overflows are discharging a mixture of wastewater and stormwater to the streams. In CSOs, pollutants can be found in the dissolved phase, such as ammonium, or bound to particulates (colloids; sediment), typical for pollutants with a high tendency to sorb (PAHs, heavy metals). In the combined systems, the stormwater acts as a dilutor, decreasing the concentrations of most of the pollutants (except for some heavy metals and PAHs). As the CSOs are produced by the overflows of combined systems, the chemical composition and pollutants present are a combination of urban wastewater and stormwater, and can therefore include ammonium, phosphorus, organic matter and/or heavy metals. Among the XOCs, the same pollutants found in separate stormwater systems (described below) are expected, together with emerging pollutants such as personal care products, antibiotics and pharmaceuticals (such as ibuprofen).

Separate stormwater systems can decrease the volume going through wastewater treatment plants, thereby reducing the possibility for (combined) sewer overflows. However, only part of it is treated before entering the streams. Separate partly treated or untreated stormwater coming from roofs, highways, roads and gardens can also be collected and discharged directly into the streams, potentially posing a higher risk compared to actual wastewater discharges (Eriksson et al., 2006; Wicke et al., 2014). Moreover, the disconnection of stormwater runoff from combined urban drainage systems results in greater volumes of untreated water discharging to the streams (Vezzaro et al., 2017). A study conducted in the city of Berlin conclud-

ed that the larger fraction of priority pollutants discharging into surface water bodies comes from the stormwater systems rather than the treated wastewater discharges (Wicke et al., 2014). The pollution loads in the separate systems are highly variable, as they depend on which type of water is being collected (lower pollution areas such as parks and roofs, or higher pollution areas such as highways or roads). XOCs such as PAHs, pesticides, plasticizers and biocides (used in wood protection products and paints) are also frequently found in stormwater systems. PCBs are also within the wide range of different substances that can be found in stormwater discharges (Bollmann et al., 2014; Eriksson et al., 2006; Vezzaro et al., 2017). Among the general pollutants, heavy metals such as Cd, Cr, Cu, Pb and Zn are frequently found in stormwater.

The chemical composition and pollutant load found in wastewater discharges also depends on different aspects: first of all, the types of industrial discharges connected to the wastewater treatment plant. Secondly, wastewater characteristics such as the system capacity and the different treatment steps available could lead to a highly variable composition of the water discharged. In general, when medium to heavy rains occur and the overall system is combined, the high hydraulic load would decrease the removal performance of the plant, increasing the number of pollutants discharged to the stream (Vezzaro et al., 2017).

### **4.2.3 Agriculture activities and aquaculture**

Agricultural areas are another well-known source of contamination for freshwater ecosystems. Pesticides are a major stressor related to this type of land use due to their negative effects on macroinvertebrates and therefore on the overall ecosystem biodiversity (Bunzel et al., 2014; Liess and Von Der Ohe, 2005; Schäfer et al., 2016). Pesticides include herbicides, fungicides, insecticides and plant growth regulators. Another major type of pollution coming from agricultural fields includes macro- and micro-nutrients derived from fertilizers (Hansen et al., 2011). Both pesticides and fertilizers can be transported into the watercourse via atmospheric transport and deposition, surface runoff, drains or groundwater. Multiple pathways lead to difficulties in deciding the points where monitoring and subsequently remediation should be performed, in addition to difficulties in understanding the mass flow from a specific agricultural field.

The presence of aquaculture discharges could also potentially impact stream water quality and lead to adverse effects on ecosystems. Two main categories of pollutants have an important role with respect to aquaculture: nutrients and pharmaceuticals. Aquacultural production could increase the concentrations of macro-nutrients (such as nitrogen and phosphorus) that can lead to the eutrophication of water bodies (Zhang et al., 2015). Pharmaceuticals are also used in fishery production as antibacterial agents to avoid the spreading of infections and increase stocking densities. Antibiotics could migrate in different environmental matrices close to the aquaculture systems, affecting the aquatic environment (Zheng et al., 2012). The most commonly used antibiotics are sulfadiazine, oxolinic acid, oxytetracycline, amoxicillin and florfenicol (Pedersen et al., 2004). In a more recent study, Sonne et al. (2017) found sulfamethiazole, sulfathiazole and sulfadiazine downstream from two fish farms in Grindsted Å.

# 5. Development of a decision support tool

The current chapter describes the methodological approach built for the purpose of dealing with contaminated sites impacting stream water quality under conditions of multiple stressors. The integrative approach was designed to help the Danish authorities and the Regions in identifying the real stream contamination drivers in a multiple stressor context. This new decision support tool was then applied to the three study cases that will be described in Chapter 6.

## 5.1 Description of the methodology

The overall integrated assessment methodology is shown in Figure 8. The approach is divided into three sections: *Desktop Screening*, *Impact Assessment* and *Assessment Support*. The methodology deals only with steps described inside the black, dashed line. The management of contaminated sites posing a risk towards surface water is still under consideration as part of the implementation of the EU Water Framework Directive. Thus, any final decisions and further handling (investigation and remediation) of the sites will not be discussed in this report, which may depend on additional factors not directly related to the chemical stressors investigated here.

### 5.1.1 Desktop Screening

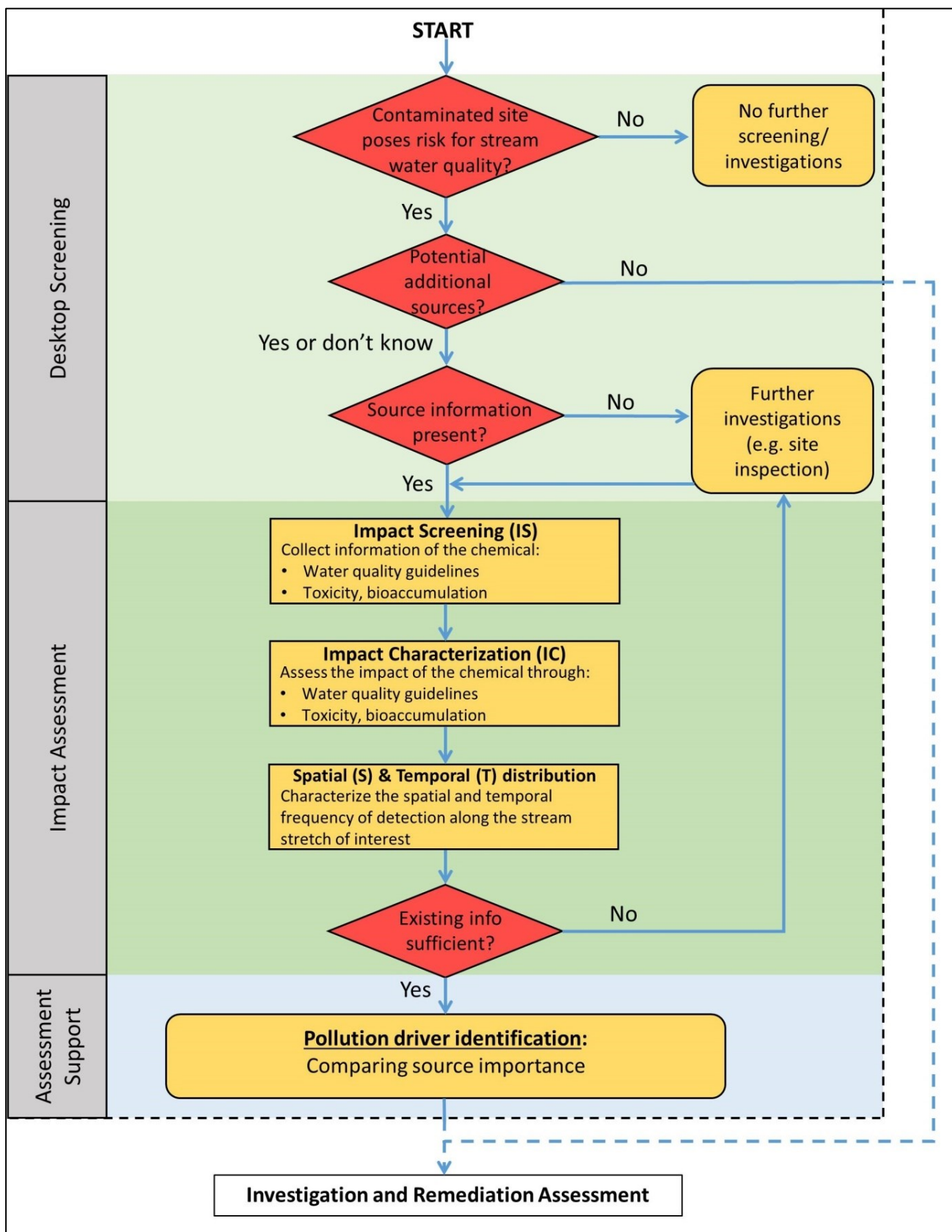
The purpose of the *Desktop Screening* is to obtain information regarding potential pollution sources along the stream section of interest. As already pointed out in Chapter 1, the initial condition to start this investigation is the presence of a site contaminated by chlorinated ethenes impacting or potentially impacting a nearby watercourse. Therefore, this is the first information to acquire in the proposed integrated approach. This is currently done by the Danish Regions by use of a screening tool and is expected to be followed by additional investigations, which is outside the scope of this report.

In the case that a contaminated site is polluting a nearby stream, the presence of potential additional sources needs to be investigated. This is accomplished by using databases such as MiljøGIS, MiljøPortalen and the Jupiter database maintained by the Geological Survey of Greenland and Denmark (GEUS). In this manner, information about discharge point locations, land use patterns, contaminated groundwater and potential additional useful information regarding the stream of interest (hydromorphology, stream type, ecological conditions, etc.) can be collected.

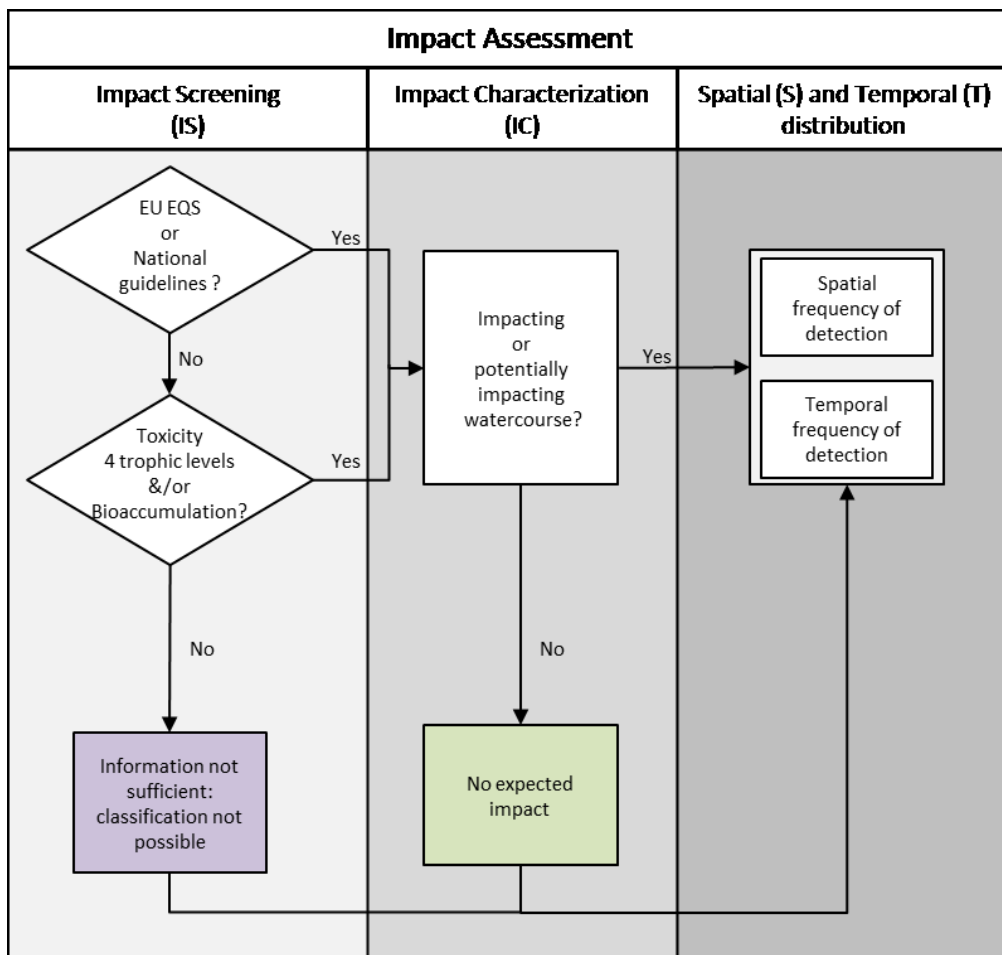
If no other sources of contamination are found, the contaminated site has to be assessed individually (see dashed blue line in Fig. 8). If additional sources are present or could potentially be present, data regarding contaminant mass discharges or chemical concentrations found in the stream should be acquired through a literature review (i.e. by looking for example to site-specific past investigations), via the previously mentioned databases (collecting useful information) or directly acquiring new data through field measurements.

### 5.1.2 Impact Assessment

The *Impact Assessment* is based on the desktop screening. This is divided into three different steps: Impact Screening (IS), Impact Characterization (IC) and finally Spatial (S) and Temporal (T) distribution. Figure 9 presents the flow diagram focused only on this part of the methodological approach. This three-step assessment is applied to each single chemical detected in the stream.



**FIGURE 8.** Schematic representation of the methodological approach proposed to evaluate the impact of contaminated sites to stream water quality under the condition of multiple stressors. Everything outside the black dashed line is not covered in the current report.



**FIGURE 9. Flow diagram for identifying the *Impact Assessment* of single compounds. The flow diagram has to be read from left to right.**

### ***Impact Screening (IS)***

The IS step collects information regarding fate and effects of chemicals in freshwater systems. First, National or EU EQS values for the chemicals of interest are collected. Then, in order to additionally take into account the ecological effects of chemicals not regulated by Environmental Quality Standards, ecotoxicity and bioaccumulation data has to be collected. Ecotoxicity is represented by the lethal dose (mortality) killing 50% of the organisms, LC50, or median effective concentration of 50% growth inhibition, EC50, of four aquatic bioindicator categories: fish, crustaceans, algae and plants. The potential for bioaccumulation was estimated from two different indices reported in the literature: the octanol-water partition coefficient ( $K_{ow}$ ) and the bioconcentration factor (BCF).

If insufficient data are available, the Impact Characterization (IC) is not possible (purple box in Figure 9) and the assessment moves directly to the third step, evaluating only the spatial and temporal distribution of the chemical in the stream.

### ***Impact Characterization (IC)***

Focusing now on the Impact Characterization, Table 6 shows the different groups in which the chemicals of interest can fall. Each group is defined in bold and identified by a color. Table 6 also shows the cut-off values assigned to each group.

**TABLE 6. Impact Characterization (IC) groups and cut-off values used.**

Impact Characterization (IC)				
<b>1</b>	<b>Impact to the watercourse even with high dilution</b> If C > Maximum Allowable Concentration (MAC) EQS			
<b>2</b>	<b>Impact to the watercourse during low flow conditions</b> If C > Annual Average (AA) EQS			
<b>3</b>	<b>Potential impact to the watercourse</b> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top;"> <i>Aquatic Toxicity</i>                      a. 96h LC50 (fish) ≤ 10 mg/l                      b. 48 h LC/EC50 (crustacean) ≤ 10 mg/l                      c. 72/96h ErC50 (Algae) ≤ 10 mg/l                      d. 72/96h ErC50 (Plant) ≤ 10 mg/l                 </td> <td style="width: 10%; text-align: center; vertical-align: middle;"><i>&amp; / Or</i></td> <td style="width: 40%; vertical-align: top;"> <i>Bioaccumulation</i>                      a. log Kow ≥ 3                      b. BCF ≥ 100                 </td> </tr> </table>	<i>Aquatic Toxicity</i> a. 96h LC50 (fish) ≤ 10 mg/l b. 48 h LC/EC50 (crustacean) ≤ 10 mg/l c. 72/96h ErC50 (Algae) ≤ 10 mg/l d. 72/96h ErC50 (Plant) ≤ 10 mg/l	<i>&amp; / Or</i>	<i>Bioaccumulation</i> a. log Kow ≥ 3 b. BCF ≥ 100
<i>Aquatic Toxicity</i> a. 96h LC50 (fish) ≤ 10 mg/l b. 48 h LC/EC50 (crustacean) ≤ 10 mg/l c. 72/96h ErC50 (Algae) ≤ 10 mg/l d. 72/96h ErC50 (Plant) ≤ 10 mg/l	<i>&amp; / Or</i>	<i>Bioaccumulation</i> a. log Kow ≥ 3 b. BCF ≥ 100		
<b>4</b>	<b>No expected impact</b> In all the rest of the cases			

The IC divides the chemicals into four groups:

1. Impact to the watercourse even with high dilution (red compound): the concentration of the chemical exceeds the MAC EQS in at least one investigated point of the stream stretch of interest. In this case concentrations are so high that they are expected to impact the watercourse in the majority of the cases, even during high flow conditions.
2. Impact to the watercourse during low flow conditions (orange compound): the concentration of the chemical exceeds the AA EQS in at least one investigated point of the stream stretch of interest. This condition is less alarming than the previous case.
3. Potential impact to the watercourse (yellow compound): if EQS values are not defined, the chemical is potentially impacting the stream stretch of interest if the short-term toxicity assessed from results of standardized tests of at least one of the four aquatic indicator species is above the benchmark value of 10 mg/l. A chemical is considered also potentially impacting the watercourse if they are characterized by medium to high potential for bioaccumulation ( $\log K_{ow} \geq 3$  or  $BCF \geq 100$ ).
4. No expected impact (green compound): if the chemical is below the EQS values or below cut-off values of aquatic toxicity and bioaccumulation as described in point 3.

### ***Spatial (S) and Temporal (T) distribution***

The Spatial (S) and Temporal (T) distribution in turn divide the chemicals into three groups each.

The S distribution is evaluated through the groups shown in Table 7:

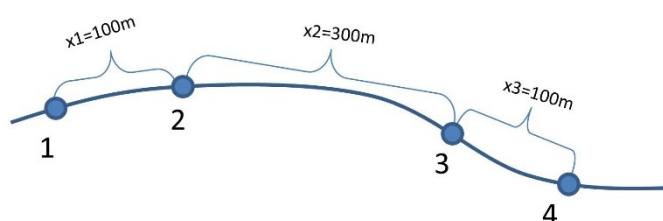
1. Widespread contamination (dark grey): if the chemical is found in more than 50% of the stream stretch of interest. This condition is true if the majority of the investigated points were contaminated by the chemical of interest.
2. Semi-widespread contamination (grey): If the pollutant is found in a portion between 10% and 50% of the stream stretch of interest.

- Limited contamination (light grey): if the pollutant is found in less than 10% of the stream stretch of interest. This condition is true only if among the investigated points only few were contaminated by the chemical of interest.

A practical example of how the percentage of the chemical's spatial distribution is determined is described below and shown in Box 1:

- Calculate the distances between the sampling points.
- If a pollutant is found in hypothetical point 1, the stretch of the vandområde influenced by that contaminant is half of the stretch between point 1 and the next sampling location, point 2. If the pollutant is also found in point 2, the stretch influenced by the pollutant in point 2 is calculated as the remaining part between point 1 and 2 plus half of the stretch between point 2 and the next sampling location, point 3.
- Finally, if the pollutant is found only in point 1 and 2, the percentage of vandområde influenced by the chemical of interest is calculated as the ratio between the sum of the two stretches and the total length of the vandområde of interest.

### Box 1



- 3 chemicals detected in the vandområde (delimited by the sampling points 1 and 4): C1, C2, C3
- C1 is found in the sampling points 1 and 2
- Spatial distribution (%) of C1 =  $\left(\frac{x_1 + \frac{x_2}{2}}{x_1 + x_2 + x_3}\right) * 100 = \left(\frac{100 + \frac{300}{2}}{100 + 300 + 100}\right) * 100 = 50\%$

The proposed method is dependent on the number of samples taken along the stream stretch of interest. More sampling points will lead to a better evaluation of the spatial distribution, as the distances between the sampling points will be shorter and the calculation of the percentage will be less approximate.

The spatial distribution as it was described above is adequate for xenobiotic organic compounds, i.e. chemical substances not naturally produced or expected to be present in the environment. In order to potentially consider also inorganic pollutants (such as heavy metals), the concentrations of inorganic compounds found in the sampling points are used in the calculation described above only if the measured concentration is above the 90% quantile found in Danish streams, as discussed in Sonne et al. (2017). The 90% quantile is a useful cut-off point that can be applied to see if the concentration found in one point falls within the range of values usually found in Danish streams (and if so, then it doesn't need to be considered in the spatial distribution calculation).



**TABLE 7. Spatial (S) distribution groups and cut-off values used.**

Spatial Distribution (S)	
<b>1</b>	<b>Widespread contamination</b> If pollutant found in > 50% of the stream stretch
<b>2</b>	<b>Semi-widespread contamination</b> If pollutant found in a portion between 10% and 50% of the stream stretch
<b>3</b>	<b>Limited contamination</b> If pollutant found in < 10% of the stream stretch of interest

The last parameter used for the evaluation of the impact of multiple stressors in streams is the Temporal (T) distribution. This parameter characterizes the temporal variation of the chemicals of interest in the water body. Moreover, addressing the occurrence of the chemicals is a key factor useful in forecasting the moment of the year with the highest and lowest concentrations. This could be beneficial for deciding when to acquire additional data through field investigations or deciding the timing for remedial efforts.

Similar to the S distribution, the Temporal (T) distribution is evaluated through the groups shown in Table 8, which are then described in more detail below.

**TABLE 8. Temporal (T) distribution groups.**

Temporal Distribution (T)	
<b>1</b>	<b>Continuous contamination</b> If pollutant released in the watercourse with no interruptions
<b>2</b>	<b>Semi-continuous contamination</b> If pollutant released depending on the season
<b>3</b>	<b>Pulse contamination</b> If pollutant released depending on the rain event

1. Continuous contamination: if the pollutant is released in the watercourse with no interruptions. This is the typical case of chemicals coming from contaminated sites, which are continuously discharged into nearby streams due to the presence of groundwater-surface water contact zones. If the contamination is continuous, the contaminant mass approach can be applied to calculate the total groundwater contaminant mass per unit of time discharging into the stream (CMD) (Milosevic et al., 2012; Rønde et al., 2017). In this case, a simple mass balance and plug flow is used to estimate the CMD:

$$CMD \left( \frac{kg}{year} \right) = C_{mix} \cdot Q_{mix}$$

Where  $C_{mix}$  and  $Q_{mix}$  are respectively the stream water concentration and flow at the point of fully mixed conditions (Aisopou et al., 2015; Sonne et al., 2017). For this project, three classes were used to classify the magnitude of the pollution load discharging into the stream (Table 9). This approach is similar to the concepts reported in Newell et al. (2011). The magnitude of Mag1-Mag3 categories is representative for known CMD's from

contaminated sites in Denmark (e.g. Miljøstyrelsen, 2016a; Rønne et al., 2017; Troldborg et al., 2012).

**TABLE 9. Contaminant mass discharge (CMD) magnitude classification applied in the current project.**

Magnitude Category	CMD (kg/year)
Mag 1	< 1
Mag 2	1 to 10
Mag 3	> 10

2. Semi-continuous contamination: if the pollutant is released depending on the season. Contaminants discharging into the stream could be higher in a specific part of the year, while being almost irrelevant at other times of the year (independently from the stream water discharge). This case can be associated with pesticides coming from agricultural lands, for example, as the highest concentrations are usually detected after rain events during the spraying seasons (Rasmussen et al., 2013). This can be identified by using event-triggered sampling campaigns as described by McKnight et al. (2012).
3. Pulse contamination: if the pollutant is released depending on the rain event. Chemicals associated with urban settlements, such as PAHs, emerging pollutants or biocides, could fall into this category as they can be discharged into the stream through separate storm water systems or CSOs after rain events. Detecting these compounds requires high intensity sampling schemes or flow proportional sampling schemes, as described by Vezzaro et al. (2017).

The three categories briefly described above have the same color as it is not possible to classify which of the mentioned temporal distributions reflects the worst condition for the stream. Continuous contaminations are expected to cause a chronic impact to the stream, as they impact the receiving water body over a long time period (months or years). However, concentrations can be low. On the other hand, intermittent pulses of contamination are recognized to be impacting in the short term period, due to the magnitude of stormwater pollutant loads (Gasperi et al., 2012).

### 5.1.3 Assessment Support

The *Assessment Support* helps the regulator to make a decision on which category of pollutant (and source) may be driving the stream's contamination in conditions of multiple stressors. Thus, in this final step, the information gained in the *Impact Assessment* is presented and the expected or known source(s) is reported.

Table 10 shows an example of how the *Assessment Support* could be visualized, considering that each study case will be different in terms of category of pollutants, compounds and expected or known sources. The column "Expected or known sources" is based on the potential sources of stream water contamination shown in Figure 2, Chapter 1.

**TABLE 10. Example of how the *Assessment Support* can be visualized.**

	Compounds	Expected or known sources	IC	S	T
Category of pollutant 1	Compound 1	Source 1 Description			Continuous (CMD calculation)
	Compound 2				Continuous (CMD calculation)
	Compound 3				Continuous (CMD calculation)
Category of pollutant 2	Compound 4	Source 2 Description			Semi-continuous/Pulse
	Compound 5				Pulse
	Compound 6				Pulse

The assessment is aimed at end-users at the regulatory level. However, once the sources driving the contamination of the stream are defined, the prioritization of remedial actions will depend on the national strategy to manage surface water contamination.

## 6. Refined screening of existing contaminated sites

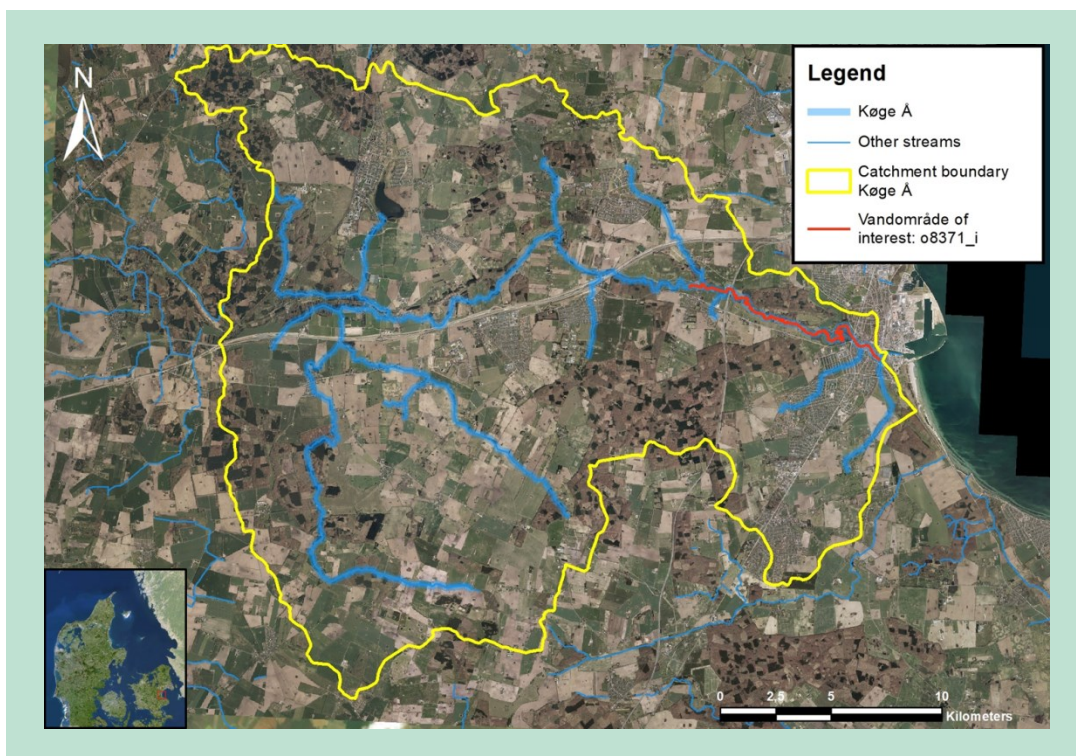
The streams initially described in Chapter 2 need to be investigated in more detail to understand if, besides a contaminated site, other pollution sources are potentially causing water impairment. The current chapter describes the refined screening performed for three of the eight cases, specifically: Køge Å, Skensved Å and Kirke Å.

The choice between the eight cases was based on different factors. First, all three chosen “vandområder” have a *poor-to-bad* ecological status, indicating already a degraded biological condition of the streams. The remaining streams initially taken into account have at least a *moderate* ecological status. Moreover, the stream stretches of Køge Å and Skensved Å are very close to each other, although representing different land uses conditions: Køge Å passes through the urban area of Køge, which indicates the potential presence of urban pollution sources. Skensved Å, on the other hand, is surrounded by agricultural fields. Kirke Å was chosen as it is located in the western part of Denmark (Region Midtjylland) where multiple sources could act together. The ecological status of the stream is also the worst among the eight cases initially selected. Finally, these three cases were chosen in order to consider different geological settings. The geology of the southwest part of Denmark is dominated by coarse-grained glacial outwash deposits from the large glaciation of Denmark. On the other hand, the region of Sjælland is dominated by low permeability soils of clayey tills formed due to glacial deposits often containing fractures and sand lenses (Kessler et al., 2012; Pedersen et al., 2011).

### 6.1 Køge Å

Køge Å is a stream classified as type 2 located in the Region of Sjælland, having a length of 20,6 km and an average width of 10 m. The catchment area of Køge Å is 181,68 km<sup>2</sup> and all the collected water of the basin drains into the Bay of Køge, located 40 km south of Copenhagen, before flowing into the Baltic Sea. Since Køge Å flows directly into the sea, it is affected by the tides, which contribute to the rise and fall of the stream flow depending on the time of the day. Figure 10 shows Køge Å stream, including the focus area (red line), and the catchment boundary.

Previous investigations will be described first, before giving an overview on the potential point and diffuse sources of pollution for Køge Å that could aggravate the chemical and ecological conditions of the stream



**FIGURE 10.** Overview of Køge Å, including tributaries (blue line), and the focus area defined in the map as Vandområde Køge Å o8371\_i (red line). The area inside the yellow line represents the catchment for Køge Å.

### 6.1.1 Results from previous studies in Køge Å

The assessment covers only the stream stretch of interest (red line in Fig. 10), where in previous investigations chlorinated compounds were found exceeding the AA EQS.

The overall ecological status of this water area is defined as *poor*, indicating already a stream impacted by anthropogenic activities (Table 11) and far from the objective of obtaining a good ecological status. The DSFI and DFISa reveal a *moderate* status of the macroinvertebrate and fish community in the stream, but the plant status was reported as *poor*. No information regarding the benthic algae has been obtained yet.

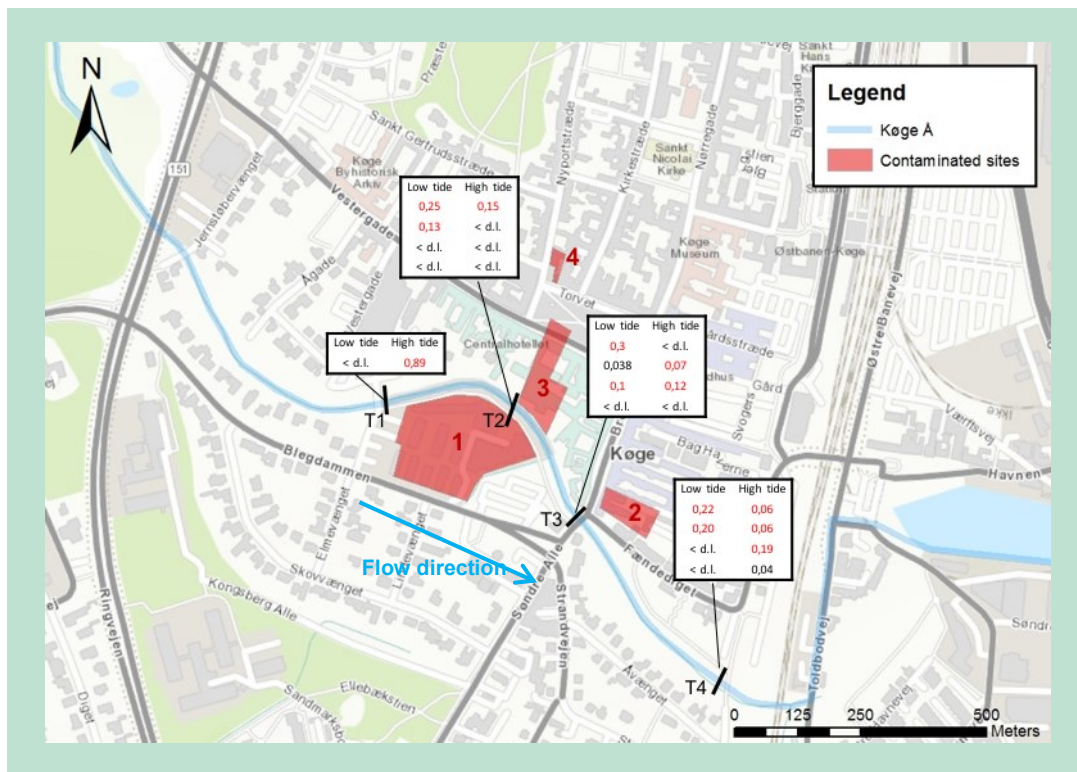
**TABLE 11.** The four ecological indices for Køge Å section o8371\_i which together form the overall ecological status.

	Benthic invertebrates	Fish	Plants	Benthic algae	<i>Overall</i>
Køge Å o8371_i	Moderate	Moderate	Poor	Not Known	Poor

The general chemical conditions in the stream have not been assessed in the past; therefore, no information regarding ammonium, nutrients, dissolved oxygen, as well as BOD<sub>5</sub> is available.

Regarding the XOCs, different investigations have been made previously within the city of Køge due to the presence of four contaminated sites close to the harbor polluting the soil and the upper groundwater aquifer. The locations of the contaminated sites are shown in Figure 11. The screening tool used by the EPA characterized these sites as potentially causing stream water contamination due to the close proximity between the contaminated site and the stream. Therefore, groundwater and stream water samples have been collected in recent

years to detect possible interactions between stream water and groundwater. A field campaign in 2004 showed concentrations up to 8800 µg/l and 60 µg/l for PCE and VC, respectively, in the groundwater beneath hotspot 4, while in the latest campaign of 2015, a PCE concentration of 19,000 µg/l was measured beneath hotspot 3. It was not possible to define the exact groundwater flow direction of the upper contaminated aquifer based on available data.



**FIGURE 11. Locations of the four identified contaminated sites polluting Køge Å and the concentrations (µg/l) of vinyl chloride (VC) found in the stream during high tide and low tide for the different transects (T1-T4) (results taken from Miljøstyrelsen, 2016a). <d.l. means below detection limit, which is 0,020 µg/l for VC. The red numbers indicate the points where concentrations were detected higher than the AA EQS of 0,05 µg/l.**

Stream water samples were also collected from Køge Å to investigate if concentrations were above the EQS. The samples were taken both in low tide and high tide conditions, and the results can be seen in Figure 11 for VC. Each box represents the concentrations found in the stream during low tide (first column) and high tide (second column). Each row represents the concentrations found in the investigated points of the transect, from the left bank (first row) to the right bank (last row) in accordance with the flow direction. Overall, concentrations of VC were exceeding the AA EQS during both low tide and high tide in more than one sampling point. Concentrations of TCE, PCE and cis-DCE were also found exceeding their respective freshwater AA EQS (complete results shown in Appendix A). During low tide, the highest concentration of VC was detected in transect T3 close to the left bank. During high tide, the contamination is pushed further upstream: VC in transect T1 (sampled in the middle of the stream) was found exceeding the stream water quality criteria by a factor of 17,8.

Due to the tides, the accessibility conditions and the water depth it was not possible to place piezometers and define the locations of the contact zones. However, the concentrations in the stream are assumed nevertheless to be caused by polluted groundwater partly discharging in the river through contact zones not clearly defined. Moreover, it was not possible to understand which sites contributed the most to the contamination of Køge Å, as it is likely that the

pollution plumes overlap. However, the site-specific investigation revealed that the contribution of site 1 shown in Figure 11 was negligible, as the concentrations close to the right bank in transect T2 were found below detection limit.

### 6.1.2 Screening of other possible sources

This section characterizes and investigates potential pollution sources within the “vandområde” of interest. This screening approach helps to 1) locate and classify the different sources and 2) select among these the stressors that may have the largest impact on the nearby stream.

An overview of the land use in the area, shown in Fig. 12 gives a first insight of the potential sources present close to the stream section of interest. Upstream of the urban area containing the contaminated sites, the land is covered with agricultural fields, represented as yellow in the map below. Agriculture affects water quality mainly due to release of pesticides and nutrients. This diffuse source of contamination could enter the stream through numerous pathways, including the separate stormwater discharge points along the stream (purple circles in Figure 12) or via direct surface runoff or tile drain systems, as the agricultural fields were found to be located within just a few meters of the stream. The green area located north of Køge Å could act as a buffer zone reducing the run off and/or extent of spray drift of agricultural chemicals coming from the crops located to the north. Due to the specific periods of pesticide application, seasonal variations need to be taken into account when pollution loads are investigated.



**FIGURE 12. Identification of potential point and diffuse sources of pollution together with the land use pattern close to the stream stretch of interest.**

Close to the contaminated site, the urban pattern prevails. During wet weather, stormwater runoff discharges directly into the stream or into the harbor through underground or superficial drains. Moreover, during medium and large storms, sewer systems could overload and usually emergency outlets are built to prevent flooding in the city. After a first screening investigation using MiljøPortalen and MiljøGIS, it was possible to map the stormwater and CSO discharges

(yellow circles) along the stream stretch (Figure 12). The complete list of sources identified as relevant for this area of interest are given in Table 12.

No previous investigations on XOCs have been made in Køge Å, except for the chlorinated compounds and their degradation products related to the contaminated sites in Køge. After this initial screening, the next step is to define which categories of pollutants are the most important to investigate, in addition to characterizing and comparing sources acting differently in time and space.

**TABLE 12. List of sources, pathways and discharge points along Køge Å.**

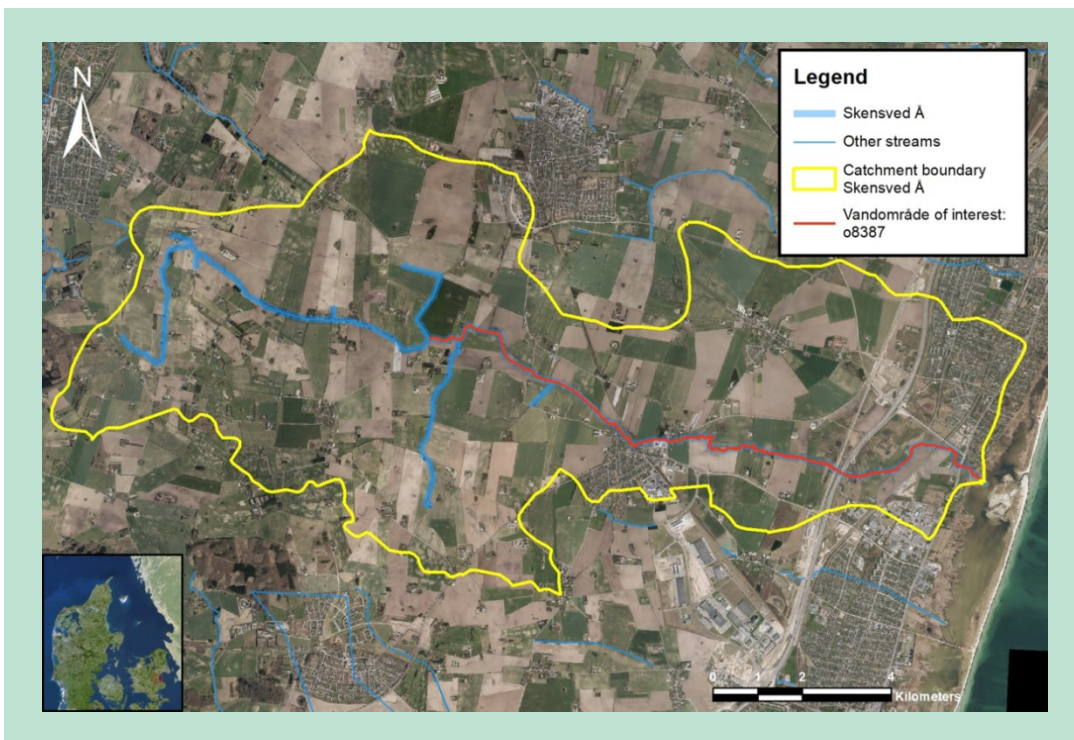
Source	Pathway	Discharge points
<i>Point sources</i>		
Contaminated sites	Groundwater	- (*)
Urban stormwater	Pipe outlets, direct discharge	24
CSOs	Pipe outlets, direct discharge	3
<i>Diffuse sources</i>		
Agricultural fields	Groundwater, surface run-off, drain systems	- (*)

(\*): Exact discharge location not identifiable.

## 6.2 Skensved Å

The second case selected is Skensved Å, also located in the Region of Sjælland (Figure 13). Skensved Å is only 6 km north of Køge Å. This gives the possibility to compare the land use pattern, distribution of sources and status within the same geographical region. The catchment area of Skensved Å is much smaller compared to Køge Å. It collects the water from ca. 38,5 km<sup>2</sup> of land and the boundary is shown in yellow in Figure 13. This stream flows past the town of Lille Skensved and also drains into the Bay of Køge. The mean water flow in Skensved Å was found to be 156 l/s, with large seasonal variations reported in the past investigations. In 2004, for example, the stream flow dropped from 1744 l/s in early February to 3,8 l/s in June (Christensen and Raun, 2005). The vandområde of interest is defined with the ID number o8387 and shown in red in Figure 13. The length of the stretch was reported to be 9,3 km, classified as Type 2 and not highly modified. Therefore, good ecological and chemical status is the objective to reach in order to follow the national environmental requirements.





**FIGURE 13.** Overview of Skensved Å (thick blue line), its catchment boundary (yellow line) and the stream stretch of interest (red line) defined as vandområde o8387.

### 6.2.1 Results from previous studies in Skensved Å

Skensved Å has been evaluated for the concentrations of general water quality parameters such as inorganic ions and nutrients, but also for XOCs, in particular chlorinated solvents and pesticides.

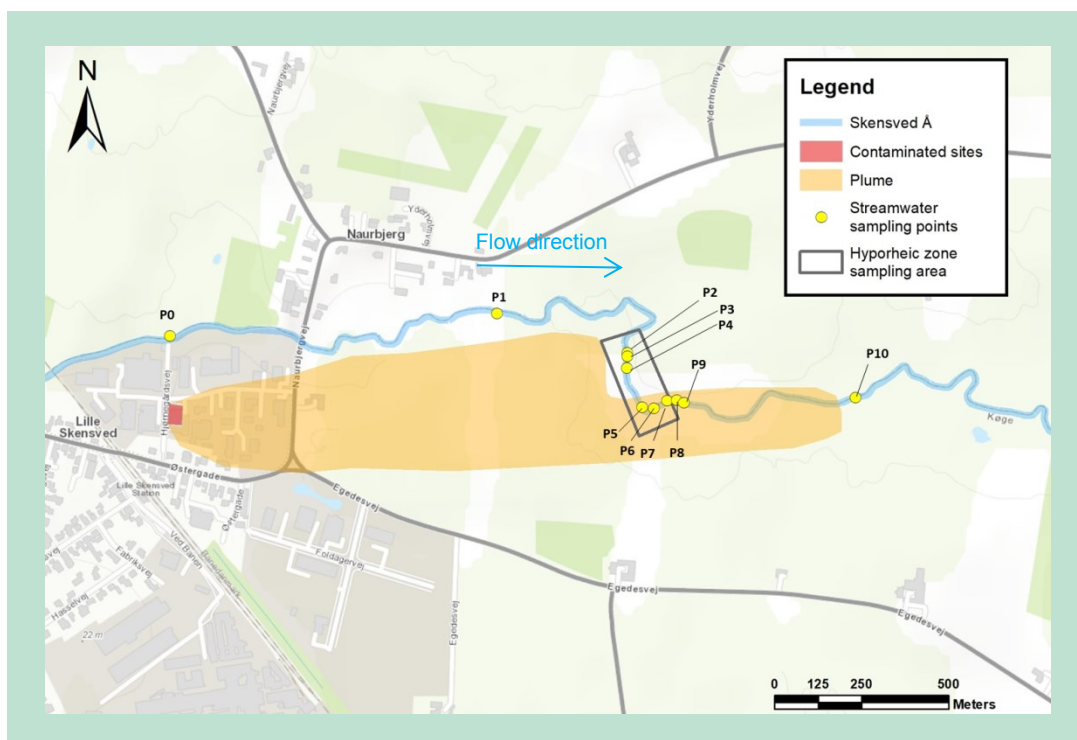
With respect to streams classified as Type 2, the overall ecological status is determined using the biological indices described in Chapter 3. According to the DSFI and DFSIa, the benthic macroinvertebrate and fish community were found to have a *good* and *poor* status respectively, while no information regarding plants and benthic algae has been obtained yet. Therefore, the overall ecological status is indicated as *poor*. Table 13 shows the indices defining the ecological conditions in Skensved Å.

**TABLE 13.** The four ecological indices for Skensved Å section o8387 which together form the overall ecological status.

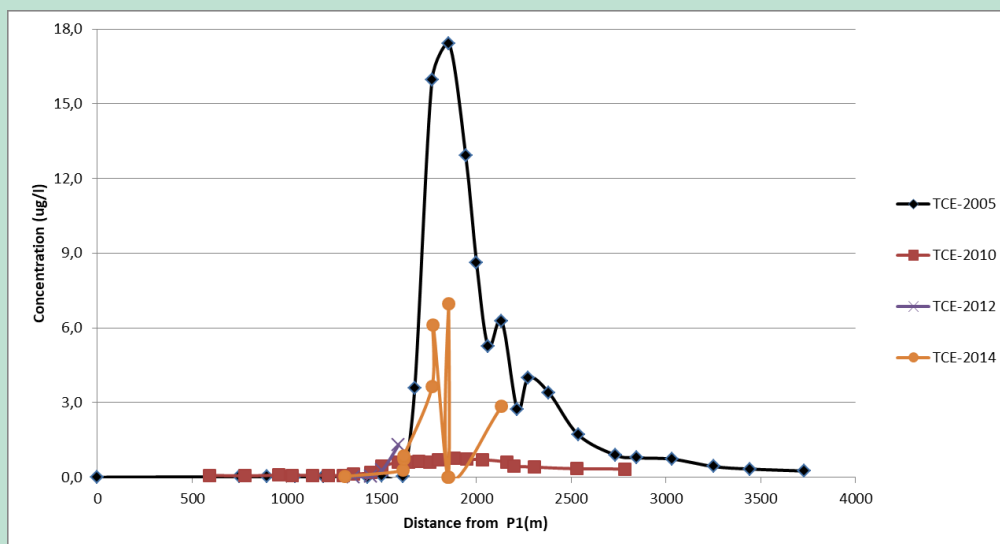
	Benthic invertebrates	Fish	Plants	Benthic Algae	<i>Overall</i>
Skensved Å o8387	Good	Poor	Not Known	Not Known	Poor

The stream has been investigated over the past 20 years due to the presence of a chlorinated solvents plume generated from a leaking tank located at a former auto lacquer shop, which had used these products to degrease metal components between 1974-1993 (Christensen and Raun, 2005). The plume extends up to 1000 m downstream (Figure 14), spreading in the upper aquifer before entering Skensved stream through different contact points in the streambed. Since the site is located in an area with protected drinking water interests, a remediation strategy of pump-and-treat has been implemented from 1999 to 2009. The hydraulic control of the plume reduced the amount of chlorinated solvents discharging in the stream. However, the containment action finished ca. 9 years ago, therefore the plume could potential-

ly begin spreading again raising the concentrations of chlorinated solvents in the stream. This effect has been investigated over the last few years in part through a monitoring campaign conducted by DTU Environment that showed an increase in TCE in the stream water. Figure 15 shows the concentrations from 2005 to 2014 (distance 0 refers to the point P0 shown in Figure 14). Concentrations decreased drastically from 2005 to 2010, but then the concentrations of TCE were elevated again in 2014, with concentrations up to ca. 7 µg/l found close in P8. Moreover, during the campaign of 2014, VC has been reported in P6 and P8 at concentrations of 0,041 and 0,048 µg/l, respectively (the complete results of the 2014 campaign can be found in Appendix B).



**FIGURE 14. Representation of the contaminated site location and plume, together with the sampling points of the stream water campaign in 2014 and the hyporheic zone area investigated by DTU Environment from 2012 to 2017.**



**FIGURE 15. Skensved stream water TCE concentrations for campaigns conducted in 2005 (dark blue line), 2010 (red line), 2012 (purple line) and 2014 (orange line); unpublished data courtesy of DTU Environment.**

Measurements of concentrations in the hyporheic zone can provide information about the discharge of pollutants into the stream, as the hyporheic zone is the interface between groundwater and stream water and these three compartments are well connected when contact zones are present. The hyporheic zone at this site was first investigated by Christensen and Raun (2005), and additional measurements have been done from 2012 by DTU Environment students. The latest results from 2017 show high concentrations of TCE detected in the piezometers with a depth between 20 and 40 cm. The sampling points located inside the dark grey rectangle in Figure 14 showed concentrations up to 42,4 µg/l. If the hyporheic zone concentrations are compared with the TCE EQS for surface water and groundwater, the detected concentrations were more than 4 and 40 times above the guideline value, respectively. The complete results of the hyporheic zone campaign in 2017, together with the sampling locations, are reported in Appendix C.

### 6.2.2 Screening of other possible sources

Other potential sources discharging in the stream stretch of interest can be initially investigated by looking at the land use pattern of the area. Figure 16 shows the land pattern characteristics for the area of interest. As it can be seen from the map and already reported by McKnight et al. (2012), agricultural fields prevail among the other land uses, accounting for more than 90% of the total catchment. This shows the possibility of having agricultural pesticides and nutrients as major potential pollutants for the stream water ecosystem along the entire stretch.

The GEUS Jupiter database provides a geographical information system with borehole information and groundwater monitoring analyses. In the area close to Skensved Å, groundwater is used for drinking water purposes and the analysis of the raw water from the groundwater treatment plants CP Kelco and Lille Skensved Vandværk (exact location in Figure 16) revealed the presence of pesticides in the aquifer. Table 14 lists the detected pesticides in the aquifer close to Skensved Å.



**FIGURE 16.** Representation of the land use pattern surrounding the stretch of interest at Skensved Å. Potential point sources of pollution and location of the water treatment plants where the presence of pesticides in the aquifer was revealed can also be seen.

**TABLE 14.** List of detected pesticides in the aquifer close to Skensved Å ( $\mu\text{g/l}$ ). Results were taken from the water analysis of the boreholes supplying the water treatment plants (location shown in Figure 16) close to the area of interest.

	2-4 dichlorphenol	Bentazone	Mechlorprop	BAM
Skensved vandværk Plant DGU nr. 104.598	- 0,08 (2017)	- 0,012 (2017) - 0,011 (2009)	- 0,011 (2009)	- 0,013 (1998)
CP Kelco Plant DGU nr.104.542	- 0,014 (2007) - 0,017 (2002)	- 0,012 (2017) - 0,037 (2010) - 0,02 (2007) - 0,045 (2002)		- 0,056 (2016) - 0,022 (2013) - 0,071 (2010) - 0,089 (2007) - 0,074 (2003)

McKnight et al. (2012) reported findings of pesticides in the stream water and applied the SPEcies At Risk (SPEAR) index for evaluating ecological status (Liess and Von Der Ohe, 2005). This index ( $\text{SPEAR}_{\text{pesticides}}$ ) indicated that Skensved stream is “far from obtaining good ecological status” as the scores showed a *poor* and a *poor-to-bad* ecological status before and after the spraying season (comparing March and August samples, respectively). By using the screening tool Toxic Units (TU), the results showed that the suspended sediments were contaminated by pesticides and the TU values obtained, ranging from -0,14 and -0,92, were far above the threshold of -3 (McKnight et al., 2012). Above this threshold, shifts in community composition of the benthic macroinvertebrates begin to occur (Liess et al., 2008).

Another source potentially impacting the water quality of Skensved Å is the presence of urban settlements and infrastructures in the surroundings. A town such as Lille Skensved and the highway E47 crossing the stream could release urban pollutants to Skensved Å, increasing the anthropogenic pressure on the stream.

Figure 16 shows the point source locations discharging in Skensved Å. Besides the contaminated site already described, CSOs (orange circles) and separate stormwater (purple circles) discharges are found along the entire stretch. No clear information regarding these point sources was available. Private discharges (green circles) are also present along Skensved Å. These pipes/open drains are not connected to the drainage system of the municipality and are typically coming from farms or isolated houses. Moreover, on the north side of the stream close to the contaminated site there is an industry, Pro-Glue A/S (light green square), providing adhesives for hygiene, food, brewing and pharmaceutical industries. The wastewater is discharged after treatment into Skensved Å, potentially increasing the pollutant loads.

Overall, the sources identified in the area of interest are listed in Table 15.

**TABLE 15. List of sources, pathways and number of discharge points at Skensved Å.**

Source	Pathway	Discharge points
<i>Point sources</i>		
Contaminated sites	Groundwater	- (*)
Urban stormwater	Pipe outlets, direct discharge	17
CSOs	Pipe outlets, direct discharge	3
Private discharges	Ditches/drains	5
Industrial discharges	Pipe outlets	1
<i>Diffuse sources</i>		
Agricultural fields	Groundwater, surface run-off, agricultural drains	- (**)

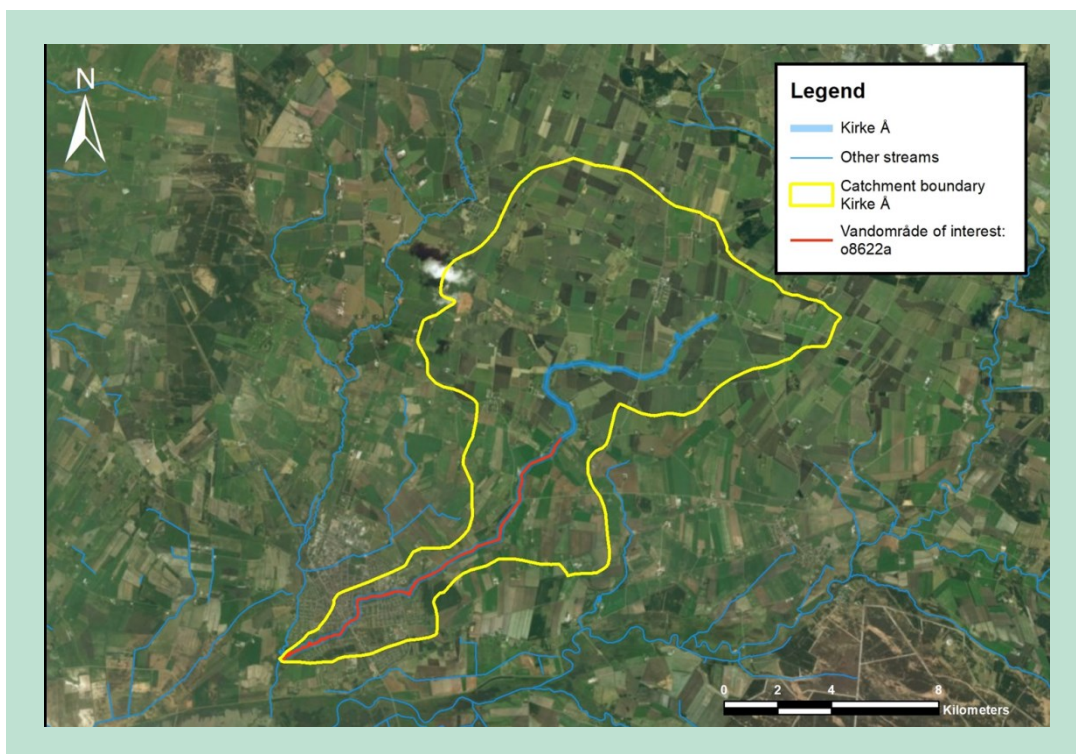
(\*): Discharge location between P4 and P10 in Figure 14.

(\*\*): Exact discharge location not identifiable.

### 6.3 Kirke Å

Kirke Å is located in the Region of Midtjylland and passes through the town of Skjern. The drainage basin of Kirke Å covers an area of approximately 43,15 km<sup>2</sup>, and connects to the larger basin of Ganer Å before flowing into Hestholm Sø.

The investigation of potential point and diffuse sources was again made only for the area of interest, shown in Figure 17, which contains the contaminated site described in Chapter 6.3.1. The extension of the considered vandområde is 8,5 km, represented by the red line in Figure 17. This part of Kirke Å is classified as type 2 with a width and depth of respectively 4 and 1 m (Lemaire, 2016). In October 2015, the average flow was reported as 370 l/s (Miljøstyrelsen, 2016a). Since Kirke Å is not classified as highly modified, it is required to achieve good ecological and chemical status in the stream.



**FIGURE 17. Overview of Kirke Å, its catchment area and the stream stretch of interest, defined as Vandområde o8622a.**

### 6.3.1 Results from previous studies in Kirke Å

Different investigations have been performed in Kirke Å over the past years, with the aim of investigating the biological and chemical condition of the stream.

The ecological status of this water area is defined as *bad*. This result was reached as the Danish Fish Index for Streams (DFIS) indicated a *bad* status. The DSFI is classified as *moderate*, indicating an ecological impact on the macroinvertebrate community. No information regarding the benthic algae and plant indexes have been recorded. Table 16 shows the information collected regarding the ecological status of Kirke Å.

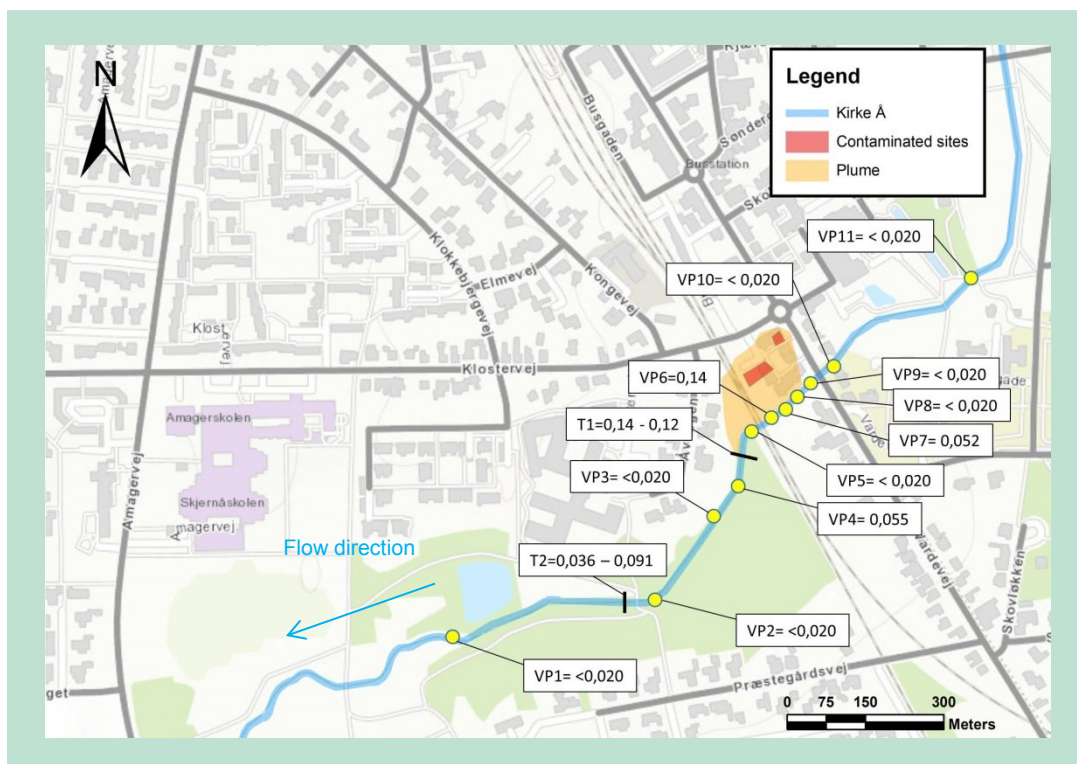
**TABLE 16. The four ecological indices for Kirke Å which together form the overall ecological status.**

	Benthic invertebrates	Fish	Plants	Benthic algae	<u>Overall</u>
Kirke Å o8622a	Moderate	Bad	Unknown	Unknown	Bad

The general chemical condition of the stream has not previously been assessed; therefore, no information regarding ammonium, nutrients, dissolved oxygen or BODs is available.

The previous investigations in Skjern have focused on the contaminated sites located north of the stream, shown in Figure 18. The sites include a former dry cleaning facility and a disposal site operating from 1939 to 1970 (Lemaire, 2016). The soil and the upper aquifer have been contaminated by chlorinated solvents, forming a plume discharging into Kirke Å. This was confirmed through a Distributed Temperature Sensing (DTS) analysis, a multi-point thermocouple-probe, in conjunction with the sampling of groundwater, stream water and hyporheic zone water. Figure 18 shows the concentrations (µg/l) of vinyl chloride found in the stream water in October 2015 (Miljøstyrelsen, 2016a). Concentrations were found above the limit of

0,05 µg/l also outside the mixing zone (10 \* width of the stream= 30-50 m). Some points close to the contaminated sites were found unpolluted (e.g. VP3 in Figure 18), while others much further downstream were found with concentrations of VC (transect T2 for example) above AA EQS. This is indicative for the high spatial variation common for the groundwater contaminated with CAHs entering surface water. PCE, TCE and DCE have also been analyzed in the stream water, however, concentrations were found below the detection limit of 0,020 µg/l in almost every investigated point.



**FIGURE 18. Representation of the contaminated sites and the plume polluting Kirke Å, together with the stream water concentrations for vinyl chloride (µg/l) detected during the Orbicon campaign in October 2015 (Miljøstyrelsen, 2016a). Abbreviations: VP=sampling point, T=transect.**

### 6.3.2 Screening of other possible sources

As already done for Køge Å and Skensved Å, the first step of the screening is to study the land use pattern in the area where Kirke Å flows. Since the project refers to the vandområder defined by the Ministry of Environment and Food, the analysis will focus on the stretch represented in Figure 17 in red. However, as Kirke Å is a sub-catchment within the larger catchment of Ganer Å, to identify the upstream and downstream boundary conditions, the potential sources before and after the vandområde of interest will also be shown.

Figure 19 shows the land use cover close to Kirke Å. The contaminated site is located in the town of Skjern, represented as grey in the map. However, similar to Køge's pattern, in the upper part of the vandområde the land is primarily used for agricultural activities (yellow pattern in the map). Pesticides and nutrients could discharge into the stream due to direct surface runoff, through tile drains and/or separate stormwater discharges and via the groundwater-surface water interface. On the contrary, the downgradient section of the vandområde is dominated by streets and buildings that could potentially pollute the stream with urban contaminants such as biocides, PAHs or heavy metals.

Figure 19 shows also the potential point sources affecting the stream together with the contaminated site described in chapter 6.3.1.



**FIGURE 19.** Land use pattern close to Kirke Å and potential point sources of contamination discharging into Kirke Å, including the contaminated sites, CSOs, stormwater, industrial and former wastewater discharges.

No investigations on XOCs have been made in Kirke Å, besides the chlorinated compounds and their degradation products related to the contaminated sites in Skjern.

Inside the vandområde, there are 32 separate stormwater drains discharging in the stream. Almost all the drains are collecting the water from streets. Moreover, a CSO discharge is also present upstream of the contaminated sites. No information regarding the overflow frequency or the chemical status of this outlet could be found.

After the confluence with Ganer Å, that runs from north to south, the wastewater discharge point coming from Skjern PapirFabrik A/S (green square in Figure 19) flows into the stream. This factory produces different kinds of paper products (coreboard, greyliner, sheets, grey-board) from recycled wastepaper. However, it seems that the wastewater coming from this industry is connected to the public wastewater treatment plant of Tarm, without discharging directly into Kirke Å stream (information about discharge couldn't be found on Miljøportalen). Furthermore, downstream from the vandområde there is also a drain that was discharging the wastewater from a no longer active treatment plant (red triangle in Figure 19).

Overall, the sources identified in the area of interest are listed in Table 17.



**TABLE 17. List of sources, pathways and number of discharge points at Kirke Å.**

Source	Pathway	Discharge points
<i>Point sources</i>		
Contaminated sites	Groundwater	- (*)
Urban Stormwater	Pipe outlets, direct discharge	32
CSOs	Pipe outlets, direct discharge	1
<i>Diffuse sources</i>		
Agricultural fields	Groundwater, surface run-off, agricultural drains	- (**)

(\*): Discharge location between VP9 and T1 in Figure 18.

(\*\*): Exact discharge location not identifiable.

# 7. Investigation approach and methods

In this section, the field plan and methods will be described in detail as they have been applied to two of the three case study sites (results presented in Chapter 8). The information collected from previous investigations and through the initial screening of the sites of interest helped in the planning of the field activities. Only two of the three streams (Køge Å and Skensved Å) were selected for further investigation through a field campaign, a decision reached for a number of reasons. Firstly, Køge Å and Skensved Å are in the same general geographic region and therefore close to each other. This helped in carrying out the field investigation, reducing the costs incurred due to e.g. transportation. More importantly, these two streams represent different land-use scenarios, as Skensved's landscape is characterized predominantly by agricultural activities while Køge Å is located in a mixed land use pattern, with the stream first flowing through agricultural fields and then the city of Køge. Kirke Å was not further investigated due to limitations associated with the duration and budget of the project. Instead, Kirke Å, together with Køge Å and Skjern Å, was chosen to function as an example for a final testing of the methodological approach, described in Chapter 5.

The field campaign conducted at Køge Å and Skensved Å focused on 5 main classes of pollutants:

- General water quality parameters
- Heavy metals
- Chlorinated solvents and degradation products
- Pesticides and degradation products
- PAHs

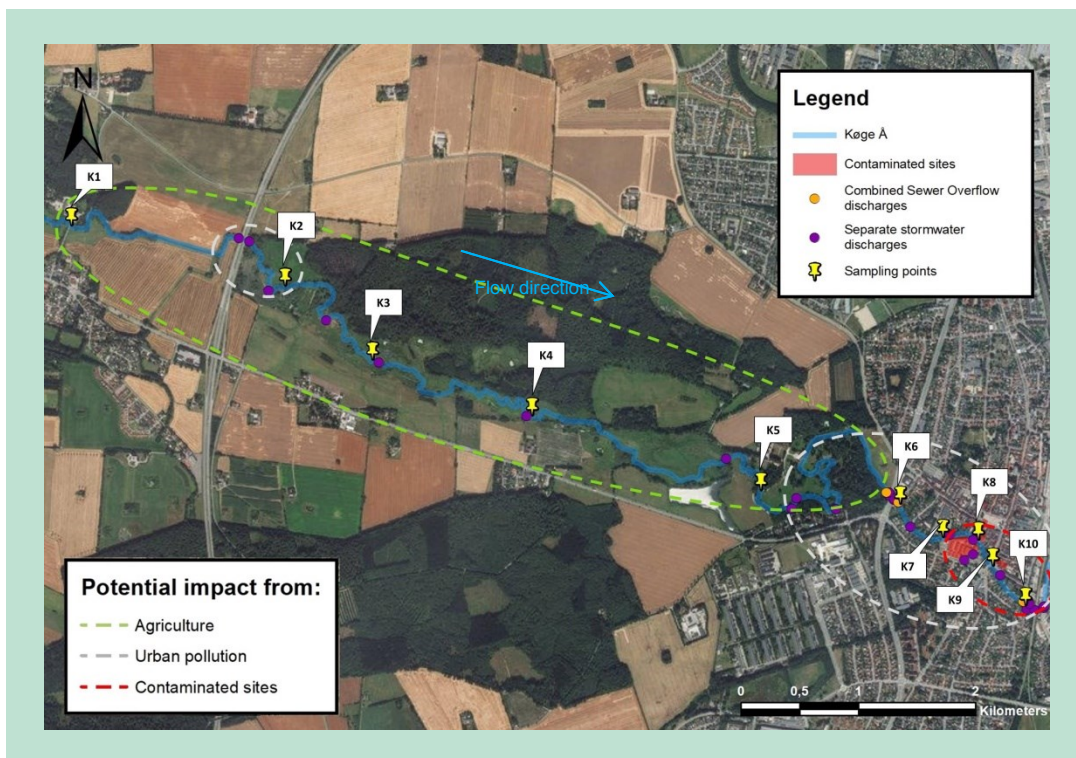
These categories have been chosen based on the potential pollution sources identified in Chapter 6. Table 18 lists the motivation behind the selection of each pollutant's category, while Appendix D presents the complete list of chemicals analyzed.

**TABLE 18. Categories of pollutants investigated during the field campaign at Skensved Å and Køge Å.**

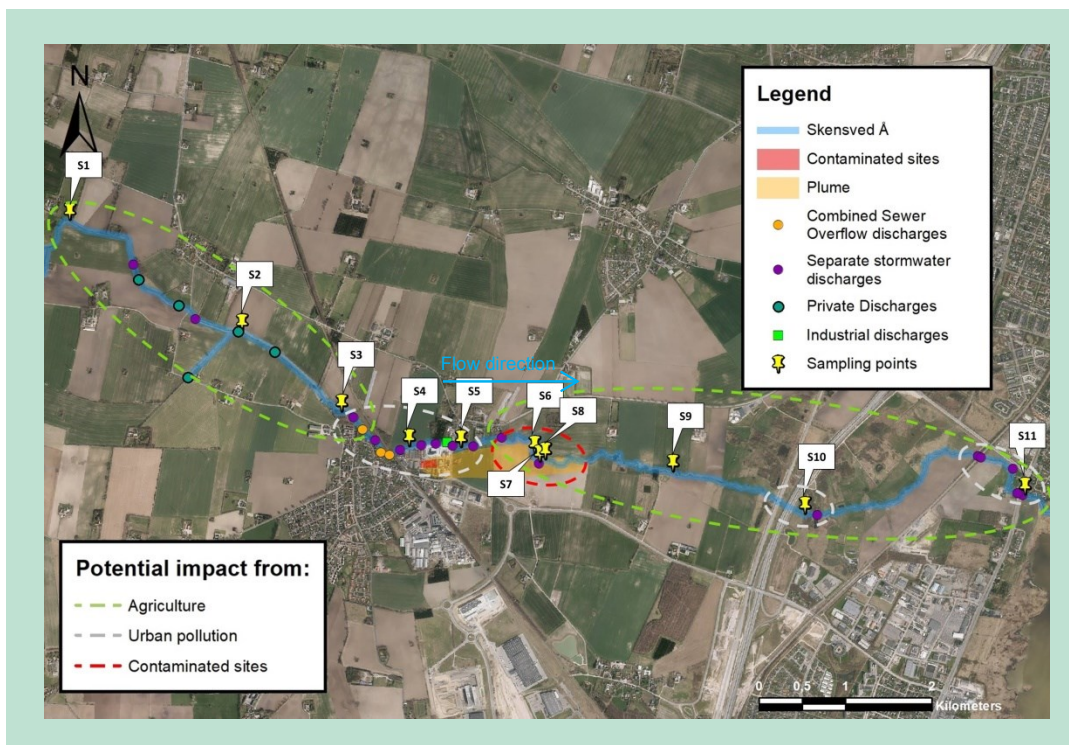
Category	Chemical analysis	Filtration	Motivation
<i>General pollutants</i>			
General water quality parameters	<ul style="list-style-type: none"> <li>- Nutrients</li> <li>- Macro-ions</li> <li>- Suspended solids (SS)</li> <li>- NVOC</li> <li>- BOD5/COD</li> </ul>	Not filtered	<ul style="list-style-type: none"> <li>- General knowledge about water status</li> <li>- Provides information about parameters that could indicate wastewater contribution</li> </ul>
Heavy metals – dissolved concentrations	<ul style="list-style-type: none"> <li>- As      - Pb</li> <li>- Cd      - Ni</li> <li>- Cr      - Zn</li> <li>- Cu</li> </ul>	Filtered - 0,45 µm	<ul style="list-style-type: none"> <li>- Provides information regarding natural heavy metal concentrations and anthropogenic contributions</li> </ul>
<i>XOCs</i>			
Chlorinated solvents and degradation products – dissolved	<ul style="list-style-type: none"> <li>- Perchloroethene (PCE)</li> </ul>	Filtered - 0,45 µm	<ul style="list-style-type: none"> <li>- Update data regarding contaminated sites' contribution to stream impair-</li> </ul>

concentrations	- Trichloroethene (TCE) - Degradation products		ment
Pesticides and degradation products – total concentrations	- Insecticides - Fungicides - Herbicides - Biocides	Not filtered	- Provides information regarding agricultural contribution to stream pollution - Provides information regarding pesticides related to urban applications
PAHs – total concentrations	- PAHs identified as priority hazardous substances by the WFD - PAHs listed in the Danish legislation for freshwater quality (BEK 439 19/05/2016)	Not filtered	- Provides information regarding urban and traffic source contribution (e.g. road dust, vehicle emissions, industrial processes, coking plants) to stream pollution

The field investigations at Køge Å and Skensved Å were conducted during weeks 48 and 49 (2017). Figures 20 and 21 illustrate the locations of the sampling points; locations are denoted K1-K10 and S1-S11 for Køge Å and Skensved Å, respectively. Coordinates can be found in Appendix E. The sampling locations were also chosen with the goal of covering the entire stretch of interest described in Chapter 6, providing “upstream” (potential) background concentrations and allowing the linkage of pollutants to sources. Sampling points denoted with the number 1 represent the most upstream point investigated, which corresponds to the beginning of the “water corridor” of interest.



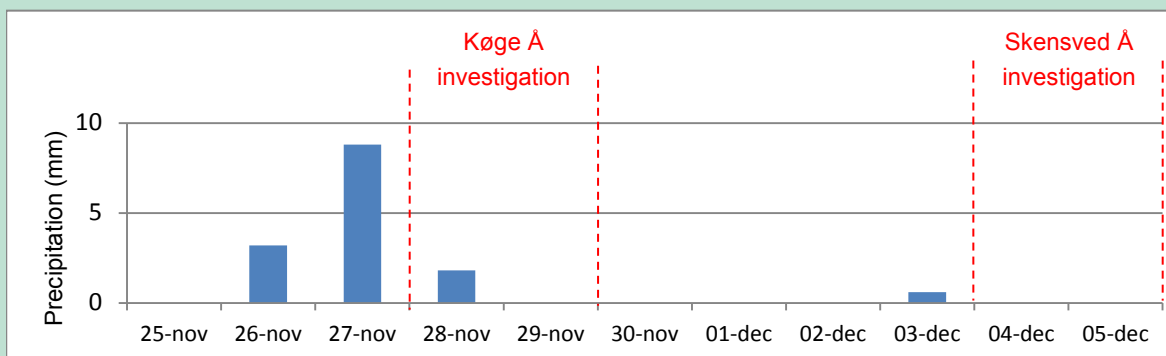
**FIGURE 20.** Map showing the potential affected stream stretches to different pollution sources (colored dashed lines) and the location of the sampling points K1-K10 along Køge Å. Stream flow direction is from left to right.



**FIGURE 21. Map showing the potential affected stream stretches to different pollution sources (colored dashed lines) and the location of the sampling points S1-S11 along Skensved Å. Stream flow direction is from left to right.**

The screening focused on the collection of water samples and field measurements of oxygen, pH, electrical conductivity (EC) and temperature. Moreover, the stream water flow was evaluated for some of the investigated points using an “OTT MF pro” portable velocity sensor (Hydromet, 2015). The flow of Køge Å was measured in K1, while for Skensved Å it was investigated in 3 points: S2, S4 and S9.

Figure 22 shows the daily rainfall data before and during the field campaigns, provided by rain gauges that are part of the Danish SVK network and collected since 1979 by the Danish Meteorological Institute (DMI) and the Water Pollution Committee (Spildevandskomiteen, SVK). Køge Å was investigated during the first two days of week 48 (28<sup>th</sup> and 29<sup>th</sup> of November) and characterized by wet weather conditions, since a rain gauge station close to the area of interest indicated 13,8 mm of rain in the days before the field investigation. The Skensved Å sampling campaign was performed in week 49, in almost dry weather conditions.



**FIGURE 22. Overview of the rain events before and during the field investigations performed in Køge Å and Skensved Å.**

Considering the potential and known pollution sources in Køge Å and Skensved Å, it was possible to visually illustrate the potential spatial impact of a determined source on a specific part of the water area of interest. This is shown in Figures 20 and 21 by the colored dashed lines: the stream reach within the green dashed line is thought to be primarily affected by agricultural activities, while the reach within the grey and red dashed lines by urban pollution and contaminated sites, respectively. The Laboratory ALS Denmark A/S analyzed the water samples for the general water chemistry, chlorinated compounds, pesticides and PAHs, while the heavy metals have been analyzed in the DTU Environment laboratory.

The collection of the samples was done using dedicated flasks provided by the environmental laboratories. Flasks were slowly filled without turbulence using a sampling tube put at the bottom of the flask, in order to avoid air in the bottle. Images of the stream water sampling at station K3 and K5 (Figure 23) and S2 and S5 (Figure 24) are shown below.



**FIGURE 23. Photos from the field work investigation at Køge Å. Left: stream close to sampling point K3. Right: sampling point K5.**



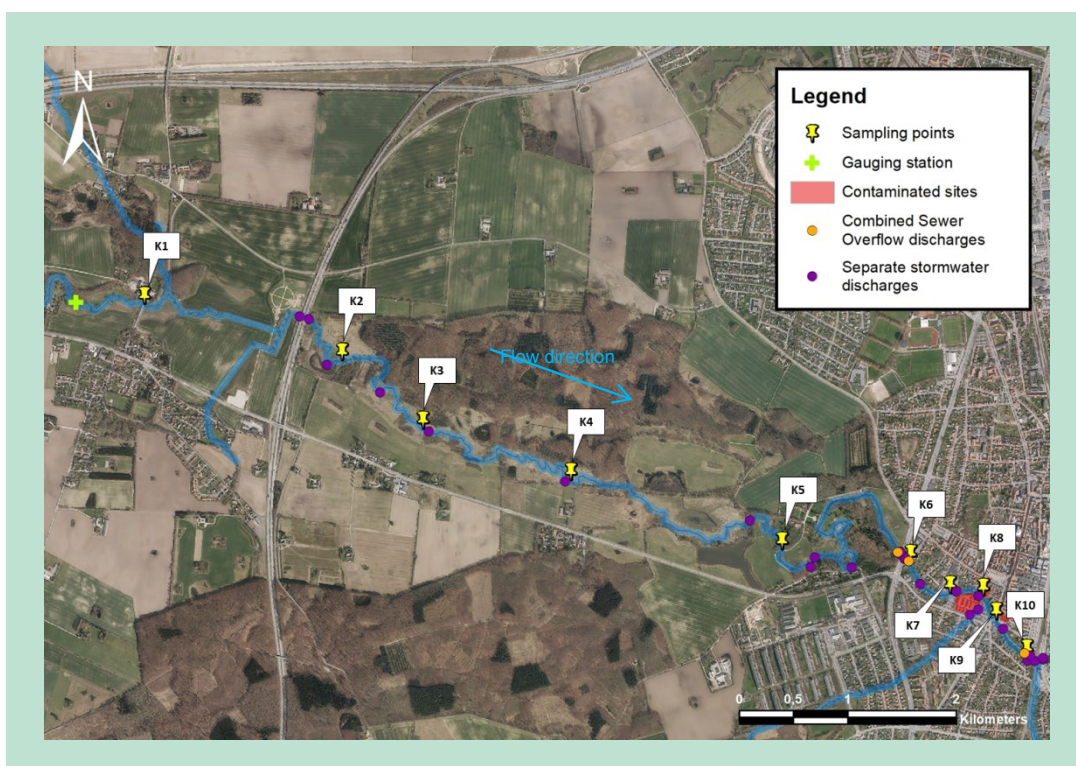
**FIGURE 24.** Photos from the field work investigation at Skensved Å. Left: sampling point S2. Right: sampling point S5.

# 8. Results and discussion regarding the field investigation

This Chapter presents the results related to the investigations carried out in Køge Å and Skensved Å. Supplementary data can be found in Appendices F and G, respectively.

## 8.1 Køge Å

Figure 25 presents an overview for the stream corridor of interest together with the potential point sources of pollution and the gauging station.

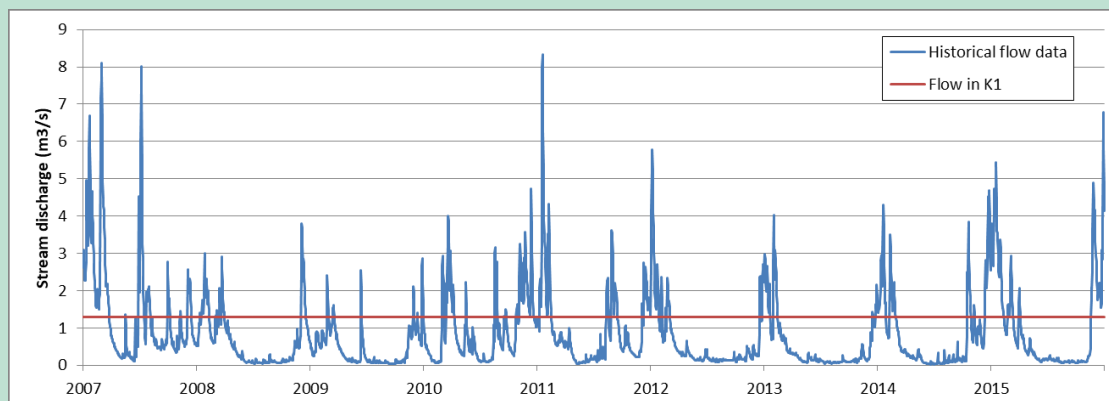


**FIGURE 25.** Map showing the location of the sampling points, point sources of contamination and the stream flow gauging station.

### 8.1.1 Stream flow, general water quality and nutrients

The stream flow was monitored only at station K1, as this was the only point where it was possible to enter the stream to measure the stream profile and velocity. When moving further downstream, Køge Å increases in both the width and depth making it difficult to measure the stream profile using the portable velocity system. In K1, the stream flow was found equal to  $1,285 \text{ m}^3/\text{s}$ . Compared to the historical data recorded by a gauging station 200 m upstream of K1 (shown in Figure 26), the result recorded in this study was found to fall above the average flow of  $0,84 \text{ m}^3/\text{s}$ . The measured discharge is also above 78% of the daily flow records, indicative for a not-extreme wet weather discharge. This matches that in the days leading up to the sampling campaign, a total rainfall of 13,8 mm had been reported by rain gauging stations in the area close to Køge Å. Specifically, 3,2, 8,8 and 1,8 mm of rain were registered by DMI gauging stations the 26<sup>th</sup>, 27<sup>th</sup> and 28<sup>th</sup> of November, respectively (Figure 22 in Chapter 7).

The flow measured in K1 during the field campaign is slightly higher than the typical dry weather baseline discharge of November, indicating a slight rainfall influence.



**FIGURE 26. Historical flow registered from 2007 to 2015 (blue line) and flow registered in K1 during the field campaign (red line).**

Table 19 shows the ranges of results for the water quality parameters and the nutrients measured along the entire investigated stretch. The levels of nutrients found in the stream are in line with the typical concentrations found in Denmark. Ammonium in K2 was found to be particularly high (3,9 mg/l) compared to the average concentrations found elsewhere in the stream, possibly indicating an agricultural source of contamination due to the absence of other anthropogenic sources such as wastewater discharges or landfills in the area.

**TABLE 19. Water quality parameters measured in November 2017. Complete results can be found in Appendix F.**

<b>Macro-ions (mg/l)</b>		<b>Nutrients and Organic Matter (mg/l)</b>	
Ca <sup>2+</sup>	97-100	NVOC	8,9-12
Mg <sup>2+</sup>	5,2-5,8	BOD5	<1
K <sup>+</sup>	2,6-2,8	COD	19-26
Na <sup>+</sup>	15-20	SS	410-450
F <sup>-</sup>	0,22-0,23	Total-P	0,098-0,21
SO <sub>4</sub> <sup>2-</sup>	28-30	NO <sub>3</sub> <sup>-</sup>	21-28
Cl <sup>-</sup>	30-36	NH <sub>4</sub> <sup>+</sup>	0,015 - 3,9
<b>Real time measurements</b>		<b>Metals (mg/l)</b>	
pH (-)	7,89-7,96	Fe	0,24-1,1
Ec (µS/cm)	583-633	Mn	0,08-0,062
Oxygen (mg/l)	9,8-11,32		
Temperature (°C)	5,2-5,8		



### 8.1.2 Chlorinated compounds and degradation products

Chlorinated solvents and degradation products have also been investigated along the vand-område of interest. The results are shown in Figure 27. The stream was found contaminated by tetrachlorethylen (PCE), cis-1,2-dichlorethene (cis-DCE) and vinyl chloride (VC). As expected, chlorinated solvents and degradation products were detected downstream, close to the contaminated sites highlighted in red in Figure 27. K8 was the most contaminated point (VC: 0,066 µg/L), with concentrations of VC slightly exceeding the national AA EQS of 0,05 µg/l. cis-DCE and VC were also found respectively in K9 and K10, with concentrations of 0,031 and 0,025 µg/l.

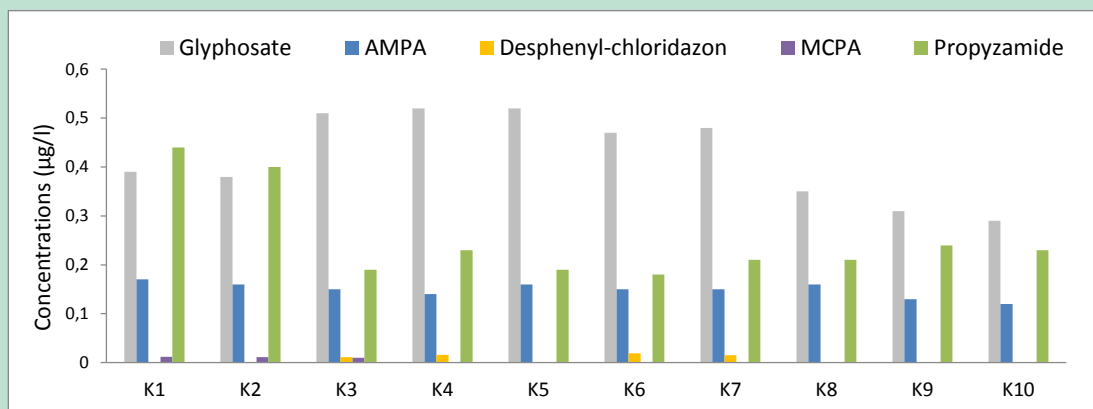
Results are in agreement with the previous investigations of chlorinated solvents and degradation products carried out in Køge Å in 2015 and described in Chapter 6.1.1



**FIGURE 27. Concentrations of chlorinated compounds and degradation products found in Køge Å close to the contaminated sites. Detection limit (d.l.) is 0,020 µg/l. Results are expressed in µg/l.**

### 8.1.3 Pesticides

Among the long list of pesticides and degradation products investigated in this study (reported in Appendix D), the following were detected in Køge Å: glyphosate, AMPA, desphenyl-chloridazon, MCPA and propyzamide. Figure 28 shows the concentrations found in the different sampling points. The detection limit for all the investigated pesticides is 0,010 µg/l.



**FIGURE 28. Overview for the pesticide concentrations, including metabolites, detected in Køge Å at the sampling stations K1-K10.**

In Appendix H, the description of the pesticides detected in Køge Å can be reviewed. The table presented in Appendix H includes information about the type of pesticide (herbicide, fungicide, insecticide, metabolite...etc.), application period, general description of the chemical, usage in Denmark, current EU/Danish permissions and maximum annual sales registered in Denmark.

Glyphosate was detected in all the investigated points of Køge Å. The highest concentrations of this herbicide were detected in K3 (0,51µg/l), K4 and K5 (both 0,52 µg/l). The lowest concentration (0,29 µg/l) was detected in K10, the most downstream investigated point of the stretch and therefore far from the agricultural fields located further upstream.

The concentrations of AMPA, the primary transformation product of glyphosate, were lower compared to the parent compound. The maximum and minimum concentrations were detected in K1 and K10, respectively, with values of 0,17 and 0,12 µg/l. Along the stretch the concentrations were found more constant compared to glyphosate, even if the lowest concentration was always found in the most downstream point of the stretch (K10).

Desphenyl-chloridazon, the primary metabolite of the banned herbicide chloridazon, was also detected. NIRAS investigated the presence of desphenyl-chloridazon in August 2017, estimating at least 60 waterworks with concentrations of this degradation product above the limit value of 0,1 µg/l (information obtained from the website of NIRAS in 2017). Although the concentrations are one order of magnitude lower than the concentrations of glyphosate and AMPA, in K3, K4, K6 and K7, the concentrations were found above the detection limit. The highest concentration was found in K6 (0,019 µg/l), while the lowest in K3 (0,011µg/l).

The herbicide MCPA was found in K1, K2, K3 with concentrations slightly above the detection limit (from 0,010 to 0,012 µg/l). The highest concentration was found in K1. This part of the stretch is surrounded by agricultural fields and farms, possibly explaining why the highest concentration was found there.

Propyzamide was also detected in the surface water at every investigated point of Køge Å. Concentrations vary between 0,18 and 0,44 µg/l, with the maximum concentrations detected in the upstream part of the vandområde. K1 and K2 had the highest concentrations of this herbicide, respectively 0,44 and 0,40 µg/l. After K2 the concentrations seem to decrease, and the lowest concentration was found in K6 (0,18 µg/l).

### 8.1.4 PAHs and heavy metals

PAHs and heavy metals have also been investigated in K1-K10. The complete results can be seen in Appendix F.

Sixteen PAHs have been analyzed to detect the contribution of the urban source to the stream pollution. All the investigated compounds were below the detection limit of 0,010 µg/l.

Lastly, concentrations of heavy metals (Table 20) were found rather constant along the entire investigated vandområde. Low concentrations of dissolved As, Ni, Zn and Cu were detected, in every point below the AA EQS and in line with the median concentrations detected in Danish streams (Table 20). Dissolved Cr and Pb were below the detection limit of 0,10 µg/l in every investigated point. Cd was also found below the detection limit in almost every point except K3, where 0,21 µg/l was detected in the stream. Cd in K3 is therefore exceeding the AA EQS.

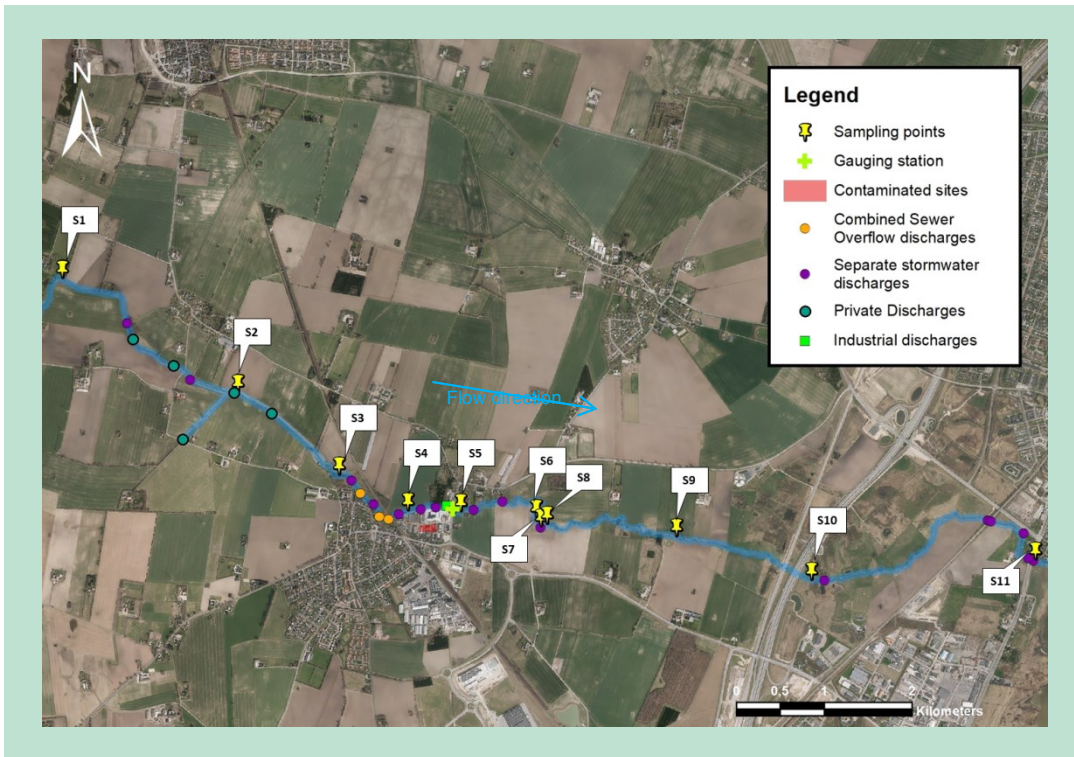
**TABLE 20. Range (minimum and maximum) of measured dissolved heavy metals along Køge Å together with the Annual Average (AA) and Maximum Allowable Concentration (MAC) EQS. Detection limit (d.l.) is 0,10 µg/l. Results are expressed in µg/l.**

	Concentrations in Køge Å	Median concentrations in Danish streams (*)	EQS: AA - MAC
Cr	< d.l.	0,165	3,4 - 17
Ni	1,14 - 1,49	1	4 - 34
Cu	1,63 - 2,48	1,05	4,9 - 4,9
Zn	3,61 - 7,25	7,75	7,8 - 8,4
As	0,65 - 0,72	1,1	4,3 - 43
Cd	< d.l. - 0,21	0,005	0,08 - 0,45
Pb	< d.l.	0,029	1,2 - 14

(\*): DCE (2016).

## 8.2 Skensved Å

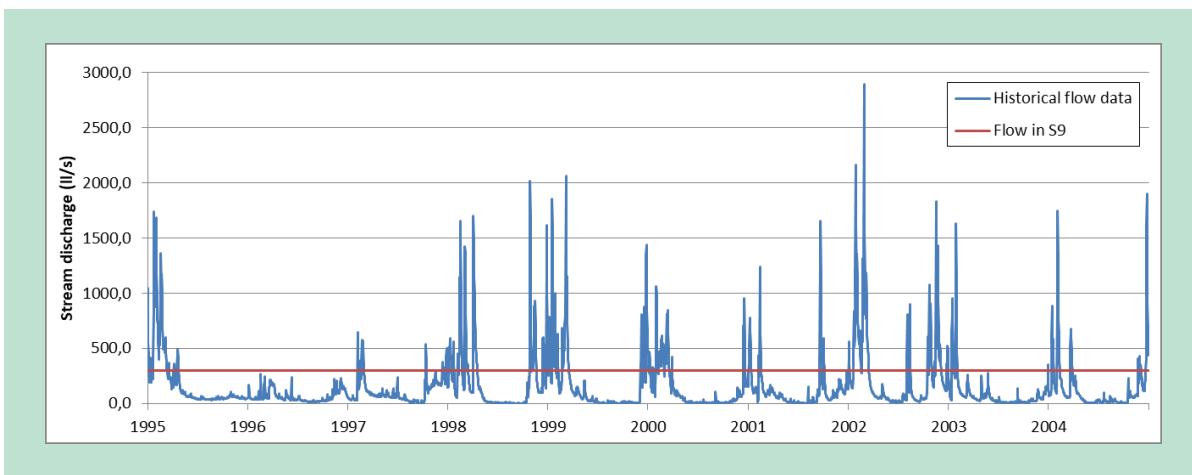
Figure 29 illustrates the overall studied stretch of Skensved Å, together with the sampling locations, the stream gauge and the potential point sources of contamination.



**FIGURE 29.** Map showing the overall studied stretch of Skensved Å, the sampling locations, the potential point sources of pollution and the gauging station that collected stream flow data from 1984 to 2004. Stream flow direction is from left to right.

### 8.2.1 Stream flow, general water quality and nutrients

The stream discharge was measured in three points, S2, S4 and S9 in the field campaign. The flow passing through these sections was found to be 284, 284 and 301 l/s respectively. Figure 30 shows the historical flow data taken from a gauging station upstream the stretch of interest and the flow measured in S9.



**FIGURE 30.** Skensved Å historical flow data registered from 1995 to 2004 by the gauging station shown in Figure 29 (blue line) and the flow measured during the field campaign in point S9 (red line).

The flow is low compared to the peaks registered in the past years. The maximum discharge ever recorded was 2857 l/s, far above the measured flow. The campaign was conducted during an almost dry weather period, as in the days before the sampling campaign only one light

rain event (shown in Figure 22, Chapter 7) was registered the 3<sup>rd</sup> of December by a nearby rain gauging station. However, the measured flow is above the average (156,9 l/s) and above 87% of the historical recorded flows. To sum up, the flow is still in line with the typical autumn conditions registered in the past years.

The general water quality and nutrients levels are shown in Table 21. Analyses of macro-ions, nutrients, organic matter and metals were performed for S2, S4 and S9.

**TABLE 21. Skensved Å water quality parameters measured in December 2017. Complete results can be found in Appendix G.**

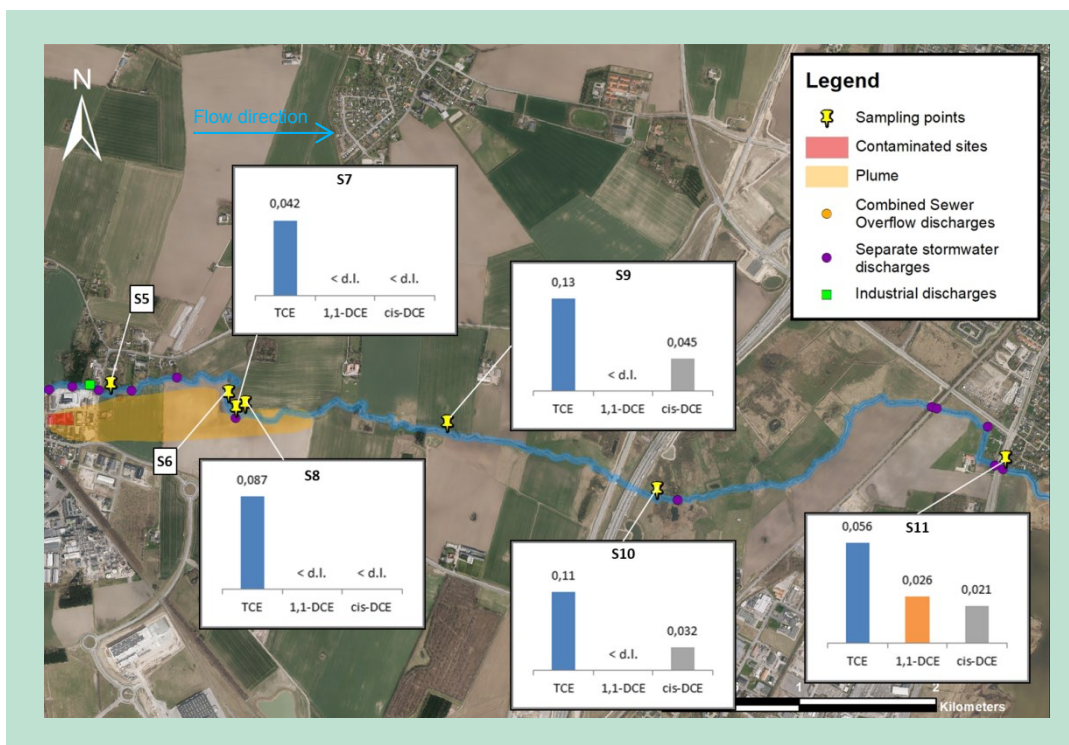
<b>Macro-ions (mg/l)</b>		<b>Nutrients and Organic Matter (mg/l)</b>	
Ca <sup>2+</sup>	120-130	NVOC	6,1-6,5
Mg <sup>2+</sup>	8,1-8,8	BOD	<1
K <sup>+</sup>	2,7-2,8	COD	13-16
Na <sup>+</sup>	15-17	SS	490-510
F <sup>-</sup>	0,27-0,28	Total-P	0,081-0,096
SO <sub>4</sub> <sup>2-</sup>	36-40	NO <sub>3</sub> <sup>-</sup>	30-31
Cl <sup>-</sup>	29-34	NH <sub>4</sub> <sup>+</sup>	0,075-0,099
<b>Real time Measurements</b>		<b>Metals (mg/l)</b>	
pH (-)	7,61-7,97	Fe	0,21-0,23
Ec (µS/cm)	747-835	Mn	0,037-0,050
Oxygen (mg/l)	10,95-12,24		
Temperature (°C)	4,3-7,4		

## 8.2.2 Chlorinated compounds and degradation products

Skensved Å was found contaminated by chlorinated solvents and degradation products in the middle of the stretch of interest, where the plume in the upper aquifer coming from the contaminated site in Lille Skensved is known to discharge into the stream. Figure 31 illustrates the concentrations of chlorinated compounds and degradation products along Skensved Å. Only the sampling points S5-S11 are shown, as from the past investigations it is known that the groundwater contaminated plume discharges approximately after point S5.

TCE was found in stations S7, S8, S9, S10, S11. The highest and lowest concentration of TCE were found in S9 and S7, respectively 0,13 and 0,042 µg/l. The highest discharge from the contaminated groundwater seems to be between S8 and S10 since in S9, TCE increases one order of magnitude before decreasing gradually further downstream (compare value at S11).

Two potential degradation products of TCE were also found contaminating Skensved Å. Concentrations of cis-DCE were found above the detection limit of 0,020 µg/l in S9, S10 and S11, and are most likely associated with the contaminant plume. Of note, 0,026 µg/l of 1,1- DCE was detected in S11. This could suggest that the plume's contamination spreads in the stream water all the way up to this location (above the detection limit), but since this degradation pathway is unusual (Chambon et al., 2013), it could also signal the presence of another source located closer to this sampling point.



**FIGURE 31. Concentrations of chlorinated compounds and degradation products found in Skensved Å downstream from the contaminated site. Detection limit (d.l.) is 0,020 µg/l. Results are expressed in µg/l.**

Most of the chlorinated compounds and degradation products are regulated through the European or National EQS. In this case, none of the investigated compounds exceeded the AA EQS, as shown in Table 22.

**TABLE 22. Range of concentrations of chlorinated compounds and degradation products found in Skensved Å together with the Annual Average (AA) and Maximum Allowable Concentration (MAC) EQS.**

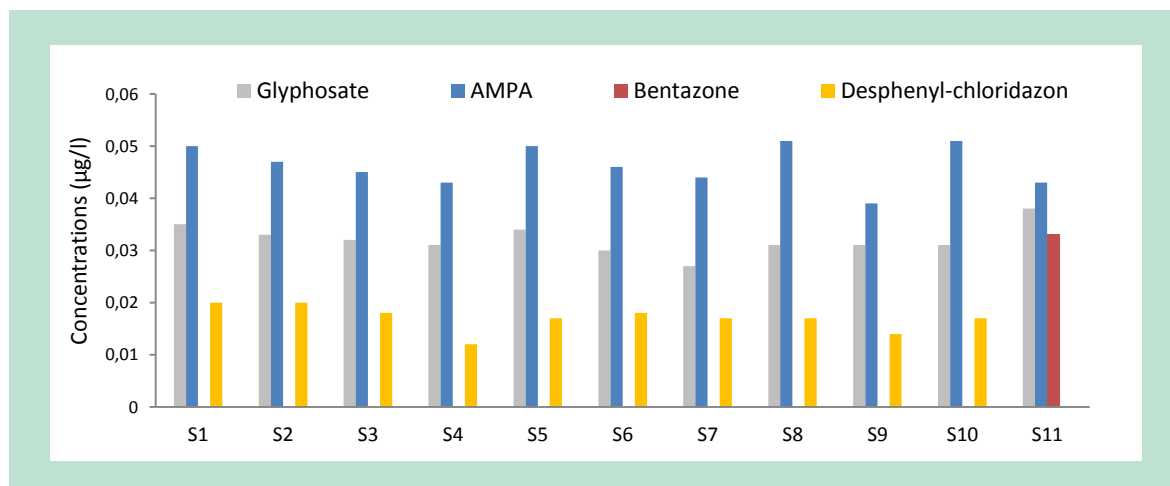
	Min – Max concentrations (µg/l)	EQS: AA - MAC
Trichlorethylene (TCE)	0,042 - 0,13	10 - /(*)
1,1-Dichlorethylene (1-1 DCE)	0,026	6,8 – 68
cis-1,2-dichlorethylene (cis-DCE)	0,021-0,045	6,8 – 68

(\*): EQS not defined.

### 8.2.3 Pesticides

Pesticides were investigated along the entire stretch at the sampling points S1-S11. Two herbicides and two degradation products were detected: glyphosate, AMPA, bentazone and desphenyl-chloridazon. In Appendix H the description of the pesticides detected in Skensved Å can be seen, together with some more information regarding the application period, the type of pesticide, the usage and sales in Denmark.

Similarities with the compounds found in Køge Å can be seen, as glyphosate, AMPA and desphenyl-chloridazon were detected also in Køge Å. Figure 32 shows the concentrations found in each investigated point.



**FIGURE 32. Overview for the pesticide concentrations, including metabolites, detected in Skensved Å at the sampling stations S1-S11.**

Glyphosate was found contaminating the entire stretch of interest. The highest and the lowest concentrations were found in S11 and S7, respectively 0,038 and 0,027 µg/l. The concentrations were in general almost constant along the stretch.

AMPA, the degradation product of glyphosate, had the highest concentrations along the stretch of interest, even above the parent product. As with glyphosate, AMPA was found in every investigated point. The highest concentration detected was 0,051 µg/l, found in two different sampling points: S8 and S10; the lowest concentration was found in S9 (0,039 µg/l).

Desphenyl-chloridazon was found in every investigated point except S11, where the concentration detected was below the detection limit of 0,010 µg/l. The highest concentrations were found upstream, in S1 and S2 (0,020 µg/l) while the lowest concentration was detected in S4.

Bentazone was the only herbicide found in Skensved Å that had not been detected in Køge Å. Compared to the other pesticides found and described above, bentazone has a national EQS that needs to be respected. S11 was found contaminated with 0,033 µg/l of bentazone, which however did not exceed the AA EQS of 45 µg/l.

## 8.2.4 PAHs and heavy metals

Skensved Å was found contaminated by PAHs in more than one sampling point. Table 23 reports the total concentrations of PAHs found in the stream, together with the AA and MAC EQS associated. Orange and red cells indicate the concentrations exceeding the AA and MAC guideline EQS, respectively.

**TABLE 23. Results of PAHs concentrations detected in Skensved Å together with the Annual Average (AA) and Maximum Allowable Concentration (MAC) guideline values. < d.l. means below detection limit, that is 0,010 µg/l. The orange and red values are the concentrations exceeding the AA and MAC EQS, respectively.**

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	EQS: AA - MAC
Naphthalene	0,11	<d.l.	<d.l.	0,011	0,013	0,014	0,021	0,013	<d.l.	<d.l.	<d.l.	2 - 130
Acenaphthylene	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	1,3 - 3,6
Acenaphthene	0,018	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,014	0,015	<d.l.	<d.l.	<d.l.	3,8 - 3,8
Fluorene	0,020	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,019	<d.l.	<d.l.	<d.l.	<d.l.	2,3 - 21,2
Phenanthrene	0,094	<d.l.	0,066	<d.l.	0,013	0,012	0,099	0,044	0,010	0,056	0,012	1,3 - 4,1
Anthracene	0,046	<d.l.	<d.l.	0,012	<d.l.	<d.l.	0,043	0,021	<d.l.	<d.l.	<d.l.	0,1 - 0,1
Fluoranthene	0,082	<d.l.	0,16	0,024	0,011	0,011	0,14	0,056	0,017	0,13	0,017	0,0063 - 0,12
Pyrene	0,11	<d.l.	0,10	0,017	<d.l.	0,012	0,13	0,066	0,018	0,13	0,016	0,0046 - 0,023
Benzo(a)anthracene	0,030	<d.l.	0,020	<d.l.	<d.l.	<d.l.	0,019	0,012	<d.l.	0,030	<d.l.	0,012 - 0,018
Chrysene	0,043	<d.l.	0,027	<d.l.	<d.l.	<d.l.	0,028	0,024	<d.l.	0,059	<d.l.	0,014 - 0,014
Benzo(b+j+k)fluoranthene	0,11	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,060	0,055	0,015	0,11	0,019	0,00051 - 0,051
Benz(a)pyrene	0,043	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,025	0,018	<d.l.	0,035	<d.l.	0,00017 - 0,27
Indeno(1,2,3-cd)pyrene	0,034	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,014	0,016	<d.l.	0,049	<d.l.	0,00017 - /(*)
Dibenzo-(a,h)anthracene	0,034	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,013	0,011	<d.l.	0,030	<d.l.	0,0014 - 0,018
Benzo(ghi)perylene	0,043	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,016	0,021	0,012	0,051	<d.l.	0,00017 - 0,0082
Benz(e)pyrene	0,058	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,033	0,026	0,011	0,073	<d.l.	/(*) - /(*)

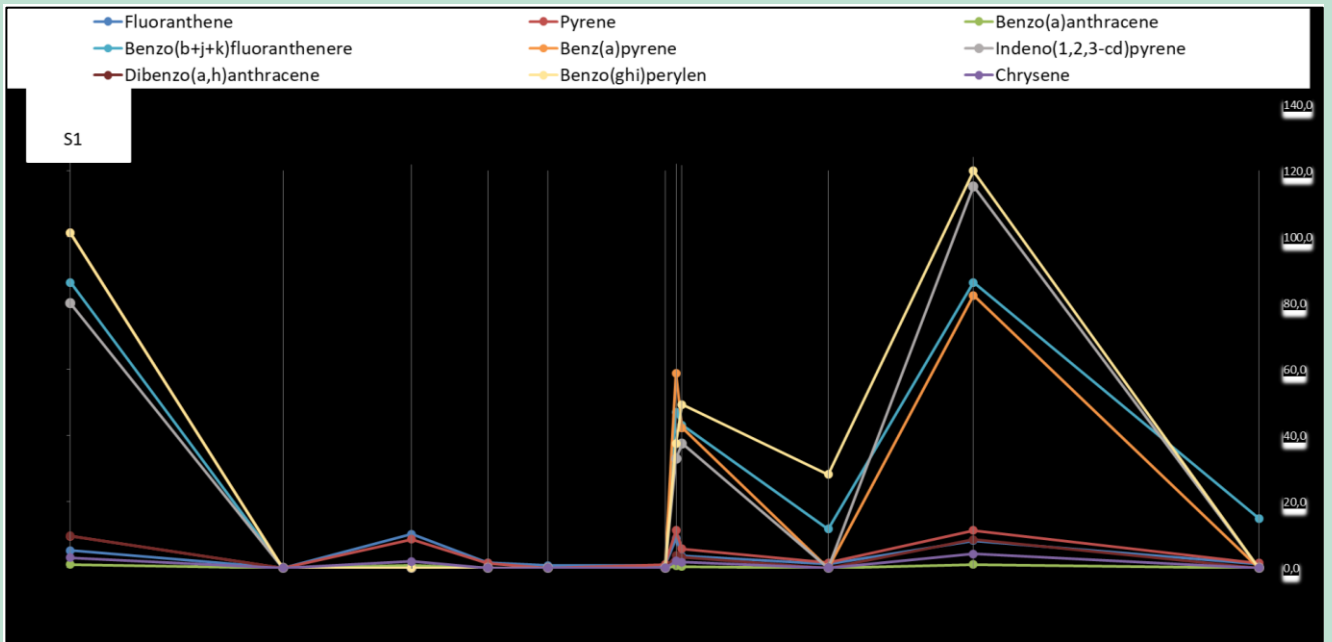
(\*) EQS not defined.

The current investigation found high total concentrations of PAHs in different sampling points. Fluoranthene, pyrene and benzo(b+j+k)pyrene had the highest concentrations, reaching 0,16, 0,13 and 0,11 µg/l, respectively. S2 is the only point where all the investigated PAHs were found below the detection limit of 0,010 µg/l. S1, S7, S8 and S10 are the points with the highest number of PAHs exceeding the freshwater guideline values, and are thereby considered to be the most impacted points.

Figure 33 shows the concentrations normalized with respect to the relative AA EQS taking into account the distance between the sampling points. The most impacted points are S1, S7 and S10, where some PAH concentrations are more than 200 times above their guideline value (i.e. benzo(ghi)perylene, benzo(b+k+j)fluorathene, indeno(1,2,3-cd)pyrene).

The pattern of Figure 33 suggests three main sources of contamination before S1, S7 and S10, due to the high concentrations found. After every peak, the sampling point immediately after is characterized by lower concentrations, suggesting a fast sedimentation process for these contaminants that are predominantly bound to the solid phase.





**FIGURE 33.** PAH concentrations over distance in the stream water at Skensved. The concentrations are normalized with respect to the Annual Average (AA) guideline values set by the Water Framework Directive ( $C/C_{EQS}$  on the y-axis). Note that the 0 distance location on the x-axis corresponds to sampling site S1 in Figure 29.

Regarding the heavy metals, high concentrations of zinc and lead were detected along the stream stretch of interest. Table 24 shows the concentrations found in Skensved Å.

**TABLE 24.** Results of the heavy metals' concentrations ( $\mu\text{g/l}$ ) found in Skensved Å together with the freshwater Annual Average (AA) and Maximum Allowable Concentration (MAC) EQS. Detection limit (d.l.) is  $0,10 \mu\text{g/l}$ . The orange and red values are the concentrations exceeding the AA and MAC EQS respectively.

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	EQS: AA - MAC
<b>Cr</b>	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	3,4 - 17
<b>Ni</b>	1,46	1,33	1,47	1,57	1,58	1,55	1,61	2,18	1,88	1,82	2,39	4 - 34
<b>Cu</b>	1,68	1,92	1,55	1,75	1,65	1,77	1,55	3,17	2,41	1,63	1,65	4,9 - 4,9
<b>Zn</b>	17,84	29,44	11,67	4,25	6,02	5,48	5,94	9,77	16,71	37,45	20,25	7,8 - 8,4
<b>As</b>	0,72	0,73	0,67	0,67	0,68	0,65	0,7	0,91	0,66	0,7	0,71	4,3 - 43
<b>Cd</b>	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,08 - 0,45
<b>Pb</b>	<d.l.	<d.l.	2,85	<d.l.	<d.l.	<d.l.	<d.l.	0,1	<d.l.	<d.l.	0,26	1,2 - 45

Zn was found exceeding the freshwater MAC EQS in 7 of the 11 sampling points. The highest concentration was found in S10, exceeding the guideline value by a factor of 4,5. Pb was also found exceeding the AA EQS in S3, as its concentration was found to be  $2,85 \mu\text{g/l}$ .

### 8.3 Comparison between Køge Å and Skensved Å cases

Based on the results related to the data acquisition presented in Chapters 8.1 and 8.2, the current paragraph discusses and compares the findings of contaminants in Køge Å and Skensved Å.

Overall, Køge Å was found contaminated by chlorinated compounds, pesticides and one heavy metal (cadmium):

- As expected, the chlorinated solvents and degradation products spread in Køge Å due to the discharge of contaminated groundwater into the stream. Contact zones have never been investigated due to the large size of the stream and the depth. The chlorinated solvent contamination of stream water starts downstream from the contaminated sites, since before K8 concentrations were below the detection limit. VC was the only compound exceeding the AA EQS, confirming the major role of the contaminated sites in the pollution of Køge Å.
- Pesticides, on the other hand, were quite diffused all over the vandområde of interest. This suggests a diffuse source problem for the watercourse that cannot be simplified by looking at a small stretch, as pesticides were found from the uppermost sampling point down to the end of the investigated reach. Most of the pesticides are not regulated by freshwater EQS and this complicates the impact assessment of the chemicals. However, concentrations were found up to 0,52 ug/l, which can be considered a high value if the groundwater threshold of 0,1 ug/l for single pesticides is taken into account. If the groundwater quality standard was considered, the concentrations found in water would have exceeded the threshold by a factor of 5.
- Overall, the flow conditions of Køge Å could be an important factor that has to be taken into account during the assessment. The flow discharge during the field investigation was in line with the autumn historical conditions, representing neither an extreme nor a drought condition. Concentrations of pesticides and chlorinated solvents could be even higher in the case of low flow conditions, typically present during spring and autumn.

On the other hand, Skensved Å was found contaminated by chlorinated solvents, pesticides, PAHs and heavy metals:

- Chlorinated solvents were found below the freshwater EQS, but the extent of the contamination spreads down to the end of Skensved Å, as TCE and two degradation products (1,1-DCE and cis-DCE) were detected in the most downstream sampling point (S11). However, the presence of 1,1-DCE in S11 raises some doubts about whether the concentrations found in Skensved Å are related to the same source studied in the report and shown in Figure 31. As reported by Pant and Pant (2010), cis-DCE is the dominant metabolite formed in the reductive dechlorination of PCE and TCE, while 1-1 DCE is the least prevalent intermediate. Besides being a unusual degradation product of TCE/PCE, concentrations of 1,1-DCE were measured far from the expected discharge location of the contaminated groundwater plume. This analysis suggests the presence of a second source downstream the contaminated site of Lille Skensved that has not been detected previously.
- Pesticides were also detected in the stream water. Concentrations are one order of magnitude lower than in Køge Å, which suggests a lower impact on the stream water quality. Bentazone was one of the pesticides detected in Skensved Å. Past groundwater investigations showed a contamination of bentazone in the boreholes close to Skensved Å (Table 14), suggesting a contamination coming from the groundwater.

- The sampling campaign revealed high total concentrations of PAHs, exceeding the AA EQS in more than one sampling point. However, the dry weather conditions before the sampling campaign (precipitation data in Figure 22) are in contrast with the results obtained, raising the question of which is the actual source contaminating the stream water. As reported in different studies such as Feng et al. (2007) and Sarria-Villa et al. (2016), remobilization of PAHs (especially low molecular weight PAHs) during resuspension of contaminated sediments could be a possible explanation for the high concentrations detected in Skensved Å. Many processes such as an increase in the turbulence or groundwater discharge from the streambed could release organic and inorganic contaminants. A sediment investigation could be useful to gain information on the relationship between the water and sediment compartments.
- High concentrations of Zn and Pb were found in Skensved Å, exceeding the freshwater EQS. Elevated levels of zinc could be related to both piglet manure and urban sources. A recent national monitoring study in Denmark revealed that the use of zinc in pig production increased the soil concentrations, and this could have increased the leaching and runoff of zinc from fields fertilized with pig manure to freshwater systems (Jensen et al., 2016). Finally, both Zn and Pb could be more related to stormwater discharges from urbanized areas, as reported by Gasperi et al. (2012) and Li et al. (2009).

# 9. Application of the approach to the three study cases

The methodological approach described in Chapter 5 was applied to the three study cases largely described and investigated in the past chapters: Køge Å, Skensved Å and Kirke Å.

In order to use the simple formula presented in Chapter 5 for the calculation of CMD, fully mixed conditions have to be fulfilled at the sampling points. This is not known for the two locations due to limited information regarding the exact discharge locations of the contaminated groundwater. Instead, the CMD was calculated based on the concentrations found in each sampling location and the manual flow measurements calculated during the field campaign. This gives a range of contaminant mass discharges useful to have a general idea of the magnitude of the pollution load discharging into the stream that can be classified based on the magnitude classification system defined in Chapter 5.

## 9.1 Køge Å

As previously described, before the current project, Køge Å had been investigated only to detect chlorinated solvents and degradation products originating from the contaminated sites close to the stream. Once more information regarding additional sources was acquired through a literature review (Chapter 6.1) and field investigations (Chapter 8.1), the *Impact Assessment* was performed. EQS and data regarding aquatic toxicity and bioaccumulation for each chemical found in the stream are reported in Appendix I (information regarding aquatic toxicity and bioaccumulation were added only for the cases where no EQS value existed for the specific chemical).

Table 25 shows the *Assessment Support* applied to the Køge Å case study site. The stream was found contaminated by chlorinated solvents and degradation products, pesticides and degradation products and one heavy metal (cadmium).

The detected chlorinated compounds (PCE, cis-DCE and VC) are known to be coming from the contaminated sites shown in Figure 27 due to contaminated groundwater entering the stream via groundwater-surface water contact zones. According to the IC analysis, VC has an *impact to the watercourse during low flow conditions*, as the concentrations are above the AA EQS. PCE and cis-DCE have *no expected impact* to the watercourse, as the detected concentrations are below their respective AA EQS in every investigated point. The S analysis revealed that all the detected chlorinated solvents were causing a limited contamination, as they were detected in less than 10% of the vandområde of interest (light grey). Regarding the T distribution, the current investigation confirmed the results of the past years: the contaminated sites close to the streams discharge without interruption into Køge Å. Therefore, the contamination is defined as *continuous* and it was possible to calculate the CMD, shown in Table 25 under the column T. Using the magnitude classification presented in Table 9 in Chapter 5, PCE, cis-DCE and VC CMDs fall into Mag 2 category, as the calculated CMDs were between 1 and 10 kg/year.

The expected sources of pesticides polluting Køge Å are the agricultural fields close to the stream. Pesticides could enter the stream water compartment via surface run-off, groundwater discharge and remobilization of contaminated sediments. All the detected pesticides do not have EQS values regulating concentrations in the environment. Therefore, the impact was assessed through the ecotoxicity and bioaccumulation properties. Glyphosate, desphenyl-

chloridazon, MCPA and propyzamide cause a *potential impact* to the water course. The results of standardized tests of at least one of the four aquatic indicator species were found above the benchmark value of 10 mg/l. According to the bioaccumulation properties, the log  $K_{ow}$  of propyzamide (3,43 l/kg) was also found above the benchmark value of 3. AMPA have no expected impact on the stream water quality. The S analysis gave further information regarding the spatial occurrence of the chemicals. Glyphosate, AMPA and propyzamide were found in more than 50% of the sampling locations along the stretch of interest, showing a *widespread* contamination of these chemicals (dark grey). Desphenyl-chloridazon and MCPA were found in 42 % and 43% of the stream stretch, falling into the *semi-widespread* contamination category (grey). According to the T classification (last column in Table 25), pesticides are classified as *semi-continuous* as it is expected that higher concentrations could be found in Køge Å during and/or after the spring spraying season. This hypothesis has to be confirmed through further investigations.

Among the analyzed heavy metals, cadmium was found to have an *impact to the watercourse during low flow conditions*, as the concentration in K3 (0,21 µg/l) exceeds the AA EQS (0,08 µg/l). Cadmium is also contaminating a fraction between 10 and 50 % of the stream stretch of interest (11%), thus the contaminations is defined as *semi-widespread*. All the other heavy metals had concentrations below the 90% quantile found in Danish streams and thus the spatial distribution was not calculated. Heavy metals were classified both as *pulse* and *continuous* pollutants, as they are expected to enter the stream intermittently through stormwater and CSO discharges, but especially for some of them (Zn, As, Ni, Cu), the source of contamination could be geogenic and therefore also discharging continuously into Køge Å through the groundwater. If close agricultural fields are fertilized with manure containing high concentrations of Ni, Cu and Zn, the source of contamination of these heavy metals could be also diffuse.

**TABLE 25. Assessment Support results as applied to the Køge Å case study site.**

	Compounds	Expected or known sources	IC	S	T
Chlorinated compounds	Tetrachlorethylene (PCE)	Point source Contaminated site(s)			Continuous (CMD=1,38 kg/y)
	Cis-1,2-dichlorethylene (cis-DCE)				Continuous (CMD=1,26-1,74 kg/y)
	Vinyl chloride (VC)				Continuous (CMD=1,01-2,67 kg/y)
Pesticides	Glyphosate	Diffuse source Agricultural fields			Semi-continuous
	AMPA				Semi-continuous
	Desphenyl-chloridazon				Semi-continuous
	MCPA				Semi-continuous
	Propyzamide				Semi-continuous
Heavy Metals	Ni	Point source direct discharges Stormwater separate systems and CSOs		-	Pulse/ Continuous
	Cu	Geogenic source		-	Pulse/ Continuous
	Zn	Diffuse source Agricultural fields		-	Pulse/ Continuous
	As	(Ni, Cu, Zn)		-	Pulse/ Continuous

	Cd				Pulse/ Continuous
	Pb			-	Pulse/ Continuous

## 9.2 Skensved Å

The same procedure was carried out for Skensved Å study case. EQS and data regarding aquatic toxicity and bioaccumulation for each chemical found in Skensved Å are reported in Appendix I (information regarding aquatic toxicity and bioaccumulation were added only when EQS values did not exist for the specific chemical).

After acquiring enough data and information regarding the chemical properties, the impact, as well as the spatial and temporal distribution of the compounds detected in Skensved Å could be assessed; the *Assessment Support* is visualized in Table 26. Differently from Køge Å case study, Skensved Å is impacted by more pollutant categories: chlorinated solvents and degradation products, pesticides, PAHs and heavy metals.

Chlorinated solvents are known to be related to the contaminated site in Lille Skensved, described in detail in Chapter 6.2.1. However, the detection of 1,1-DCE close to the delta of Skensved Å and far from the discharge area of the groundwater plume suggests the presence of a second source downstream the contaminated site of Lille Skensved that has not been studied previously. The detected chlorinated solvents (TCE, 1,1-DCE and cis-DCE) were found in every point below the AA EQS, thus these compounds have *no expected impact* to the watercourse. According to the S analysis, the spatial distribution of the detected chlorinated solvents reveals a *semi-widespread* contamination, as the fraction of stream influenced by TCE, 1,1-DCE and cis-DCE is 45,4%, 11% and 39 % respectively. The T distribution of the chlorinated solvents is shown in the last column of Table 26. The CMD was calculated for the chlorinated solvents, due to their *continuous* contamination. According to the magnitude classification system presented in Table 9 in Chapter 5, TCE CMD can be classified as Mag1-Mag2, while both 1,1-DCE and cis-DCE fall into the class Mag 1.

Pesticides are expected to be linked to the agricultural fields close to the banks of Skensved Å. The main pathways of contamination are surface run-off and contaminated groundwater discharge. Remobilization of pesticides bound to the sediment phase could also play an important role. All the pesticides detected in Skensved Å are not regulated by EQS standards. According to IC analysis, glyphosate and desphenyl-chloridazon show a *potential impact*, as their aquatic toxicity values were exceeding the benchmark of 10 mg/l for crustaceans and algae. Bentazone and AMPA have *no expected impact* on the water course. According to the S analysis, three pesticides (glyphosate, AMPA and desphenyl-chloridazon) cause a *widespread* contamination (dark grey), as they were detected in more than 50% of the stream stretch (100, 89 and 100 % respectively), while bentazone was detected in 11% of the vandområde of interest, falling into the *semi-widespread* contamination category (grey). Regarding the T analysis, former investigations in Skensved Å related to pesticides showed seasonal variations in concentrations into the stream (Mcknight et al., 2012), thus the pesticides are classified as *semi-continuous* contaminants.

The expected sources of PAH contamination are the CSOs and separate stormwater systems that discharge into the stream during wet weather conditions. Seven PAHs (fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b+j+k)fluoranthene, dibenzo(a,h)anthracene and benzo(ghi)perylene) are *impacting the stream even during high dilution* conditions, as they are exceeding the MAC EQS values in at least one investigated point. Benz(a)pyrene and indeno(1,2,3)pyrene exceed the AA EQS and thus *impact* Skensved Å *during low flow conditions*. Benzo(e)pyrene is not regulated through EQS standards, but the ecotoxicity tests and bioaccumulation properties show a *potential impact*. According to the S analysis, five PAHs

(phenanthrene, fluoranthene, pyrene, benzo(ghi)perylene and benzo(e)pyrene) show a *widespread* contamination, while all the other detected PAHs a *semi-widespread* contamination, highlighting that all the investigated stretch is influenced by PAHs. Since the PAHs are released depending on the rain event, the contamination is defined as *pulse*.

Lastly, the heavy metals found in Skensved Å could be related to geogenic, diffuse (if close agricultural fields are fertilized with manure containing high concentrations of heavy metals such as Ni, Cu and Zn) and point sources (CSOs and separate stormwater pipe outlets). Zinc is *impacting the stream even with high dilution* conditions, as it exceeds the AA EQS, while Pb exceeds the AA EQS in one investigated point, falling into the orange category *impact to the watercourse during low flow conditions*. According to the S analysis, Zn cause a *widespread* contamination, as it was detected in 69% of the vandområde of interest. Pb was found in a portion below 10% of the stream stretch of interest, falling into the *limited* contamination category. Cu was also considered in the S calculation, as the concentration found in S8 (3,17 µg/l) was above the 90% quantile found in Danish streams (2,5 µg/l according to DCE (2015)). Therefore, Cu contamination is classified as *limited*. Regarding the T analysis, heavy metal concentrations could be related to both *continuous* and *pulse* contaminations.

**TABLE 26. Assessment Support results as applied to the Skensved Å case study site.**

	Compounds	Expected or known sources	IC	S	T
Chlorinated compounds	Trichlorethylene (TCE)	Point source Contaminated site(s)			Continuous (CMD= 0,4-1,2 kg/y)
	1,1-dichlorethylene (1,1-DCE)				Continuous (CMD= 0,2 kg/y)
	cis-1,2-dichlorethylene (cis-DCE)				Continuous (CMD= 0,2-0,4 kg/y)
Pesticides	Glyphosate	Diffuse source Agricultural fields			Semi-continuous
	AMPA				Semi-continuous
	Bentazone				Semi-continuous
	Desphenyl-chloridazon				Semi-continuous
PAHS	Naphtalene	Point source direct discharges Stormwater separate systems and CSOs			Pulse
	Acenaphtene				Pulse
	Fluorene				Pulse
	Phenanthrene				Pulse
	Anthracene				Pulse
	Fluoranthene				Pulse
	Pyrene				Pulse
	Benzo(a)anthracene				Pulse
	Chrysene				Pulse
	Benzo(b+j+k)fluoranthene				Pulse
	Benz(a)pyrene				Pulse
	Indeno(1,2,3-cd)pyrene				Pulse
	Dibenzo(a,h)anthracene				Pulse
	Benzo(ghi)perylene				Pulse

	Benzo(e)pyrene				Pulse
<b>Heavy Metals</b>	Ni	<b>Point source direct discharges</b> Stormwater separate systems and CSOs		-	Pulse/ Continuous
	Cu				Pulse/ Continuous
	Zn	<b>Geogenic source</b>  <b>Diffuse source</b> Agricultural fields (Ni, Cu, Zn)			Pulse/ Continuous
	As			-	Pulse/ Continuous
	Cd			-	Pulse/ Continuous
	Pb				Pulse/ Continuous

### 9.3 Kirke Å

Kirke Å was analyzed only through a preliminary desktop investigation, without performing an in-depth site inspection of the potential additional sources described in Chapter 6.3. Therefore, it was found that not enough information and data exist to perform the *Impact Assessment*, as past studies focused only on the contamination related to the contaminated site.

Due to the lack of data regarding other potential additional sources of contamination, the answer to the question: "Source information present?" shown in the methodological approach visualized in Figure 8 in the section *Desktop Screening* was "No". Thus, to evaluate the major pollution sources, further site-specific measurements are required.



# 10. Closing remarks and future perspectives

## 10.1 Positive aspects of the proposed methodological approach

- This project confirmed the necessity of studying the anthropogenic impact to surface waters through an integrated and comprehensive approach. The Køge Å and Skensved Å study cases both indicate the presence of multiple stressors acting differently in space and time and impacting or potentially impacting at different scales the water quality of the streams. Thus, for both Køge Å and Skensved Å (and potentially in Kirke Å) it could be shown that: 1) the contaminated sites investigated in the past years are not the only sources impairing the stream, and 2) new potential sources not considered previously were mapped and addressed.
- Few published studies have approached the challenge of identifying the sources and correlating the impacts of pollutants detected in surface water in a multiple stressor context (see e.g. Barber et al., 2006; Escher et al., 2017; Kuzmanović et al., 2016; Sonne et al., 2017), highlighting the inherent difficulty in ranking and differentiating the sources. The 3 phases approach proposed here could be considered a more holistic source-pathway-receptor methodology able to support the assessment of water quality and facilitate a better understanding of the anthropogenic contribution to stream water pollution. The sources initially screened in the first phase (i.e. *Desktop Screening*) could in most cases be linked to the pollutants found in the streams during the site-specific field investigations. This principle could be useful in directing the prioritization of future high resolution (time/space) measurements and supporting future stream restoration efforts.
- The pollutants found in the stream could generally be evaluated in the second phase (i.e. *Impact Assessment*), as the Impact Characterization could provide an understanding of which pollutants to be aware of. Including the environmental fate and toxicity of chemicals not regulated by EQS enables a more comprehensive assessment of the potential risk to the environment and human health for non-regulated (e.g. emerging) pollutants for which monitoring data in the aquatic environment are still needed.
- In addition to characterizing the impact of a pollutant through its EQS or ecotoxicity/bioaccumulation data, the second phase of the methodological approach enables an evaluation of the spatial and temporal occurrence of the chemicals entering the stream. This type of information could be of further assistance in the planning and optimization of future water quality monitoring campaigns, i.e. determining macro-, micro- and representative monitoring locations (Khalil and Ouarda, 2009) with the aim of delineating “worst-case” scenario conditions.
- The third phase of the proposed approach (i.e. *Assessment Support*) collects the results gained in the *Impact Assessment* and reports the characteristics and information of the expected or known source(s). This last phase enables both linking (where possible) the detected chemicals back to their respective sources thus providing decision support to the regulator regarding which category of pollutant (and source) may be driving stream’s contamination under conditions of multiple stress, but thereby also serves as a gap analysis, to guide future data acquisition campaigns where linkages could not be made.

## 10.2 Limitations of the proposed methodological approach

- The method was tested on two case study sites by first evaluating measurements from past investigations (desktop study), followed by acquiring additional data through one additional site-specific survey. The resulting “snapshot” of the status of the receiving waterbody may in reality not be enough to uniquely identify the real pollution drivers, or may miss that these drivers can change according to e.g. season. With such a variety of potential sources and chemicals, and the necessity of looking at a larger scale (compared to the impact from a single contaminated site impacting surface water), it is difficult to predict and evaluate the major pollutant drivers from a single investigation. A better understanding of the spatial and temporal variations of pollutant loads and dilution conditions is therefore needed, which can be gained e.g. by conducting a series of site-specific field campaigns to enable representative data collection, as well as through modelling of the dominant processes affecting water quality. In particular, challenges exist regarding the collection of good quality measurements for pulse and diffuse contamination due to the inherent difficulties in choosing representative monitoring locations, the presence of multiple pathways and the limitations in monitoring resources (e.g. cost burden).
- It became clear through the course of this study that investigations concentrating solely on the stream water compartment will not be comprehensive enough to make definitive conclusions linking pollutants in streams back to their respective sources. Therefore, to truly enable a more comprehensive integrated approach, the sediment compartment and hyporheic zone compartment should be taken into account, as discussed and tested in Sonne et al. (2017).
- “How to deal with chemicals not investigated?” Although it can be difficult to decide which chemicals to monitor for, it is often not possible to conduct investigations for all chemicals due to technical and financial limitations, a problem faced also in this study. It is therefore recognized that the chance will remain that a specific chemical(s) driving impacts may simply not be assessed due to the increasing number of XOCs found in the environment, and considering that more than 85,000 chemicals are in production and use worldwide (McKnight et al., 2015). Moreover, the limited information regarding emerging pollutants and hazard potentials still challenges the standardization of chemical identification methods. Due to limitations in cost and time, expanding the list of targeted analytical methods for more individual compounds may not be the most efficient nor useful approach, as it may not be able to address e.g. transformation by-products (Muz et al., 2017b). Alternative approaches are being proposed, such as the use of non-target screening methods for the identification of “new” chemicals potentially driving impacts, where examples exist for anti-androgenic compounds (Muschket et al., 2018) and aromatic amines (Muz et al., 2017a). New compounds were identified thereby through fragmentation approaches that involved the screening of chemicals with specific modes of actions (Muschket et al., 2018) or common functionalities (Muz et al., 2017b). However, the additional costs associated with such innovative techniques for determining toxic burden, where each sample is split apart into the (potentially) hundreds of chemical components that can then be e.g. tested in an ecotoxicology lab to determine pollution drivers, may make them impossible to realize and implement in large-scale national water quality monitoring campaigns.
- Cumulative effects of complex compound mixtures were not considered. Joint toxicity of mixtures might cause adverse and toxic effects even if all the individual chemicals in the mixture have concentrations below the No Observed Effect Concentration (NOEC) or the EQS (Gustavsson et al., 2017). Cumulative effects of mixtures should be considered during environmental risk assessments, as multiple biological studies have shown quantifiable toxic and unpredictable effects resulting from complex mixtures of chemicals such as pesticides, pharmaceuticals, heavy metals, polyaromatic hydrocarbons and plasticizers on different

trophic levels even when individual effects appear negligible (Carvalho et al., 2014; Fagin, 2012). Concentration Addition (CA) models could be used to further assess the risk related to the combined effect of chemical mixtures, as shown in Bopp et al. (2015) and Kortenkamp et al. (2009). This application of this method can be considered as a conservative, first-tier (screening-level) evaluation, as confirmed by the reviews of Belden et al. (2007) and Rodney et al. (2013).

### 10.3 Future perspectives

- So far, only water bodies impacted by contaminated sites containing chlorinated compounds discharging to streams via groundwater were assessed. Other contaminated sites, such as landfills, gas stations and machine pools could be discharging pollutants to streams and warrant further investigation.
- Yearly field investigation campaigns are not sufficient to understand the overall behavior of seasonal and pulse contaminations. They may additionally misrepresent the worst-case scenario, leading to incorrect conclusions regarding the status of a water body. Due to limitations in budget and time, it was not possible to decide the timing of the sampling campaign depending on all the characteristics of the investigated sources. For example, if the potential impact from CSOs and separate stormwater outlets should be fully addressed, it is recommended to plan and optimize the monitoring campaign in order to catch the contribution during both dry and wet weather conditions. This would help in understanding the contaminant mass discharge related to a single stormwater/CSO outlet for a specific rain event.
- Better planning and integration of methods is needed for evaluating the status of streams under worst-case scenarios for various sources of anthropogenic stream water pollution drivers and to avoid incorrect conclusions regarding stream water pollution drivers. For example, Vezzaro et al. (2017) suggest to address and evaluate the negative effects of CSOs on receiving water bodies through an approach that first assesses the hydraulic parameters (e.g. maximum flows, volumes, frequency of overflows) and then, if CSO discharges could potentially affect the receiving water body, event-based and high time resolution water quality monitoring actions could be planned. For agriculturally-based inputs such as pesticides, numerous studies indicate that sampling campaigns should be conducted especially in April-June (during the main pesticide application period in Denmark) in order to catch pesticides entering streams via tile drains and/or surface runoff through the use of event-triggered water samplers, and in August for capturing inputs from groundwater (McKnight et al., 2012; Rasmussen et al., 2013).
- Multiple compartment assessments are highly recommended, also for the sites investigated in this report, to enable a better linkage of pollutants and their respective sources and dominant transport pathways. Sampling groundwater, sediment and the hyporheic zone compartments would therefore increase the possibility of addressing the pathway of contamination, obtaining a more holistic picture of the chemical quality of the stream, as shown for example in Bigi (2017), Sonne et al. (2017) and Stutter et al. (2007). This will moreover be crucial in paving the way towards suggesting potential remedial actions that are capable of reducing and/or preventing the discharge of contamination at the sources that matter, and may be the most cost-effective solution for some source types.

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# Appendix

## A. Concentrations of chlorinated solvents and degradation products in Køge Å (µg/l)

Transect	TCE		PCE		VC		cis-DCE	
	High Tide	Low Tide	High Tide	Low Tide	High Tide	Low Tide	High Tide	Low Tide
T1	0,18	<d.l.	0,46	0,022	0,89	<d.l.	0,87	<d.l.
T2	<d.l.	<d.l.	0,045	0,056	0,15	0,25	0,10	0,12
	<d.l.	<d.l.	0,027	0,051	<d.l.	0,13	<d.l.	0,11
	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
	<d.l.	<d.l.	0,027	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
T3	<d.l.	0,043	0,052	0,078	<d.l.	0,3	0,051	0,14
	<d.l.	<d.l.	0,032	0,048	0,071	0,038	0,063	0,062
	0,037	<d.l.	0,084	0,072	0,12	0,1	0,12	0,12
	<d.l.	<d.l.	<d.l.	0,038	<d.l.	<d.l.	<d.l.	0,033
T4	<d.l.	<d.l.	0,041	0,091	0,059	0,22	0,041	0,15
	<d.l.	0,065	0,049	0,12	0,063	0,20	0,090	0,20
	0,035	<d.l.	0,097	<d.l.	0,19	<d.l.	0,19	<d.l.
	<d.l.	<d.l.	<d.l.	<d.l.	0,04	<d.l.	0,052	<d.l.

## B. Stream water concentrations of chlorinated solvents (µg/l) from the 2014 campaign in Skensved Å

Point	Coordinates (UTM 33N)		Chlorinated solvents								
	X	Y	PCE	TCE	cis-DCE	trans-DCE	1,1-DCA	CA	VC	1,1,1-TCA	1,1,-DCE
P1	320018,86	6155693,05	<d.l.	0,032	0,022	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,000
P2	320228,31	6155620,37	<d.l.	0,276	0,091	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
P3	320228,04	6155615,31	<d.l.	0,715	0,189	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,019
P4	320226,75	6155595,88	<d.l.	0,867	0,200	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,012
P5	320248,73	6155531,17	<d.l.	3,630	0,951	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,045
P6	320267,62	6155529,18	0,027	6,101	1,557	<d.l.	<d.l.	<d.l.	0,041	<d.l.	0,016
P7	320289,55	6155540,19	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
P8	320305,50	6155540,75	0,047	6,964	1,727	<d.l.	<d.l.	<d.l.	0,048	<d.l.	0,073
P9	320317,09	6155535,77	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
P10	320597,00	6155533,00	<d.l.	2,841	0,786	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0,034

**C. Hyporheic zone concentrations ( $\mu\text{g/l}$ ) of chlorinated solvents from the 2017 campaign in Skensved Å**

Piezometer	Depth (cm)	Coordinates (UTM 33N)		Chlorinated solvents						
		X	Y	PCE	TCE	cis-DCE	trans-DCE	1,1-DCE	CA	VC
piezometer 1	40	320228	6155610	0,089	18,188	2,586	<0,02	0,090	<0,02	<0,02
piezometer 2	40	320226	6155600	0,071	12,967	1,997	<0,02	0,070	<0,02	<0,02
piezometer 3	20	320251	6155526	0,095	42,389	5,614	<0,02	0,352	<0,02	<0,02
piezometer 4	40	320269	6155530	0,118	38,167	5,381	<0,02	0,295	<0,02	<0,02
piezometer 5	40	320299	6155539	<0,02	13,637	1,851	<0,02	0,062	<0,02	<0,02
piezometer 6	40	320298	6155544	<0,02	16,484	2,134	<0,02	0,068	<0,02	<0,02
piezometer 7	40	320299	6155542	0,038	11,670	1,608	<0,02	0,054	<0,02	<0,02
piezometer 8	20	320309	6155540	<0,02	7,542	1,018	<0,02	0,038	<0,02	<0,02
piezometer 9	40	320315	6155538	<0,02	7,631	1,458	<0,02	0,057	<0,02	<0,02

**D. Complete list of analyzed compounds**

Compound	Detection limit	Analysis method
<b>PAHs</b>		
Naphtalene	0,010 $\mu\text{g/l}$	GC/MS
Acenaphtylene	0,010 $\mu\text{g/l}$	GC/MS
Acenaphtene	0,010 $\mu\text{g/l}$	GC/MS
Fluorene	0,010 $\mu\text{g/l}$	GC/MS
Phenanthrene	0,010 $\mu\text{g/l}$	GC/MS
Anthracene	0,010 $\mu\text{g/l}$	GC/MS
Fluoranthene	0,010 $\mu\text{g/l}$	GC/MS
Pyrene	0,010 $\mu\text{g/l}$	GC/MS
Benzo(a)anthracene	0,010 $\mu\text{g/l}$	GC/MS
Chrysene	0,010 $\mu\text{g/l}$	GC/MS
Benzo(b+j+k)fluoranthene	0,010 $\mu\text{g/l}$	GC/MS
Benz(a)pyrene	0,010 $\mu\text{g/l}$	GC/MS
Indeno(1,2,3-cd)pyrene	0,010 $\mu\text{g/l}$	GC/MS
Dibenzo(a,h)anthracene	0,010 $\mu\text{g/l}$	GC/MS
Benzo(ghi)perylene	0,010 $\mu\text{g/l}$	GC/MS
Benz(e)pyrene	0,010 $\mu\text{g/l}$	GC/MS
<b>Chlorinated solvents and degradation products</b>		
Tetrachlorethylene	0,020 $\mu\text{g/l}$	HS GC/MS
Trichlormethane (Chloroform)	0,020 $\mu\text{g/l}$	HS GC/MS
Tetrachlormethane	0,020 $\mu\text{g/l}$	HS GC/MS
1,1,1-trichlorethane	0,020 $\mu\text{g/l}$	HS GC/MS
Trichlorethylene	0,020 $\mu\text{g/l}$	HS GC/MS
Vinylchloride	0,020 $\mu\text{g/l}$	HS GC/MS
1,1-dichlorethylene	0,020 $\mu\text{g/l}$	HS GC/MS
trans-1,2-dichlorethylene	0,020 $\mu\text{g/l}$	HS GC/MS

cis-1,2-dichlorethylene	0,020 µg/l	HS GC/MS
1,2-dibromethane	0,020 µg/l	HS GC/MS
1,2-dichlorethane	0,020 µg/l	HS GC/MS
1,1-dichlorethane	0,020 µg/l	HS GC/MS
Chlorethane	0,10 µg/l	HS GC/MS
Pesticides, regional package 2		
2,4-D	0,010 µg/l	LC/MS
2,4-dichlorphenol	0,010 µg/l	GC/MS
2,6-dichlorphenol	0,010 µg/l	GC/MS
4-CPP, (4-Chlorprop)	0,010 µg/l	LC/MS
4-nitrophenol	0,010 µg/l	LC/MS
Aminomethylphosphonsyre, AMPA	0,010 µg/l	LC/MS
Atrazine	0,010 µg/l	LC/MS
2,6-Dichlorbenzamid (BAM)	0,010 µg/l	LC/MS
Bentazon	0,010 µg/l	LC/MS
Carbofuran	0,010 µg/l	LC/MS
Chloridazon	0,010 µg/l	LC/MS
Prochloraz	0,010 µg/l	LC/MS
Captan	0,010 µg/l	GC/MS
Prometryn	0,010 µg/l	LC/MS
Propachlor	0,010 µg/l	LC/MS
Azinphos-methyl	0,010 µg/l	GC/MS
Mevinphos	0,010 µg/l	GC/MS
Malathion	0,005 µg/l	GC/MS
Parathion-ethyl	0,005 µg/l	GC/MS
Chlorthiamid	0,010 µg/l	LC/MS
Desphenyl-chloridazon	0,010 µg/l	LC/MS
Desethylatrazine	0,010 µg/l	LC/MS
Desethylterbutylazine	0,010 µg/l	LC/MS
Desisopropylatrazine	0,010 µg/l	LC/MS
Dichlorprop(2,4-DP)	0,010 µg/l	LC/MS
Dimethoat	0,010 µg/l	LC/MS
Dinoseb	0,010 µg/l	LC/MS
Diuron	0,010 µg/l	LC/MS
Glyphosate	0,010 µg/l	LC/MS
Hexazinone	0,010 µg/l	LC/MS
Hydroxyatrazine	0,010 µg/l	LC/MS
Isoproturon	0,010 µg/l	LC/MS
Lenacil	0,010 µg/l	LC/MS
Linuron	0,010 µg/l	LC/MS
MCPA	0,010 µg/l	LC/MS
Mechlorprop (MCP)	0,010 µg/l	LC/MS
Metamitron	0,010 µg/l	LC/MS
Metribuzin-desamino-deketo	0,010 µg/l	LC/MS
Metribuzin-deketo	0,010 µg/l	LC/MS
Pendimethalin	0,010 µg/l	GC/MS

Pirimicarb	0,010 µg/l	LC/MS
Propyzamide	0,010 µg/l	LC/MS
Simazine	0,010 µg/l	LC/MS
Terbutylazine	0,010 µg/l	LC/MS
<b>Inorganic analysis package</b>		
pH	0,1 pH	DS/EN ISO 10523:2012
Conductivity	1 mS/m	DS/EN 27888
Calcium, Ca <sup>2+</sup>	0,5 mg/l	ICP DS/EN ISO 11885
Magnesium, Mg <sup>2+</sup>	0,3 mg/l	ICP DS/EN ISO 11885
Potassium, K <sup>+</sup>	0,05 mg/l	ICP DS/EN ISO 11885
Sodium, Na <sup>+</sup>	0,1 mg/l	ICP DS/EN ISO 11885
Iron, Fe	0,01 mg/l	ICP DS/EN ISO 11885
Manganese, Mn	0,001 mg/l	ICP DS/EN ISO 11885
Ammonium+ammonia, NH <sub>4</sub> <sup>+</sup>	0,004 mg/l	SM 17udg. 4500-NH3
Nitrite, NO <sub>2</sub> <sup>-</sup>	0,001 mg/l	DS/EN 26777:2003
Nitrate, NO <sub>3</sub> <sup>-</sup>	0,4 mg/l	SM17udg. 4500-NO3 H
Oxygen, dissolved, O <sub>2</sub>	0,1 mg/l	DS 2205
Total phosphorous, P	0,003 mg/l	DS/EN ISO 6878:2004 del 7
Chloride, Cl <sup>-</sup>	0,5 mg/l	SM17udg. 4500-Cl -E
Fluoride, F <sup>-</sup>	0,03 mg/l	DS 218,MOD
Sulfate, SO <sub>4</sub> <sup>2-</sup>	0,5 mg/l	SM17udg. 4500-SO4
Bicarbonate, HCO <sub>3</sub> <sup>-</sup>	3 mg/l	DS/EN ISO 9963-1:1996
Aggressive carbon dioxide, CO <sub>2</sub>	2 mg/l	DS 236
Suspended solids	0,2 mg/l	DS 207:1985
NVOC	0,1 mg/l	DS/EN 1484:1997
COD	5 mg/l	DS/ISO 15705:2006
BOD <sub>5</sub> , recipient	0,4 mg/l	DS/EN 1899-2
<b>Heavy metals</b>		
Arsenic	0,10 µg/l	ICP-MS
Cadmium	0,10 µg/l	ICP-MS
Copper	0,10 µg/l	ICP-MS
Chromium	0,10 µg/l	ICP-MS
Nickel	0,10 µg/l	ICP-MS
Lead	0,10 µg/l	ICP-MS
Zinc	0,10 µg/l	ICP-MS

**E. Stream water sampling locations in Køge Å and Skensved Å. Coordinates are in UTM 33N**

<b>Sampling location</b>	<b>X</b>	<b>Y</b>
<b>Køge Å</b>		
K1	317379,565	6150813,923
K2	318401,840	6150478,886
K3	318810,860	6150106,012
K4	319572,619	6149805,781
K5	320666,090	6149398,344
K6	321336,325	6149305,588
K7	321537,665	6149135,923
K8	321709,263	6149116,219
K9	321773,560	6148986,810
K10	321925,640	6148789,746
<b>Skensved Å</b>		
S1	317230,781	6157236,183
S2	318333,532	6156462,817
S3	318964,490	6155909,205
S4	319399,863	6155663,444
S5	319739,567	6155643,117
S6	320224,964	6155587,223
S7	320253,070	6155524,414
S8	320291,866	6155540,372
S9	321125,432	6155427,347
S10	321983,938	6155114,967
S11	323433,824	6155184,712

## F. Complete results from the field investigation performed in Køge Å

	Unit	K1	K2	K3	K4	K5	K6	K7	K8	K9	K10
<b>Macro-ions, nutrients and metals</b>											
Calcium, Ca <sup>++</sup>	mg/l	98	97	100	99	100	100	100	99	99	100
Magnesium, Mg <sup>++</sup>	mg/l	5,2	5,3	5,3	5,4	5,8	5,8	5,7	5,6	5,6	5,8
Potassium, K <sup>+</sup>	mg/l	2,8	2,8	2,7	2,6	2,6	2,7	2,6	2,6	2,6	2,7
Sodium, Na <sup>+</sup>	mg/l	16	16	15	15	17	18	18	18	19	20
Iron, Fe	mg/l	0,77	1,1	0,33	0,32	0,27	0,25	0,26	0,24	0,25	0,29
Manganese, Mn	mg/l	0,054	0,062	0,023	0,014	0,008	0,009	0,008	0,008	0,008	0,010
Ammonium+ammonia, NH <sub>4</sub> <sup>+</sup>	mg/l	0,045	3,9	0,047	0,031	0,029	0,017	0,015	0,038	0,016	0,017
Nitrite, NO <sub>2</sub> <sup>-</sup>	mg/l	0,049	0,043	0,060	0,062	0,064	0,066	0,063	0,061	0,059	0,056
Nitrate, NO <sub>3</sub> <sup>-</sup>	mg/l	22	21	26	28	22	22	21	21	21	21
BOD <sub>5</sub>	mg/l	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Total phosphorous, P	mg/l	0,20	0,21	0,13	0,12	0,10	0,098	0,10	0,11	0,11	0,12
COD	mg/l	26	26	23	22	19	20	21	20	20	21
Chloride, Cl <sup>-</sup>	mg/l	32	31	30	30	33	34	34	35	36	36
Fluoride, F <sup>-</sup>	mg/l	0,22	0,23	0,23	0,23	0,22	0,23	0,22	0,23	0,23	0,23
Sulfate, SO <sub>4</sub> <sup>--</sup>	mg/l	28	28	29	28	30	30	30	29	29	29
Suspended solids	mg/l	450	420	420	410	430	420	420	410	410	430
NVOC	mg/l	12	12	10	9,5	8,9	9,2	8,9	9,1	9,0	9,1
<b>PAHs</b>											
Naphthalene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Acenaphthylene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Acenaphthene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Fluorene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Phenanthrene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	0,010	<0,010	<0,010	<0,010
Anthracene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Fluoranthene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Pyrene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Benzo(a)anthracene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Chrysene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Benzo(b+j+k)fluoranthene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Benz(a)pyrene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Indeno(1,2,3-cd)pyrene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Dibenzo(a,h)anthracene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Benzo(ghi)perylene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Benz(e)pyrene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
<b>Chlorinated compounds and degradation products</b>											
Trichloromethane (Chloroform)	µg/l	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
1,1,1-trichlorethane	µg/l	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
Tetrachloromethane	µg/l	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
Trichlorethylene	µg/l	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
Tetrachlorethylene	µg/l	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	0,034	<0,020	<0,020
Chlorethane	µg/l	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10
Vinyl chloride	µg/l	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	0,066	<0,020	0,025
1,1-dichlorethylene	µg/l	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
trans-1,2-dichlorethylene	µg/l	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
cis-1,2-dichlorethylene	µg/l	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	0,043	0,031	<0,020
1,2-dibromethane	µg/l	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
1,2-dichlorethane	µg/l	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
1,1-dichlorethane	µg/l	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
4-chlor-2-methylphenol	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
<b>Pesticides</b>											

2,4-D	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
2,4-dichlorphenol	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
2,6-dichlorphenol	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
4-CPA, (4-Chlorprop)	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
4-nitrophenol	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Aminomethylphosphonsyre, AMPA	µg/l	0,17	0,16	0,15	0,14	0,16	0,15	0,15	0,16	0,13	0,12
Atrazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
2,6-Dichlorbenzamid (BAM)	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Bentazone	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Carbofurane	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Chloridazon	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Prochloraz	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Captan	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Prometryn	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Propachlor	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Azinphos-methyl	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Mevinphos	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Malathion	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Parathion-ethyl	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Chlorthiamid	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Desphenyl-chloridazon	µg/l	<0,010	<0,010	0,011	0,016	<0,010	0,019	0,015	<0,010	<0,010	<0,010
Desethylatrazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Desethylterbutylazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Desisopropylatrazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Dichlorprop(2,4-DP)	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Dimethoat	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Dinoseb	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Diuron	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Glyphosate	µg/l	0,39	0,38	0,51	0,52	0,52	0,47	0,48	0,35	0,31	0,29
Hexazinon	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Hydroxyatrazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Isoproturon	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Lenacil	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Linuron	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
MCPA	µg/l	0,012	0,011	0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Mechlorprop (MCPA)	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Metamitron	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Metribuzin-desamino-deketo	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Metribuzin-deketo	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Pendimethalin	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Pirimicarb	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Propyzamide	µg/l	0,44	0,40	0,19	0,23	0,19	0,18	0,21	0,21	0,24	0,23
Simazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Terbutylazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
<b>Heavy metals</b>											
Cr	µg/l	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
Ni	µg/l	1,28	1,49	1,37	1,23	1,16	1,22	1,17	1,14	1,14	1,14
Cu	µg/l	2,27	1,86	2,48	2,17	1,63	1,71	1,66	2,15	1,88	1,64
Zn	µg/l	7,2	6,94	7,25	3,8	6,8	3,61	4,22	6,44	4,55	5,53
As	µg/l	0,73	0,72	0,72	0,72	0,65	0,66	0,68	0,69	0,68	0,69
Cd	µg/l	<0,1	<0,1	0,21	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
Pb	µg/l	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1

## G. Complete results from the field investigation performed in Skensved Å

	Unit	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
<b>Macro-ions, nutrients and metals</b>												
Calcium, Ca <sup>++</sup>	mg/l	-	120	-	120	-	-	-	-	130	-	-
Magnesium, Mg <sup>++</sup>	mg/l	-	8,1	-	8,4	-	-	-	-	8,8	-	-
Potassium, K <sup>+</sup>	mg/l	-	2,7	-	2,7	-	-	-	-	2,8	-	-
Sodium, Na <sup>+</sup>	mg/l	-	15	-	15	-	-	-	-	17	-	-
Iron, Fe	mg/l	-	0,23	-	0,22	-	-	-	-	0,21	-	-
Manganese, Mn	mg/l	-	0,050	-	0,048	-	-	-	-	0,037	-	-
Ammonium+ammonia, NH <sub>4</sub> <sup>+</sup>	mg/l	-	0,099	-	0,095	-	-	-	-	0,075	-	-
Nitrite, NO <sub>2</sub> <sup>-</sup>	mg/l	-	0,065	-	0,067	-	-	-	-	0,075	-	-
Nitrate, NO <sub>3</sub> <sup>-</sup>	mg/l	-	31	-	31	-	-	-	-	30	-	-
BOD5, recipient	mg/l	-	<1	-	<1	-	-	-	-	<1	-	-
Total phosphorous, P	mg/l	-	0,096	-	0,081	-	-	-	-	0,089	-	-
COD	mg/l	-	16	-	14	-	-	-	-	13	-	-
Chloride, Cl <sup>-</sup>	mg/l	-	29	-	31	-	-	-	-	34	-	-
Fluoride, F <sup>-</sup>	mg/l	-	0,27	-	0,27	-	-	-	-	0,28	-	-
Sulfate, SO <sub>4</sub> <sup>--</sup>	mg/l	-	36	-	40	-	-	-	-	40	-	-
Suspended solids (SS)	mg/l	-	490	-	510	-	-	-	-	500	-	-
NVOC	mg/l	-	6,5	-	6,3	-	-	-	-	6,1	-	-
<b>PAHs</b>												
Naphthalene	µg/l	0,11	<0,010	<0,010	0,011	0,013	0,014	0,021	0,013	<0,010	<0,010	<0,010
Acenaphthylene	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Acenaphthene	µg/l	0,018	<0,010	<0,010	<0,010	<0,010	<0,010	0,014	0,015	<0,010	<0,010	<0,010
Fluorene	µg/l	0,020	<0,010	<0,010	<0,010	<0,010	<0,010	0,019	<0,010	<0,010	<0,010	<0,010
Phenanthrene	µg/l	0,094	<0,010	0,066	<0,010	0,013	0,012	0,099	0,044	0,010	0,056	0,012
Anthracene	µg/l	0,046	<0,010	<0,010	0,012	<0,010	<0,010	0,043	0,021	<0,010	<0,010	<0,010
Fluoranthene	µg/l	0,082	<0,010	0,16	0,024	0,011	0,011	0,14	0,056	0,017	0,13	0,017
Pyrene	µg/l	0,11	<0,010	0,10	0,017	<0,010	0,012	0,13	0,066	0,018	0,13	0,016
Benzo(a)anthracene	µg/l	0,030	<0,010	0,020	<0,010	<0,010	<0,010	0,019	0,012	<0,010	0,030	<0,010
Chrysene	µg/l	0,043	<0,010	0,027	<0,010	<0,010	<0,010	0,028	0,024	<0,010	0,059	<0,010
Benzo(b+j+k)fluoranthene	µg/l	0,11	<0,010	<0,010	<0,010	<0,010	<0,010	0,060	0,055	0,015	0,11	0,019
Benz(a)pyrene	µg/l	0,043	<0,010	<0,010	<0,010	<0,010	<0,010	0,025	0,018	<0,010	0,035	<0,010
Indeno(1,2,3-cd)pyrene	µg/l	0,034	<0,010	<0,010	<0,010	<0,010	<0,010	0,014	0,016	<0,010	0,049	<0,010
Dibenzo(a,h)anthracene	µg/l	0,034	<0,010	<0,010	<0,010	<0,010	<0,010	0,013	0,011	<0,010	0,030	<0,010
Benzo(ghi)perylene	µg/l	0,043	<0,010	<0,010	<0,010	<0,010	<0,010	0,016	0,021	0,012	0,051	<0,010
Benz(e)pyrene	µg/l	0,058	<0,010	<0,010	<0,010	<0,010	<0,010	0,033	0,026	0,011	0,073	<0,010
<b>Chlorinated compounds and degradation products</b>												
Trichlormethane (Chloroform)	µg/l	-	-	-	-	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
1,1,1-trichlorethane	µg/l	-	-	-	-	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
Tetrachlormethane	µg/l	-	-	-	-	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
Trichlorethylene	µg/l	-	-	-	-	<0,020	<0,020	0,042	0,087	0,13	0,11	0,056
Tetrachlorethylene	µg/l	-	-	-	-	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
Chlorethane	µg/l	-	-	-	-	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10
Vinyl chloride	µg/l	-	-	-	-	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
1,1-dichlorethylen	µg/l	-	-	-	-	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	0,026
trans-1,2-dichlorethylen	µg/l	-	-	-	-	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
cis-1,2-dichlorethylen	µg/l	-	-	-	-	<0,020	<0,020	<0,020	<0,020	0,045	0,032	0,021
1,2-dibromethan	µg/l	-	-	-	-	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
1,2-dichlorethan	µg/l	-	-	-	-	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
1,1-dichlorethan	µg/l	-	-	-	-	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020	<0,020
4-chlor-2-methylphenol	µg/l	-	-	-	-	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
<b>Pesticides</b>												



2,4-D	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
2,4-dichlorphenol	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
2,6-dichlorphenol	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
4-CPP, (4-Chlorprop)	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
4-nitrophenol	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Aminomethylphosphonsyre, AMPA	µg/l	0,050	0,047	0,045	0,043	0,050	0,046	0,044	0,051	0,039	0,051	0,043
Atrazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
2,6-Dichlorbenzamid (BAM)	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Bentazone	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	0,033
Carbofuran	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Chloridazon	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Prochloraz	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Captan	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Prometryn	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Propachlor	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Azinphos-methyl	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Mevinphos	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Malathion	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Parathion-ethyl	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Chlorthiamid	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Desphenyl-chloridazon	µg/l	0,020	0,020	0,018	0,012	0,017	0,018	0,017	0,017	0,014	0,017	<0,010
Desethylatrazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Desethylterbutylazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Desisopropylatrazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Dichlorprop (2,4-DP)	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Dimethoat	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Dinoseb	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Diuron	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Glyphosate	µg/l	0,035	0,033	0,032	0,031	0,034	0,030	0,027	0,031	0,031	0,031	0,038
Hexazinone	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Hydroxyatrazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Isoproturon	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Lenacil	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Linuron	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
MCPA	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Mechlorprop (MCP)	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Metamitron	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Metribuzin-desamino-deketo	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Metribuzin-deketo	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Pendimethalin	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Pirimicarb	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Propyzamide	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Simazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
Terbutylazine	µg/l	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010	<0,010
<b>Heavy metals</b>												
Cr	µg/l	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
Ni	µg/l	1,46	1,33	1,47	1,57	1,58	1,55	1,61	2,18	1,88	1,82	2,39
Cu	µg/l	1,68	1,92	1,55	1,75	1,65	1,77	1,55	3,17	2,41	1,63	1,65
Zn	µg/l	17,84	29,44	11,67	4,25	6,02	5,48	5,94	9,77	16,71	37,45	20,25
As	µg/l	0,72	0,73	0,67	0,67	0,68	0,65	0,7	0,91	0,66	0,7	0,71
Cd	µg/l	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
Pb	µg/l	<0,1	<0,1	2,85	<0,1	<0,1	<0,1	<0,1	0,1	<0,1	<0,1	0,26

**H. Pesticides detected in Skensved Å and/or Køge Å in the field investigation. The table includes information about the type of pesticide, the application period, general description of the chemical, use in Denmark, current EU/Danish status, maximum annual sales**

Compound	CAS number	Type	Detected in	Application period in DK	Description	Use in Denmark	Current EU status/DK (if different)	Max. annual sales- tones
Glyphosate	1071836	Herbicide	Køge Å Skensved Å	1975 - present	<ul style="list-style-type: none"> <li>Most widely used herbicide in the world and in Denmark</li> <li>Pre- or post-harvest to control the growth of annual and perennial weeds</li> </ul>	Cereals, public gardens, grassland, roadside grass	Permitted	1638 (*)
AMPA	1066519	Metabolite (glyphosate)	Køge Å Skensved Å	-	<ul style="list-style-type: none"> <li>Primary transformation product of glyphosate</li> </ul>	-	-	-
Desphenyl-chloridazon	6339191	Metabolite (chloridazon)	Køge Å Skensved Å	1964-1996 (chloridazon)	<ul style="list-style-type: none"> <li>Primary transformation product of the herbicide chloridazon</li> <li>used for pre-plant, pre-emergence and early post emergence use</li> </ul>	beet, beetroot , onion	Permitted/Banned (chloridazon)	-
MCPA	94746	Herbicide	Køge Å	1956 - present	<ul style="list-style-type: none"> <li>Selective and widely used post-emergence phenoxy herbicide</li> <li>Used for the formulation of other compounds such as 2,4-D and MCPB</li> </ul>	Cereals, peas, grassland, golf courses, public gardens, orchards	Permitted	965 (*)
Propyzamide	23950585	Herbicide	Køge Å	1992- present	<ul style="list-style-type: none"> <li>Provides effective control annual and perennial weeds</li> <li>Acts on the roots of the target plant</li> </ul>	rape, loganberry, pear, plum and raspberry	Permitted	45 (**)
Bentazone	25057890	Herbicide	Skensved Å	1974 - present	<ul style="list-style-type: none"> <li>Selective herbicide</li> <li>In the national list of water pollutants to be controlled</li> </ul>	Cereals, peas, clover, corn	Permitted	93 tones(*)

(\*) Miljøstyrelsen (2013).

(\*\*) Miljøstyrelsen (2017).

**I. Environmental Quality Standards (EQS), aquatic toxicity and bioaccumulation of the pollutants found in Køge Å and Skensved Å. Aquatic toxicity and bioaccumulation were reported only if an EQS did not exist for the specific chemical**

Compound	CAS number	Found in	EQS <sup>(a)</sup> (µg/l)		Lowest reported value of aquatic toxicity (mg/l)				Bioaccumulation	
			AA	MAC	Crustacean (D.Magna) (48h LC/EC50)	Fish (96h LC50)	Algae (72/96h EC50)	Plant (72/96h EC50)	Log K <sub>ow</sub> (l/kg)	BCF
<b>Chlorinated solvents and degradation product</b>										
Trichlorethylene (TCE)	79-01-6	Skensved Å	10	-	-	-	-	-	-	-
Tetrachlorethylene(PCE)	127-18-4	Køge Å	10	-	-	-	-	-	-	-
Vinylchloride (VC)	75-01-4	Køge Å	0,05	0,5	-	-	-	-	-	-
1,1-dichlorethylene (1,1-DCE)	75-35-4	Skensved Å	6,8	68	-	-	-	-	-	-
cis-1,2-dichlorethylene (cis-DCE)	156-59-2	Køge Å, Skensved Å	-	-	79 <sup>(c)</sup>	135 <sup>(b)</sup>	59,69 <sup>(d)</sup>	-	1,86 <sup>(b)</sup>	8 <sup>(b)</sup>
<b>Pesticides</b>										
AMPA	1066-51-9	Køge Å, Skensved Å	-	-	690 <sup>(e)</sup>	520 <sup>(e)</sup>	90 <sup>(e)</sup>	-	- 2,17 <sup>(i)</sup>	-
Bentazone	25057-89-0	Skensved Å	45	450	-	-	-	-	-	-
Desphenyl-chloridazon	6339-19-1	Køge Å, Skensved Å	-	-	49 <sup>(c)</sup>	35 <sup>(f)</sup>	5,1 <sup>(d)</sup>	-	-	-
Glyphosate	1071-83-6	Køge Å, Skensved Å	-	-	4,1 <sup>(d)</sup>	22 <sup>(e)</sup>	3,52 <sup>(d)</sup>	24 <sup>(d)</sup> (168h)	- 3,4 <sup>(b)</sup>	1,4-5,9 <sup>(g)</sup>
MCPA	94-74-6	Køge Å	-	-	180 <sup>(d)</sup>	6,6 <sup>(d)</sup>	21,67 <sup>(d)</sup>	4,24 <sup>(d)</sup> (168h)	2,73 <sup>(j)</sup>	<1 <sup>(k)</sup>
Propyzamide	23950-58-5	Køge Å	-	-	5,6 <sup>(d)</sup>	10,6 <sup>(d)</sup>	0,287 <sup>(d)</sup>	0,95 <sup>(d)</sup> (168h)	3,43 <sup>(b)</sup>	6-20 <sup>(b)</sup>
<b>PAHs</b>										
Naphthalene	91-20-3	Skensved Å	2	130	-	-	-	-	-	-
Acenaphthylene	208-96-8	Skensved Å	1,3	3,6	-	-	-	-	-	-
Acenaphthene	83-32-9	Skensved Å	3,8	3,8	-	-	-	-	-	-
Fluorene	86-73-7	Skensved Å	2,3	21,2	-	-	-	-	-	-
Phenanthrene	85-01-8	Skensved Å	1,3	4,1	-	-	-	-	-	-
Anthracene	120-12-7	Skensved Å	0,1	0,1	-	-	-	-	-	-
Fluoranthene	206-44-0	Skensved Å	0,0063	0,12	-	-	-	-	-	-

Pyrene	129-00-0	Skensved Å	0,0046	0,023	-	-	-	-	-	-
Benzo(a)anthracene	56-55-3	Skensved Å	0,012	0,018	-	-	-	-	-	-
Chrysene	218-01-9	Skensved Å	0,014	0,014	-	-	-	-	-	-
Benzo(b+j+k)fluoranthene	205-82-3	Skensved Å	0,00051	0,051	-	-	-	-	-	-
Benzo(a)pyrene	50-32-8	Skensved Å	0,00017	0,27	-	-	-	-	-	-
Indeno(1,2,3-cd)pyrene	193-39-5	Skensved Å	0,00017	-	-	-	-	-	-	-
Dibenzo(a,h)anthracene	53-70-3	Skensved Å	0,0014	0,018	-	-	-	-	-	-
Benzo(ghi)perylene	191-24-2	Skensved Å	0,00017	0,0082	-	-	-	-	-	-
Benzo(e)pyrene	192-97-2	Skensved Å	-	-	0,33 <sup>(d)</sup>	-	-	-	6,70 <sup>(h)</sup>	-
Heavy Metals										
Ni	7440-02-0	Køge Å, Skensved Å	4	34	-	-	-	-	-	-
Cu	7440-50-8	Køge Å, Skensved Å	4,9	4,9	-	-	-	-	-	-
Zn	7440-66-6	Køge Å, Skensved Å	7,8	8,4	-	-	-	-	-	-
As	7440-38-2	Køge Å, Skensved Å	4,3	43	-	-	-	-	-	-
Cd	7440-43-9	Køge Å	0,08-0,25	0,45-1,5	-	-	-	-	-	-
Pb	7439-92-1	Skensved Å	1,2	14	-	-	-	-	-	-

<sup>(a)</sup>: BEK nr. 439 of 19/05/2016.

<sup>(b)</sup>: PubChem Chemical Database.

<sup>(c)</sup>: Sonne et al. (2017).

<sup>(d)</sup>: ECOTOX Chemical Database.

<sup>(e)</sup>: European Glyphosate Environmental Information Source (EGEIS): Aquatic ecotoxicity of glyphosate and formulated products containing glyphosate.

<sup>(f)</sup>: PAN Pesticides Database – the value refers to the parent compound chloridazon.

<sup>(g)</sup>: Contardo-Jara et al. (2009).

<sup>(h)</sup>: GSI Chemical Database.

<sup>(i)</sup>: Traas and Smit (2003).

<sup>(j)</sup>: EPA (2004).

<sup>(k)</sup>: Naylor R. (1996).



### **Investigating stream water quality under conditions of multiple stress**

Contaminated sites are among one of the major environmental problems in Denmark, contaminating soil, groundwater and surface water bodies located nearby. Recently, screening tools and risk assessment methods have been developed to support the Danish Regions in evaluating the impact contaminated groundwater originating from these sites may have on Danish streams (Miljøprojekt nr. 1846, Miljøprojekt nr. 1604 ). However, investigations related to stream water affected by contaminated sites have to-date only covered single sources of contaminants.

This report provides a decision support tool for assessing the importance of contaminated sites in relation to other potential sources impacting the streams, with the aim of identifying the impact drivers in a multiple stressor context.



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