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A simple screening tool to assess the impacts of combined sewer overflows on freshwater – A Danish case

Master Thesis in Advanced Hydrosystem

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Approval

This thesis has been prepared over six months at the Section for Indoor Climate, Department of Civil Engineering, at the Technical University of Denmark, DTU, in partial fulfilment for the degree Master of Science in Engineering, MSc Eng.

It is assumed that the reader has a basic knowledge in the areas of hydraulics.

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Date

Abstract

With the progress of urban wastewater treatment, wet weather discharges coming from urban impervious surfaces represents an increasing percentage of the load of contaminants potentially discharged to the European stream network Pistocchi 2020. Moreover, the number of contaminants is increasing in the past years due to an increasing everyday use of products such as cosmetics, pharmaceuticals and pesticides. These contaminants found in the rivers are often referred to as CEC (Contaminants of Emerging Concern) and beyond being harmful for the environment, CEC also present a threat for human health Delli Compagni et al. 2020. Climate change is also playing an important role as it is projected to cause more precipitation (hence urban runoff volume) in the North of Europe Bisselink et al. 2018. Weather is also expected to become more unpredictable, with longer dry spells and more intense storms potentially enhancing both build-up and wash-out of pollution from urban surfaces Heinrich and Gobiet 2011.

The aim of this thesis, according to the request moved by the European Union expressed in the Water Framework Directive (Directive 2000/60/EC) of having more data about water quality (Art.27), is to provide a first estimation of micro-pollutant concentration in Danish rivers. Improving stormwater treatment to reduce wet weather discharges is not only key to pollution control, but also a no-regret option for a more sustainable use of water. Taking into account vertical gardens and green areas become fundamental to reduce urban runoff Pistocchi, Zalewski, and Bidoglio 2017.

Points sources contribute to about 10 percent of the yearly discharges of nitrogen and phosphorous to Danish water environment and wet weather discharges represent a non-negligible fraction of this contribution (Jensen et al. 2018; Thodsen et al.2018). Danish system is constant in monitoring the situation in Denmark providing micropollutant loads that are estimated by the municipalities every year using mathematical models. These data are collected in the PULS database (punktkildedatabase) managed by the ministry of Environment and Food of Denmark.

Even if Danish system is very accurate in collecting every year the discharged volumes and micropollutants loads it lacks in specifying if these micropollutants once discharged into the river are diluted enough or not.

The implementation of detailed models to calculate s concentration is often difficult, costly, and cannot be applied on a big scale (regional/national level). Therefore, simple, indicative quantifications methods are needed to estimate CSO (Combined Sewer Overflow) and river discharges of CEC, enabling a quick estimation of their impacts in natural water bodies. This is the aim of the Joint Research Centre (JRC); giving a first quantification of pollution conveyed by urban runoff at European continental scale using a simple model based on event mean concentration (EMC).

This thesis aims at developing a simple model as well to give a rough quantification of CEC concentrations from overflow discharges on natural water bodies, and thereby estimating their impacts and their dilution in the river. Specifically, this thesis will:

- Investigate the different modelling approaches to estimate CEC concentrations in the Mølle Å river.
- Apply the above mentioned model at a big scale i.e. Denmark

One of the research question of the study was also comparing the obtained results with the JRC's ones calculated for European cities to see if there were similarities between the two models.

The comparison would have also been important to explore the possibility of applying the model in other countries where no freely open data are available as in Denmark in case the results matched. Unluckily the comparison would be made in the next steps of the study because it has not been possible to have the data by the time of this thesis. This simple model is based on a set of assumptions and is thus affected by a higher uncertainty respect to the Danish model, but it provides an indication of a potential problem.

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Chiara Scarpellini, MSc Civil Engineering, DTU
Creator of this thesis template.

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1 Introduction

Modelling the river concentration coming from the CSO discharges is not an easy task. Combined sewage is a mixture of domestic sewage and stormwater runoff and it is usually conveyed away from urban areas through underground sewer systems and treated at wastewater treatment plants (WWTP). Nevertheless, during medium and large storms the underground sewer systems are overloaded and so they convey part of the water straight to the river to protect the city from possible flooding. These outlets that discharge directly into the rivers are called combined sewer overflows. On an annual basis only a minor fraction of the total combined sewage volume is discharged through these structures but during heavy rains their contribution play a significant role in the amount of water conveyed to the rivers compared to dry weather conditions. Together with emissions are denoted as wet weather discharges.

Wet Weather Discharges are more and more in the limelight because of the implementation of related environmental legislation in Denmark and across the EU during the period 1987-2000 mainly focuses on continuous emissions. The Water Framework Directive (2000/60/CE) moved the focus from single discharge points to a more holistic evaluation of the ecological status of the receiving water body. Furthermore it is very important to monitor wet weather discharges because they are continuously increasing and with them, the amount of micropollutants they carry. The volumes discharged into the rivers are increasing according to two main reasons; urbanization and climate change. The first one intensifies the pressure on receiving water bodies caused by wet weather discharges because of the continuously increasing percentage of impervious surfaces in urban areas. These indeed lead to a rise in the runoff flows and volumes because they limit the infiltration into the soil. Climate Change plays an important role as well in worsening the situation as it is projected to cause more precipitation (hence urban runoff volume) in the North of Europe. The hydrologic cycle is expected to become more impulsive with longer dry spells and more intense storms Heinrich and Gobiet 2011.

Integrated management of urban water have been promoted for decades at the European level, promoted by legislation such as the Water Framework Directive "DIRECTIVE 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2000 establishing a framework for Community action in the field of water policy" 2000-10-23. However, given the difficulties of current monitoring protocols to detect impacts of urban wet-weather discharges (SSSO-Separate Storm Sewer outlets and CSO-Combined Sewer Overflows),integrated models have been proposed as effective tools for planning and implementing integrated solutions and achieving the desired quality status (e.g. Gilli et al.,2019). The implementation of complex models indeed, requires importance resources for data collection, model implementation and validation. Thus, these tools are not always the best options for screening activities, where urban water managers need to identify critical areas for prioritizing their investments.

This work presents itself as a simple screening model able to provide a first quantification of pollution conveyed by urban runoff at a small scale. The study exploits data that are freely available in the Danish context (modelled flows in natural streams and wet-weather discharges, measured concentrations) to screening the potential threat caused by micropollutants to the chemical status of Danish natural streams. This simple screening model doesn't take into account the chemical degradation of the micropollutants but is a model just based on dilution and advection. It allows thought to identify stream stretches were environmental Quality Standards (EQS) can potentially be exceeded as consequence of wet-weather discharges. Althought taking advantage from the ”rich data” calculated by the Danish government, the proposed simple approach can be adapted to the measured/modelled data in other countries such as the ones fro the Joint Research Centre to provide a first identification of the areas negatively impacted by urban wet-weather discharges. The localization of these area is of key importance to address and highlight critical ones. On these areas, one individualized, will be prioritized the available resources and on them more sophisticated models would be applied.

2 Theoretical Background

This work will focus its attention in analyzing the concentration of micropollutants coming from wet weather discharges from Combined Sewer Overflows (CSO). This chapter has the aim of providing the reader some basic knowledge on how water quality is usually estimated in rivers and why is becoming more and more important to keep under control the parameters that describe it. Water quality characterization is primarily done by surface water sampling and chemical analysis. The main legislation regulating water quality safeguard at an European scale is the Water Framework Directive “DIRECTIVE 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2000 establishing a framework for Community action in the field of water policy” 2000-10-23. Cities and other high density human settlements discharge a constant flux of pollutants through outlets from wastewater treatment plants, while additional pollutant fluxes are discharged during rain events through outlets from separated drainage systems (stormwater) and combined sewer overflows, CSO (mixed of stormwater and wastewater) that take place only during a limited number of events per year.Sewer Systems can be:

1. Separate, divided in:
    - Sanitary sewers: designed to carry sewage (wastewater) from houses or industries to a Waste Water Treatment Plant (WWTP).
    - Storm drains: designed to collect and transport excess rain to a receiving water body (river, lake or sea) without being treated without being treated but assuming that the rain will dilute it.
2. Combined Sewer Systems are instead sewer systems designed to collect sanitary sewage and stormwater runoff in a single pipe system. During dry weather, sewage is delivered to WWTP while during storms, if the capacity of the pipe is overcame, excess flow is spilled into receiving water bodies.

CSO discharges are intermittent with a significantly lower frequency respect to rain events. It is estimated that in Denmark CSOs discharge 5-10 times/year against the 110-130 rainy days per year *DMI* 2019.

Wet weather discharges were studied intensively during the past years because it has been recognised how much emissions coming especially from CSOs impact small creeks and lakes Eriksson, Baun, and Mikkelsen 2007a. The implementation of environmental legislation aiming at safeguarding the quality status of the water both in Denmark and in the rest of Europe however is still nowadays mainly focus on continuous emissions. Even if not still regulated by legislation, intermittent discharges play an important role in affecting the overall quality of the receiving water body and need to be kept under control.

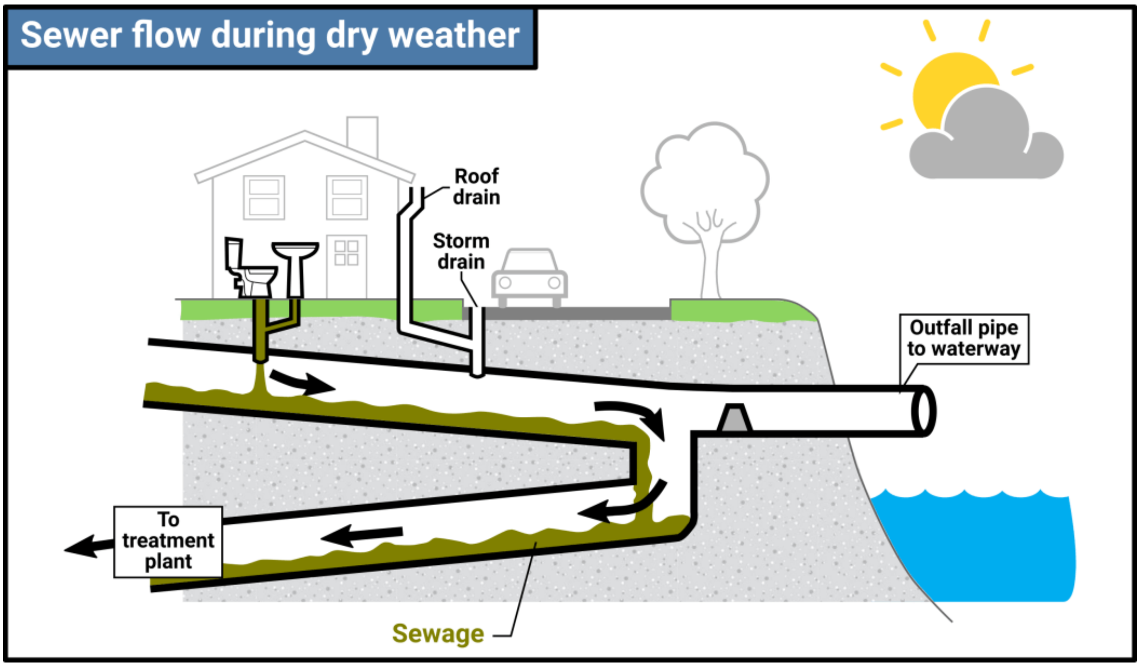


Figure 2.1: Combined Sewer Overflow during dry weather: both sewage from domestic/industrial sources and rain go to the WWTP. *Ecoss.org* n.d.

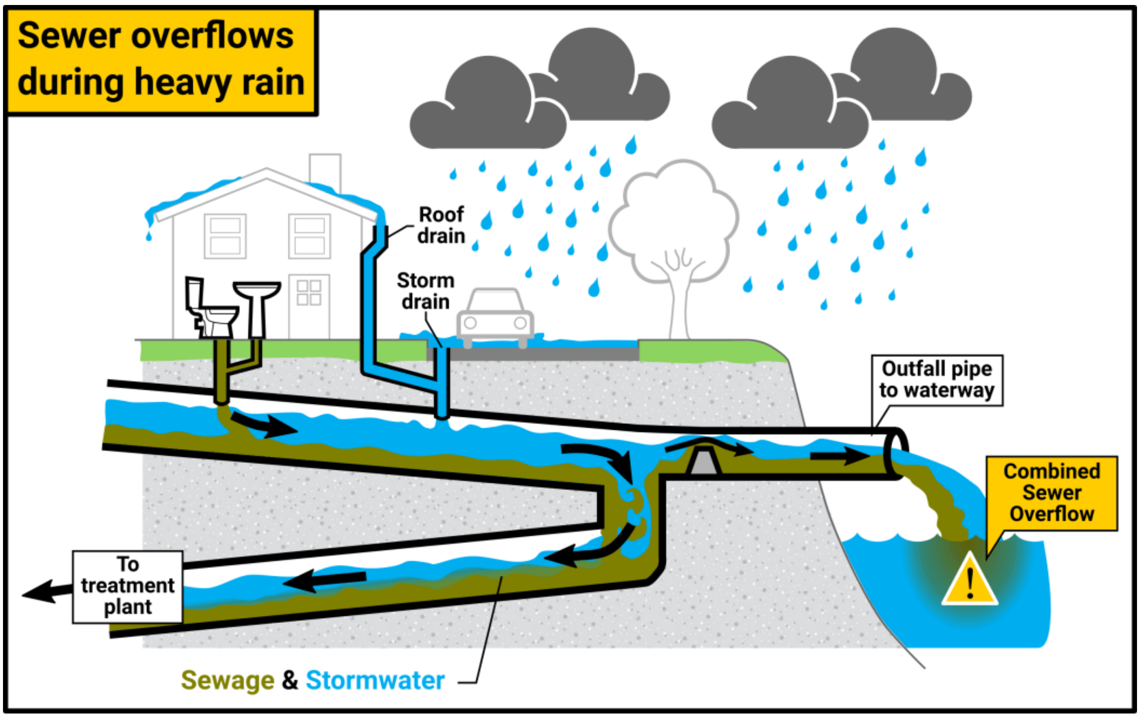


Figure 2.2: Combined Sewer Overflow during wet weather: the increased flow caused by the storm water runoff exceeds the sewage system, untreated wastewater is forces into receiving water bodies through CSO outfalls. *Ecoss.org* n.d.

2.1 Importance of clean water

As population is continuously growing there is the necessity of increasing food supply. According to FAO by 2030 the world will require 60% more food, which 80% will be provided by intensifying agriculture through irrigation. *FAO. Water:source of food security* 2002 It is becoming urgent then understanding where to find the water sources to irrigate the new crops destined to agriculture as the easily available water sources are widely exploited. Irrigation, differently from drinking water supply can relate on water with a lower quality. This can create the opportunity to use different water sources such as the reuse of reclaimed wastewater Delli Compagni et al. 2020. Reuse of reclaimed wastewater (RWW) for agricultural irrigation limits the exploitation of fresh water sources necessary for drinking and already scarce. Wastewater would also be rich of essential plant nutrients (e.g., P and N) useful for cultivating but harmful for the river status as they increase the eutrophication in the river's surface. Even though, using this water would be necessary in the future to supply water to new cultivation crops and safeguard the sources of fresh drinking water, at the same time, it could be extremely dangerous. Indeed, in the past minimum quality standards were suggested in order to guarantee the health of plants and to avoid human health impacts *FAO. Wastewater treatment and use in agriculture* 1992. These recommendations however can't be used anymore nowadays as they don't reflect the status of the river that is now threatened by new substances. Regardless of conventional micropollutants such as heavy metals and toxic elements, the attention is rising in the last years on new constituents labelled as contaminant of emerging concern (CECs). These are pharmaceuticals, biocides and fertilizers.

2.2 Micropollutant

A micropollutant is any pollutant that can cause a toxic effect at a very small concentration. Many organic pollutants, such as, organochlorine pesticides (OCPs), polychlorinated biphenyl (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are detected in the environment at low concentrations. Due to their large-scale production and usage, toxicity, bioaccumulation and persistence in the environment, they can cause harmful effects to organisms and to human health. Atmospheric deposition, industrial and urban activity presents the main sources of environmental pollution.

Analyzing rivers' water what comes out is the always new presence in water of new compounds. These new micropollutants have been labelled as Contaminant of Emerging Concerns by water quality professionals. Contaminants of emerging concern (CECs) is a general term that covers a broad class of different types of chemical compounds, including medicines, personal care or household cleaning products, flame retardants, lawn care and agricultural products *Contaminants of emerging concerns* n.d. These diverse compounds are classified as "emerging" because they are often newly identified manufactured or naturally occurring chemicals and typically are not regulated under current environmental laws. They have garnered much attention lately from scientists due to their widespread occurrence in surface water and their potentially deleterious effects in aquatic life at low concentration (<1µg/L). Probably, these new substances were already presents in the water from decades but their presence is acquiring now a rising importance because of the threat they pose. Another key reason of the increase in the attention and further monitoring of the quality of the water is due to the need of utilizing this water for irrigating crop fields. Irrigation can rely on water with lower quality compared to drinking water supply, creating the opportunity for exploiting alternative water sources. It is of mandatory importance the reuse of reclaimed wastewater (RWW) for agriculture irrigation as this limits the exploitation of high quality fresh water. This would also allow the provision of essential plant nutrients such as P and N contained in RWW, which otherwise would be discharged into rivers and oceans, increasing eutrophication and harming marine environment.

2.3 Water Quality Standards

The Water Framework Directive has the aim of protecting the environment from the adverse effects of urban waste water and industrial discharges. The directive makes it a legal requirement to clean the waste water from communities of more than two thousand population equivalent and sets the rules on how stringent the treatment must be. A revision of the Directive was schedule on 21/07 and was planned to address those areas of improvements that have been identified by the Joint Research Centre (JRC). The aim of the check out was also the one of align the Directive with the points outlined in the European Green Deal.

2.3.1 AA EQS and MAC EQS

EQS is an environmental medium quality standard for specific substances, which sets concentration thresholds below which, no adverse impact on the medium occurs, and which takes explicit account of available dilution at different discharge locations Inglezakis et al. 2016. The Environmental Quality Standards (EQS) for Danish streams are defined in the Bekendtgørelse BEK 1625 19/12/2017 which is an integration of the European EQS directive (2013/39/EU). For some of the substances of the study, EQS are not defined at the European level yet, but their values have been retrieved from the Swiss Ecotox Centre, 2020.
EQS are expressed as Maximum Allowed Concentration (MAC-EQS), i.e. a value that should never be exceed, and an Annual Average (AA-EQS), a value that should not be exceeded on a yearly basis. These two values represent respectively the acute toxicity and the chronic toxicity. Where the former relates to adverse effects that occur within 14 days of exposure and the latter relates to adverse effects resulting from long term exposure to the substance.

2.4 Water Quality Data

The water quality data used for this work have been provided by Mutzner et al. 2021. Mutzner et al. in their work highlight the need to identify critical contaminants and quantify pollutant concentrations in wet-weather discharges to assess effective control strategies. Urban wet-weather either coming from combined sewer overflows (CSO) or separate sewers (SWO) carry traces of contaminants which can pose a threat for receiving water bodies. As stated in their work the monitoring campaigns to estimate the amount of pollutants conveying in the rivers are still limited as most contain small, local data-set both in terms of sampled discharge events and spatial coverage. Their study aims, as this one, basing on data-driven statistical analysis of existing measurements, at informing regulators and future policy makers about the need to increase the monitor efforts. The data gathered for the study come from 63 sites, 506 monitored events and more than 42.000 observations that have been provided as raw data by the authors of every country. The raw data were transformed to consider the difference in the limit of quantification (LOQ) or detection (LOD) in the data-sets. Contaminant concentrations<LOQ were treated as missing values and estimated using regression on order statistics (ROS). ROS was applied if there were more than 3 observations per site and less than 80% missing data. Then have been assessed the contaminants that i) are often found when looked for (they need to have at least once>LOQ at site) and ii) are found in concentrations, above the environmental water quality limits, calculated as a required dilution factor (DF). The dilution factor has been calculated using a 90% percentile EMC concentration of all sites divided by the environmental chronic water quality standard (CQS). The higher is the result of DF the more problematic a contaminant is expected to be for the water bodies.

CAS	Substance	10% Conc [μg/L]	Median [μg/L]	90% Conc [μg/L]
39475-55-3	Chlorpyrifos	1.6E-04	4.0E-04	1.7E-03
101802-54-4	Pentachlorophenol	2.0E-01	4.3E-01	8.6E-01
140-66-9	4-tert-Octylphenol	3.0E-02	6.8E-02	1.6E-01
120-12-7	Anthracene	1.4E-03	1.5E-02	1.5E-01
6699-27-0	Benzo[a]pyrene	2.7E-03	4.7E-02	8.0E-01
82208-43-3	DEHP	3.1E-01	1.1E+00	4.2E+00
27100-33-0	Bisphenol A	4.4E-02	1.8E-01	7.8E-01
76774-50-0	Fluoranthene	1.4E-02	1.9E-01	2.8E+00
63278-70-6	Carbendazim	2.4E-04	1.4E-02	7.0E-01
102962-29-8	Diuron	2.2E-03	3.0E-02	3.6E-01
138261-41-3	Imidacloprid	4.6E-03	1.6E-02	8.0E-02
81271-94-5	Cadmium	1.2E-02	1.7E-01	8.1E-01
195161-82-1	Chromium	4.3E-01	2.9E+00	1.7E+01
7440-50-8	Copper	5.2E+00	6.0E+01	2.7E+02
21595-53-9	Nickel	7.1E-01	2.9E+00	1.2E+01
7439-97-6	Mercury	7.0E-03	2.5E-02	8.7E-02
19229-95-9	Zinc	1.3E+01	2.4E+02	1.5E+03
886-50-0	Terbutryn	7.8E-04	7.9E-03	8.0E-02
7439-92-1	Lead	9.2E+00	3.1E+01	1.4E+02
15307-86-5	Diclofenac	8.3E-03	9.1E-02	5.3E-01

Table 2.1: Estimated micropollutant concentrations percentiles estimated by researchers at DTU through raw data coming from 63 sites and 506 events.

2.4.1 EU Legislation

The main European directives relevant to the management of urban stormwater runoff are:

- The EU Water Framework Directive (WFD) from 2000 "DIRECTIVE 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2000 establishing a framework for Community action in the field of water policy" 2000-10-23.
- The EU Floods Directive (FD) from 2007 "DIRECTIVE 2007/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2007 on the assessment and management of flood risk" 2007-10-23.
- The Environmental Quality Standards Directive (EQSD) from 2008, which is a daughter directive of the WFD. "DIRECTIVE 2008/105/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directive 2000/60/EC of the European Parliament and of the Council" 2008-12-16

The aim of the WFD is the one of protecting all water systems and assure that they are in a good ecological-chemical status. The ecological status is defined in terms of the quality of the biological community e.g flora, fish fauna ecc. Chemical status is instead determined on the compliance or not of the river micropollutant concentration with the Environmental Quality Standards (EQSs) established for the chemical substances. A relevant part of the WFD implementation is the production of the River Basin Management Plans (RBMPs) which aim is describing the current status of the water environment and program the interventions that need to be addressed in the future.The latest studies (still on progress) highlight that only 40% of European surface water have achieved the label of good ecological status, the number drop to 38% for the chemical status Kristensen et al. 2018. An important factor that may hinder such statuses is emissions of wet weather discharges from urban areas, notably combined sewage containing both domestic and storm water Vezzaro et al. 2018. The introduction of the WFD in 2000 has brought to the limelight the importance of protecting natural recipients, this operation is though still hindered by the different legislation and organizational paths across the member countries Sage, Berthier, and M. 2015.

Typical pollutant concentrations are listed for a range of typical water quality criteria, including priority pollutants and new emerging contaminants. The legislation regulating the monitoring of discharges from WWTPs include the EU Wastewater directive (91/271/EEC) and its danish implementation (BEK nr 1469 af 12/12/2017).

2.4.2 Denmark

Even if Denmark had an ambitious start with the application of WFD, later its implementation has slowed down due to cost-effective focus and agricultural interests. It is estimated that just the 24% of rivers satisfy the WFD requirement of good ecological status Bourblanc et al. 2012. While the EU regulation mainly aims at monitoring compliance with discharge limits (i.e. concentrations expressed as Emission Limit Values- ELV), the Danish legislation also enforces a monitoring of discharged loads. Discharged pollutant loads (N,P,BOD5) are taxed (Skatteministeriet,2016), creating an economic incentive for the reduction of pollutant outlet concentrations significantly below the allowed ELV. In Denmark, each municipality should report annually the total discharged volumes and pollutant loads from all wet-weather discharges in their municipality for selected water quality indicators (5-day Biological Oxygen Demand (BOD5), Chemical Oxygen Demand (COD), total nitrogen (N). and total phosphorous (P)). These indicators are related to short-term acute effects, such as oxygen depletion (COD, BOD5), or to long-term accumulative effects, such as eutrophication (N,P). These data are collected in the PULS database, managed by the ministry of Environment and Food of Denmark. The decision to undertake this study comes from the fact that even if the Danish system is very precise and accurate in monitoring the micropollutant loads it lacks in investigating the fate of these once discharged into the rivers. Indeed, there are no data about the micropollutant concentrations in the water bodies. Even if the micropollutant loads are under the Danish thresholds this doesn't mean that they won't pose a threat to the river stretch when these are discharged because the dilution is not taken into account. In Denmark there are 19773 wet-weather discharge points spread across the municipalities; almost 5000 CSO structures about 14500 outlets from separate systems (data for 2016, (Miljøstyrelsen,2018)).

Item		
Substance	MAC EQS [μg/L]	AA EQS [μg/L]
Clorpyrifos	0.03	0.1
Pentachlorophenol	0.4	1
4-Tert-Octylphenol	0.1	Non Defined
Anthracene	0.1	0.1
Benzo[a]pyrene	0.00017	0.27
DEHP	1.3	Non Defined
Bisphenol A	0.1	10
Fluoranthene	0.0063	0.12
Carbendazim	0.44	0.7
Diuron	0.2	1.8
Imidacloprid	0.013	0.1
Cadmium	0.25	1.5
Chromium	4.9	17
Copper	4.9	4.9
Nickel	4	34
Mercury	0.07	0.07
Zinc	7.8	8.4
Terbutryn	0.065	0.34
Lead	1.2	14
Diclofenac	0.05	Non Defined

Table 2.2: micropollutant MAC and AA thresholds for Denmark taken from Danish legislation *BEK nr 1625 af 19/12/2017* n.d. and integrated with data coming from the SWISS ECOTOX CENTRE for the pharmaceuticals.

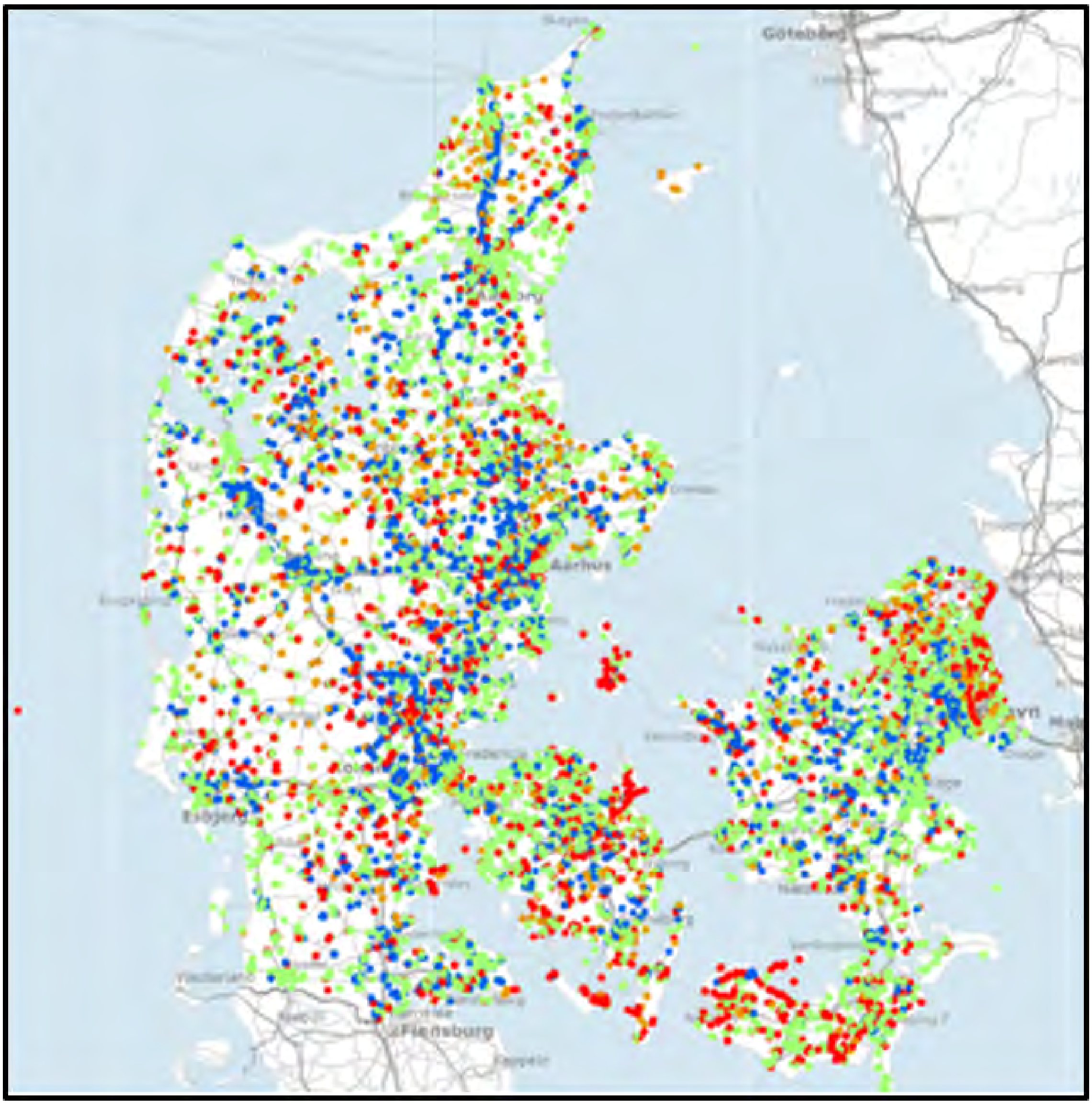


Figure 2.3: Denmark's map from *HIP model* n.d. reporting all the 19773 wet weather discharges.

In this image are shown the 19773 wet weather discharges in Denmark. The red spots indicates the combined sewer overflows with a catchment, the orange ones the ones without catchment. Blue and green spots instead indicate respectively the separate discharges with catchments and without.

2.4.3 JRC Model

The Joint Research Centre (JRC) is an European Commission's science and knowledge service. JRC estimates annual loads of 5-days biochemical oxygen demand (BOD5), nitrogen(N), phosphorous (P) and total suspended solids (TSS) using a simple event mean concentration (EMC).This model was initially proposed, in 1976, by Heaney et al. Their aim is the one of giving a rough quantification of the urban runoff coming from the most important european cities. There is the need for this kind of models since urban runoff is difficult to represent through precise mathematical models. The practical alternative they developed is based on the Event Mean Concentration to represent the pollutant content of urban runoff. The mass of the pollutant discharged into the receiving water body is then calculated assuming that all runoff coming from a given type of land use carry a constant equivalent concentration equal to the event mean concentration. The generic ith pollutant carried by urban runoff [M][T]-1 is computed as:

$$L_i = \sum_{i=1}^{n} EMCi, j \tag{2.1}$$

3 Modelling Approach

3.1 General concepts of wet weather discharges modelling

3.2 Assumption of the screening model for Mølle Å

To understand if there is a problem in Denmark's rivers related to pollution coming from wet weather discharges from CSOs and understanding the validity of the test, the screening model has been applied to the Mølle Å. The model assumes some assumptions to stay on the safe side. The test proposed in this work is a screening one, it does not mean to be precise, but it aims to highlight, in case of a problem, where this can be most likely located. If using strong assumptions it is found that micropollution concentration are over the thresholds it can reasonably be said that there is the need for a further investigation in Denmark's river to be done with more precise models.
The micropollutant concentration have been firstly calculated basing on these hypothesis:

1. Not considering the discharge upstream the CSOs.
2. Considering a quantile micropollutant concentration equal to 90%.
3. Considering the thresholds just for a chronic exposure.

The formula used with this first assumptions is:

$$C = \frac{C_{CSO} Q_{CSO}}{Q_{RIV} + Q_{CSO}} \tag{3.1}$$

In this formula 3.1 what happen upstream the examined CSO is not taken into account, meaning that the concentration upstream is considered equal to zero.
The same test over the Mølle Å has been then repeated restricting the hypothesis to obtain a rough understanding of the magnitude of the problem.
The assumptions this time were:

1. Considering river discharge coming from upstream the CSO
2. Considering also a quantile micropollutant concentration of 50
3. Taking into account also the thresholds for an acute exposure

The formula we use to calculate the micropollutant concentration is the following:

$$C = \frac{C_{UPS} Q_{UPS} + C_{CSO} Q_{CSO}}{Q_{RIV} + Q_{CSO}} \tag{3.2}$$

Where:

- Q_{CSO}: Indicates wet weather discharges through the CSO, these data are taken from the PULS database.
- C_{CSO}: Are the quantile micropollutant concentration, we have assumed, in our screening model, 90% and 50%.
- Q_{UPS} or Q_R: Is the river discharge in the point of the river where is the CSO considered, data come from PULS database.

The formula 3.2 takes into account the dilution and accumulation that happen in the river stretch between a CSO and the following one.

3.3 Assumption of the screening model for Denmark

After the first test on Mølle Å, the model has been extended to all Denmark. When expanding the model to all Denmark some CSOs such as the ones discharging into the sea or lakes have been removed because they were not significant for the screening. The removal of such CSOs has been done on QGIS cutting the layer according to Denmark's coastline profile. All the points outside the profile have been cut out, the points on the lakes instead have been removed manually.

The islands of Bornholm, Saltholm, Samsø and Læsø have not been included in the screening.

In the figure here below 3.1 can be seen all Denmark discretized in 46746 points for 2785 streams according to the HIP model *HIP model* n.d.In the red rectangle in the top right is zoomed the Mølle Å that is discretized according to the HIP model in 138 points.

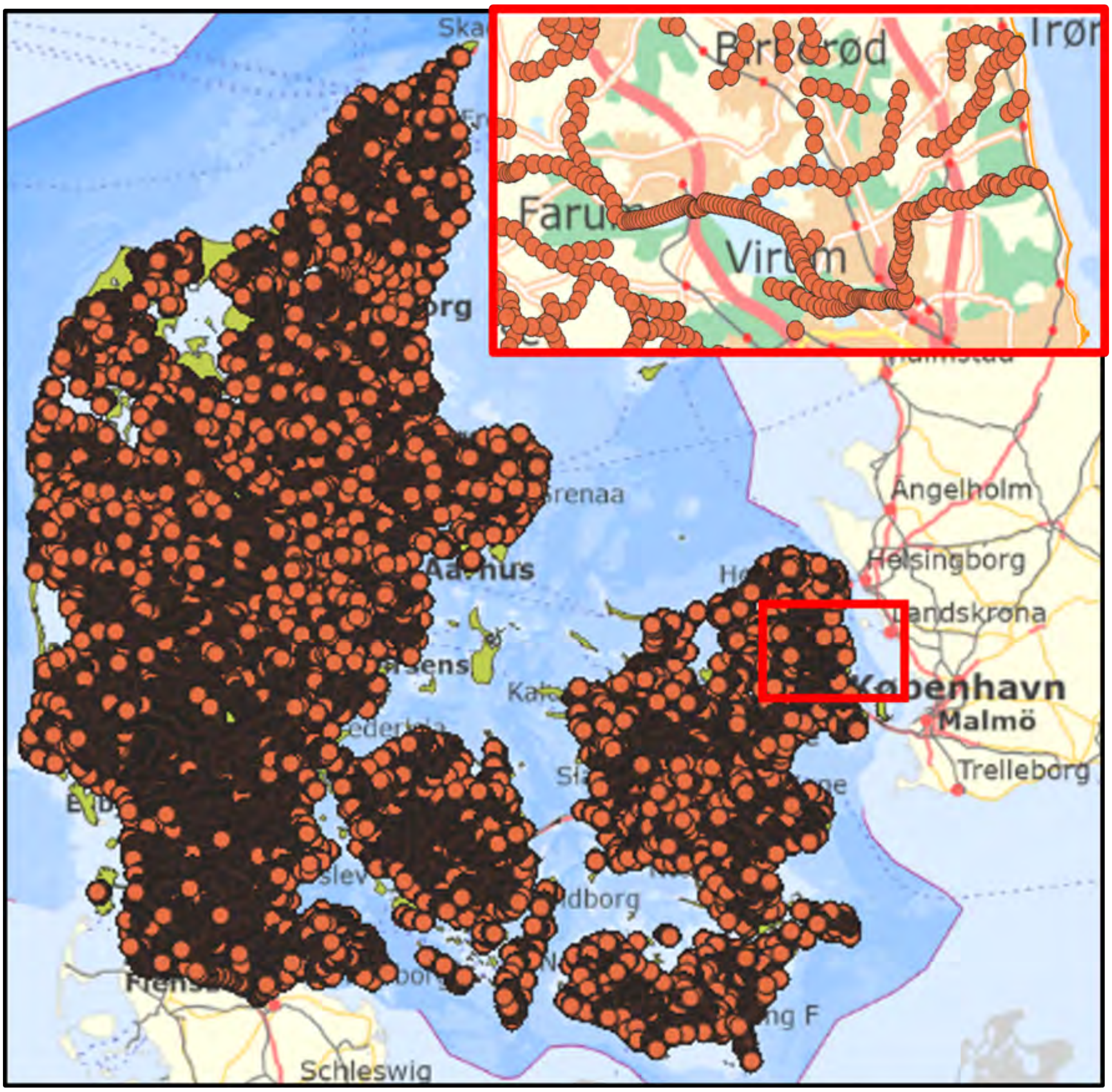


Figure 3.1: *HIP model* n.d. discretization of all Denamrk's rivers. Fpcus on Mølle Å on the top right-hand side. Image from QGIS

3.4 Durations and Volumes from Mølle Å

As already mentioned in the previous chapters, the Danish database PULS provides information about the total discharged volumes over the years but it never mentions the number of times the CSOs are active during the year nor the volume discharged per event. Calculating and modelling the CSOs concentration is not an easy task then as the *punktkilde* database just provides the integral value of the volume. For this project calculations in order to apply the formula 3.2 a temporal factor indicating the number of events per year was needed.
Indeed, as can be seen in the formula 3.3, the PULS database just provides the total yearly Volume discharged by the CSOs then a temporal factor is needed in order to convert this to a discharge per event.

$$Q_{CSO} = \frac{V}{T} \tag{3.3}$$

Where:

- V: Total annual volume from PULS database $[m^3]$.
- T: Temporal factor taking into account the times CSOs are discharging per year. To be determined.
- Q_{CSO}: CSO's discharge per every event $[\frac{m^3}{event}]$

In order to determine a possible number of events per year and the discharge released by an archetype event, it has been asked the Lyngby-Taarbæk water utilities for the data regarding the duration and volumes discharged by the CSOs on the Mølle Å.
The yearly CSO volume have been downscaled to single events discharging by using event duration and magnitude calculated by the municipality with 10 year simulated discharges. Considering 16 nodes from the records sent by the municipalities of Lyngby-Taarbæk, in figure 2.3 it can be seen that the majority of them have been discharging around 323 times in 10 years meaning they discharge aroud 30 times a year. The CSOs considered are 16 and they have the following codes:
20ARB01; 00OR100; 08BRS01; 05BRM01; 00OLYF01; 31ARA01; 34XRH01; 34XRJ01; 34XRI01; 23ARV00; 27CRA01; 26ARB01; 28XRA01; 29CRD99; 15ART03; 29BRL99; 32ARA01

Dividing the total number of events by 10 years, is estimated that the CSOs that have been considered for the study discharge on average 24,29 times per year. However, this data is far from the literature data for Denmark reporting that, on average, CSOs discharge around 10/15 times a year. Also the value estimated simply dividing by 10 the amount of events registered over 10 years does not take into account that lot of events registered have a very short duration, then their contribution can be neglected for the purpose of this study.

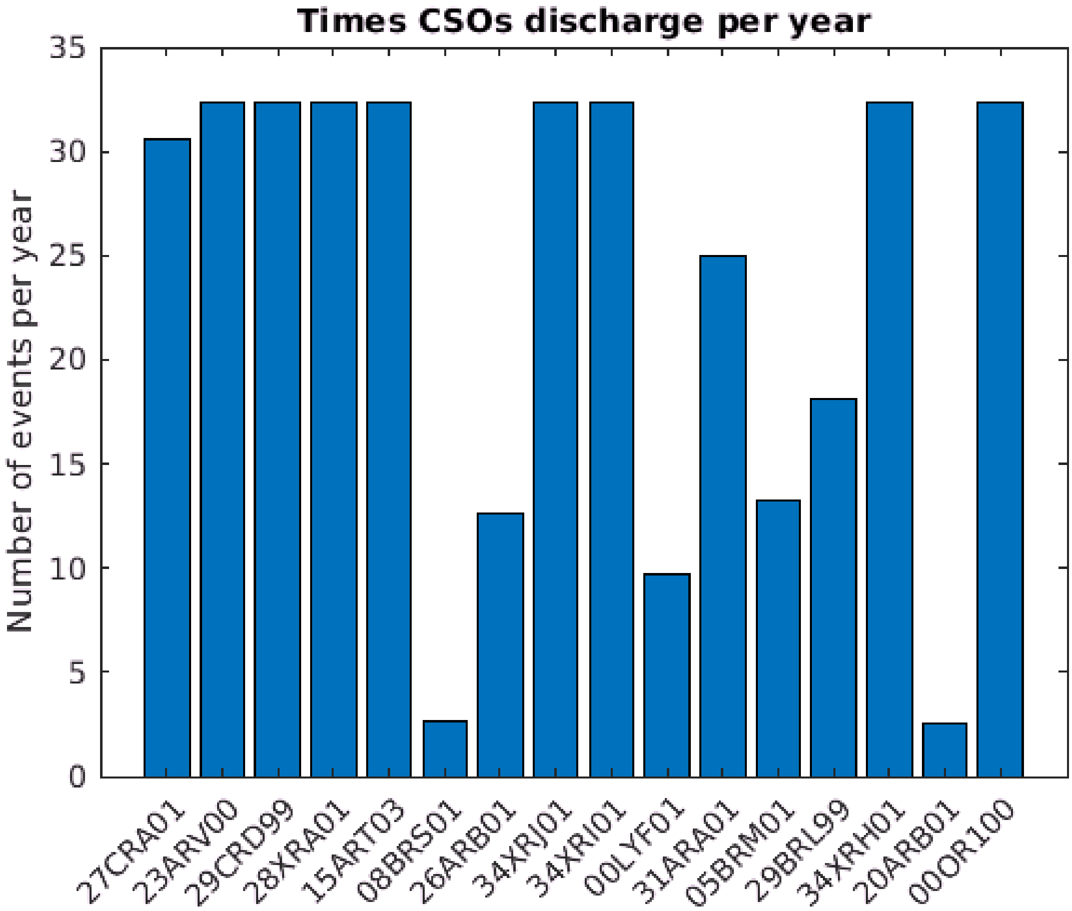


Figure 3.2: Histogram of CSO discharging events over 10 years. These data have been provided by the Lyngby-Taarbække Water Utility.

In 3.2 the histogram indicate the duration of the events for which the CSOs were active. Observing the graphs it can be seen that, taking as example the archetype CSO $00OR100$, the median duration is about 11.70[hr] and the average is 13 [hr].
Four examples of the CSOs discharging in Mølle Å are shown in this chapter, the other graphs can be found in Appendix A.

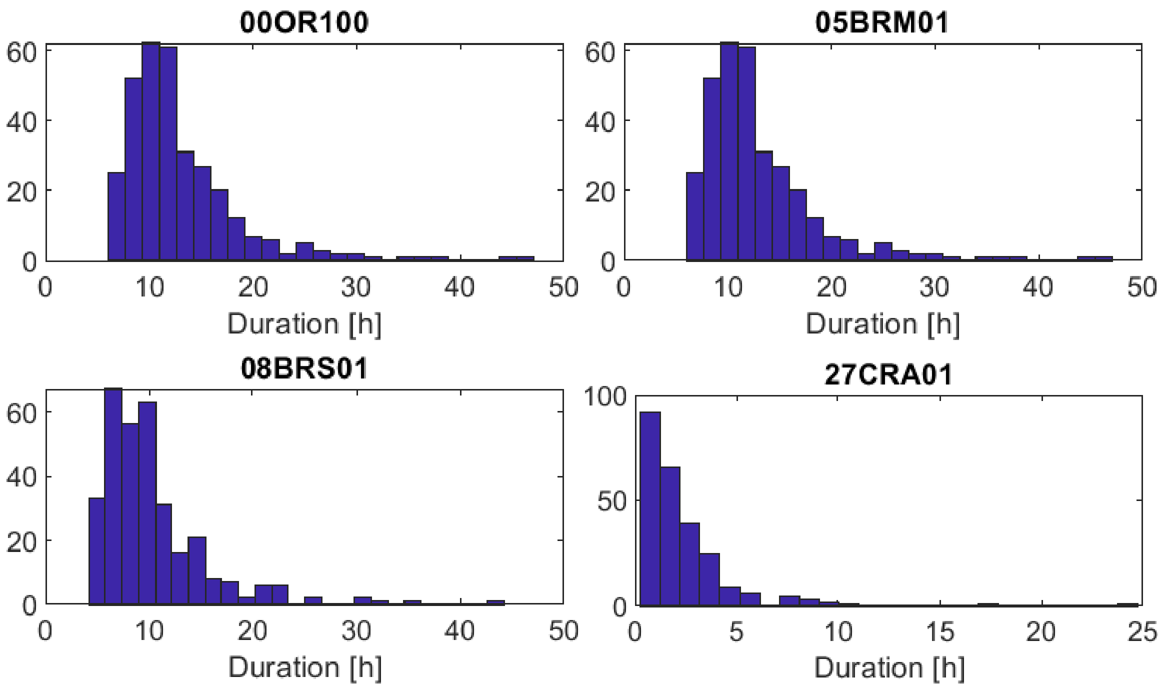


Figure 3.3: Samples of CSOs discharging duration measured in h coming from 4 CSOs. The data have been provided by Lyngby-Taarbække Water Utility.

In 3.3 are shown the duration of of the events.

In the graphs below 3.4 are instead displayed the amounts of volumes discharged per event. Using as example the same CSOs used for the duration it results that the median volume per event is 53897.81[m^3] and the average 64112.89 [m^3].

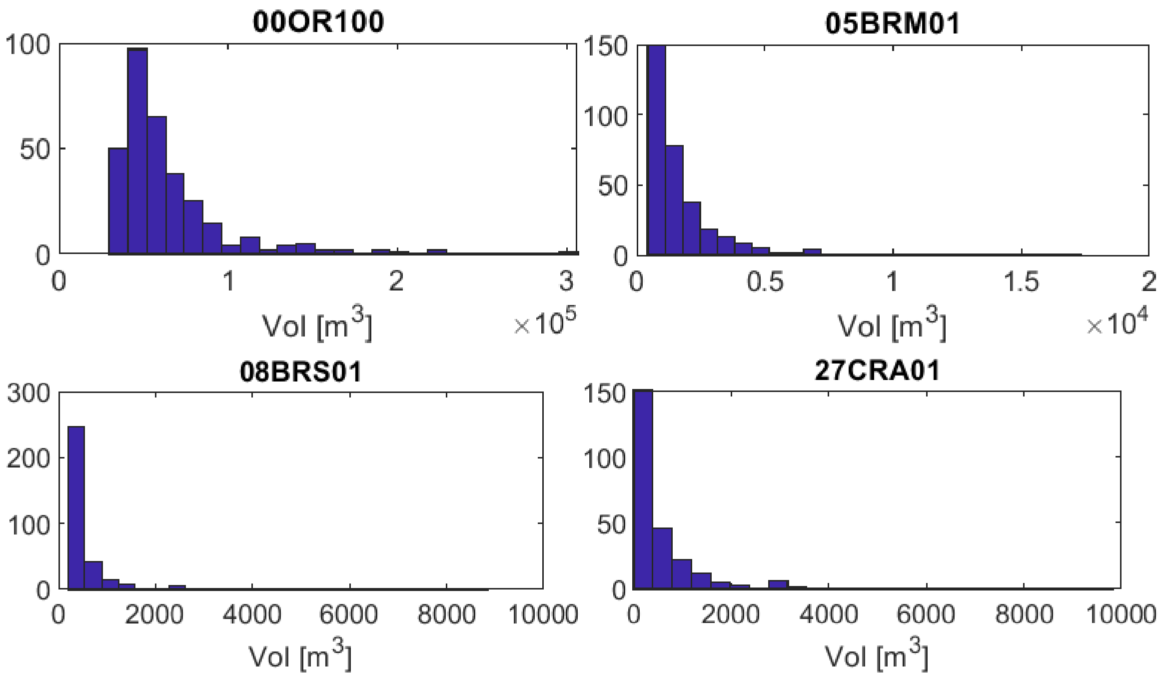


Figure 3.4: Volume discharged per event espressed in m^3 every time the CSO was active, data from Lyngby-Taarbække Water Utility.

The municipalities of Lyngby-Taarbæk have provided the data for the calculations of the number of events per year; times that the CSOs have been active (discharging) along the year. These data consist in the duration and magnitude of the events calculated by using 10-year simulated discharges provided by Lyngby-Taarbæk water utilities for the Mølle Å. In this image 3.5 it is shown the fraction of total volume discharged from every CSO; how much every CSOs contribute in terms of the total volume discharged during the year.

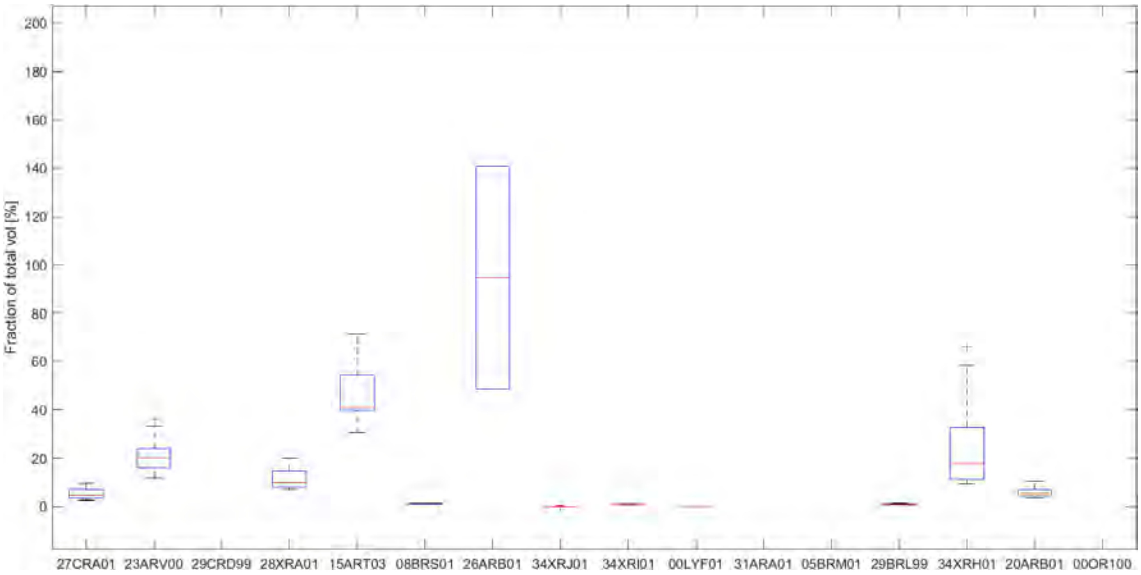
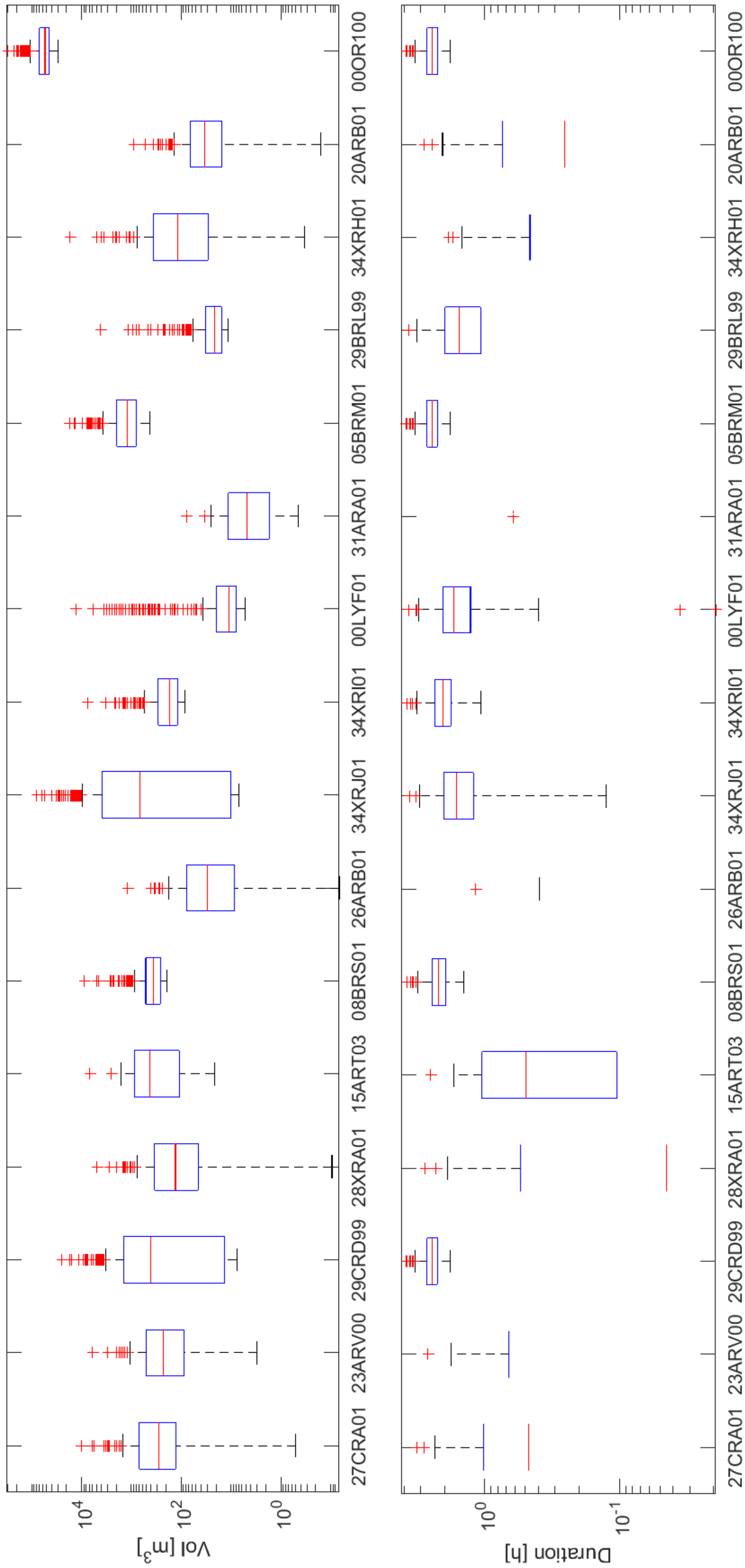


Figure 3.5: Fraction of total volume

As previously said just taking the number of events over 10 years and dividing them for 10 does not give a satisfactory estimation of the possible number of events. For this study indeed, we are not interested in the too short or too long events, as it can be seen from the images 3.6 that represents respectively the boxplot of the volumes discharged by the CSOs (left-hand side) and the durations (right-hand side).
As it can be noted there are lot of shorts events, that together with the too long events have been neglected for the calculations of this study as the scope was the one of defining the archetype duration and volume. As it can be noted in figure 3.6a the CSO indicated with the code 00OR100 i discharging way more than the others, this happen because this one is the overflow of the WWTP itself.
The archetype duration result to be 3h and it is estimated that the 5% of the total volume is discharged per every event. This data has been applied for all Denmark.



(a) Volumes CSOs (b) Duration CSOs

Figure 3.6: Volume and Duration CSOs registered in the WWTP of the municipality of Lyngby-Taarbæk

4 Case Study

4.1 Catchment description

4.1.1 Molle A catchment basin

The simple river model has been firstly tested on Mølle Å, a peri-urban stream located north of the city of Copenhagen.The Mølle Å is a small river in North Zealand, Denmark, which runs 36 kilometers from the west of Bastrup Sø near Lynge to the Øresund between Taarbæk and Skodsborg.The source of the river is Hettings Mose between the lakes of Buresø and Bastrup Sø. From the source the river drops 29 metres until it reaches the sea. After Bastrup Sø, the river runs to a swampy area to Farum Sø. For a period it becomes "Fiskebæk Å", passing under the Hillerød motorenway (E16) and Frederiksborgsvej before reaching Denmark's deepest lake, Furesø, with a depth of 38 metres. Afer passing through Frederksdal Storskov, the river runs under Nybrovej until it meets the lake of Lyngby Sø *Mølleåen* n.d. The river passes through lots of lakes and the presence of these need to be accounted during the application of the screening model to the river because their presence affect the concentration's results. Indeed even if the concentration of the micropollutants can result high in some stretches of the river the presence of the lakes shows us that these are diluted enough. The river is a Natura 2000 protected area, and it crosses several urban areas, with over 124 total CSOs structures discharging into it. The stream is discretized in 138 nodes in the HIP model.

4.1.2 Denmark

After a first application of the screening model to Mølle Å, the model has been extented to All Denmark. For lack of data in this screening have not been included the islands of Bornholm, Saltholm, Samsø and Læsø. The total amount of rivers result to be 2785 of which some are just small streams; this can be easily said according to the fact that no CSOs have been encountered alongside their path. The total amount of CSOs for all the above mentioned area are 4648 that drop to 4190 if we remove the ones discharging into the sea or lakes. For the study have been considered just the CSOs actively discharging that are 787, all the remaining ones showing NaN as disharge for the year 2019 have been removed. The Danish area considered in this study have been discretized in 46746 points in the HIP model.

4.2 Data Collection and Analysis

4.2.1 Data Collection

The screening model obtained from this work can be defined as an hybrid one. Its aim is the one of providing a basic knowledge about the general status of the river water quality wise. The scope of this study wants to pursue a similar aim as the Joint Research Centre's one: accept the request made by European Union about the necessity of having more simple screening models to have a partial understanding about the substance concentration in EU rivers Sørensen et al. 2021. The work proposes a simple way of calculating the MPs concentrations discharged by wet weather discharges from CSOs in the river using existing data. The term hybrid wants to state the fact that even if the model claims itself as simple it is based on publicly available data coming from the PULS database and estimated through precise mathematical models. As part of the digitization strategy proposed by the Danish Government, several environmental data are public available.
These include:

- Modelled flow data for all Danish streams, obtained by the Hydrological Information and Prediction system *HIP model* n.d. These are calculated by using the National Water Resource Model, a tridimensional representation of the integrated water cycle (including rainfall-runoff, groundwater and surface water, urban water contributions) with a 100 m grid resolution. Model results are available for over a 30 years period with monthly resolution for a total of 46746 points for 2785 streams.
- Modelled wet-weather discharges. These results are generated from the 98 Danish municipalities by using detailed hydrodynamic models, providing the yearly discharged volume for each of the 4,500 CSO and 14,500 SSSO (Vezzaro et al., 2019). All this information is available on the Danish Environmental Portal *Danmarks Miljøportal* n.d.
- Measured concentrations of micropollutants from monitoring campaigns performed by the Danish Environmental Protection Agency *BEK nr 1625 af 19/12/2017* n.d. and *Miljøstyrelsen* n.d. Given the limited number of monitored sites and events, these measurements were integrated with those reviewed by Mutzner et al. (2021),especially for what concerns pharmaceutical MPs.

Type	Resolution	Source
30 years simulated flow data for all Denmark*	Spatial: approx 100 m Temporal: 1 month	GEUS (hip.dataforsyningen.dk)
CSO Discharge	Yearly value (All Denmark)	PULS Database (arealinformation.miljoportal.dk)
CSO Discharge	Event data (10 years simulations)	Lyngby Taarbæk Water Utility (LTF)
MPs concentrations in CSO water	Event data	DK Environmental Agency (Miljøstyrelsen) Swiss legislation for pharmaceuticals

Table 4.1: Table summarising data sources

The first step of the model implementation has been plotting the coordinates of all Denmark's CSOs on QGIS. The same operation has been repeated for all the points in which the 2785 Danish rivers have been discretized to simulate the discharge values.
Initially, the screening has been applied just on Mølle Å to test its validity.
After both sets of points have been displayed on QGIS every CSO has been associated to the closest discretized point where the volume measurements have been simulated from the municipalities. The association has been done using the command distance to nearest hub in QGIS as it can be seen in image 4.1. Every simulated point is identified in the PULS database by a code which is stating the municipality, the region of belonging and a code to identify the position of the point in the river respect to the other points in which the river is discretized.

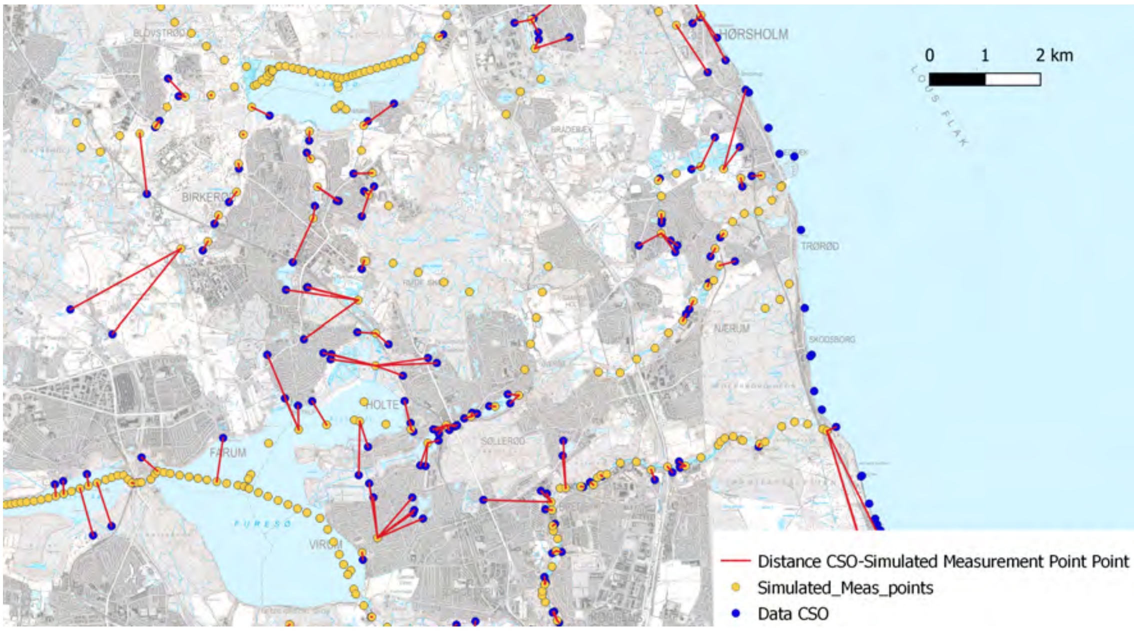


Figure 4.1: Association on QGIS of overflows to the closest point in which the measures of flow were simulated. Image from QGIS

When the CSO has been associated with the closest simulated point alongside the river, it has been associated to the CSO the same numerical code.
After this operation all the csv file has been exported on Matlab were all the calculations have been performed.
The observed scenarios for Mølle Å are the ones presented in Chapter 2 which formulas are respectively 3.1 and 3.2. A simple advection model was created, starting from the stream discretization of the HIP model. For each known discharge point, the concentration in the i-th river section was calculated by using a simple advection model.

The CSO concentration is calculated from the distributions estimated by Mutzner et al. (2021) as 50% and 90% percentiles. The yearly CSO volume have been downscaled to single events discharging by using event duration and magnitude calculated by using 10-year simulated discharges provided by Lyngby-Taarbæk water utilities for the Mølle Å stream as seen in Chapter 3. Accordingly, an archetype discharge event was defined to have a duration of 3 hours and a volume corresponding to the 5% of the annual average. The simulated concentrations were compared against EQS values defined by European and Danish legislation (with integration from Swiss guidelines when official guidelines were not available). A total of 20 micropollutants were selected based on the risk-assessment performed in Mutzner et al.(2021).

5 Results

Differently from Denmark's ministry, this study doesn't just investigate the presence in water of COD, BOD5, N and P but 20 micropollutants are taken into account. In the next sub-chapters are shown first the concentrations of micropollutants alongside the Mølle Å, then the results obtained in all Denmark.

5.1 Screening application to Mølle Å

In the first figure here below 5.1 are shown, in the figure above, the yearly average discharges alongside the river as reported in the PULS database [m^3/year] while in the one below the various red spots indicate the CSO discharge per year. Looking at the first graph in the x-axes are the distances along the river [m], this goes from $-1.5x10^4$ and $1.5x10^4$ and it doesn't indicates the distance itself but the code with which are indicated the various points for which have been computed the river discharges. In the y-axes instead there are the values of the river discharges calculated by the municipalities through accurate mathematical models. The second graph shows instead the CSOs associated to every point when the measures are calculated. As previously seen the association has been done according to the minimum distance, displaying points on QGIS. We assume that the overflows discharge in the point of the river where are calculated the volume discharges.

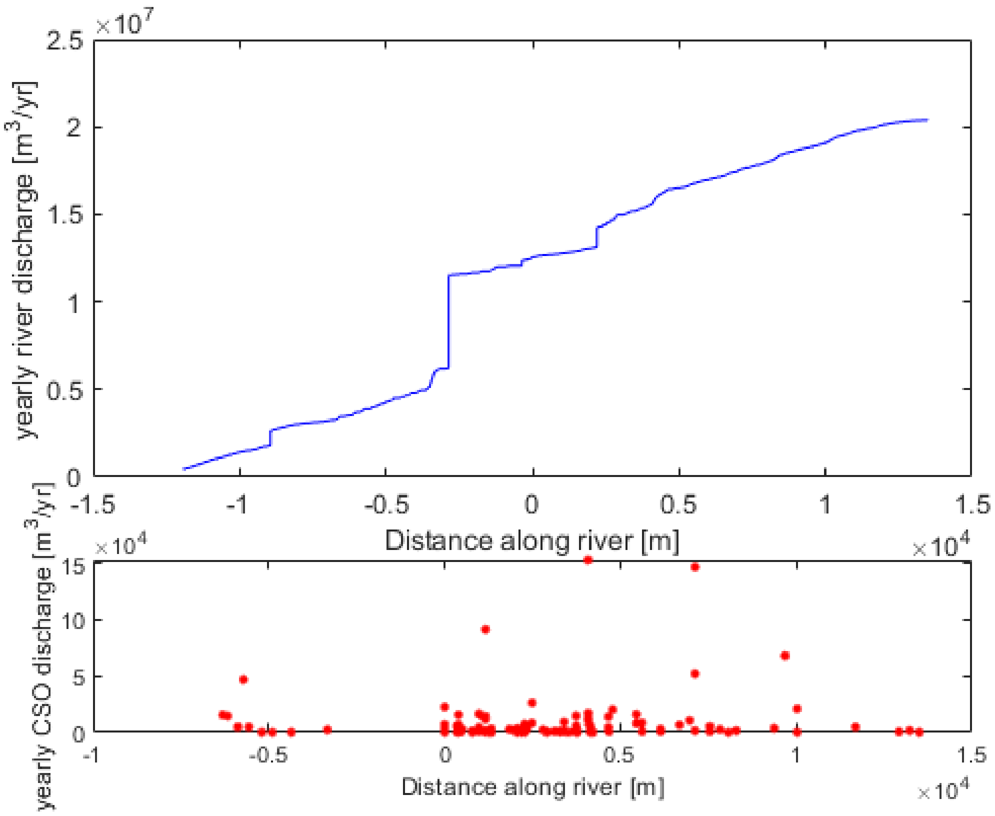


Figure 5.1: The graph at the top shows how the river discharge going from the source to the river mouth.The graph below shows where are located the CSOs alongside Mølle Å and how much they discharge per year. Image from Matlab

In the following pages are reported the graphs displaying the MP concentrations alongside the Mølle Å. The upper graph for every MP reports the micro-pollutant concentration with the hypothesis of not considering the background of the CSOs; meaning not considering the river discharge above it. The graph below instead reports the MP concentration taking into account the river discharge above the CSOs. As it can be seen from the graph in this case the MP concentration rises from the river's source to the river mouth. The red straight line in the graph indicates the threshold for an acute exposure AA-EQS while the blue line the limit for a chronic exposure MAC-EQS. The orange line indicates the MP concentration in the river assuming that the micropollutant estimated quantile concentration is 50% while the blue line indicates an estimated quantile concentration equal to 90%. In the graphs are also reported respectively in light green and yellow the MP concentrations considering a quantile of 50% and 90% in case the lakes are not taken into account. It was important to study these case so to realize how much the dilution provided by the lakes was belittling the problem in Mølle Å. The points taken into account for the screening alongside Mølle Å for which the municipalities have computed the yearly discharged volume are 138.
In fig 5.2 are displayed on the above figure the MP concentrations in case no background is considered for Benzo[a]pyrene while in the one below are considered the concentrations considering the accumulation or dilution.
In fig5.3 are displayed in the figure above the MP concentrations for Copper not considering the background of the measured points and in the one below the one considering the background. Copper is one of the MPs to take more under observations because is overcoming the limit for acute exposition also in the case where no accumulation is considered. In the other images we can see how Fluoranthene 5.4, Lead 5.5 and Zinc 5.6 are behaving alongside Mølle Å.
While in the last two graphs, Diclofenac 5.7 and Bisphenol A 5.8 these substances are just overcoming the limits in case no lakes are considered.
All the results and the percentages of points overcoming the thresholds are reported in the tables 5.1 for the case in which background is not taken into account and 5.2 for all the cases considering the background; accumulation of concentrations or dilution provided by the river.

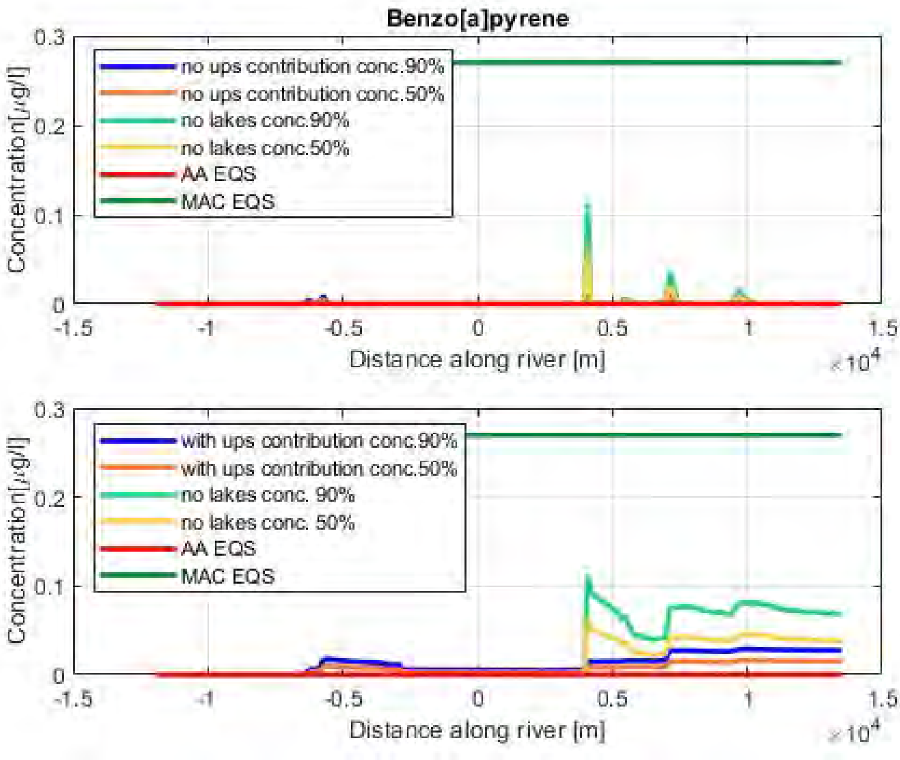


Figure 5.2: Benzo[a]pyrene

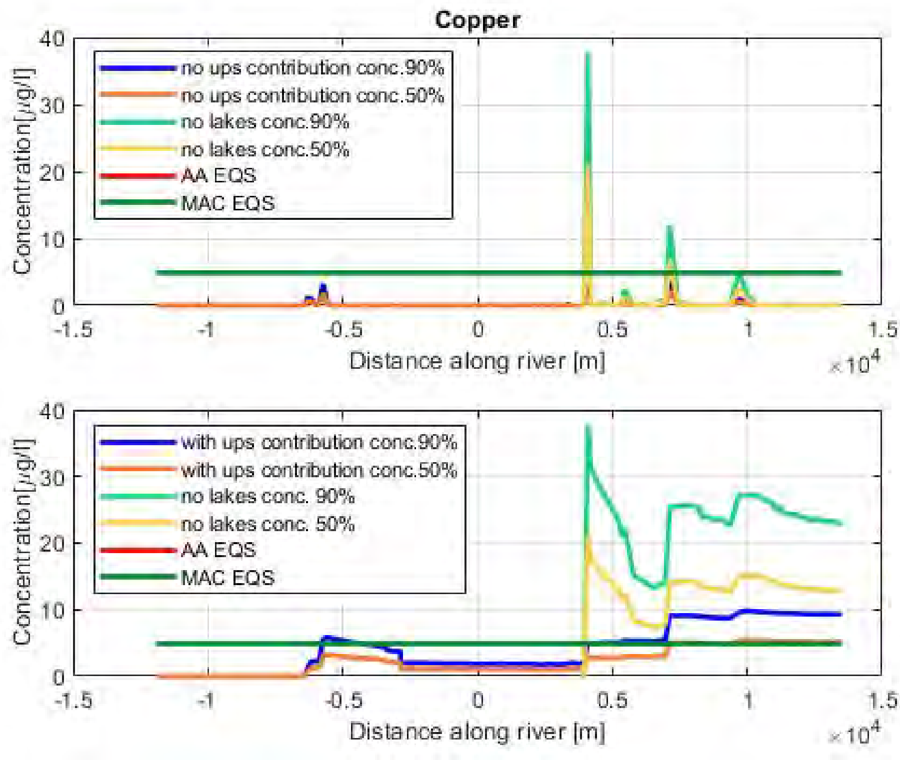


Figure 5.3: Copper

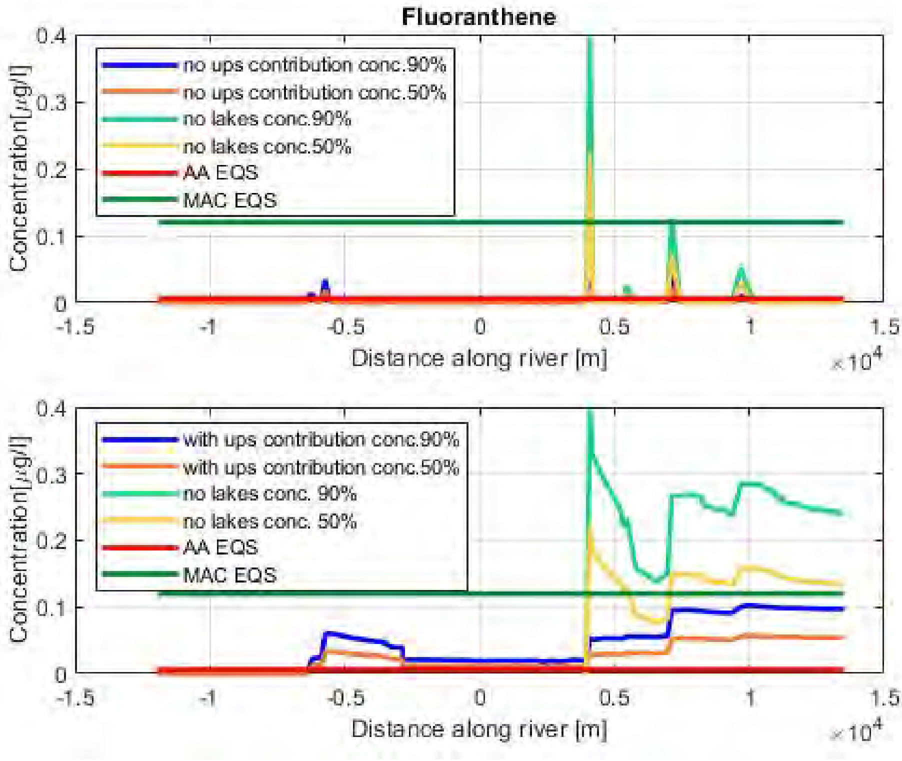


Figure 5.4: Fluoranthene

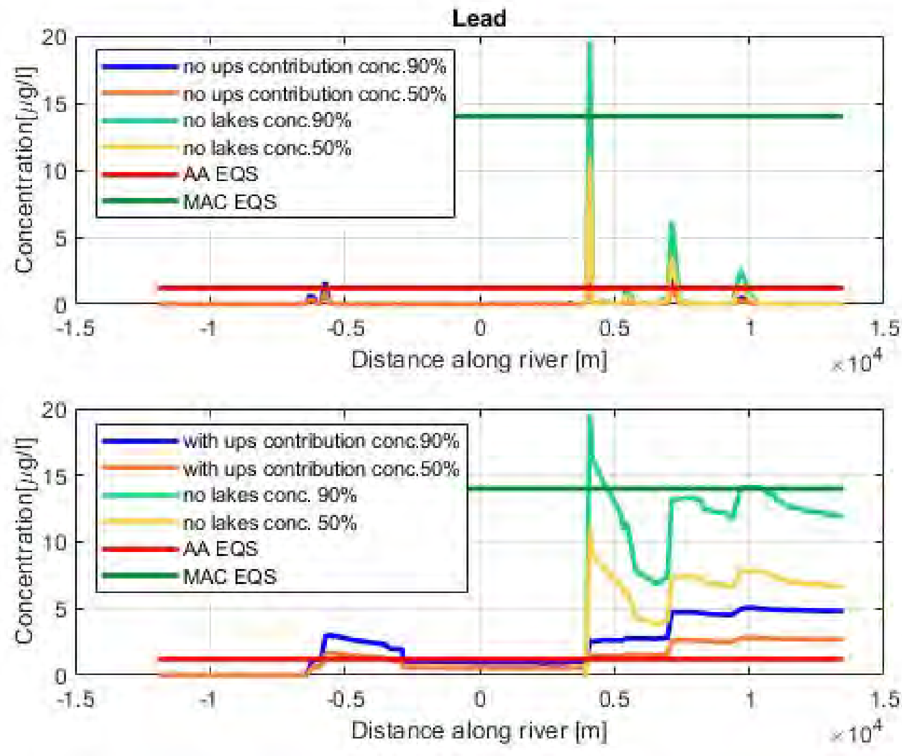


Figure 5.5: Lead

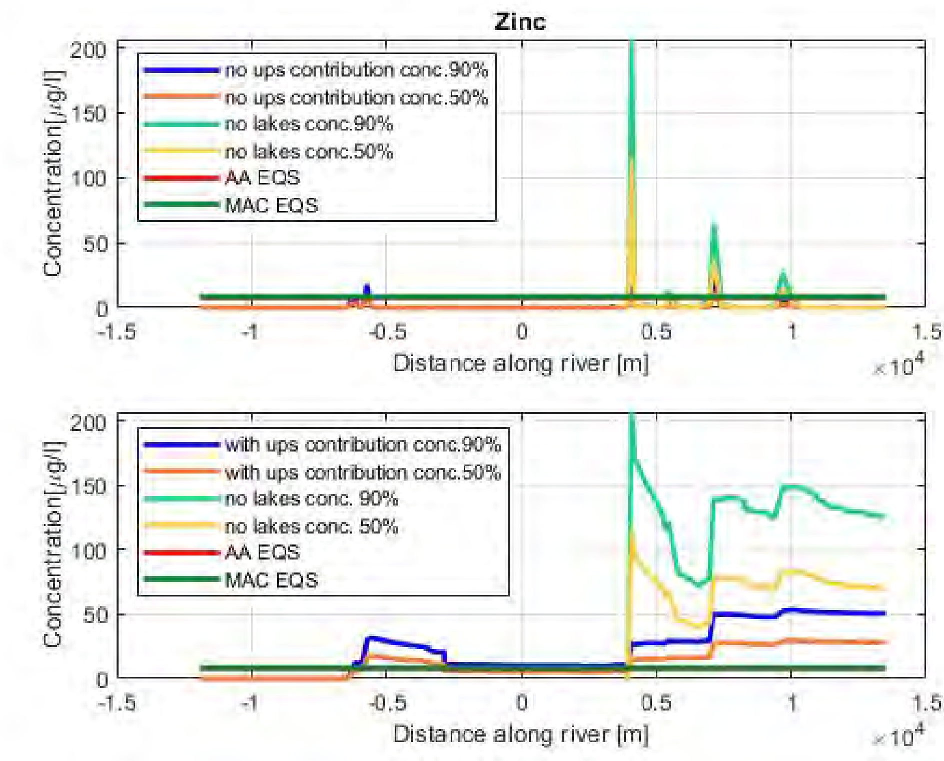


Figure 5.6: Zinc

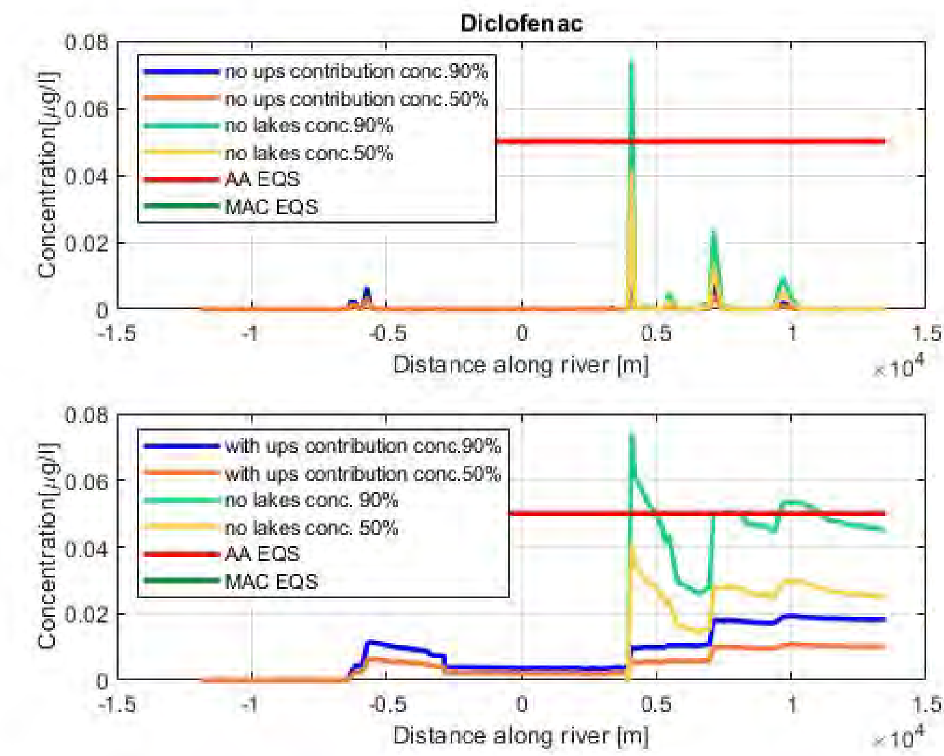


Figure 5.7: Diclofenac

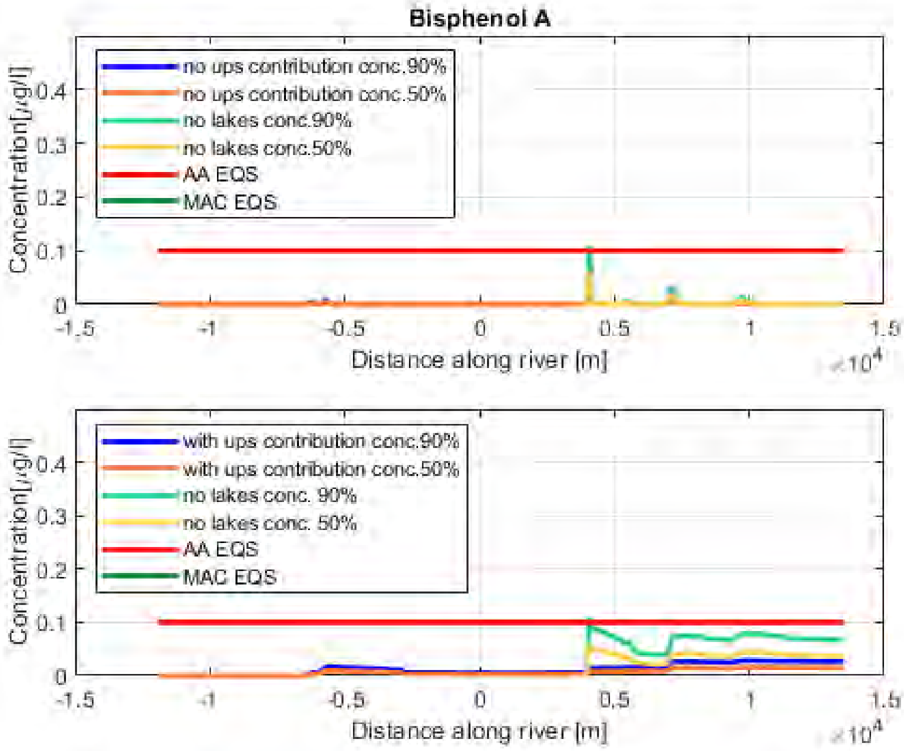


Figure 5.8: Bisphenol

Here below we can see in fig. 5.9 how the Zinc concentration varies alongside the river. This graph has been obtained plotting on QGIS the Zinc concentrations obtained taking into account for every CSO the upstreaming concentration. As it can see from the image the concentration drops by the lakes because here it undergoes a dilution and it increases again more and more towards the river mouth. The darker is the color the higher is the concentration of Zinc, but this doesn't mean that it overcomes the AA limit that for the Zinc is 7.8 [μg/L].
In fig. 5.11 instead it can be seen in which points the Zinc concentration goes above the threshold. The red dots indicate values of concentration higher than the AA limit while the others points evidence a MP's concentration below the AA limit.

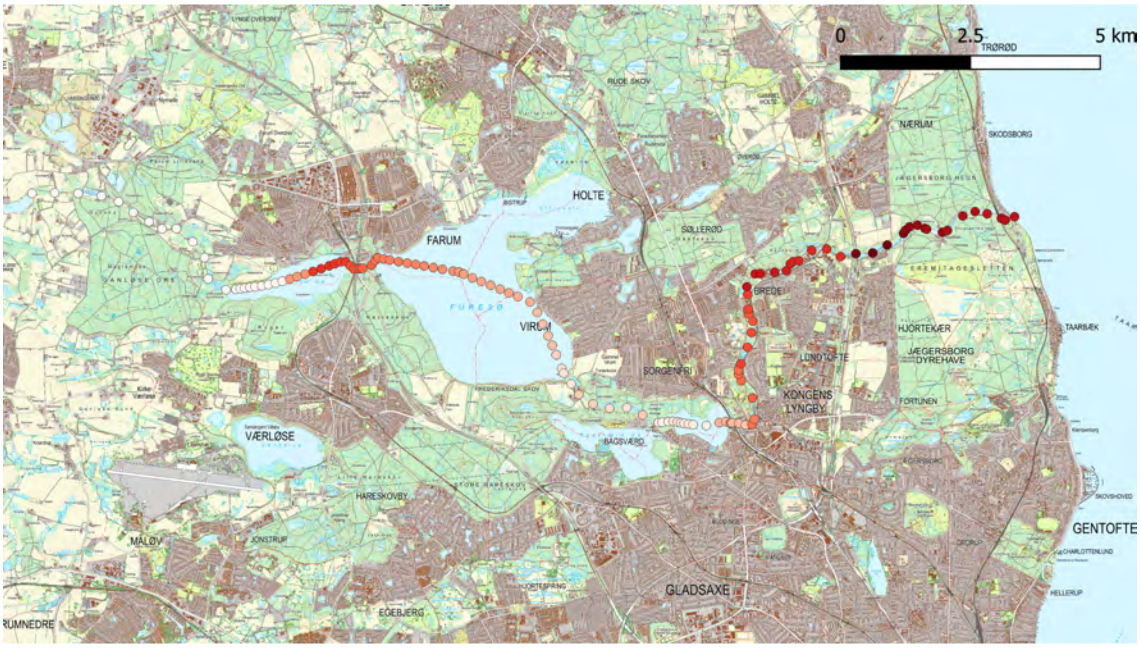


Figure 5.9: Zinc concentration alongside Mølle Å displayed on QGIS

Figure 5.10: Zinc 90% percentile concentration above AA-EQS threshold

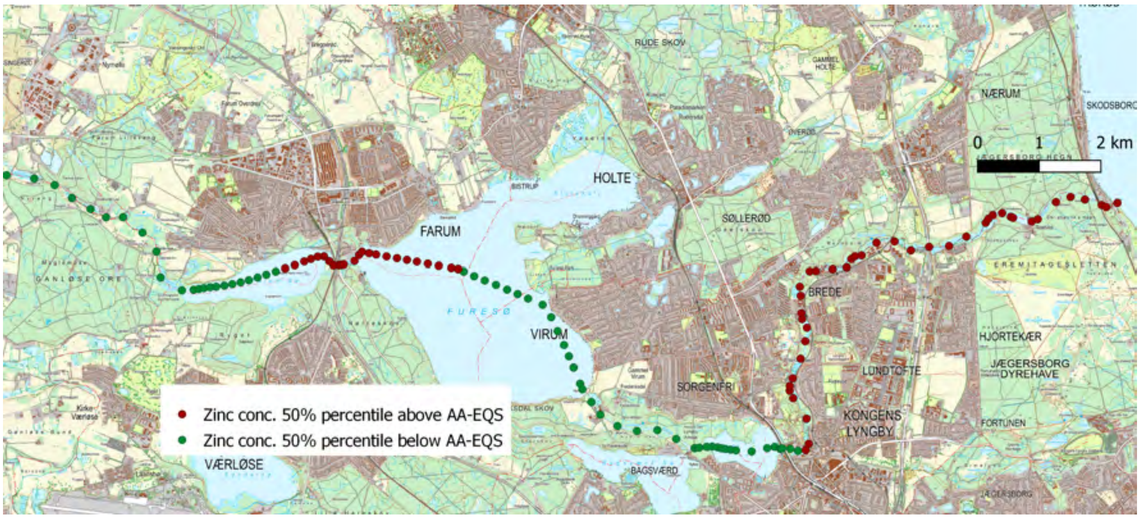


Figure 5.11: Zinc 50% percentile concentration above AA-EQS threshold

5.1.1 Testing of assumptions: using MP concentration equal to 50% percentile

After applying the screening model to the Mølle Å considering a percentile concentration of 90%, the screening has been repeated on the same river considering this time a percentile concentration of 50%. The project started considering a percentile concentrations of 90% because being its aim the one of providing a rough estimate of the river stretches most affected by high concentrations of micropollutants it was necessary to stay on the safe side. Reducing the percentile concentration allows to better frame the magnitude of the problem highlighted in the previous case. The substances overcoming the limits are the same of the 90% percentile case; Benzo[a]pyrene, Copper, Fluoranthene, Lead and Zinc but less are the points whose concentrations is above the AA threshold. However as we can see in the tables 5.1 and 5.2 the percentage of points above the limits is still signicative.

5.1.2 Testing of assumptions: lakes

Alongside the Mølle Å from the municipality of Bastrup where is located the river's source to the river's mouth there are lot of lakes. The most important are Bastrup Sø, Farum Sø, Furesø and Lyngby Sø. The presence of the lakes is of crucial importance and it has to be taken into account in the study because lakes provide lot of discharge to the river. To check what the scenario would have been without the dilution provided by the presence of the lakes, the screening on the Mølle Å has been repeated going through the same script but using as input just the points of the river from the municipality of Lyngby (just below the Lyngby Sø) to the river's mouth. In this case, not considering the water intake coming from the lakes, there are more substances, and in more river stretches, going above the threshold. Besides Benzo[a]pyrene, Copper, Fluoranthene, Lead and Zinc, we have also Diclofenac and Bisphenol A going overcoming the Acute Exposure threshold. The percentages are reported in the tables 5.1 and 5.2 and the behaviour of the concentrations without considering the lakes can be observed in the figures above from 5.2 to 5.8.

	90% * AA_EQS	90% * MAC_EQS	50% * AA_EQS	50% * MAC_EQS	90% * AA_EQS no lakes	90%* MAC_EQS no lakes	50%* AA_EQS no lakes	50%* MAC_EQS no lakes
Benzo[a]pyrene	83.3%	-	83.3%	-	95.34%	-	95.34%	-
Copper	39.13%	39.13%	18.11%	18.11%	95.34%	95.34%	95.34%	95.34%
Fluoranthene	83.3%	-	83.3%	-	95.34%	95.34%	95.34%	95.34%
Lead	48.55%	-	44.93%	-	95.34%	79.6%	95.34%	79.6%
Zinc	82.60%	82.60%	47.83%	47.83%	95.34%	95.34%	95.34%	95.34%
Diclofenac	-	-	-	-	81.39%	-	81.39%	-
Bisphenol A	-	-	-	-	27.90%	-	27.90%	-

Table 5.1: Percentages of points overcoming limits in case no background discharge is considered

	90% * AA_EQS	90% * MAC_EQS	50% * AA_EQS	50% * MAC_EQS	90% * AA_EQS no lakes	90%* MAC_EQS no lakes	50%* AA_EQS no lakes	50%* MAC_EQS no lakes
Benzo[a]pyrene	83.3%	-	83.3%	-	95.34%	-	95.34%	-
Copper	39.13%	39.13%	18.11%	18.11%	95.34%	95.34%	95.34%	95.34%
Fluoranthene	83.3%	-	83.3%	-	95.34%	95.34%	95.34%	95.34%
Lead	48.55%	-	44.93%	-	95.34%	79.6%	95.34%	79.6%
Zinc	82.60%	82.60%	47.83%	47.83%	95.34%	95.34%	95.34%	95.34%
Diclofenac	-	-	-	-	81.39%	-	81.39%	-
Bisphenol A	-	-	-	-	27.90%	-	27.90%	-

Table 5.2: Percentages of points overcoming the limits in case dilution and accumulations are considered

5.2 Screening application to Denmark

After a first testing of the screening on the Mølle Å, the simple model has been applied to the whole Denmark, providing an initial screening of the areas potentially impacted by urban discharges and requiring then major attention by stakeholders and policy makers. The results shown here below highlight the potential of this simple model to individualize critical areas, where urban water managers should concentrate their attention to reduce wet weather discharges and thus maximize the quality of the river status. The total freshwater streams considered are 2785 and the CSOs structures 787. As was reported in Chapter 2 the total CSOs in Denmark are around 5000 but part of these are discharging into the sea or lakes or nonactives. The former have been removed cutting the CSOs layer in QGIS according to the Danish coastline profile while the latter have been removed on Matlab as they don't present data. Therefore the work ended up considering for the study 787 CSOs.

Here below in table 5.3 are presented the number of rivers having at least one active CSO. The present rivers have at least one point whose concentration of MPs overcome the AA-EQS threshold. It can be noted that for the majority of the micropollutants the number of rivers overcoming the threshold in at least one point is very high, around 600 rivers over the 787 having active CSOs.

This result is very high but reasonable as most of the rivers in Denmark have a low flow rate (this can also be seen by the fact that most of the rivers have few CSOs or none) and thus they likely have areas in which the concentrations are high due to a little dilution. Furthermore, it has to be keep in mind that the the simulation has been done considering a 90% percentile to stay on the safe side.

	Number of river exceeding over 787
Chlorpyrifos	1
Pentachlorophenol	588
4-Tert-Octylphenol	586
Anthracene	586
Benzo[a]pyrene	591
DEHP	589
Bisphenol A	591
Fluoranthene	591
Carbendazim	586
Diuron	588
Imidacloprid	591
Cadmium	589
Chromium	590
Copper	591
Nickel	589
Mercury	586
Zinc	591
Terbutryn	586
Lead	591
Diclofenac	591

Table 5.3: Rivers exceeding the AA threshold in Denmark having at least one active CSO

In figure 5.12 are represented the boxplot of the fractions of rivers exceeding the thresholds; how many points are overcoming the limit per river. The median in most of the cases is about 0.5-0.6 meaning that most of the points overcoming the limit belong to the same river.

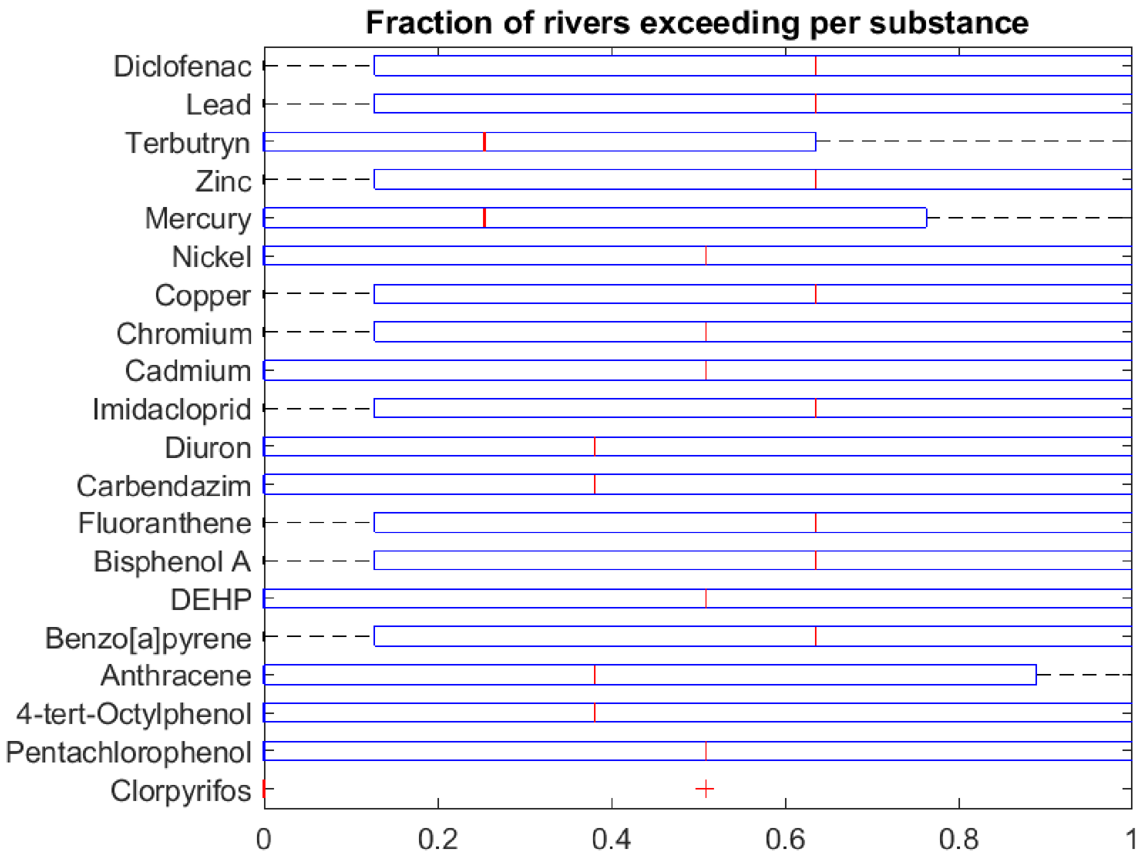


Figure 5.12: Fraction of river exceeding per micropollutant

Figure 5.13 has been obtained plotting the maximum concentration values for each river per every substance. This values have then been divided by the AA-EQS threshold of every pollutant to find the risk quotient; defining how much the maximum concentration in every river was overcoming the Annual Average limit. The same graph 5.14 has been plotted for the median values for every river over the AA-EQS limit per substance.
The range of the x-axes has been set from 0 to 10 to better focus on the concentrations of more plausible values of concentration. Indeed the values of concentration of heavy metals and especially Benzo[a]pyrene are way higher respect to the others. Speaking in particular about Benzo[a]pyrene, its high value is due to some approximation of the model that doesn't reflect the behaviour of this micropollutant in water. The model indeed, is too simple to offer a big picture of the Benzo[a]pyrene's charateristics in water as it doesn't make distinctions between suspended and particulate. The actual concentration of Benzo[a]pyrene indeed, is estimated to be low in water as the most of it settles down at the bottom of the river (bed sediment).
Hovewer, even if the model partially represents the real behaviour of the micropollutants the concentration values especially for heavy metals are high.
Because of their high degree of toxicity, zinc, lead, and mercury rank among the priority metals that are of public health significance. These metallic elements are considered systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure. Even if the model is based on strong assumptions is still reasonable thinking that

the concentrations of especially heavy metals and Benzo[a]pyrene are to further investigate because high.

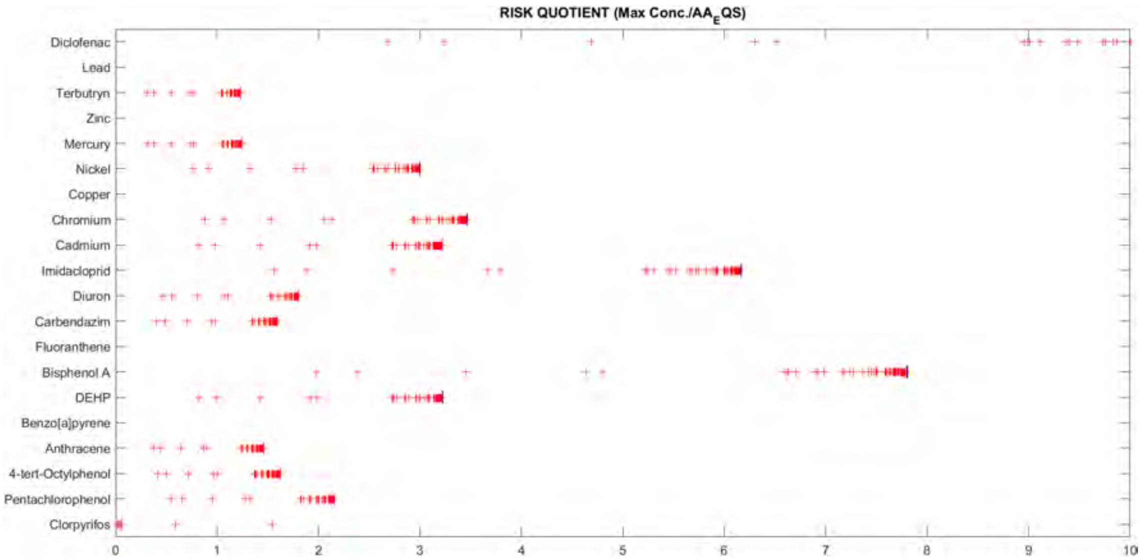


Figure 5.13: Maximum Concentration over AA-EQS threshold

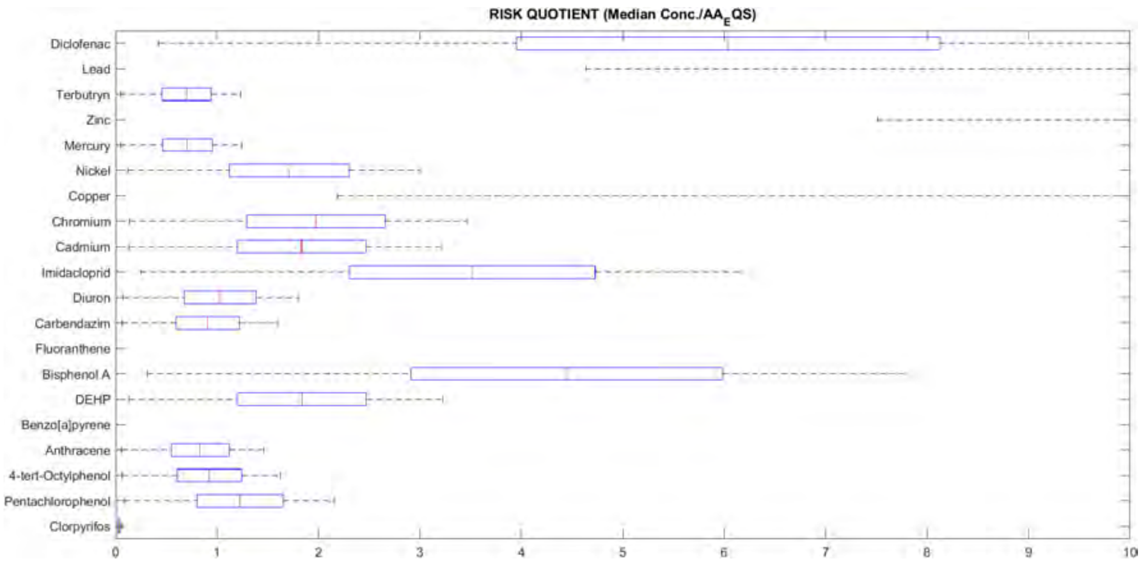


Figure 5.14: Median Concentration over AA-EQS threshold

6 Discussion and Further Outlooks

The preliminary results shown in this elaborate illustrate the potential of this simple modelling approach to highlight critical areas, where urban water managers should focus their resources to reduce wet-weather discharges and thereby maximize the improvement in the river chemical and environmental status.

When performing the simulation considering also the dilution/accumulation concentration coming from the discharge upstream the considered measurement point, the upstream CSO's discharge has been neglected because its contribution would have been small. This hypothesis could have been valid if the contribution given by the CSO would have been way smaller than the river's one, but it has resulted that this hypothesis can't be applied in Denmark. Here indeed, given the scarce discharge present in lot of rivers, the two values are sometimes comparable, thus, the upstream CSO discharge can't be neglected and need to be taken into account in the next improvements of the model.

The presented simplified screening has several assumptions limiting its application to an initial screening purpose but there are lots of ranges and assumptions that can be used to explore other potentialities of the model. Several aspects can be addressed to improve the robustness of its results:

- Expansion with stochastic emission models. The use of fixed CSO concentrations does not reflect the high temporal variability of wet-weather discharges.
  A Monte-Carlo approach can be implemented, with CSO concentrations sampled from the distributions estimated by Mutzner et al., (2021)
- Addition of simple environmental processes (e.g. first order degradation, solid/water partition) would improve the estimation of the micropollutant concentrations in the water phase
- Forward uncertainty analysis: the modelling results should be presented as risk of EQS exceedance, in order to clearly illustrate the structural uncertainties linked to the modelling approach.

The presented work is a simple advection transport model it doesn't take into account the chemical and weathering phenomena that the micropollutants might undergo during their permanence in water. These processes such as biodegradation, sinking and evaporation can be simulated making some assumptions in the model and they would be interesting to take into account in the following developments of it.

In further improvements of the model also it would be interesting taking into account oxygen depletion and ammonia toxicity, which can pose an immediate threat to the environment and kill the fishes instantaneously.

7 Conclusions

This master thesis aim has been the one of bringing into the limelight the possible threat posed by wet weather discharges coming from combined sewer overflows. Micropollutants released from urban areas into surface waters through combined sewer overflows constitute an important risk either for human health and for the chemical status of the rivers and they absolute need more attention from the institutions and decision makers.

The impact of this concentrations indeed is nowadays underrated. Micropollutant's concentrations in Denmark are measured at the outlet of the pipe instead of in the river, therefore the size of the latter is never taken into account. According to this guideline thus all the river stretches are treated in the same way. This regardless of the fact that some stretches of the river can endure the micropollutant concentration discharges they receive because the river discharge is enough to dilute it, while in other cases the same concentrations can be fatal for the aquatic ecosystem of the river stretch due to the scarce dilution provided by the river.

The scope of this thesis has been the one of giving a first estimation of the micropollutant's concentrations in Danish rivers. This has been done through a screening simple model able to individualize the areas of the river most affected by high micropollutant concentrations because of their scarce discharges and as consequence low dilution.

The output of this study highlights the danger constituted by wet weather discharges coming from combined sewer overflows calculating:

- the locations in the river where there are high concentrations of micropollutants.
- the concentrations of the 20 micropollutants studied.

It came out indeed, that on a total of 20 micropollutants studied, 5 are posing an important threat for the chemical status of the river as their concentrations overcome the EQS thresholds in several parts of the river. The number of micropollutants rise up to 7 if we don't consider in the study the presence of the lakes that offer a generous dilution. It is therefore reasonable to further investigate with samples or more precise models the estate of the river in those areas.

Focusing on Mølle Å and taking into account the most realistic scenario meaning considering the concentrations coming from upstream it comes out that for the five substances overcoming the AA-EQS limit this happen on average on 93 points out of the 138 points in which Mølle Å is discretized (65.22%). Most of the Mølle Å's stretches are affected by high micropollutant concentrations if a 90% percentile is considered. The river stretches that seem not to be affected by the problem are just the ones close to the river's source when we still don't have an high accumulation of micropollutant's concentration.
If instead a 50% percentile micropollution concentration is considered different areas have been resulted affected my high concentrations. These are mostly located right when the river leaves the lakes, thus when less dilution is provided. We can see indeed that in case we remove the lakes the average of points above the AA threshold rise up to 83.72%.

Regarding the study conducted on all Denmark it comes out that a very high number of rivers have at least one CSO discharging a concentration that once arrived into the river is not diluted enough, almost 600/787 rivers that have at least one CSO. In most of the cases this concentration values is three times higher than the AA-EQS limit one. The chemical condition assessments have so far been carried out in Denmark by comparing measured concentrations in the water areas obtained under the NOVANA program with established environmental quality requirements. However, monitoring all water areas basing solely on measured concentration is a very demanding operation in terms of resources and time Sørensen et al. 2021.

This project wanted to present itself as a first attempt of offering an alternative to most sophisticated models or limiting their application to specific areas where high micropollutant concentrations most likely be.

This thesis had the aim of exploring the possibilities of building up a screening model just relying on publicly available data coming from the PULS database. It must be seen thus as the first step into a larger task.

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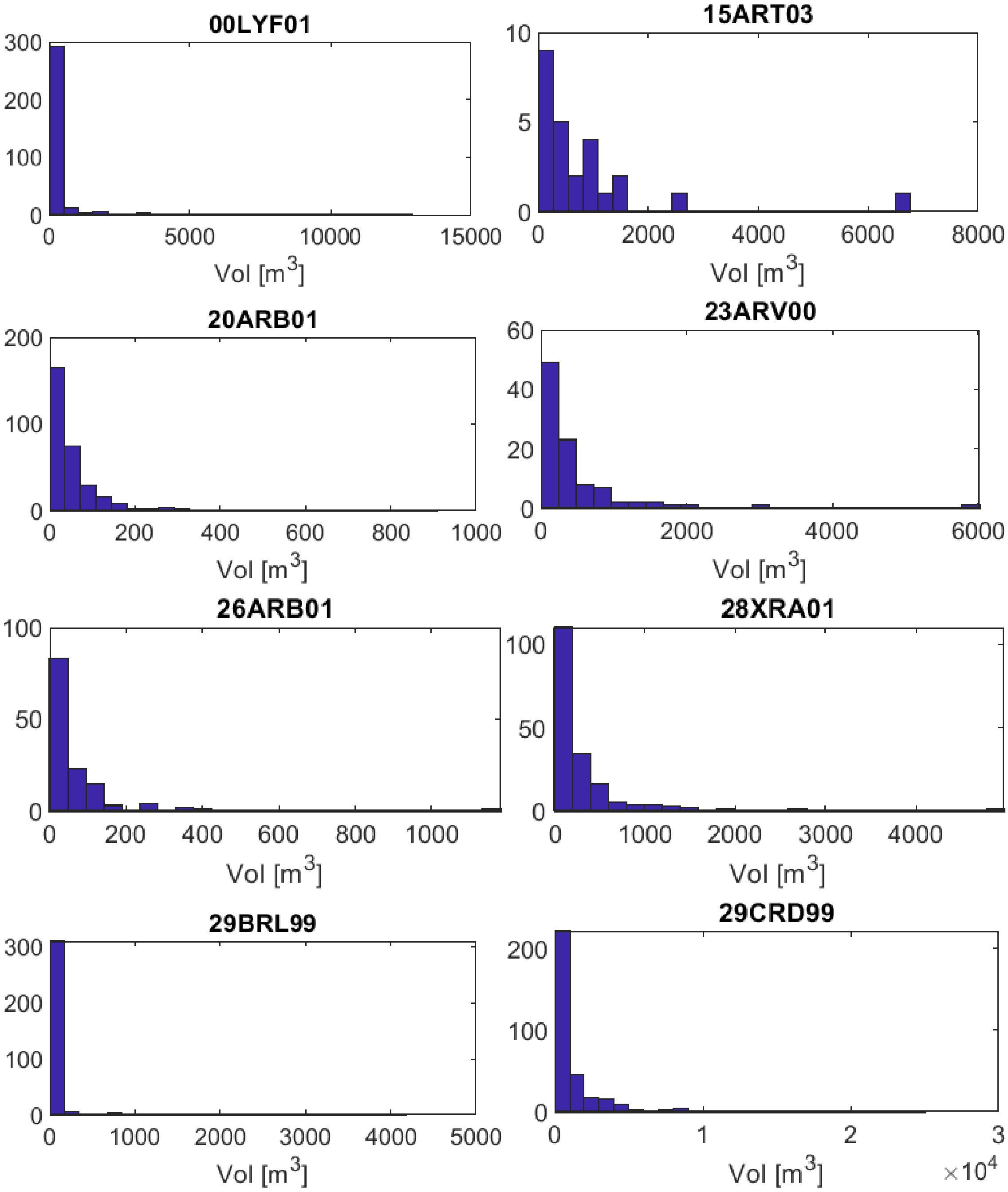
A Appendix

A.1 Graphs and charts



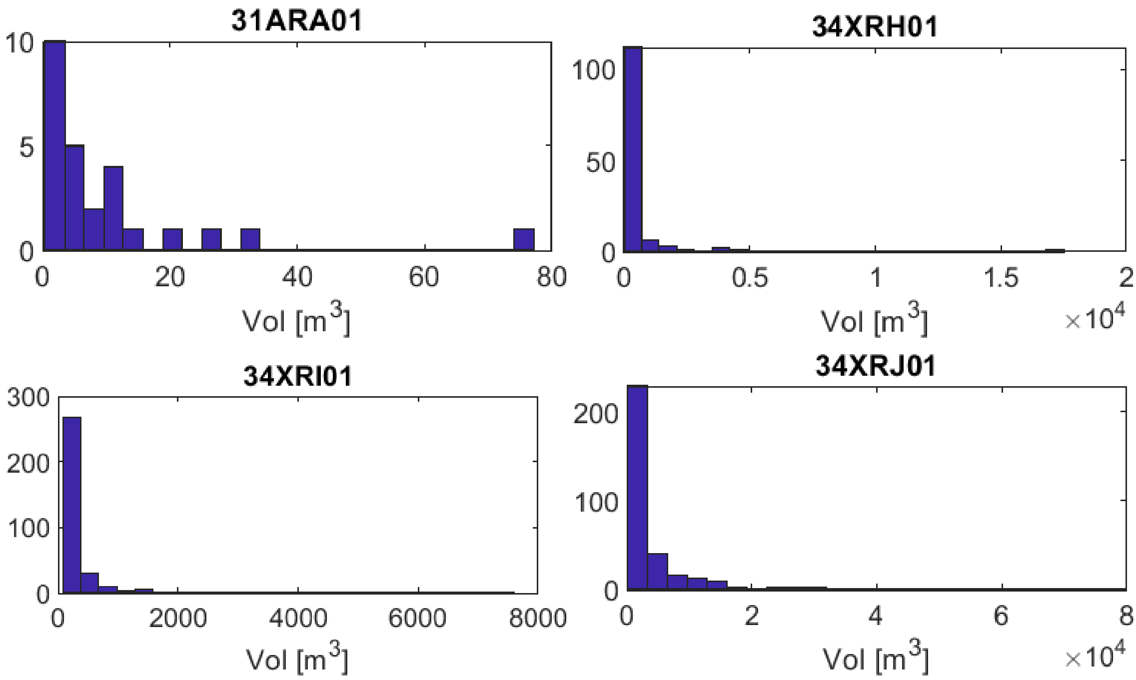
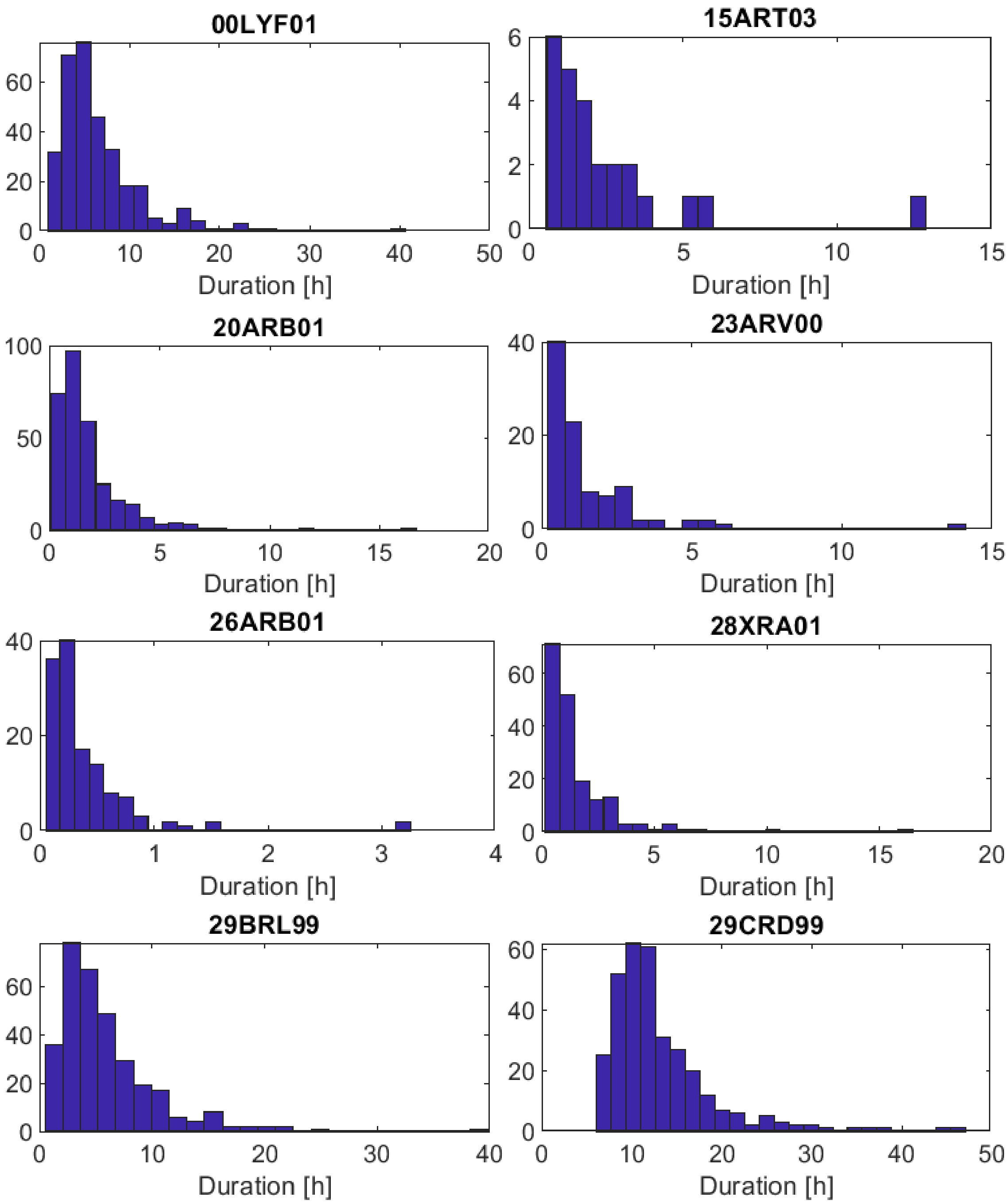


Figure A.1: Some images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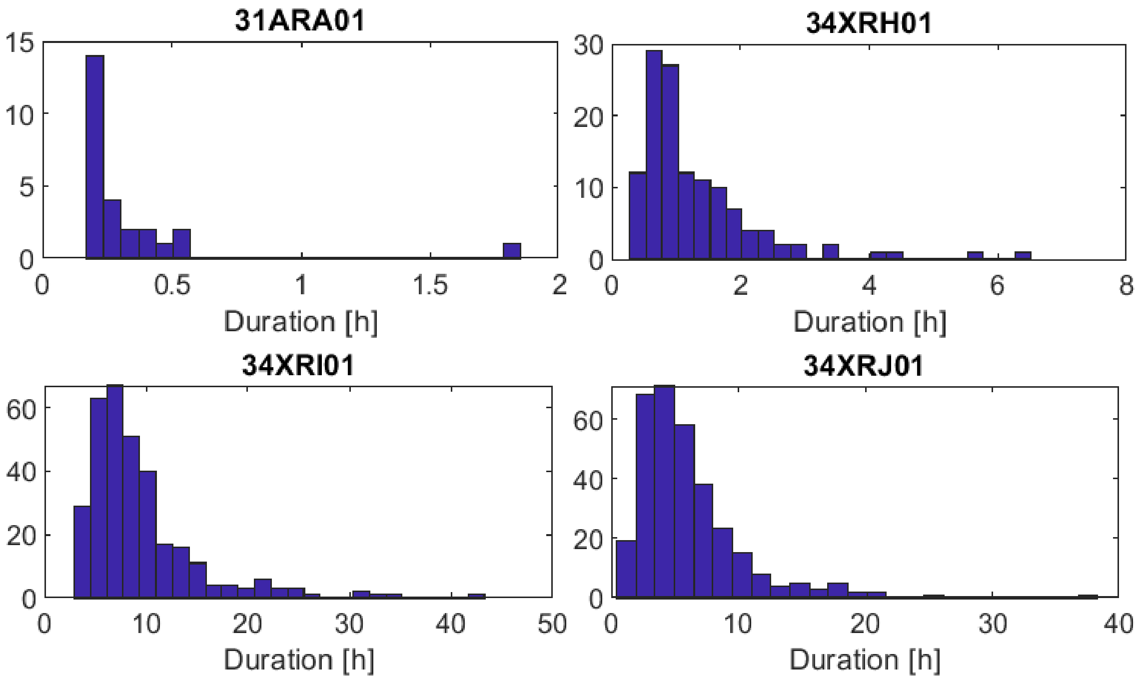

Figure A.2: Some images

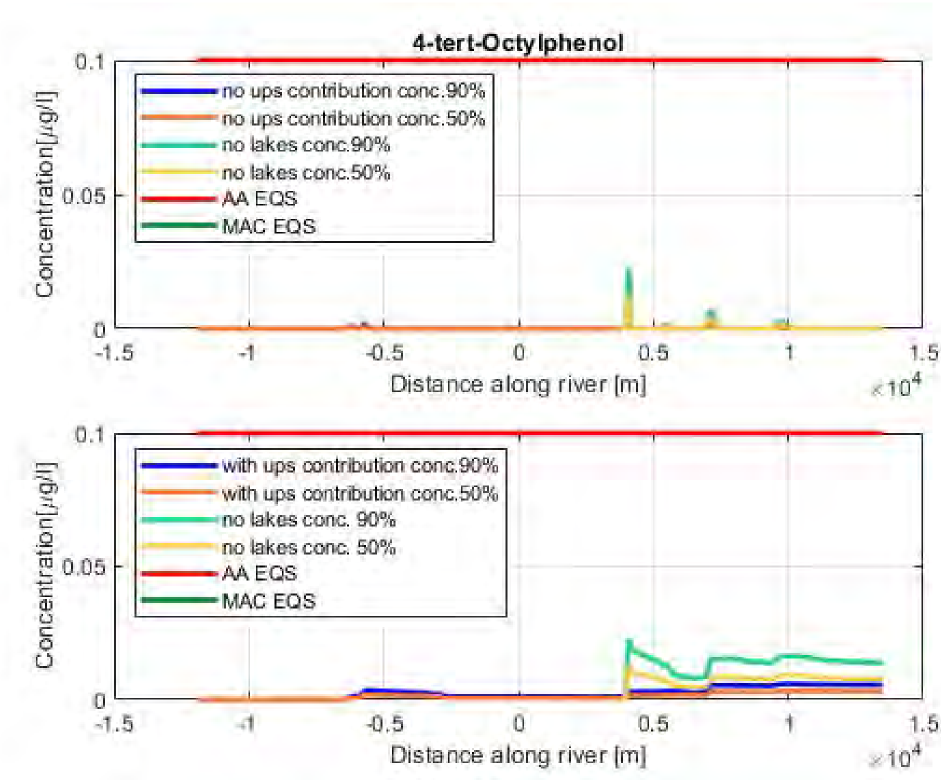

Figure A.3: 4-Tert-Octylphenol

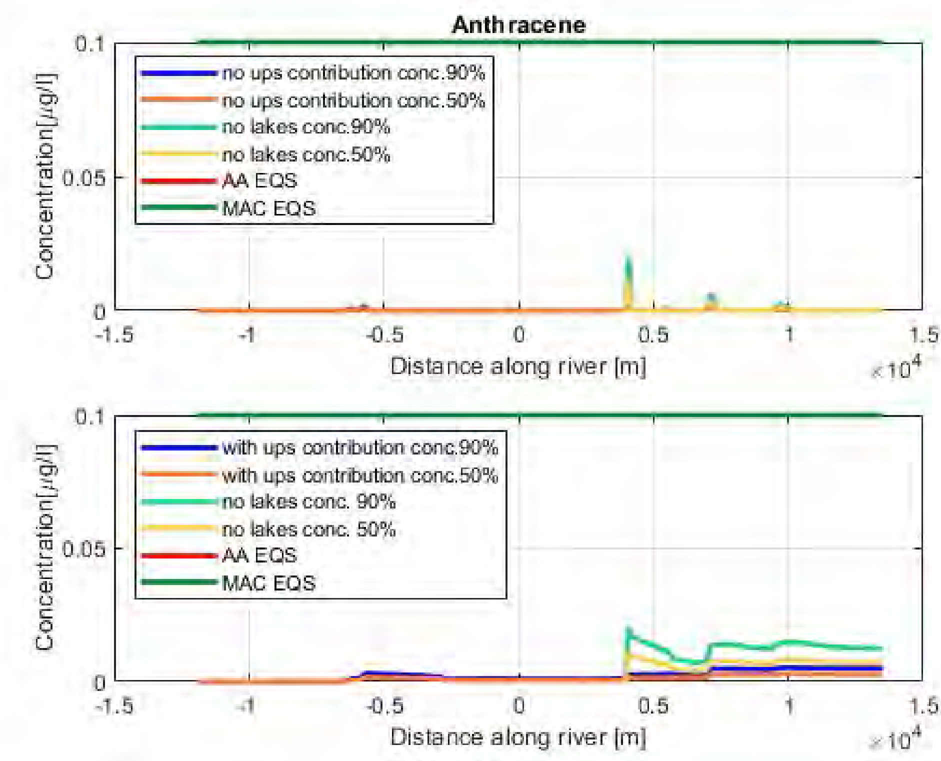

Figure A.4: Anthracene

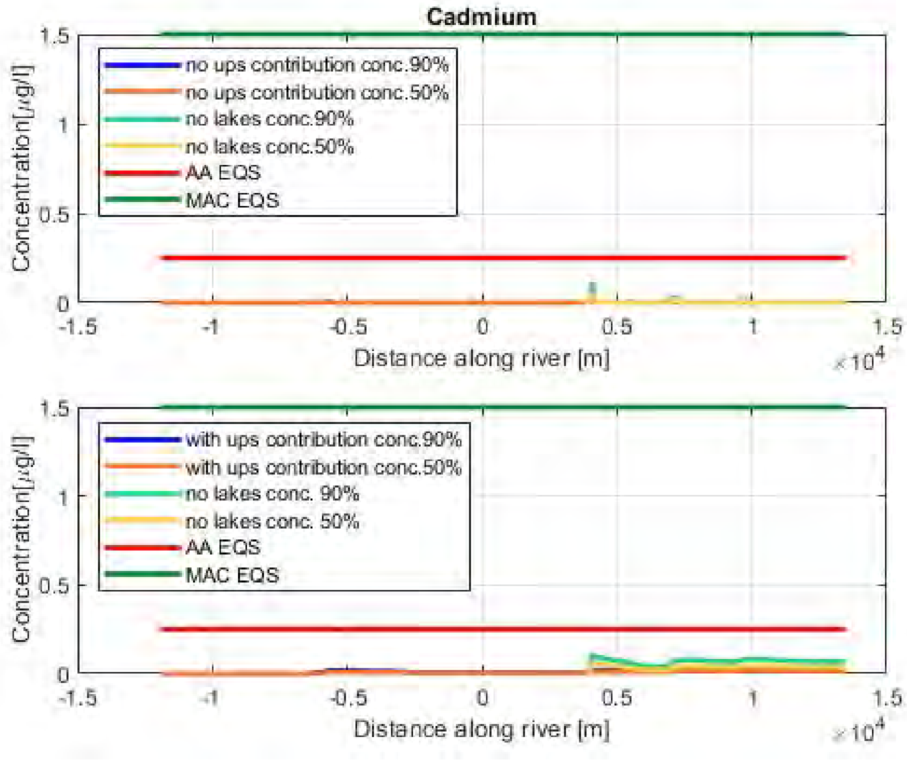

Figure A.5: Cadmium

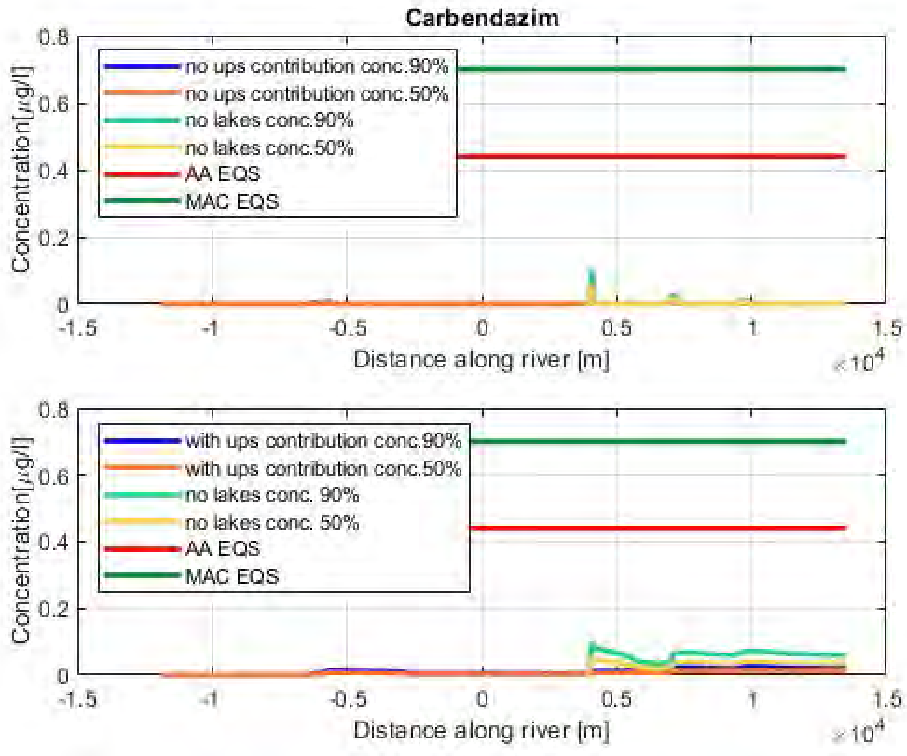

Figure A.6: Carbendazim

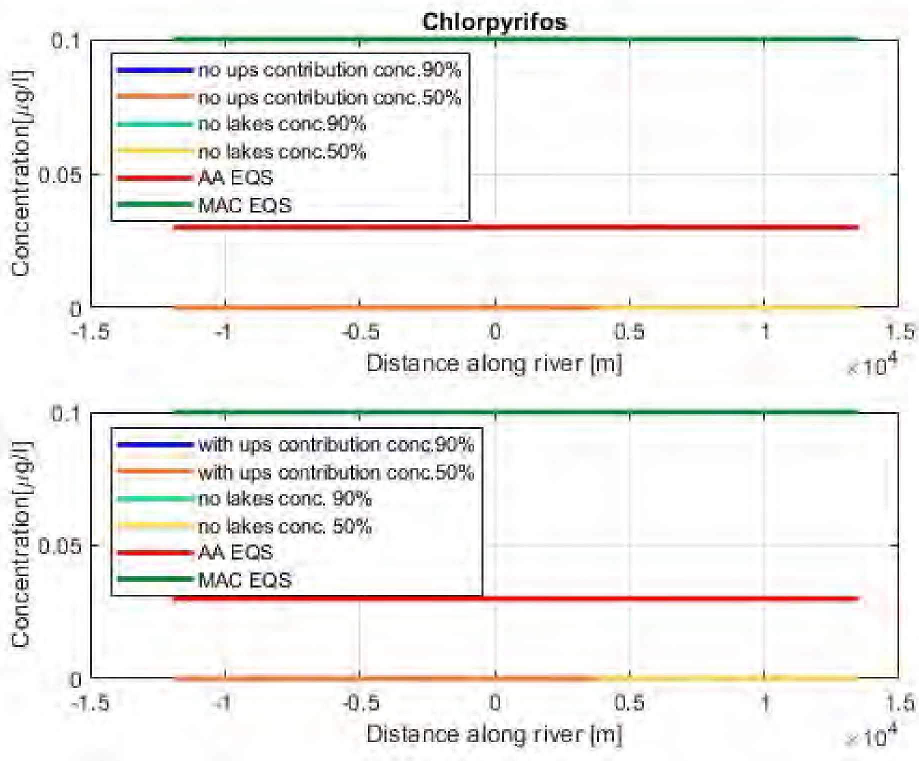

Figure A.7: Chlorpyrifos

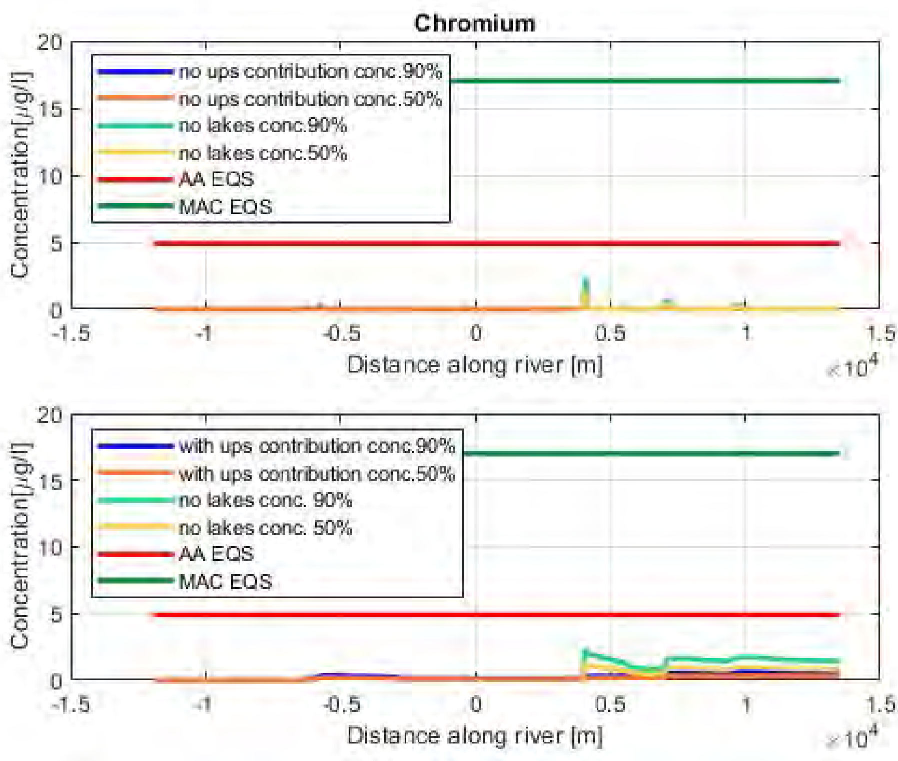

Figure A.8: Chromium

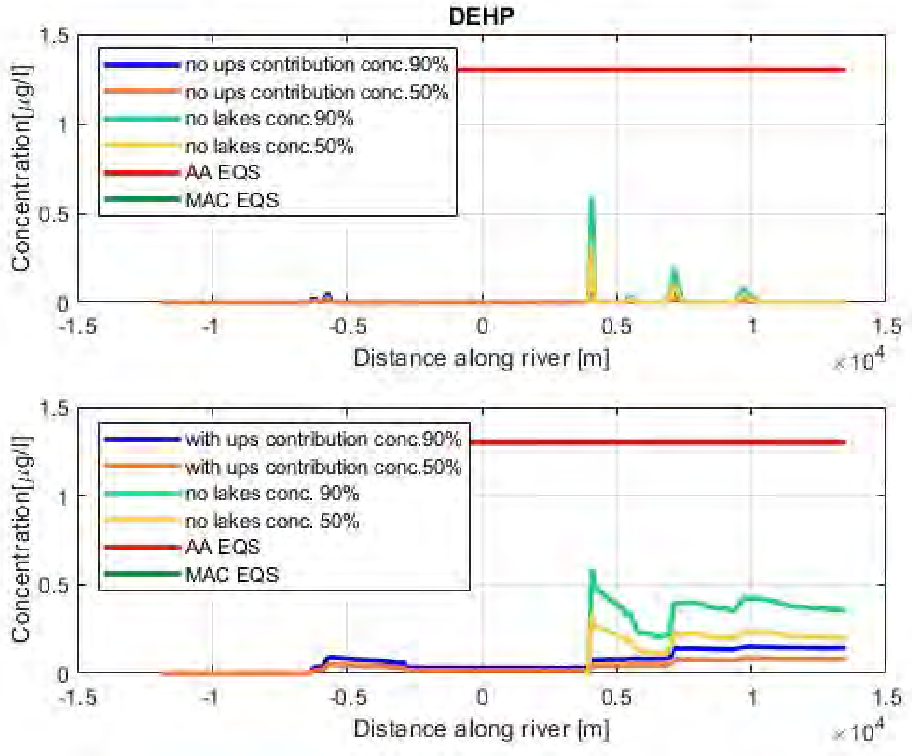

Figure A.9: DEHP

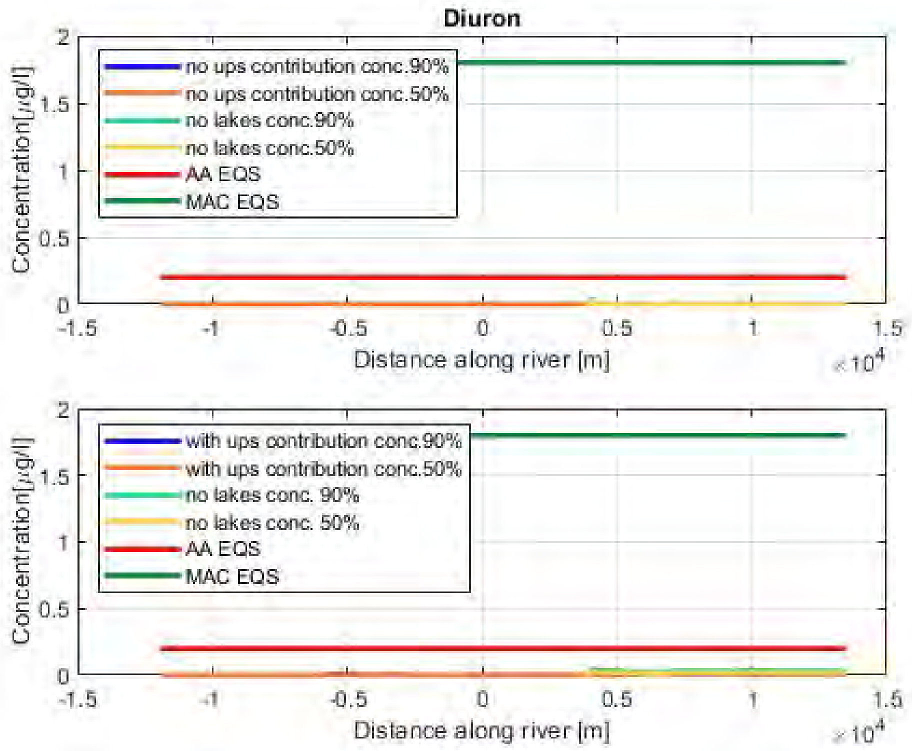

Figure A.10: Diuron

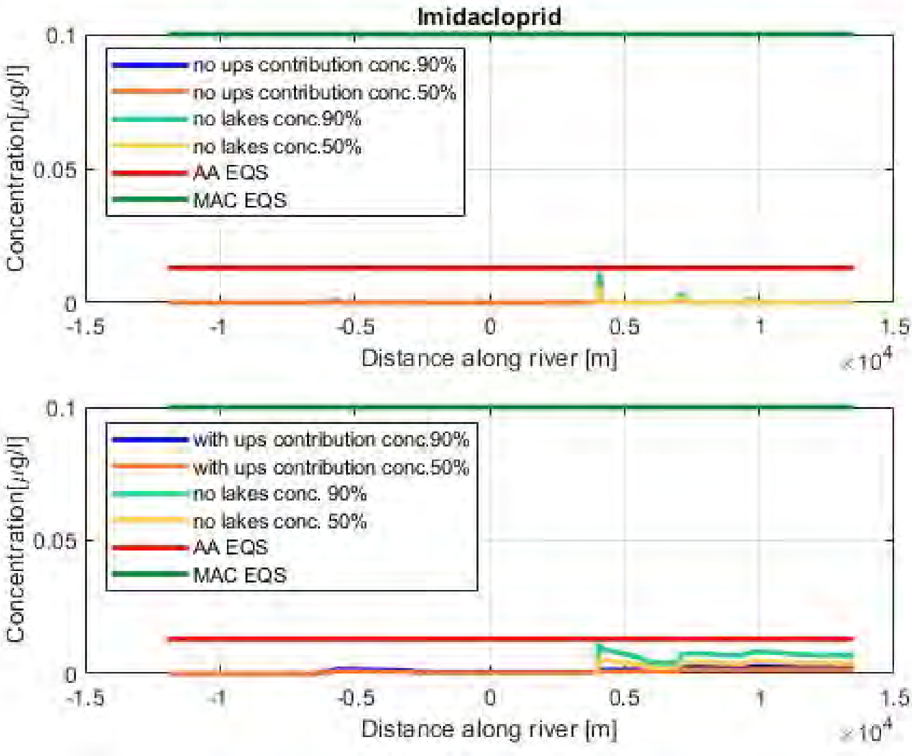

Figure A.11: Imidaclopryd

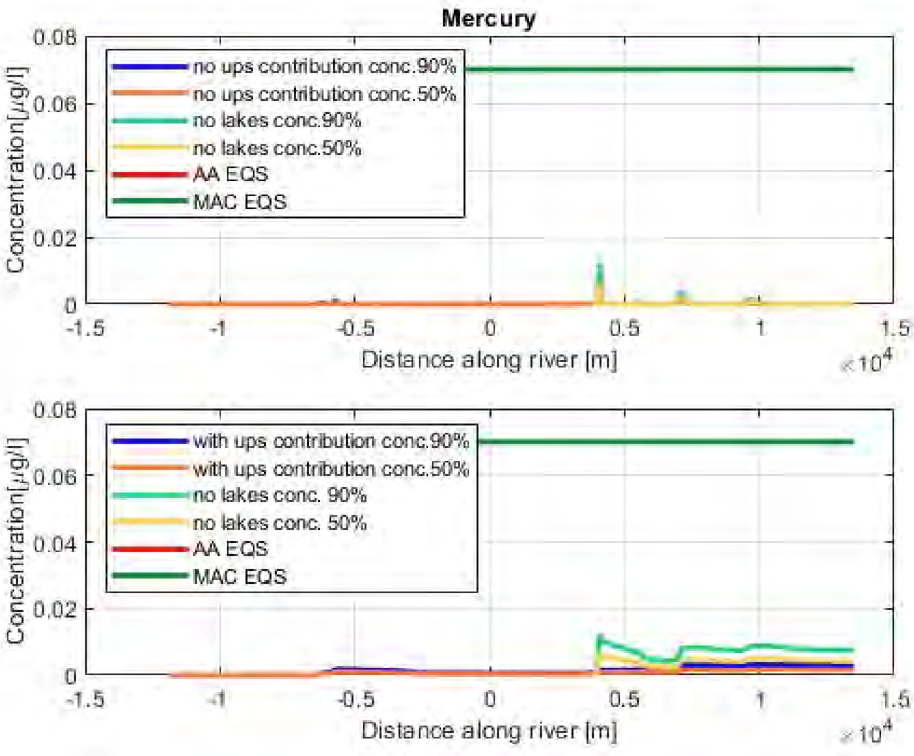

Figure A.12: Mercury

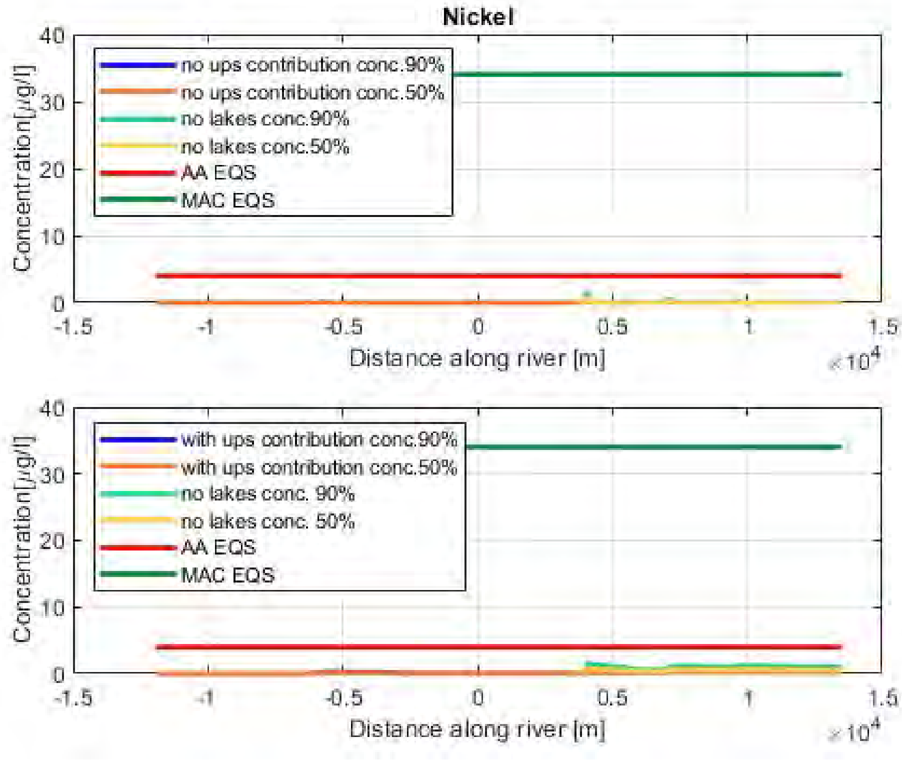

Figure A.13: Nickel

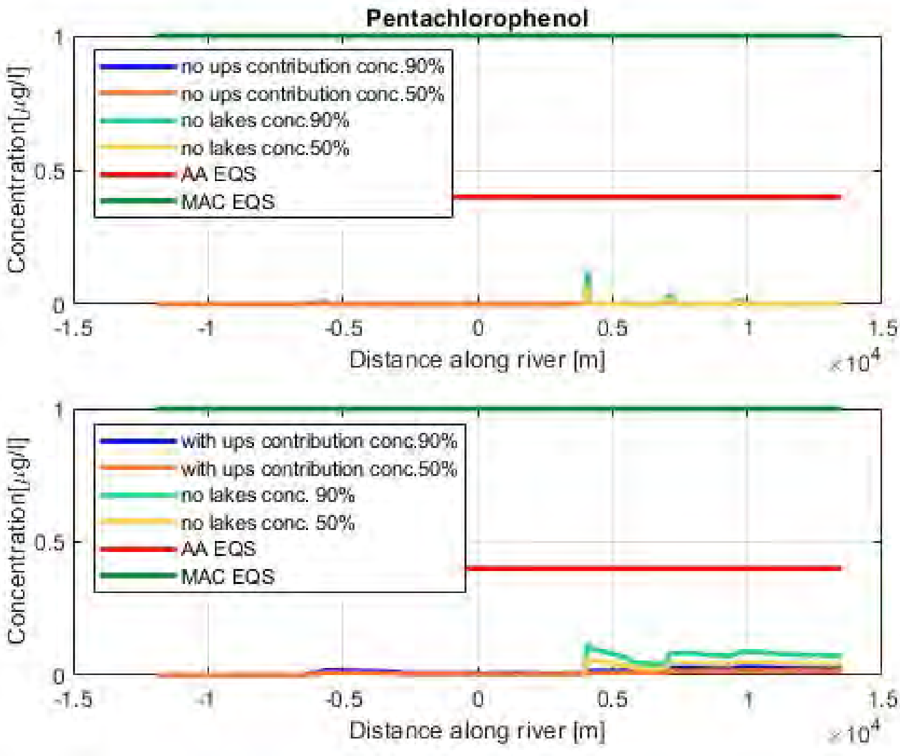

Figure A.14: Pentachlorophenol

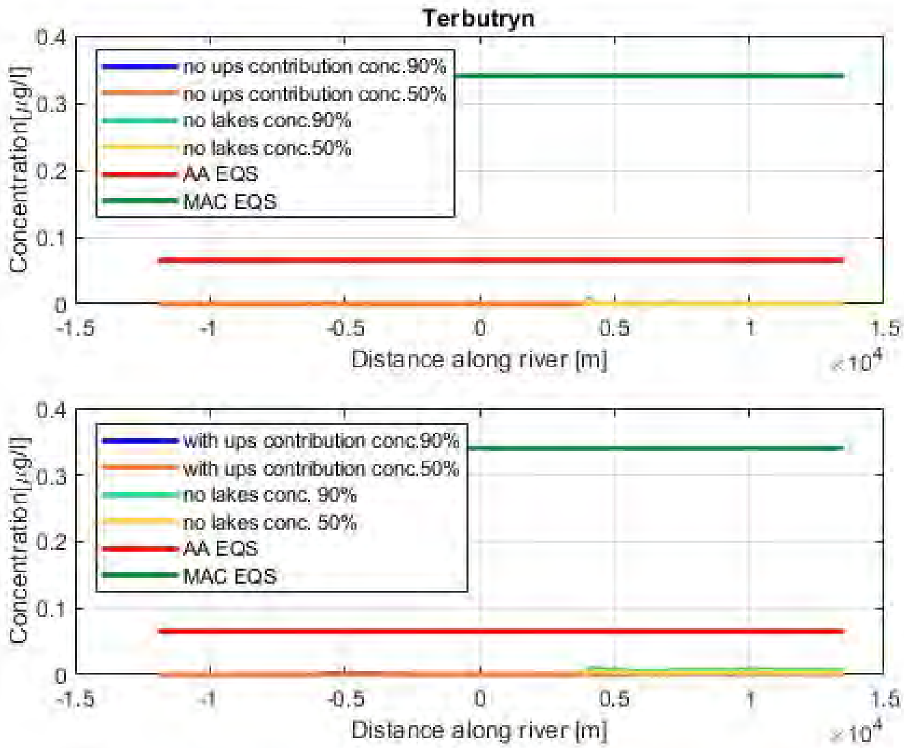

Figure A.15: Terbutryn

A.2 Listings and codes

The code reports the computations done for the Mølle Å to compute the concentrations.

```

clear all
close all

% import conc data 90%
importConcData90
EQSvalues %Chronic values
MACvalues %Acute values
% import conc data 50%
importConcData50

% read river nodes
importFlowData_HIP

% find their position along the river stretch
rivLoc= regexp([CalculationPoint{:}], '(?:(-\d*|\d*)\.\d)', 'match');
rivLoc=rivLoc';
rivLoc=(str2double(rivLoc));

% order stations
[rivLoc,idx]=sort(rivLoc);
River_Discharge=River_Discharge(idx);
x=x(idx);
y=y(idx);
CalculationPoint=CalculationPoint(idx);


% import CSO data
importCSOdata

csoLoc= regexp([CSOdischargePoint{:}], '(?:(-\d*|\d*)\.\d)', 'match');
csoLoc=csoLoc';
csoLoc=(str2double(csoLoc));

%% ========================================================

% visualize flow along river stretch
figure
h(1)=subplot(3,1,1:2);
plot(rivLoc,River_Discharge,'b-')
xlabel('Distance along river [m]')
ylabel('yearly river discharge [m^3/yr]')
hold on

h(2)=subplot(3,1,3);
plot(csoLoc,CSODischargem3year,'r.','MarkerSize',10)
xlabel('Distance along river [m]')
ylabel('yearly CSO discharge [m^3/yr]')

%% ========================================================
matrix=[csoLoc,CSODischargem3year]


%% =============== make calculations with upstream contribution =======

concRiv_NO=zeros(length(rivLoc),length(CAS)); % scenario with no upstream
    contribution
concRiv_UPS=zeros(length(rivLoc),length(CAS)); % scenario with upstream
    contribution
```

```
concRiv_NO50=zeros(length(rivLoc),length(CAS)); %scenario with no upstream contribution and 50% micropollutants conc.
concRiv_UPS50=zeros(length(rivLoc),length(CAS)); %scenario with ups contrib. and 50% micropollutants conc.
points_over_threshold_90=[];
points_over_threshold_50=[];
for idxPoll=1:length(CAS) % loop over substances
    % for each river point, find corresponding CSO (if any) and make
    % calculations

    for i=2:length(rivLoc) % loop over all river points
        idxCSO=find(csoLoc==rivLoc(i));
        if isempty(idxCSO) % no CSO in this river stretch
        % with upstream contribution
             concRiv_UPS(i,idxPoll)= concRiv_UPS(i-1,idxPoll) * River_Discharge(i-1) /...
                 River_Discharge(i);
             concRiv_UPS50(i,idxPoll)= concRiv_UPS50(i-1,idxPoll)* River_Discharge(i-1)/...
                 River_Discharge(i);
        else % there is a match, then make mass balance
            volCSO=0;
            for j=1:length(idxCSO) % loop if several CSO discharge on same point
                volCSO=volCSO+CSODischargem3year(idxCSO(j));
            end
            % no upstream contribution
            concRiv_NO(i,idxPoll)= (concRiv_NO(i,idxPoll) * River_Discharge(i) + ...
                                ConcugL_90(idxPoll)* volCSO ) / ...
                                (River_Discharge(i) + volCSO);
            concRiv_NO50(i,idxPoll)=(concRiv_NO50(i,idxPoll)* River_Discharge(i)+ ...
                                ConcugL(idxPoll)*volCSO)/...
                                (River_Discharge(i) + volCSO);
            % with upstream contribution
            concRiv_UPS(i,idxPoll)= (concRiv_UPS(i-1,idxPoll) * River_Discharge(i-1) + ...
                                   ConcugL_90(idxPoll)* volCSO ) / ...
                                   (River_Discharge(i) + volCSO);

            concRiv_UPS50(i,idxPoll)= (concRiv_UPS50(i-1,idxPoll)* River_Discharge(i-1)+...
                                   ConcugL(idxPoll)*volCSO)/ ...
                                   (River_Discharge(i) + volCSO);
        end
    end
    EQS_NO=zeros(length(rivLoc),1);
    EQS_NO(find(concRiv_NO(:,idxPoll)>AA_EQS(idxPoll)))=1;
    EQS_NO50(find(concRiv_NO50(:,idxPoll)>AA_EQS(idxPoll)))=1;
    EQS_NO(find(concRiv_NO(:,idxPoll)>MAC_EQS(idxPoll)))=1;
    EQS_NO50(find(concRiv_NO50(:,idxPoll)>MAC_EQS(idxPoll)))=1;

    EQS_UPS=zeros(length(rivLoc),1);
    EQS_UPS(find(concRiv_UPS(:,idxPoll)>AA_EQS(idxPoll)))=1;
    EQS_UPS(find(concRiv_UPS(:,idxPoll)>MAC_EQS(idxPoll)))=1;
    points_over_threshold_90=[points_over_threshold_90,sum(EQS_UPS)];
    EQS_UPS50=zeros(length(rivLoc),1);
    EQS_UPS50(find(concRiv_UPS50(:,idxPoll)>AA_EQS(idxPoll)))=1;

    points_over_threshold_50=[points_over_threshold_50,sum(EQS_UPS50)]
    figure
```

```
    hh(1)=subplot(2,1,1);
    hold on
    plot(rivLoc,concRiv_NO(:,idxPoll),'c','LineWidth',2)
    plot(rivLoc,concRiv_NO50(:,idxPoll),'g--','LineWidth',2)
    legend('no ups contribution conc.90%','no ups contribution conc.50%','Location','NorthWest')

    title(Substance{idxPoll})

    hh(2)=subplot(2,1,2);
    hold on
    plot(rivLoc,concRiv_UPS(:,idxPoll),'c','LineWidth',2)
    plot(rivLoc,concRiv_UPS50(:,idxPoll),'g--','LineWidth',2)
    legend('with ups contribution conc.90%','with ups contribution conc.50%','Location','NorthWest')


    for j=1:2
        axes(hh(j))
        plot([min(rivLoc) max(rivLoc)],ones(2,1)*AA_EQS(idxPoll),'r-','LineWidth',2,...
            'DisplayName','AA EQS')
        hold on
        plot([min(rivLoc) max(rivLoc)],ones(2,1)*MAC_EQS(idxPoll),'b-','LineWidth',2,...
            'DisplayName','MAC EQS')
        ylabel('Concentration[\mug/l]')
        xlabel('Distance along river [m]')
    end
    set(hh,'Box','on','XGrid','on','YGrid','on')

    % create output file for QGIS

    namefile=join(['outputGIS_' Substance{idxPoll} '.csv']);
    %header
    writematrix('x;y;concNO;concUPS;EQS_NO;EQS_UPS',namefile,'Delimiter','semi','QuoteStrings',false)
    %write the data
    writematrix([x y concRiv_NO(:,idxPoll) concRiv_UPS(:,idxPoll) EQS_NO EQS_UPS],namefile,'WriteMode','append','Delimiter','semi')

 end

points_over_threshold_90
points_over_threshold_50
sum90=sum(points_over_threshold_90);
sum50=sum(points_over_threshold_50);
```

Listing A.1: First screening on Mølle Å to test the model

```

clear
clc

%Import CSOs data
ImportCSOs

ID_number=[];
string=[];
discharge = [];
vanfoerinCSO.VarName7=erase(vanfoerinCSO.VarName7,"_Downstream")

for i=2:length(vanfoerinCSO.VarName7)

    %extract numbers from string
%      number = cellfun(@(x)str2double(regexp(x,'\d*\.\d*','match')),
    vanfoerinCSO.VarName7(i));
    dis = vanfoerinCSO.VarName12(i);
    %extract literal part from string
    str= strsplit(vanfoerinCSO.VarName7(i), '_');
    number=str2num(str(end));
    n=length(str);
    str1=join(str(1,1:(n-2)), '');
    %%%
    ID_number=[ID_number;number];
    string=[string;str1];
    discharge = [discharge; dis];
end

T=table(string,ID_number, discharge);
```

Listing A.2: modelling CSO data according to position

Modelling concentration in all Denmark

```
clear
clc

%Load all simulated points alongside rivers
ImportAllRivers
%Extract just the values of 2019
[row, ~] = find(pinco.aar == 2019);
All_Rivers=pinco(row, :);
ID_number=[];
string1=[];
All_Rivers.beregnings=string(All_Rivers.beregnings);
p = arrayfun(@(i)strncmpi(All_Rivers.beregnings{i}(end:-1:1),'maertsnwod',10)
    ,(1:1:size(All_Rivers,1))','uniform',true);
All_Rivers = All_Rivers(~p,:);

for i=1:length(All_Rivers.beregnings)
    i;
    %extract numbers from string
    %number = cellfun(@(x)str2double(regexp(x,'\d*\.\d*','match')),All_Rivers.
        beregnings(i));
    %extract literal part from string
    str= strsplit(All_Rivers.beregnings(i), '_');
    number=str2num(str(end));
    n=length(str);
    str1=join(str(1,1:(n-2)), '');
    ID_number=[ID_number;number];
    string1=[string1;str1];
end

SimulatedPoints=table(string1,ID_number,All_Rivers.vandfoerin);

nameRivers=unique(SimulatedPoints.string1);
for i=1:length(nameRivers)
    summaryRiver(i).name=nameRivers(i);
    idxRiv=find(SimulatedPoints.string1==nameRivers(i));
    summaryRiver(i).points=SimulatedPoints.ID_number(idxRiv);
    summaryRiver(i).Q=SimulatedPoints.Var3(idxRiv);

    %removing doublettes
    [s,IA,ss] = unique(summaryRiver(i).points);
    summaryRiver(i).Q=summaryRiver(i).Q(IA);
    summaryRiver(i).points=summaryRiver(i).points(IA);
end

All_Points= struct2table(summaryRiver,'AsArray',true);
for i=1:length(All_Points.points)
    k=length(All_Points.Q{i});
    for j=1:k
        All_Points.Q{i}(j,1)=All_Points.Q{i}(j,1)/0.05;
    end
end

save('All_Points')
```

Listing A.3: modelling discahrges of points coming from all Denmark

```
clear
clc

%upload Simulated Measurement Points of all Denmark
load ('All_Points.mat')
```

```
%upload CSOs data of all Denmark
load('Name_Code.mat')
%creating a matrix with the columns for the volumes and concentrations
for ci=1:length(All_Points.points)
    nrows=length(All_Points.points{ci});
    All_Points.CSOvol{ci}=zeros(size(All_Points.points{ci}));
    All_Points.ConcUPS90{ci}=zeros(size(All_Points.points{ci}));
    All_Points.ConcNo90{ci}=zeros(size(All_Points.points{ci}));
    All_Points.ConcUPS50{ci}=zeros(size(All_Points.points{ci}));
    All_Points.ConcNo50{ci}=zeros(size(All_Points.points{ci}));
    All_Points.Over{ci}=zeros(size(All_Points.points{ci}));
end
%associate CSO to River Points according to the code
for i=1:length(Name_Code.Name)

 idxPoint=find(Name_Code.Name(i)==All_Points.name(:));
 k=length(Name_Code.Codes{i});
 for j=1:k
     if find(Name_Code.Codes{i}(j,1)==All_Points.points{idxPoint})
         idxDischarge=find(Name_Code.Codes{i}(j,1)==All_Points.points{idxPoint
             });
         All_Points.CSOvol{idxPoint}(idxDischarge,1)=Name_Code.Discharge{i}(j
             ,1);
     else isempty(idxDischarge);

     end
 end
end

%%
sub_over_threshold90=[];
PointsOverThresholdperRiver=[];
matrix_concentrations=[];
Conc50
Conc90
Substances
EQSvalues
PointsOverThresholdPerSubstance=[];
%loop over the micropollutants
for idxPoll=1:20
%loop over the rivers
for ii=1:length(All_Points.points)
   if find(All_Points.name{ii}==Name_Code.Name(:))
       idxCSO=find(All_Points.name{ii}==Name_Code.Name(:));
        kkk=length(All_Points.points{ii});
        volCSO=0;
%loop over the points evry river has been discretized
    for jj=2:kkk
        idx=find(Name_Code.Codes{idxCSO}==All_Points.points{ii}(jj,1));
        if isempty(idx) %no CSO in this river stretch
             All_Points.ConcUPS90{ii}(jj,1)=All_Points.ConcUPS90{ii}((jj-1),1)
                 *All_Points.Q{ii}(jj-1,1)/...
                 All_Points.Q{ii}(jj);
        else %there is a match, then make mass balance
            volCSO=volCSO+All_Points.CSOvol{ii}(jj,1);
             All_Points.ConcUPS90{ii}(jj)=(All_Points.ConcUPS90{ii}(jj-1)*
                 All_Points.Q{ii}(jj-1)+ Conc_90.ConcugL_90(idxPoll)* volCSO)
                 /...
                 (All_Points.Q{ii}(jj) + volCSO);
             All_Points.ConcUPS50{ii}(jj)=(All_Points.ConcUPS50{ii}(jj-1)*
                 All_Points.Q{ii}(jj-1)+ Conc_50.ConcugL_50(idxPoll)* volCSO)
                 /...
```

```
                 (All_Points.Q{ii}(jj) + volCSO);
             All_Points.ConcNo90{ii}(jj)=(All_Points.ConcNo90{ii}(jj)*
                 All_Points.Q{ii}(jj)+ Conc_90.ConcugL_90(idxPoll)* volCSO)
                 /...
                 (All_Points.Q{ii}(jj) + volCSO);
             All_Points.ConcNo50{ii}(jj)=(All_Points.ConcNo50{ii}(jj)*
                 All_Points.Q{ii}(jj)+ Conc_50.ConcugL_50(idxPoll)* volCSO)
                 /...
                 (All_Points.Q{ii}(jj) + volCSO);
             % check how many points are over the threshold

        end
        All_Points.Over{ii}=All_Points.ConcUPS90{ii}>AA_EQS(idxPoll);
        All_Points.total{ii}=sum(All_Points.Over{ii});
    end

    else isempty(idxCSO)

   end
end
%count the number of rivers that have at least one point over the
%threshold for every substance
rivers_over_threshold=[];
for d=1:length(All_Points.total)
    if All_Points.total{d}>0;
        dd=1;
    else
        dd=0;
    end
rivers_over_threshold=[rivers_over_threshold,dd];
end
PointsPerSubstance=sum(rivers_over_threshold);
%on 787 rivers having at a least a CSO, rivers per substance are
%ovecoming the AA threshold
PointsOverThresholdPerSubstance=[PointsOverThresholdPerSubstance,
    PointsPerSubstance];
PointsOverThresholdperRiver=[PointsOverThresholdperRiver,All_Points.total];
matrix_concentrations=[matrix_concentrations,All_Points.ConcUPS90];
end
```