Univerza
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*Fakulteta za gradbeništvo in geodezijo*

UNIVERZITETNI PODIPLOMSKI ŠTUDIJSKI
PROGRAM VARSTVO OKOLJA

DOKTORSKI ŠTUDIJ

Kandidatka:

**DARJA ISTENIČ, univ. dipl. biol.**

# ČIŠČENJE NIZKO OBREMENJENIH VODA Z RASTLINSKIMI ČISTILNIMI NAPRAVAMI

Doktorska disertacija štev.: 208

# TREATMENT OF LOW POLLUTED WATERS WITH CONSTRUCTED WETLANDS

Doctoral thesis No.: 208

Soglasje k temi doktorske disertacije je dala Komisija za doktorski študij na 11. redni seji 11. septembra 2008. Za mentorja je bil imenovan prof. dr. Boris Kompare, za somentorja pa prof. dr. Danijel Vrhovšek, Limnos d. o. o.
Na 4. seji 25. marca 2010 je Komisija za doktorski študij dala soglasje k pisanju disertacije v angleškem jeziku in imenovanju novega somentorja prof. dr. Hansa Brixa z Univerze v Aarhusu.

Ljubljana, 12. november 2010

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**Komisijo za oceno ustreznosti teme doktorske disertacije v sestavi**

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**IZJAVA O AVTORSTVU**

Podpisana **DARJA ISTENIČ, univ. dipl. biol.**, izjavljam, da sem avtorica doktorske disertacije z naslovom: **»ČIŠČENJE NIZKO OBREMENJENIH VODA Z RASTLINSKIMI ČISTILNIMI NAPRAVAMI«.**

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Ljubljana, 12. novembra 2010

…………………………………..
(podpis)

## BIBLIOGRAPHIC-DOCUMENTALISTIC INFORMATION

**UDC:** **502/504:628.32(043.3)**

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**Supervisor:** **prof. dr. Boris Kompare**

**Co-supervisor:** **prof. dr. Hans Brix**

**Title:** **Treatment of low polluted waters with constructed wetlands**

**Notes:** **184 p., 35 tab., 48 fig., 2 app.**

**Keywords:** **stormwater, wet detention pond, sand filter, wetland plants, sediment accumulation**

### Abstract

The thesis deals with the treatment performance and pollutant fate in four traditional stormwater detention ponds and three stormwater detention ponds with additional technologies for enhanced elimination of dissolved and colloidal pollutants. The additional technologies integrated were sand filters, sorption filters and addition of precipitation chemicals along with plantation of wetland plants. Water samples were analysed for water quality parameters, heavy metals (Zn, Cu, Pb, Cd, Hg, Ni, Cr) and polycyclic aromatic hydrocarbons (PAHs). Sediment samples were taken in each pond and analysed for organic contents, P, Fe, Mn, Ca, Na, K, Al, Pb, Zn, Cd, Ni, Cr, Cu and PAHs. Nutrients and heavy metals were analysed also in plant tissues sampled at the banks of the ponds, free water and sand filters. The results showed efficient elimination of suspended solids and total phosphrous from stormwater in all studied systems and improved elimination of soluble pollutants in upgraded wet detention ponds. Pollutants accumulated in the sediment; wetland plants enhanced sedimentation and accumulation of pollutants in the sediment. Heavy metals accumulated in the plants' roots with no marked translocation into aboveground tissues and hence presented no threat for bioaccumulation. *Rumex hydrolapathum* accumulated the highest concentrations of heavy metals in the roots (concentration factor of 4.5 and 5.9 for Zn and Ni, respectively) and *Iris pseudacorus* the lowest (concentration factors below one). *Typha* sp. and *Phragmites australis* were also found to be appropriate species for phytoremediation of stormwater runoff. Heavy metal concentrations in the plants were correlated with concentrations of heavy metals in the water and sediment.

## BIBLIOGRAFSKO-DOKUMENTACIJSKA STRAN IN IZVLEČEK


| | |
|---|---|
| **UDK:** | **502/504:628.32(043.3)** |
| **Avtor:** | **Darja Istenič, univ.dipl.biol.** |
| **Mentor:** | **prof.dr. Boris Kompare** |
| **Somentor:** | **prof. dr. Hans Brix** |
| **Naslov:** | **Čiščenje nizko obremenjenih vod z rastlinskimi čistilnimi napravami** |
| **Obseg in oprema:** | **184 str., 35 pregl., 48 sl., 2 pril.** |
| **Ključne beside:** | **meteorna voda, mokri zadrževalni bazen, peščeni filter, močvirske rastline, kopičenje sedimenta** |


**Izvleček:**

Disertacija obravnava učinkovitost čiščenja in usodo onesnažil v štirih običajnih bazenih za zadrževanje meteorne vode in treh zadrževalnikih meteorne vode z dodatnimi tehnologijami za izboljšano odstranjevanje raztopljenih in koloidnih onesnažil. Vključene dodatne tehnologije so bili peščeni filtri, sorbcijski filtri in dodatek kemikalij za precipitacijo skupaj z zasadnjo močvirskih rastlin. V vzorcih vode so bili analizirani parametri kakovosti vode, težke kovine (Zn, Cu, Pb, Cd, Hg, Ni, Cr) in policiklični aromatski ogljikovodiki (PAH). V vsakem zadrževalniku so bili odvzeti vzorci sedimenta in analizirana vsebnost organskih snovi, P, Fe, Mn, Ca, Na, K, Al, Pb, Zn, Cd, Ni, Cr, Cu in PAH. Hranila in težke kovine so bile analizirane tudi v rastlinskih tkivih vzorčenih na brežinah zadrževalnikov, prosti vodi in na peščenih filtrih. Rezultati so pokazali učinkovito odstranjevanje suspendiranih snovi in celokupnega fosforja iz meteorne vode v vseh proučevanih sistemih ter izboljšano odstranjevanje raztopljenih onesnažil v nadgrajenih zadrževalnih bazenih. Onensažila so se akumulirala v sedimentu; močvirske rastline so pospešile sedimentacijo in kopičenje onesnažil v sedimentu. Težke kovine so se kopičile v koreninah rastlin brez očitne translokacije v nadzemna tkiva ter s tem niso predstavljale nevarnosti za bioakumulacijo. Najvišje koncentracije težkih kovin so se akumulirale v koreninah *Rumex hydrolapathum* (koncentracijski faktor 4.5 in 5.9 za Zn oziroma Ni) in najnižje v *Iris pseudacorus* (koncentracijski faktorji manjši od ena). *Typha* sp. in *Phragmites australis* sta se prav tako izkazali kot ustrezni vrsti za fitoremediacijo odtoka meteornih vod. Koncentracije težkih kovin v rastlinah so bile v korelaciji s koncentracijami težkih kovin v vodi in sedimentu.

## ACKNOWLEDGMENT

First, I would like to thank to prof. dr. Danijel Vrhovšek for employing me at his company LIMNOS Ltd. as a PhD student and to The Ministry of Higher Education, Science and Technology for funding my studies. The work at LIMNOS has always been dynamic and has enriched me with broad new knowledge. I would like to express my special thanks to my supervisors – prof. dr. Boris Kompare and prof. dr. Hans Brix for accepting the role of (co)supervision and being always prepared to share their rich knowledge with me. I am grateful to prof. Kompare for accepting my ideas about research theme and supporting my work. The cooperation with my co-supervisor prof. dr. Hans Brix at Plant Biology Department at Aarhus University, Denmark, was an exceptional work experience. I would like to express sincere gratitude to prof. Brix for accepting me in his group, including me in an interesting project that was financed by EU LIFE fund and enabling the work went smoothly and professionally. Hereby I would like to give my special gratitude to a crucial person in my PhD studies, doc. dr. Tjaša Griessler Bulc who enabled me the contact with prof. Brix and encouraged me for an important step. An acknowledgement also goes to AD-FUTURA agency, which funded my research visits to Denmark. Next, I would like to give my special thanks to dr. Carlos Arias from Aarhus University for guidance and help in the fieldwork and in the laboratory and for all the advices he gave me. I would like to express my thanks to the entire group at Plant Biology Department at Aarhus University for accepting me among them and especially to the excellent crew of technical stuff for help in the laboratory. I would also like to thank to the directress of LIMNOS Mrs. Marjana Vrhovšek for truthful cooperation and to all present and past LIMNOS group for being a productive and co-operational team of co-workers and friends.

Being a PhD student was not only a rich educational or scientific practice but also a life experience of all kinds. I am grateful to my mum, dad and sister, to my beloved friends that I met in Denmark and those from home for supporting and encouraging me in stressful moments.

## ZAHVALA

Na začetku bi se rada zahvalila prof. dr. Danijelu Vrhovšku, da me je zaposlil v njegovem podjetju LIMNOS d.o.o. kot doktorsko študentko ter Ministrstva za visoko šolstvo, znanost in tehnologijo za financiranje mojega študija. Delo na LIMNOS-u je bilo vedno dinamično in me je obogatilo s širokimi novimi znanji. Posebno bi se rada zahvalila mojima mentorjema – prof. dr. Borisu Komparetu in prof. dr. Hansu Brixu, da sta sprejela vlogi mentorstva oz. somentorstva in bila vedno pripravljena deliti njuno bogato znanje z mano. Hvaležna sem prof. Komparetu, da je sprejel moje ideje o raziskovalni tematiki in podprl moje delo. Sodelovanje z mojim somentorjem prof. dr. Hansom Brixom na oddelku za rastlinsko biologijo Univerze v Aarhusu, Danska, je bila izjemna delovna izkušnja. Iskreno sem hvaležna prof. Brixu, da me je sprejel v svojo skupino, vključil v zanimiv projekt financiran s strani EU LIFE programa in omogočil, da je delo potekalo gladko in profesionalno. Na tem mestu bi se rada posebej zahvalila ključni osebi v mojem doktorskem študiju, doc. dr. Tjaši Griessler Bulc, ki mi je omogočila kontakt s prof. Brixom in me spodbudila k pomembni odločitvi. Zahvala gre tudi agenciji AD-FUTURA za financiranje mojih raziskovalnih obiskov na Danskem. Posebno zahvalo bi rada izrekla tudi dr. Carlosu Ariasu iz Univerze v Aarhusu za vodenje in pomoč pri delu na terenu in v laboratoriju ter za vse nasvete, ki mi jih je dal. Hvaležna sem tudi celotni skupini oddelka za rastlinsko biologijo, da so me sprejeli medse in še posebej odlični skupini tehničnega osebja za pomoč v laboratoriju. Rada bi se zahvalila tudi direktorici LIMNOS-a ga. Marjani Vrhovšek za korektno sodelovanje in vsej sedanji in pretekli ekipi podjetja, da smo (bili) produktivna in sodelujoča skupina sodelavcev in prijateljev.

Biti doktorska študentka ni bilo le bogato izobraževalno ali znanstveno delo ampak tudi vsakovrstna življenjska izkušnja. Hvaležna sem moji mami, atiju in sestri, mojim dragim prijateljem, ki sem jih spoznala na Danskem ter tistim doma za podporo in spodbujanje v stresnih trenutkih.

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## ABBREVIATIONS AND SYMBOLS

AC – accumulation coefficient
ANOVA – analyzes of variance
BMP – Best Management Practice
BOD – biochemical oxygen demand
CF – concentration factor
COD – chemical oxygen demand
DME – Danish Ministry for the Environment
DW – dry weight
Eh – redox potential
GC-MS – gas chromatography-mass spectrometry
HMW – high molecular weight
ICP-OES – inductive coupled plasma-optical emission spectrometry
LMW – low molecular weight
O.G. RS – Official Gazette of Republic of Slovenia
Ortho-P - orthophosphate
PAHs – polycyclic aromatic hydrocarbons
TKN – total Kjeldahl nitrogen
TN – total nitrogen
TP – total phosphorous
TSS – total suspended solids
WFD – Water Framework Directive

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# 1 INTRODUCTION

Precipitation is an essential part of the global water cycle, necessary for the recharge of surface and groundwater bodies. In a natural environment, there is an unimpeded connection between land, groundwater and surface waters (lakes, rivers, wetlands), while in urban areas this connection is interrupted by impervious surfaces. Groundwater recharge is therefore reduced, while the surface runoff in terms of total volume as well as flow peaks is increased. The increased surface runoff might cause flooding in the cities and downstream water bodies and flushes numerous pollutants, which accumulate on urban surfaces as a result of different human activities. Stormwater runoff from urban areas therefore presents a quantitative and qualitative loading for natural water bodies including groundwater, which is the main drinking water source in many countries.

In general, effects of stormwater runoff to the environment can be divided into acute and chronic effects. Hydraulic effects, oxygen depletion, organic matter discharge, bacterial pollution and toxic pollutants cause acute effects, while nutrients, accumulation of toxic substances and suspended matter cause chronic effect to the environment. Different effects of stormwater runoff pollution are listed in Table 1.

**Table 1: Different effects of stormwater runoff pollution.**

| Effect | Description and comments |
|---|---|
| Physical changes of habitats | ▪ Flooding in urban and rural areas<br>▪ Erosion caused by peak flows in receiving water bodies<br>▪ Sediment deposition in receivers |
| Depletion of dissolved oxygen | ▪ Effects on the biological communities |
| Eutrophication | ▪ Effects of nutrients (N, P) and organic matter as substrates for excessive biological growth and activity |
| Toxic pollutants impact | ▪ Effects of heavy metals and organic micropollutants |
| Risk for public health | ▪ Direct impacts by pathogenic microorganisms and viruses<br>▪ Indirect impacts through contaminated animal food |
| Aesthetic deterioration of the environment and public perception | ▪ E.g. because of accumulation of large amounts of sediments and gross solids |

Stormwater is characterised by containing relatively low, but not insignificant pollutant concentrations. Even moderate storms can generate big volumes of runoff water and thus diluting pollutant concentration. This characteristic of stormwater creates difficulties in treatment of runoff water because rather low pollutant concentrations in large volumes of water have to be reduced to even lower levels. However, in the short period of first flush event high concentrations of pollutants can occur.

## 1.1 Legislation

In order to protect natural water bodies against pollution and physical damage caused by stormwater runoff, the water has to be retained and treated. Treating stormwaters meets the requirements of Water Framework Directive (2000/60/EC) (WFD) to reach the objective of good chemical and ecological conditions in all inland and costal water. The criteria should be fulfilled by the end of 2015. Even though all European countries have to fulfil the WFD goals, the individual countries have different legislation according to stormwater collection and treatment. As the research presented in PhD thesis was carried out by a Slovenian student in Denmark, the Slovenian and Danish legislation of relevance for stormwater management are mentioned below.

In Denmark there are no outflow standards for stormwater runoff; however the emission limit values for discharge to streams, lakes and the sea have to be respected (BEK no. 921 of 08/10/1996). A brief comparison of the legislation in the two countries reveals a completely different view of the stormwater. Slovenian legislation discusses stormwater similarly to industrial discharge while Danish legislation use limiting concentrations based on fresh water quality standards. Therefore the limiting values defined by Slovenian legislation, e.g. for heavy metals, are 3 to 70-times higher compared to Danish standards.

In Slovenia, stormwater runoff is regulated by two decrees. Decree on the emission of substances in the discharge of meteoric water from public roads (O.G. RS, 47/2005) is defining measures for emission reduction with the discharge of stormwater and limiting values for emissions from public roads into waters and sewerage system. For questions not defined by this decree, a Decree on the emission of substances and heat in the discharge of wastewater into waters and public sewage systems (O.G. 47/2005, 45/2007, 79/2009) is used.

## 1.2 Stormwater detention and treatment

For detention and treatment of stormwater runoff different engineering solutions can be applied, from »hard« ones such as underground concrete sewers and storage tanks to »soft« solutions that mimic natural water ecosystems. Specific pollutant characteristics in terms of their acute or accumulative effects may directly determine which engineering measures are feasible.

Due to the dispersed origin and the large volumes of stormwater that have to be treated, the strategy of nowadays stormwater treatment systems is towards a large number of low-cost decentralized facilities. Stormwater systems are often located in areas with recreational value, and must therefore be designed with urban landscape architecture in mind. Different wetland plant species create a pleasant appearance of a wet detention pond and play an active role in the removal of pollutants mainly by its presence and the physical effects this gives rise to (Brix, 1997).

A number of technologies for management of stormwater runoff are available and are described in Chapter 2. Among the different technologies, wet detention ponds are probably the most commonly used because of their simple construction and maintenance, efficient pollutant elimination and natural appearance. The main treatment process in wet detention ponds is sedimentation, enabling removal of suspended solids and associated pollutants. However, many pollutants appear in colloidal and dissolved form and their treatment in these systems is insufficient. Nowadays research is focused on the development of new and innovative technologies to upgrade the wet detention ponds in order to enhance the removal of these pollutants.

The research in the scope of this PhD thesis was carried out at seven wet stormwater detention ponds with an aim to investigate their efficiency in removal of suspended and soluble pollutants as well as to examine pollutant accumulation in the sediment and uptake by plants. The investigated systems comprised traditional wet detention ponds and wet detention ponds upgraded with additional technologies for improved removal of dissolved and colloidal pollutants enabling the comparison between different treatment approaches.

In the continuation, state of the art in the field of stormwater treatment is resumed, with the focus on wet detention ponds, their design and performance. The investigated systems are described in detail, including the additional technologies for removal of soluble and colloidal pollutants implemented in three of the tested systems. The results are divided according to the sampling and pathways of pollutants into water treatment performance, accumulation of pollutants in the sediment and plant uptake.

## 1.3 Objectives

The objective of this PhD research is to assess and compare the performance of traditional wet detention ponds and wet detention ponds with additional water quality improvement technologies for stromwater treatment. The target pollutants in this research are suspended solids, phosphorous, heavy metals and polycyclic aromatic hydrocarbons (PAHs).

The research also aims to estimate the pollutant pathways in the systems, namely accumulation of phosphorous, heavy metals and PAHs in the sediment and the relation to the plant uptake. The accumulation of PAHs in wet stormwater detention ponds has rarely been studied, thus this research contributes significantly to a better understanding of the accumulation of PAHs in the sediment and their distribution in the systems. Furthermore, the evaluation of the different additional treatment technologies implemented in upgraded wet detention ponds provides data that can be used to evaluate the appropriateness of these technologies in comparison with classical wet detention ponds. Besides this, the analysis of heavy metal uptake by plants assesses the potential risk that wet detention ponds could have for bioaccumulation of heavy metals in the food chain.

The thesis also contributes to the knowledge on heavy metal uptake by different aquatic plant species and outlines the species that are suitable for phytoremediation of stormwater runoff.

# 2 STORMWATER TREATMENT - STATE OF THE ART

Precipitation mainly appears like rain; however, in the temperate and cold climates it can also be snow, followed by runoff in snowmelt period. The main characteristic of stormwater runoff is its event-based nature. The rational formula describes the amount of runoff flow as the rainfall amount times catchment area and runoff coefficient. The runoff coefficient is a function of numerous factors, namely the infiltration through the surface, the season (presence of frost), vegetation uptake and evapotranspiration, evaporation from surfaces, micro-accumulations (puddles, pools) and similar (Kompare, 1991). Moreover, these factors are complex and depend on different characteristics and conditions, e.g. infiltration depends on surface porosity and moisture conditions, i.e. how wet the surface is prior the rainfall. Vegetation and small depressions can accumulate significant quantities of water, delaying its flow and allowing some rainwater to evaporate into the atmosphere (Lazaro, 1979); however, the accumulation of water in the surfaces varies with the season, temperature of air and surfaces, wind velocity etc. During summer, vegetation can store higher amounts of water due to bigger leaf surfaces (Kompare, 1991). Despite the complexity of runoff coefficient determination and thus the calculation of the amount of stormwater runoff, in engineering practice, runoff coefficient usually presents the percentage of impervious surfaces in total catchment area.

A detailed analysis of the input of the pollutants from stormwater runoff into environment is not possible due to the non-point source nature of the pollution. The pollutant loads and its impacts depend on the type of stormwater catchments, the dynamics of the activities in the area, precipitation pattern and inter-event dry periods when accumulation of pollutant in urban surfaces takes place. The precipitation pattern in terms of annual rainfall, seasonal distribution, rainfall event characteristic and temperature is determined mainly by climatic, orographic, and specific local conditions at a certain location. A time dependent variability of the pollutant loads is therefore expected within each single rain event and among the events. Therefore, also the standard deviation of pollutant concentrations that originate from a series of runoff events is typically of the same order of magnitude as their mean value. It is also known that snowmelt runoff contains significantly higher heavy metal concentrations compared to rain runoff.

The presence and amount of pollutants in the runoff depends on the land use in the catchment (residential area, roads, parking lots, industry etc.) resulting in a wide range of different pollutants found in stormwater runoff. Motor vehicle emissions, drips of crankcase oil, vehicle tire wear and asphalt road surfaces, roof toppings etc. are all diffuse sources of chemical contaminants in urban environments. The composition of a runoff from a highway is also affected by road surface type, traffic density and carriageway maintenance. During rainfall, the contaminants are washed from roofs, roads and other surfaces into the stormwater system and then discharged into surface waters. The pollutants in stormwater can be classified into suspended, colloidal and dissolved pollutants as well as into inorganic and organic matter. The most common pollutants are suspended solids, heavy metals, nutrients, organic micro-pollutants (polycyclic aromatic hydrocarbons, PAHs), and pathogenic microorganisms (Pitt et al. 1999, Bulc and Vrhovšek 2003). According to Pitt et al. (1999), pollutants from stormwater runoff can affect groundwater quality, especially in commercial and industrial areas where subsurface infiltration is used. Their literature review showed the presence of nutrients, certain pesticides and other organic compounds, pathogens, salts and metals in groundwater originating from urban runoff.

The most commonly heavy metals present in stormwater runoff are aluminium, cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc (Sansalone et al., 1997; Nolte and Associates. 1998). Among these, Zn, Cd, Cu, Ni, Pb, Cr are included in the list of stormwater priority pollutants established in the study of Eriksson et al. (2007). Platinum was also included in the list because of its use in vehicle exhaust catalysts. Heavy metals in stormwater runoff can be dissolved or bound to particulate matter. In road and highway runoff heavy metals (Cu, Pb, Zn) and PAHs are of particular concern due to their toxicity to aquatic organisms and persistence in the environment. Persistent pollutants in stormwater runoff are also inorganic particles that tend to accumulate in the ecosystem and affect aquatic organisms and their habitats. Diffuse sources of PAHs and heavy metals include traffic activities, tires, fluid leakage, pavement or asphalt degradation, domestic fire emissions, inappropriate dumping of waste oil and the corrosion of roofing materials.

A typical stormwater runoff pollutant concentrations and loadings according to land use (input coefficients) are presented in Table 2. The table summarises data from different studies reported by Kadlec and Wallace (2009), representing mainly American studies, by Storhaug (1996) representing results from Norway and by PH-Consult (1989), representing results from Denmark. Pollutants loads per unit area and unit time by different land use are presented in Table 3 (Horner et al., 1994; Burton and Pitt, 2002).

**Table 2: Concentrations of pollutants and mass loading rates in stormwater runoff (PH-Consult, 1989; Storhaug, 1996; Kadlec and Wallace, 2009).**

| | Urban | | Industrial | | Residential/Commercial | |
|---|---|---|---|---|---|---|
| Pollutant | Concentration (mg $L^{-1}$) | Load (kg $ha^{-1}$ $year^{-1}$) | Concentration (mg $L^{-1}$) | Load (kg $ha^{-1}$ $year^{-1}$) | Concentration (mg $L^{-1}$) | Load (kg $ha^{-1}$ $year^{-1}$) |
| $BOD_5$ | 5-56 | 90 | 9.6 | 34-98 | 3.6-20 | 31.59-135.2 |
| COD | 20-275 | - | - | - | - | - |
| TSS | 20-2890 | 360 | 93.9 | 672-954.5 | 18-140 | 84.28-797 |
| $NH_3$-N | 0.582 | - | - | - | - | - |
| TKN | 0.57-4.2 | - | - | - | - | - |
| TN | 0.7-20 | 11.2 | 1.79 | 7.8-18.06 | 1.1-2.8 | 9.144-32.18 |
| Ortho-P | 0.12 | - | 0.13 | 1.321 | 0.05-0.04 | 0.568-3.302 |
| TP | 0.02-4.3 | 3.4 | 0.31 | 2.2-3.151 | 0.14-0.51 | 1.412-4.85 |
| Cu | 0.005-0.40 | 0.049 | - | 0.077 | 0.003-0.031 | 0.045 |
| Pb | 0.001-1.20 | 0.174 | 0.202 | 0.269-2.053 | 0.001-0.214 | 0.157-2.431 |
| Zn | 0.01-2.9 | 0.630 | 0.122 | 0.98-1.240 | 0.005-0.17 | 0.218-1.88 |
| Cr | 0.001-0.17 | 0.28 | - | 0.044 | 0.001-0.012 | 0.026 |
| Cd | 0.0001-0.003 | 0.16 | - | 0.024 | 0.0001-0.0005 | 0.013 |
| Fe | 8.7 | - | - | - | - | - |
| Hg | 0.00005-0.0012 | 0.043 | - | 0.065 | - | 0.038 |
| Ni | 0.003-0.19 | 0.032 | - | 0.030 | 0.001-0.011 | 0.029 |
| PAH | 0.0001-0.0027 | - | - | - | 0.00001-0.0003 | - |
| Oil and grease | 2.6 | - | - | - | - | - |

Dealing with stormwater detention and treatment facilities, the types of sewer network and urban drainage system are of significant importance. Each drainage network has its specific characteristics. In general, there are two main types of systems with quite different performance of stormwater discharge, which directly affects the decision on appropriate engineering measures. The two systems are:

- Combined sewer network
- Separate sewer network

In a combined sewer network, the municipal wastewater and stormwater runoff from urban surfaces are transported in the same network, while in separate sewer networks the two types of flows are separated in two networks. Combined sewer networks have to be designed with a relatively high capacity in order to serve for runoff purposes. The pipe diameter is bigger and overflow structures and detention basins have to be constructed. During runoff events, the excess mixture of wastewater and runoff water is temporary stored in the system or discharged untreated in an adjacent watercourse through overflow structures.

**Table 3: Typical stormwater loadings according to land use. Input coefficients are given in kg ha$^{-1}$ year$^{-1}$ (Horner et al., 1994; Burton and Pitt, 2002).**

| Pollutant (kg ha$^{-1}$ year$^{-1}$) | Commercial | Residential High-density | Residential Medium-density | Residential Low-density | Industrial | Freeway | Parking |
|---|---|---|---|---|---|---|---|
| TSS | 1,100 | 450 | 270 | 10 | 550 | 1,000 | 450 |
| TP | 1.7 | 1.1 | 0.4 | 0.05 | 1.5 | 1.0 | 0.8 |
| TKN | 7.5 | 4.7 | 2.8 | 0.3 | 3.7 | 8.9 | 5.7 |
| BOD | 70 | 30 | 15 | 1 | - | - | 53 |
| COD | 470 | 190 | 60 | 10 | 230 | - | 300 |
| Pb | 3.0 | 0.9 | 0.06 | 0.01 | 0.2 | 5.0 | 0.9 |
| Zn | 2.3 | 0.8 | 0.1 | 0.05 | 0.4 | 2.3 | 0.9 |
| Cu | 0.4 | 0.03 | 0.03 | 0.01 | 0.1 | 0.4 | 0.07 |

In a separate sewer network, a stormwater sewer system is constructed only for collection and transport of runoff water from impervious and semi-impervious surfaces, and separate sanitary sewers are constructed for collection and transport of municipal wastewater to a downstream wastewater treatment plant. The stormwater sewers only operate during wet weather periods and discharge runoff water into receiving water bodies usually with no or little treatment. In urban areas, stormwater sewers are usually constructed as underground pipes, while in rural areas they can be in the form of swales and filter strips.

Separate sewer systems are commonly used in climatic conditions with heavy and frequent rainfall, i.e. in tropical and subtropical areas, while in temperate climates combined systems prevail. However, new constructions in temperate climates nowadays favour separate systems in order to reduce the impact of combined sewer overflow and to control the load on downstream wastewater treatment plants. Until recently, stormwater runoff was considered as relatively clean water, which can be directly discharged into receiving water bodies. However, it is nowadays known that stormwater runoff can contribute to an important part of pollution in a natural environment.

Dealing with stormwater demands careful consideration of its characteristics. The stormwater treatment facility must be flexible to manage high flow rates followed by dry periods, and high pollutant concentrations in the first flush followed by diluted concentrations in the main flow. Stormwater treatment system should enable water detention, minimize the hydraulic peaks and reduce the pollutant input in downstream facilities and/or receiving waters (Hvitved-Jacobsen et al., 1994; Deutsch, J.C., 2003).

## 2.1 Best management practice overview

In this chapter a short review on the current use of stormwater best management practice (BMP) in Europe is given. The recruitment of BMPs, their descriptions and efficiency have been summarized from the Review of the Use of Stormwater BMPs in Europe 2003 elaborated in the framework of DayWater Project (Deutsch, J.C., 2003) and from the online International Stormwater BMP database. Different types of stormwater BMP and their applicability vary greatly across Europe with northern and temperate countries having the broadest variability of different measures and their high usage. On the other hand, stormwater BMPs are less well developed in southern European countries.

A variety of methods is available in order to design appropriate structural stormwater BMP. They focus on parameters and criteria important for the treatment processes, such as particle settling characteristics, capture of the first flush, residence time, periodicity, infiltration capability and treatment capacity. The later can be directed to specific priority pollutants which are the most important to be treated at a given site. Besides this, two of the major concerns when deciding for appropriate BMP are also operation and maintenance, which should be cost-effective.

During the last decades, several technologies for management of stormwater runoff have evolved. Some of the most reliable technologies, achieving good and consistent pollutant removal, are infiltration systems, wet detention ponds and constructed wetlands. Of these solutions, especially wet detention ponds are capable of meeting the above stated requirements.

BMPs are divided in two main types:

- Structural BMPs are physical structures for runoff management.
- Non-structural BMPs include different management measures for runoff mitigation.

Each of the two main types includes numerous measures, which are linked to each other. Especially in the group of structural BMPs, the border between different measures is sometimes hard to define and thus different names for similar measures in the literature can be found.

### 2.1.1 Non Structural BMP

A reduction in stormwater pollution can be reached by pollutant source control in the catchment area such as use of unleaded fuel, replacement of copper roofs, use of more environmentally friendly materials in car production etc. A list of most commonly used non-structural BMPs is given below together with possible aspects, which may be introduced or modified in order to achieve enhanced stormwater management.

- Street cleaning is carried out on a regular basis in many European countries; however, the frequency can vary greatly. Along with street cleaning frequency and the type of cleaning equipment, also BMP in gully pot emptying has to be considered.

- For the control of weeds on paved and asphalt surfaces different herbicides are used to maintain safety, prevent structural damage and keep a desired aesthetic level. The key factors affecting the runoff removal of herbicides are the type of herbicide along with its persistence and adsorption to the surface, rainfall intensity and the time period between the application of herbicide and rain event. Reduction in herbicide usage should be considered as BMP.

- De-icing salts can cause high chloride concentrations in receiving waters and consequently in groundwater aquifers. De-icing salts can also affect the performance of stormwater treatment facility with toxic effects, pollutant release from bottom sediment via ion exchange and leaching of metals and oxygen deficiency, which are the result of chemical stratification and impeded vertical mixing. One of the mitigation measures in terms of de-icing salts is to catch the first flush with high salt concentrations and release it gradually with less salty flows thus diluting the salty runoff. Snowmelt contains higher pollutant concentrations compared to runoff water. According to snow management practice, it is therefore important if the snow is dumped on land or in a nearby water body.

- In order to reach a multipurpose use of a stormwater facility and good acceptance in local environment, effective consultations and discussions between constructors, landowners, local community, regional authorities etc. is of crucial importance. Between stormwater treatment facilities, especially wet detention ponds and constructed wetlands have a great educational potential, which is already exploited in some West and North European countries. Natural stormwater systems are usually well accepted by the public. Often they are used as recreational areas and bird watching sites and are valued as flood storage facilities.

- Balance between the impermeable and permeable surfaces during urban planning and development should be restored. Measures to control the impervious area development differ in low and high-density urban areas.

- Besides stated non structural BMPs, also other measures can be taken, e.g. optimization of routine management practices like grass cutting and sediment removal, implementation of flood prevention techniques, environmentally friendly painting and use of metals in constructions, litter and debris control, etc.

### 2.1.2 Structural BMP

The main characteristics of most common structural stormwater BMPs are described here. Some of the facilities are designed only for water retention and hydraulic loads mitigation, while others enable different treatment processes to take place, e.g. accumulation and transformation of pollutants.

The tendency of stormwater treatment technologies is towards smaller, simple, robust and semi-natural systems, which can be applied at a local scale. The systems should be capable of mitigating periodical stormwater events and rather variable pollutant concentrations along time. Extended detention ponds, wet detention ponds/constructed wetlands, infiltration trenches and ponds, sand filters, porous pavement etc. are used effectively across Europe and US and are described below.

Filter drains or sand filters are areas with gravel, where rainwater drains through and is collected in a perforated pipe. The filter is usually constructed along the highways. The bottom and walls of the filter can be lined with a geotextile and the surface can be exposed or covered with a layer of soil. They are designed to remove particulate matter and associated pollutants from stormwater. On the filter medium biofilm can develop, which contributes to the removal of pollutants. With the selection of filter media with certain absorption characteristics efficiency in removal of specific pollutants can be enhanced (e.g. carbonate sands for removal of phosphorous).

Porous asphalt and paving are water permeable surfaces with high void content. An adjacent reservoir provides temporary water storage and mitigates runoff. Porous paving collects water as it falls. It can improve water quality to a certain extend and supports road traffic.

Sedimentation tanks, silt traps, oil and grit separators etc. are technical BMPs, usually used as pre-treatment structures. They are constructed as concrete structures with appropriate water depth to provide particle settling in the quiescent periods and can be connected to other stormwater facilities.

Swales are vegetated broad and shallow channels mainly used for transportation of stormwater; however, some water quality improvement can also occur through settling and infiltration into the soil. A swale can be used for infiltration in case that there is a sufficient distance between the swale and groundwater table. The infiltration capacity of a grass vegetated swale depends on groundwater level, soil porosity, sediment load and vegetation density.

Filter strips are grassed or vegetated strips of land where stormwater flows across. They are similar to swales, but have flatter banks.

Soakaways are underground chambers or rock-filled volumes where stormwater soaks into and slowly infiltrates into the surrounding soil. They provide little or no protection to groundwater especially from soluble pollutants like heavy metals, aromatic hydrocarbons, herbicides, etc.

Infiltration trenches are long and thin soakaways filled with stones or rubbles. The infiltration surface area is enlarged thus enabling better treatment performance compared to soakaways. Nowadays instead of stones for filling the underground basin, plastic boxes with high void volumes are used. From the infiltration trench, water can soak into the surrounding soil or can be collected via perforated pipes and routed to the recipient water body.

Infiltration ponds/basins are designed to retain stormwater runoff at the surface and allow it to slowly soak to the underground through the base of the pond. At the basin bottom, a special drainage system can be constructed containing gravel or sand filter beds. Infiltration pond can also include pretreatment structures like gravel chamber or oil remover. These ponds are usually vegetated with native plants (mainly grasses) which are kept at approximately 15 cm height by regular harvesting. Usually an efficient removal of suspended solids appears.

Wet detention ponds or retention ponds have a permanent water volume and temporary storage volume above it. They are designed like small and shallow natural lakes with sufficient water residence time to enable numerous treatment processes to occur. With these processes particulate and to some extend soluble pollutants are removed. Wet detention ponds can also be constructed below groundwater level, which helps to maintain a permanent water volume also in dry weather conditions. The pollutant targeted for reduction should direct the design of the pond. Shallow parts of a wet detention pond can be planted with wetland vegetation. Wet detention ponds can also be reffered as constructed wetlands. The water depth and performance vary dependent on the rainfall and the time of the year. The structure of a wetland is highly variable, with open water areas, shallow water parts (0.1-0.3 m), densely vegetated parts, small islands, etc. The high structural variability creates a high variability in type and intensity of the treatment processes occurring in the system. Natural wetlands can also be used for stormwater treatment, however the effect of the pollutants might have undesirable consequences for the natural environment (i.e. accumulation of heavy metals in the sediment) (Sriyaraj and Shutes, 2001). As the most common form of stormwater treatment, wet detention ponds are described in more detail in the next chapter.

Detention basins or extended detention basins are dry most of the time but provide stormwater storage during rainfall to attenuate peak runoff flows for the protection of downstream facilities and receiving water bodies. The difference between detention basin and extended detention basin is that extended detention basin is able to store water for longer periods compared to detention basins (up to 24 hours). The water from the pond is discharged through the outlet structure; however, a part of water can undergo evapotranspiration and infiltration to the groundwater. Infiltration to the groundwater can be prevented by lining the pond. Due to not having permanent water storage, these ponds are also named dry ponds. In dry ponds, the sedimentation of suspended particles takes place. Dry ponds can be connected to wet detention ponds into a combined stormwater system.

Lagoons are ponds designed for sedimentation of suspended solids. They are constructed by excavating of natural earth basins and can be lined with impermeable layers to protect the groundwater from infiltration. They are usually vegetated and separated from the surroundings by a fence.

Combined systems are combinations of two or more previously described systems. They can also include conventional drainage system structures as one of the parts.

A brief overview on the treatment performance of different BMPs is given in Table 4. The range in removal efficiency is wide and depends on pollutant load at the inflow. A facility with low load can have low removal efficiency, even if the outflow concentration is lower than in facilities with high loads.

**Table 4: Treatment performance of different stormwater BMP (Deutsch, 2003).**

| | % removal efficiency | | | | | |
|---|---|---|---|---|---|---|
| | TSS | Tot N | Bacteria | Hydrocarbons | Metals (total) | Metals (dissolved) |
| Filter | 60-90 | 20-30 | 20-40 | 70-90 | 70-90 | 10-20 |
| Infiltration trench/basin | 60-90 | 20-50 | 70-80 | 70-90 | 70-90 | 20-35 |
| Swales | 10-40 | 10-35 | 30-60 | 60-75 | 70-90 | 15-25 |
| Lagoon | 50-85 | 10-20 | 45-80 | 60-90 | 60-90 | 20-30 |
| Dry detention basin | 60-80 | 20-40 | 20-40 | - | 40-55 | 0-15 |
| Extended detention basin | 30-60 | 5-20 | 10-35 | 30-50 | 20-50 | 0-5 |
| 6-10 hour detention | 40-80 | 20-40 | 40-50 | 30-60 | 30-60 | 5-10 |
| 16-24 hour detention | 50-90 | 20-40 | 60-75 | 50-75 | 45-85 | 10-25 |
| Retention basin | 80-90 | 20-40 | 40-60 | 30-40 | 35-50 | 10-20 |
| Wetland | 70-95 | 30-50 | 75-95 | 50-85 | 40-75 | 15-40 |

## 2.2 Wet detention ponds for stormwater treatment

### 2.2.1 General characteristics of wet detention ponds

Wet detention ponds or wet ponds are among the most reliable and commonly established system used to mitigate the impact of stormwater runoff. They have a permanent water volume and a temporary storage volume above it, as shown in Figure 1. Continuous outflow from a wet pond occurs as long as water level is above the permanent water level. Different plant species (aquatic macrophytes) can appear in wet detention ponds (usually colonized by natural way): at the shallower marginal areas emergent and in deeper parts floating and submerged species. Wet detention ponds enable water retention and thus protect the recipient water bodies against erosion and quantity loads. Due to the longer detention time in the basin, treatment processes like biological degradation of organic matter, plant uptake and accumulation in the sediment occur (Hvitved-Jacobsen at al., 1994). Wet detention ponds, by their appearance and the processes that take place in them, mimic natural wetlands or small lakes. According to Munger et al. (1995), such a high diverse biological system has a high buffering capacity that can face hydraulic and pollutant fluctuations in stormwater runoff.

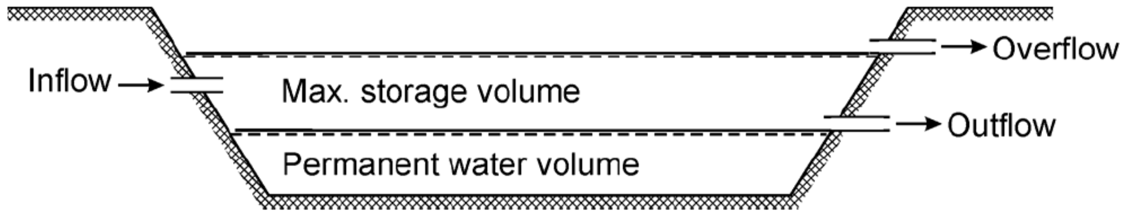


**Figure 1: A scheme of a typical wet detention pond with permanent water volume and storage volume above it. The positions of inflow, outflow and overflow pipes are shown (Hvitved-Jacobsen et al., 1994).**

### 2.2.2 Design of wet detention ponds

There are several ways of design and construction of wet detention ponds according to the hydrology of the site, targeted pollutants and desired treatment efficiency. It is imperative for the treatment performance that the entire pond volume and bottom area are utilized for pollutant removal. Two main types of wet detention ponds can be constructed, namely with horizontal and vertical water flow (Figure 2). Due to clogging problems, the type with horizontal flow is much more common.

The design of the stormwater treatment pond is resumed from LIFE Treasure, Task B, 3rd delivery: General design criteria and guidelines complied into a design manual.

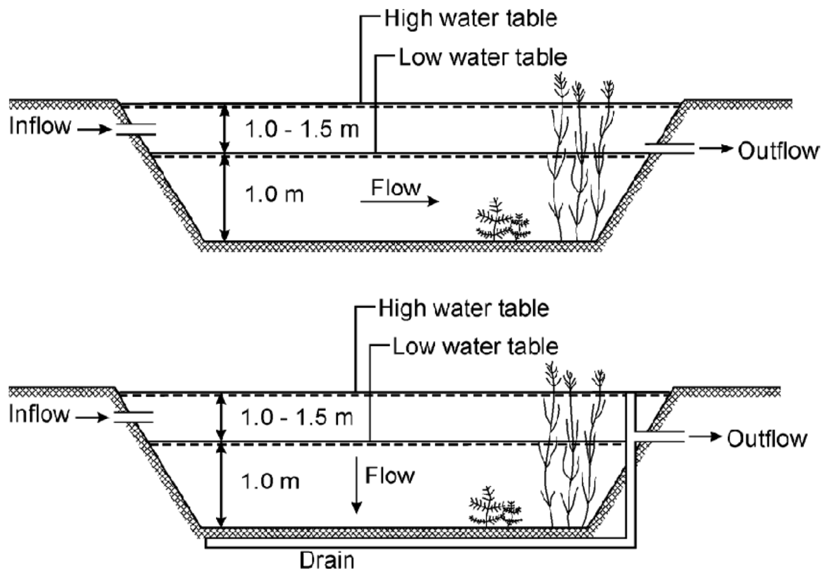


**Figure 2: Two main types of wet detention ponds, i.e. with horizontal (top) and vertical water flow (bottom) (Hvitved-Jacobsen et al., 1994).**

When designing a wet detention pond, the first step is to determine the necessary volume of the pond. Volume determination is based on empirical knowledge and can be done in different ways, briefly described below.

1. The simplest design principle for a wet detention pond is based on recommended pond surface area per impervious unit area of the contributing catchment. The specific pond area is given in $m^2$ of a pond surface per ha of impervious area in the catchment. The depth of the ponds is presumed to be constant, between 1 and 1.5 m in order to enable light penetration into the water body. Due to different hydraulic loads caused by different rainfall pattern, the ratio between the pond surface and impervious catchment area will vary from one region to another.

2. The design can also be based on rainfall characteristics and pollutant removal rates that were observed in wet detention ponds from different sites in the region. For each pond a dimensionless pond water volume, n, is calculated as a ratio between the wet detention pond volume per unit area of impervious catchment, V, ($m^3\ ha^{-1}$) and volume of water of a mean storm event per unit area, v, ($m^3\ ha^{-1}$). Based on information from different studies, an empirical relationship between dimensionless pond volume and

pollutant removal efficiency, $\gamma$, (%) is established ($\gamma$ = f(n)). The starting-point for determination of the volume of the new wet detention pond is the selected removal efficiency for target pollutant. Basing on selected removal efficiency a corresponding dimensionless pond water volume (n = V/v) is found and the pond water volume, V, can be calculated.

3. Design based on a minimum duration of the inter-event dry period is based on observation that higher removal efficiencies in wet detention ponds occur at higher residence times and at minimum mixing of the water phase. Higher residence time enables pollutant uptake by plants and microbial transformations, which are time-consuming processes, while minimum mixing of water phase enhances sedimentation. The combination of quiescent conditions and sufficient retention time can be expressed by the length of dry period between two rainfall events. The length of the inter-event dry period is compared to rainfall depth at certain return periods. The pond volume can be determined from a rainfall depth at an acceptable frequency of overflows and a length of dry period that enables quiescent water phase in the pond.

4. Wet pond design can also be based on model simulation for pollutant removal. Pollutant removal can be described as a first order kinetics in plug flow reactor as described in Equation 1. Theoretical residence time $\theta$ is defined as ratio between the distance from the inlet and average flow velocity through plug flow reactor.

$$C = C_0 \exp(-k\theta) = C_0 \cdot e^{-k\theta}$$ **Equation 1**

C = pollutant concentration at time t (g $m^{-3}$)
$C_0$ = pollutant concentration of the incoming stormwater (g $m^{-3}$)
$\theta$ = theoretical residence time in the pond (d)
k = $1^{st}$ order removal rate of the pollutant ($d^{-1}$)

This method requires a number of input data like starting value for the pond volume determined by using one of the previously described methods, but it enables the analyses of different scenarios. Besides the input of pollutants, also the hydraulic load should be included, thus representing the runoff model of a catchment.

When using methods from 1 to 3 it is important to combine both pollutant removal and hydraulic performance, while in method 4, which includes a simulation model, these two factors are already included. Design methods 1 to 3 result in a defined pond volume, i.e. the runoff volume exposed to the treatment. It is of crucial importance how this volume is interpreted – as a storage volume, as a permanent volume or the sum of both. The results from existing ponds show that the determined volume from methods 1 to 3 actually represents:

a) the storage volume for the ponds where there are specific requirements on treatment and hydraulic performance or
b) the storage volume plus 0.4 to 0.6 times the permanent volume for the ponds with no limitations for the outflow.

When designing a wet detention pond also the length to width ratio has to be appropriate to enable plug flow. The recommended length to width ratio of wet detention ponds should be above 3:1, however Vollertsen et al. (2009) reported that a wet pond with length to width ratio of 4.5:1 showed a flow pattern closer to a completely mixed reactor than to plug flow. The authors suggest that the important design parameter is more the avoidance of shortcuts between inlet and outlet than length to width ratio. Besides length to width ratio diverse nondimensional parameters should be considered, such as Reynolds and Froude number. The Reynolds number defines the flow regime as laminar or turbulent flow. Laminar flow occurs at low Reynold numbers, while turbulent flow occurs at high Reynold numbers. Turbulent flow is characterized by domination of internal forces above viscous ones in the fluid, which reduces the sedimentation velocity. However, in suspensions with flocks, turbulent flow causes more contacts between the flocks, which can have a positive effect on sedimentation. The Froude number is the ratio of forces of flow persistency to gravitational forces and determines the stability of the flow. If Froude number is too low, complete mix may occur with faint forces from the outside (e.g. light wind breeze) even though the pond has a high length to width ratio. The ponds that enable good sedimentation have Reynolds number < 2,000 and Froude number > $10^{-5}$.

Design guidelines often assume that the detention time of run-off water in a wet pond is constant, e.g. the mean detention time can be determined as equivalent to the difference between centroids of the inflow and outflow hydrographs. However, this does not represent the average detention time of the pollutant, which is especially important in the ponds with a permanent water volume. In such ponds water quality of the first stage of the outflow hydrograph represents the quality of the permanent water and is unrelated to the quality of the inflow water. Under idealized plug-flow conditions, water entering the wet detention pond will exit the system only when the new inflow water will replace the entire permanent water volume (Somes et al. 2000). Besides this, different flow velocities, mixing and wetland shape that can result in different flow paths through the pond cause a distribution of different residence times along the pond. Residence time distribution (RTD) is therefore an important parameter describing hydraulics of the wetland. Holland et al. (2004) found that the RTD is affected by changes in water depth rather than by changes in flow rate. The study also showed that higher water levels result in lower hydraulic efficiency.

Besides the determination of a pond volume and hydraulic performance, also some other design criteria should be considered. One of the main requirements for efficient treatment performance is to maintain aerobic conditions in the pond. Oxygen concentrations should be around or higher than 4 mg $L^{-1}$ but not lower than 2 mg $L^{-1}$ in order to assure a sufficient high redox potential at the sediment surface to retain pollutants like phosphorous and heavy metals. If the redox potential is too low these pollutants start to be released from the sediment and pollute the water column. The mass transfer between air and water, photosynthetic activity of phytoplankton and respiration, mainly affect the oxygen concentration in the pond. The importance of algal photosynthetic activity on dissolved oxygen concentration and pH in a stormwater wet pond was reported e.g. by Vollertsen et al. (2009).

Stormwater wet detention ponds can also represent a potential recreational area and thus have to be designed in an attractive way, i.e. the shape of the pond, planting, walking paths, bird observation towers etc. which is especially valuable in highly populated areas. Numerous wetlands and natural ponds were dried up in the past; therefore, nowadays artificial water bodies like stormwaters wet ponds can have an important contribution to the local biodiversity. Le Viol et al. (2009) in their study compared diversity of macroinvertebrates in stormwater wet ponds with natural wet ponds in a wider surrounding and found that the community in stormwater ponds was at least as rich and diverse as in natural environments. The authors therefore suggest designing the wet detention ponds also as refuges for aquatic biota and landscape connectivity between water ecosystems. Nevertheless, it should not be dismissed that in a stormwater wet pond, bioaccumulation of pollutants in the food web can appear and that not all biota is tolerant to the pollutant levels in stormwater.

As already mentioned, stormwater BMPs should be applied on a local scale, to mitigate runoff at its origin. Besides the local approach, Cohen and Brown (2007) pointed out the importance of organization of stormwater facilities on a larger scale. By a model approach, they found that using hierarchical networks for stormwater collection and treatment in a whole watershed could greatly enhance overall performance. The hierarchical network consists of small, medium and large size of wetlands to retain and treat stormwater. The model also showed that different wetland sizes have different treatment roles, namely the larger wetlands retained the biggest water volumes, middle-sized wetlands were the most efficient in phosphorous removal and the smallest wetlands were the most efficient in sediment trapping.

### 2.2.3 Treatment processes in wet detention ponds

The removal of stormwater pollutants in wet detention ponds depends on residence time (Walker, 1998). The later is variable and depends on the meteorological conditions, the hydrological characteristics of the catchments and the hydraulic characteristics of outlet structure, the permanent water pool and the temporary storage volume (Somes et al., 2000). The treatment processes in wet detention ponds are similar to those occurring in natural small, shallow lakes: e.g. pollutant accumulation in the pond sediments via sedimentation, adsorption to colloidal and particulate matter, transformations of biodegradable substances by microorganisms and uptake of pollutants by the vegetation. These treatment processes can be grouped in physical, chemical and biological processes.

#### 2.2.3.1 Physical processes

Because particulate matter in runoff represents the major pollutant and because other pollutants are largely associated with the particles, the most important physical processes in stormwater treatment in wet detention ponds are sedimentation and filtration. Particles with associated pollutants are therefore settled down from a water phase and accumulated in the bottom sediment or are retained in the filter. Reduced flow velocities in a pond enhance sedimentation (Somes et al. 2000).

Different studies, e.g. Walker and Hurl (2002) and Hares and Ward (2004) reported that sedimentation enables the removal of suspended solids and associated pollutants from the water column. The solids accumulate in the pond's sediment and are to some extent subdued to biological transformations. Due to the fact that particulate matter in stormwater occurs in lower concentrations compared to wastewater, the sedimentation occurs only by gravity with no particle association and can thus be described as laminary sedimentation.

In the study of the first flush phenomenon, Stenstrom and Kayhanian (2005) reported that the number and size of particles in a stormwater runoff decrease, with the progression of the storm, i.e. higher concentrations of particles and larger particles are washed out at the beginning of the runoff. However, the wash out of different sized particles depends on the intensity of the storm event and on deposits build up in drainage channels. Namely the greater the rain intensity the greater the erosion and transportation capacity and thus larger particles may be transported. Besides this, the dynamics of dry weather periods and intensity of previous precipitation affect the build up in drainage channels. The decrease in the number and size of particles occurs also in the pond itself. The sediment load is decreasing through the pond and material is becoming finer towards the outlet (Walker and Hurl, 2002). The number of particles in the runoff affects the amount of sorbed pollutants, which is important for elimination of pollutants from stormwater runoff (Stenstrom and Kayhanian, 2005).

Like solid and colloidal material in the inflow water deposits in the wet detention pond, similarly a layer of organic matter develops on the bottom of the pond. Organic matter accumulation comes from external sources such as organic compounds in stormwater and in situ sources such as plants and microorganism residues.

Sediment accretion at the bottom of wet ponds might vary greatly according to inflow and catchment characteristics, however also redox potential has an indirect impact on accretion of particles and thus on deposition rate. In the study by Yousef et al. (1990), which included various stormwater detention ponds, shallow and well-oxygenated ponds showed less than centimetre of sediment deposit in a year, while deeper ponds with anaerobic conditions at the bottom showed sediment accretion of 2-4 cm per year. In well-oxygenated ponds, the kinetic of biodegradation of organic matter is faster than in the anaerobic conditions, thus the layer in oxygenated ponds is already mineralized, while in anaerobic sediments decomposition of organic matter takes longer time, thus more sediment is accumulated.

Sediment accumulation in wet detention ponds was investigated also in the study by Yousef et al. (1994) in which they measured sediment depth in nine stormwater wet ponds in Florida. Based on the measured accumulation rates they estimated that excavation and removal of the sediments from wet ponds would be needed every 25 years of the operational period.

Wetland vegetation can enhance sedimentation in the wet detention pond. Hares and Ward (2004) studied the removal of heavy metals in a stormwater wet pond and pointed out that the presence of a well established reed bed with a high biomass can act to further increase residence time of stormwater in the pond and thus increase time for sedimentation, filtration and bioaccumulation processes. A low plant biomass in the pond allows the hydraulic flow to be maintained thus reducing the residence time of stormwater within the pond, which may limit the filtration and sedimentation processes.

Other processes can occur in wet detention ponds. Photodegradation is usually not referred to as a physical process, but sunlight can eliminate microorganisms, including pathogenic bacteria and viruses via ultraviolet radiation. The later also causes degradation or oxidation of some chemicals.

#### 2.2.3.2 Chemical processes

Sorption to different media is an important removal process especially for phosphorous, ammonia, hydrophobic organic chemicals, etc. Sorption of specific pollutants to filter media is described in following chapters. The process is affected by sorption material, sorption sites and the concentration of pollutants in the water, i.e. in the pore water, which can have a very different concentration than bulk water. Sorption sites are partially renewable due to accumulation of new sediments, but on the other hand, sorption can be reversible or irreversible due to mineralization of sorbed materials or formation of very strong chemical bounds.

The reaction of sorption can take two forms, namely adsorption and absorption, where adsorption is an adhesion of molecules to a surface and absorption is an incorporation of a substance into another. In stormwater treatment in wet ponds, the most important chemical process is adsorption. Adsorption between particulate, colloidal and soluble matter can be of different stability and affected by physical and chemical conditions in the surroundings (e.g. Kurniawan et al., 2006; Somerville and Norrström, 2009).

#### 2.2.3.3 Biological processes

Biological processes usually contribute little to the treatment processes but are of key importance in transformation of pollutants. Biological processes include microbiological transformation of pollutants, degradation of organic matter by decomposing macroinvertebrates and plant uptake. Biological processes become quantitatively more important in wet detention ponds with longer retention times.

Bacteria and other microorganisms are usually found in low numbers in the free water but are rather attached to the solid surfaces such as sediment-surface area, surfaces of plants, surfaces of the litter and dead standing material. The biofilm area per unit wetland area is small if there is no vegetation, higher in the presence of emergent vegetation and the highest if also the litter is considered as biofilm surface (Kadlec and Wallace, 2009). The first step towards microbial transformation or removal of a pollutant is a transfer of a pollutant to reach the direct contact with the biofilm. The microbes enable decomposition of organic matter as well as nutrient transformation (Kadlec and Wallace, 2009). It is also important to point out that microbial transformations are affected by temperature.

In wetlands, microbial nutrient transformations are especially important for nitrogen elimination. It is well known that under aerobic conditions ammonium is oxidized to nitrite and nitrate (nitrification) and under anoxic conditions nitrate is reduced to gaseous nitrogen (denitrification) and thus eliminated from the system (Vymazal, 2007). Reinhardt et al. (2006) report that in a constructed wetland denitrification contributes more than 90% to the nitrogen removal, while only 6% of nitrogen was removed via accumulation in the sediment.

An important biological process in wet detention ponds is also plant uptake. Wetland plants mainly take up nutrients needed for their metabolism. However, they take up also trace elements and store them in roots or release them via volatilization. While emergent plants take up nutrients and trace elements through their roots, submerged plants take up these elements through all plant surfaces and store them in stems and leaves, resulting in higher accumulation of heavy metals compared to emergent plants (Fritioff and Greger, 2003). It is generally accepted that performance of water treatment in a wetland is higher when plants are present (Kadlec and Wallace, 2009).

Different plant species can grow in wet ponds by natural way or by planting. The pollutant uptake and storage vary by plant species and pollutant type. The criteria for selecting of species for pollutant removal are biomass accumulation rate, surface area of the root system and persistent subsurface and aboveground biomass.

Because of the high variety of different pollutants in stormwater runoff and time variability, physical, chemical and biological processes have to be combined in order to reach desired stormwater runoff mitigation.

### 2.2.4 Pollutants and treatment efficiency of wet detention ponds

#### 2.2.4.1 Suspended solids

Since the main removal mechanism in wet detention ponds is sedimentation, the wet detention ponds generally have high efficiency in particulate matter removal (Terzakis et al., 2008; Hossain et al., 2005). Terzakis et al. (2008) compared the treatment efficiency of free-water surface, and sub-surface flow wetlands and reported a 90-91% elimination of suspended solids in subsurface and 83-88% in a free-water wetland. In accordance with this, Bratieres et al. (2008) reported a high efficiency (consistently over 95%) in suspended solids removal in a stormwater biofilter, and Hossain et al. (2005) reported an average removal of TSS in a wet detention pond to be 84%. Larger particles in stormwater runoff settle due to gravitational forces, while small particles and in particular dissolved matter might firstly be subdued to coagulation and flocculation between them before removal (Sansalone and Kim, 2008).

Organic matter is subdued to microbial and macroinvertebrate decomposition and final transformation to inorganic matter in the sediment, where it is stored.

#### 2.2.4.2 Nitrogen and phosphorous

Numerous studies report on the efficiency of wetlands in removal of different pollutants from stormwater. Kohler et al. (2004) investigated the removal of different pollutants in a wetland system created on a golf course. The wetlands were rich in macrophytes and showed efficient removal of $NO_3$, $NO_2$, $NH_4$, P, COD, TOC, Ca, Cl, Mg, Mn and Na. Efficient removal of nitrogen and phosphorous was also reported by other studies, e.g. Hvitved-Jacobsen et al. (1984) who reported a 99% accumulation of input P in the sediment and elimination of 85-90% N from the system. A crucial condition for trapping P in the sediment is a consistent and high redox potential in the surface sediment layer and for N elimination an exchange of oxic and anoxic areas. In the study of Hvitved-Jacobsen et al. (1984), the aerobic (oxidized) layer of the sediment was approximately 0.5 cm thick, followed by an anoxic layer suitable for denitrification; 0.5 cm oxic layer was apparently enough to enable P trapping and nitrification. However, differences in treatment efficiency may occur between dry weather and stormwater runoff (Scholes et al., 1999).

Carleton et al. (2001) examined the studies of 49 wetland systems designed to treat stormwater runoff. Their results showed that the removal rate constants for TP, $NH_3$ and $NO_3$ were consistent with values reported in the literature in wetlands treating wastewater. However, for $NO_3$ the calculated values were a bit lower compared to wastewater treatment, which may be a consequence of higher redox potentials in stormwater wetlands suppressing denitrification. The analysis also showed that the current design of wet detention ponds might not provide sufficient treatment for some pollutants, as removals of TP and TN were only 30 and 10%, respectively, which is contradictory to the results from Hvitved-Jacobsen (1984) mentioned in the previous paragraph.

Numerous processes affect the nitrogen elimination and retention in wet ponds, i.e. ammonia volatilisation, nitrification, denitrification, nitrogen fixation, plant and microbial uptake, mineralization (ammonification), reduction of nitrate to ammonia, anaerobic ammonia oxidation (ANAMOX), fragmentation, sorption, desorption, burial and leaching. Only certain processes enable nitrogen elimination, while others just transform nitrogen from one form to another (Vymazal, 2007). According to Vymazal (2007), constructed wetlands with vertical flow are efficient in removal of ammonia nitrogen but have limited conditions for denitrification, while constructed wetlands with horizontal water flow enable good conditions for denitrification but have limited conditions for nitrification.

Besides oxygen conditions plants can also be an important factor in nitrogen elimination. Scholz and Hedmark (2009) investigated the removal of nitrogen from stormwater in different types of planted and unplanted vertical flow constructed wetlands. Their results showed that the total inorganic nitrogen reduction was higher in planted filters compared to unplanted, and that the main mechanism of nitrogen removal was plant uptake. For both planted and unplanted filters, denitrification was low, possibly due to relatively high dissolved oxygen concentrations. However, denitrification is usually the main mechanism for nitrate removal in free water surface flow constructed wetlands (Reilly et al., 2000; Reinhardt et al., 2006). Nutrients that were taken up by plants can be removed from the system by harvesting and removing the plant biomass. This can play an important role in nutrient removal especially in systems that receive low nutrient loads (Langergraber, 2005).

Phosphorous in a wetland system is mainly accumulated in the sediment and/or in the plant biomass. Elimination of P from a wetland treatment system is possible only by harvesting of the plant biomass and removing the saturated sediment. Vaze et al. (2004) report for phosphorous in stormwater runoff from Melbourne, Australia, that around 25% of the total phosphorous load is "dissolved" (particle sizes below 0.45 μm), whereas the majority of total phosphorous is associated to particle sizes in the range from 0.01-0.3 mm. These results indicate that sedimentation cannot reduce total phosphorous concentration with more than around 75%; a conclusion, which is in the same range as generally observed treatment efficiencies for wet detention ponds. However, the treatment performance of a wet pond can be increased with application of additional sorption filters or chemical precipitation (described later).

P can be released from the sediments during anoxic conditions, however also microbial activity can cause its release. In neutral and acid conditions, microorganisms can use $Fe^{3+}$ as electron acceptor thus releasing bound P. In basic conditions, microorganisms can dissolve insoluble P by increasing the ion exchange of $OH^-$ and $PO_4^{3-}$, which arise from Fe-P or Al-P (Huang et al., 2008).

#### 2.2.4.3 Polycyclic aromatic hydrocarbons

Among the most common pollutants in the stormwater are also polycyclic aromatic hydrocarbons (PAHs). PAHs consist of two or more aromatic rings and are represented by around 100 different chemicals that usually arise during incomplete organic matter combustion (fossil fuels, wood, cigarettes etc.). Most PAHs have no known use but they appear in some products like coal tar, creosote, roofing tar, crude oil, asphalt, some medicines or dyes and plastics. Naphthalene is the most well known PAH. It is used for making dyes, in explosives, plastics, lubricants, moth repellents, etc.

There are two sources of PAHs (Brown and Peake, 2006):

- Pyrogenic PAHs are found in combustion-derived particles. Low molecular weight (LMW) 2-3 ring PAHs enriched in high molecular weight (HMW) 4-6 ring PAHs leading to LMW/HMW ratio < 1.
- Petrogenic PAHs are found in fuel oil or light refined petroleum products. LMW are dominated and thus LMW/HMW ratio is > 1.

Asphalt contains significant amounts of PAHs and has a mix of petrogenic and pyrogenic character (external source). Although considered pyrogenic by some, pyrene is also somewhat petrogenic because it is found in many petroleum products.

Hwang and Foster (2006) found that in stormwater runoff PAHs originating from combustion prevailed. Combustion specific PAHs are fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, indeno(c,d)pyrene and benzo(g,h,i)perylene. The authors report a ratio between combustion and ∑PAHs of 0.82 in the water during a stormwater flow and 0.66 in the water during a base flow.

PAHs are potentially highly carcinogenic and mutagenic and thus 16 of the most common PAHs are listed as priority pollutants by US-EPA, namely:

1. Naphthalene (NAP) is a two ring, low molecular weight and semi-volatile PAH. It is a very common PAH which also appears naturally produced by some plants, animals and fungi.
2. Acenaphthylene (ACY) is a two ring, low molecular weight PAH. It is a component of crude oil, coal tar and a product of combustion. It may be produced and released to the environment during natural fires.
3. Acenaphthene (ACE) is a two ring, low molecular weight PAH. It is a constituent of coal tar and is used in preparation of dyes, pesticides and pharmaceuticals.
4. Fluorene (FL) is a low molecular weight three ring PAH. It is manufactured artificially, although it occurs in the higher boiling fractions of coal tar. Fluorene is used to make dyes, plastics, and pesticides. It can be found in corn silk and engine exhaust gas.
5. Phenanthrene (PHEN) is a low molecular weight three ring PAH. It provides the framework for the steroids. In its pure form, it is found in cigarette smoke. Phenanthrene is used for manufacturing phenanthrenequinone (intermediate for pesticides) and manufacturing diphenic acid (intermediate for resins).
6. Anthracene (ANT) is a low molecular weight three ring PAH. It is derived from coal tar. Anthracene is used in the artificial production of the red dye alizarin. It is also used in wood preservatives, insecticides, and coating materials.
7. Fluoranthene (FLU) is a high molecular weight four ring PAH. It is largely associated with particulate matter. FLU is used in manufacturing fluorescent and vat dyes, pharmaceuticals and agrochemicals. Its presence is an indicator of lower temperature

combustion. It is a persistent PAH and should biodegrade in a few years in the presence of acclimated microorganisms.

8. Pyrene (PYR) is a high molecular weight four ring PAH. It is used in manufacturing perinon pigments.
9. Benzo[a]anthracene (BaA) is a high molecular weight four ring PAH.
10. Chrysene (CHR) is a five ring high molecular weight PAH. It is formed during burning of coal, crude oil and plant material. Chrysene is used in manufacture of some dyes.
11. Benzo[b]fluoranthene (BbF) is a five ring high molecular weight PAH. It is a site product of incomplete combustion of organic matters, especially fossil fuels and tobacco. To my knowledge there is no commercial production or known use. It has been detected in mainstream cigarette smoke, urban air, gasoline engine exhaust, emissions from burning coal and from oil-fired heating, broiled and smoked food, oils and margarine (IARC, 1973).
12. Benzo[k]fluoranthene (BkF) is a five ring high molecular weight PAH.
13. Benzo[a]pyrene (BaP) is a five ring high molecular weight PAH. Besides incomplete combustion of organic matter, it is also a component of pitch.
14. Dibenzo[a,h]anthracene (DBA) is a five ring high molecular weight PAH.
15. Benzo[g,h,i]perylene (BGP) is a six ring high molecular weight PAH. It is used to make dyes, plastics, pesticides, explosives and drugs. It has also been used to make bile acids, cholesterol and steroids.
16. Indeno[1,2,3-cd]pyrene (IND) is a high molecular weight five ring PAH.

PAHs are degraded fairly quickly in many vertebrates, less quickly and in a different way in some other life forms; however, the breakdown products of many PAHs are more hazardous than the parent compound. PAHs with four or less aromatic rings are degraded by microbes and are readily metabolized by multicellular organisms; thus, biodegradation may be the ultimate fate process. The heavier PAHs (four, five and six rings) are more persistent than the lighter (two and three rings) and tend to have greater carcinogenic and other chronic impacts (Mangas et al., 1998).

Vogelsang et al. (2006) investigated the elimination of PAHs from wastewater at five different wastewater treatment plants and found that a system with combined biological and chemical treatment removed from 94-100% of ∑16 PAHs, while systems with only chemical treatment removed 61-78% of ∑16 PAHs indicating an importance of biological degradation. The chemical treatment plants in their investigation removed up to 100% of four, five and six ring PAHs but did not remove more than 29-70% of two and three ring PAHs, indicating a significant biodegradation or evaporation of lower molecular weight PAHs.

As aromatic compounds, PAHs have low water solubility/high hydrophobicity and thus they tend to absorb to solid particles. Sorption of PAHs to soil and sediments increases with increasing organic carbon content (Environmental contaminants encyclopaedia, 1997; Evans et al., 1990). Stenstrom and Kayhanian (2005) in their study analyzed 32 particulate and soluble PAHs in stormwater runoff and found that the majority of PAHs were in the particulate phase, while soluble PAHs were rarely above the detection limit of 5 ng $L^{-1}$. Similar to this, Hwang and Foster (2006) report that 87% of the total PAHs are bound to filterable particles in the tributaries of Anacosta river, USA, receiving urban runoff. This high degree of association with particles is caused by the low water solubility of the relevant PAHs. Their study included 35 PAH species, which reached in total a concentration of 1,510-12,500 ng $L^{-1}$ during a stormwater runoff and much lower concentrations (89-457 ng $L^{-1}$) during base flow. In base flow samples, dissolved PAHs were dominant over particle-bound.

Fountoulakis et al. (2009) studied elimination of PAHs from municipal wastewater in subsurface flow, free water surface constructed wetlands and gravel filter. The main source of PAHs was stormwater runoff mixed with municipal water in a combined sewer system. The average ∑PAHs concentration in wastewater in their study was 786±514 ng $L^{-1}$ with the predominance of low and medium molecular weight compounds. The main removal mechanism was considered to be sedimentation. The mean removal efficiencies of PAHs were correlated with TSS removal efficiencies in subsurface flow wetland and in gravel filter. However, in free water surface wetland removal of PAHs was higher compared to the removal of TSS indicating that other removal processes, like photodegradation (Fasnacht and Blough, 2002), was important. In their study, Fountoulakis et al. (2009) also found that the

PAHs removal rate is decreasing with increasing temperature, which in opposite to what is generally observed for most other physical and chemical wastewater parameters.

#### 2.2.4.4 Heavy metals

During water treatment in a wet detention pond metals cannot be eliminated but are accumulated in the wetland sediment or plant tissues. Metals in water can occur in different forms of dissolved free metal ions, adsorbed onto or bound to organic and inorganic complexes. The soluble forms are the most bioavailable forms and can cause bioaccumulation in the food chain. The removal of metals from water in wetlands can result in accumulation in the sediment, which might be harmful for the organisms that live or feed on these sediments. To avoid this problem pretreatment to reduce inflow metal concentrations, installation of deep water systems or subsurface wetlands can be considered. In deep water systems with free-floating plants the sediment is deposited at great depths and is thus not available to the top feeders, and subsurface wetlands minimize the opportunity for ingestion of metals (Kadlec and Wallace, 2009).

Hares and Ward (2004) who studied heavy metal accumulation in two ponds receiving the run-off from a newly constructed motorway reported that in the period of 39 months there has been an increase in heavy metal levels within the sediment collected from both the inlet and outlet of the investigated ponds for all metals studied. The accumulation ratio (a comparison between the heavy metal concentration at 0 and 39 months of operation) was the highest for Cd, followed by Zn, Cu and Pb. Greatest accumulation was detected at the silt trap at the beginning of the system.

Depositing sediments have the ability to adsorb significant quantities of trace metals. Especially organic matter, iron and manganese oxyhydroxides act as metal adsorbents in aerated systems. Under anaerobic conditions iron and manganese oxyhydrohydes dissolves and thus release metals into the aqueous phase. This may lead to a repartitioning of metals into the sulphide or carbonate precipitates. In the conditions where metal's concentrations are in excess of sulphides, metals may complex with organic matter. Organic matter can appear in the form of surface coatings or in the form of particulates and plays an important role in metal speciation and bioavailability (Ranieri, 2004; Kadlec and Wallace, 2009). Besides, at oxic conditions, co-precipitation of heavy metals with iron, manganese, and aluminum hydroxides also relies on considerable supplies of secondary metals in the system, which might not be present.

Adsorption of metals to iron and manganese oxyhydroxides was shown also by Yousef et al. (1990) who investigated different fractions of heavy metals in stormwater wet ponds and found that for most of the metals (Zn, Cu, Ni, Cr and Cd) the dominant fraction was bound to Fe and Mn oxides. However, Pb prevailed in the exchangeable fraction and soluble and carbonate fractions were relatively low. This led them to conclude that Fe, Mn and organic content play an important role in regulating the mobility of heavy metals in the wet ponds.

Stenstrom and Kayhanian (2005) in the study of Caltrans reported that in general Cd, Cr and Pb are bound to particles, while Cu, Ni and Zn are more associated with the dissolved phase and thus cannot be removed via sedimentation. According to this, Tuccillo (2006) in the research of heavy metals in residential and highway stormwater runoff stated that Cu and Zn were predominately found in particle size fractions below 5 µm, with a rather large fraction being dissolved. Pb and Cr, on the other hand, were exclusively associated with particle size fractions above 5 µm.

As mentioned before, BMPs are more efficient in removal of pollutants sorbed to suspended solids than soluble pollutants. Comparing adsorption to plant tissues and sediments, more studies have shown that more Ni and Cr were removed by adsorption to sediments and only a small part was bound to plant tissues. Cr and Ni are also the metals, which usually reach low or even negative elimination in constructed wetlands (Nolte and Associates, 1998; Kadlec and Wallace, 2009). While the main mechanism removing Ni is sorption to organic matter, carbonates, iron and manganese oxides, the removal of Cr is mainly subdued to bacterial reduction into non-mobile form.

A strong association between heavy metals and suspended matter was shown e.g. by Scholes et al. (1998) who pointed out that the settlement of such particles and associated pollutants is an important process in removal of heavy metals from free water. The concentrations of heavy metals in the sediment in their study decreased in the following order: Zn>Pb>Ni>Cu>Cr>Cd, whit especially cadmium showing a highly mobile behaviour. Although sedimentation is the primary process in heavy metals removal from stormwater, also biological and chemical processes play a role (Walker and Hurl, 2002). Other studies also report removal of heavy metals in wet detention ponds. However, the efficiencies vary according to heavy metal species and site. E.g. Scholes et al. (1999) report 71% removal of Zn, 20-72% of Cd, 40-69% of Pb, 36-66% of Cu, 34% of Ni and 38-81% of Cr. Similar to this, Hossain et al. (2005) report 55-65% average heavy metal removal in a wet stormwater detention pond.

Retention of metals in the sediment can be modified by changes in substrate chemistry and redox potential, which is affected by wetland water depth and biological processes. Besides redox potential, also pH affects sorption/desorption of heavy metals at/from the sediment. The study by Yousef et al. (1990) showed that for most heavy metals the pH had much bigger influence on metals release compared to the redox potential. Namely, the study of the release of heavy metals from the sediment under different redox potentials from highly reduced to highly oxidized and neutral pH (7.5 to 8.0) showed less than a few percent release of metals. In contrast, a decrease of pH to 5 has been shown to enhance the release of metals significantly (Yousef et al., 1990).

The impact of redox potential (Eh) and pH on metal species form can be described by Eh-pH diagrams (also called Porbaux diagrams). Eh-pH diagrams are handy tools in understanding geochemical behaviour of the elements. The diagrams depict dominant aqueous or solid phases defined by Eh and pH axes. Porbaux diagrams for the elements analysed in the scope of this study are presented in Appendix A. The diagrams were reproduced from the Atlas of Eh-pH diagrams published by Takeno (2005).

The Porbaux diagrams can be worked out experimentally or by different geological databases and computer software and can thus show some differences according to the data source and instruments used.

As mentioned before, iron plays an important role in phosphorous and heavy metal absorption in wet detention ponds. The form of iron in a wetland system depends on redox potential and pH (Figure 3). $Fe^{3+}$ or ferric ion is the dominant form of iron under oxidized conditions (Eh > 0 at pH ≥ 6.5) and $Fe^{2+}$ or ferrous ion is the dominant form under reduced conditions. $Fe^{3+}$ forms complexes with different ligands like hydroxide ion, orthophosphate ion, humic acids etc. For example complexion with hydroxide ion results in ferric hydroxide ($Fe(OH)_3$), which is insoluble and settles to the bottom or stays in the bulk water adsorbed to organic matter. Under anaerobic conditions, ferric iron is reduced to ferrous iron, which is more soluble. Consequently, dissolved iron and associated anions are released into the bulk water. Soluble ferrous iron might be caught to insoluble form with hydrogen sulphide anion ($HS^-$) forming ferrous sulphide (FeS).

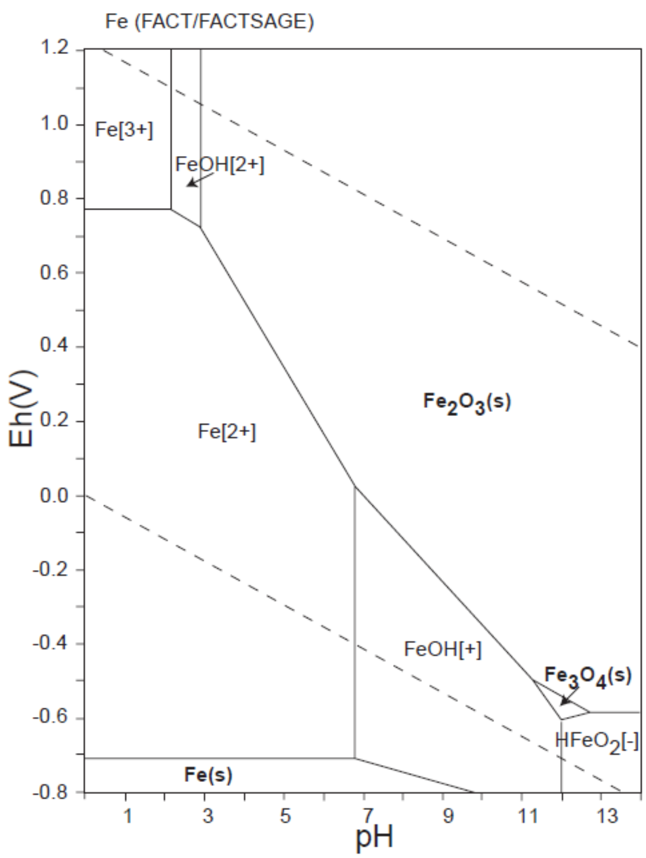


**Figure 3: Porbaux diagram for iron (Takeno, 2005).**

Metals are stored also in plants. Most of the metals found in plants are stored in the roots and rhizomes, just some small amounts may find their way to stems and leaves. Consequently, harvesting aboveground parts does not enable effective removal of metals from the wetland.

However, with the root's death some fraction of the metal may be permanently buried (Kadlec and Wallace, 2009).

Among ten investigated emergent macrophyte species, Ellis et al. (1994a) suggest *Typha latifolia* and *Sparganium* sp. as the most efficient in Pb and Zn uptake. In their experiment *T. latifolia* showed an uptake of Zn and *Sparganium* sp. of Zn and Pb in their underground tissues. Also *Eleocharis* sp. was efficient in root Pb accumulation, while the least efficient species in the uptake of Pb and Zn was *Iris* sp. Ellis et al. (1994a) suggested the use of *T. latifolia* also because of greater plant biomass per unit area that the other investigated species. *Typha* accumulated 300 and 150 mg Zn per $m^2$ for roots and shoots respectively, followed by *Sparganium* sp., which accumulated 60 and 80 mg Zn per $m^2$ for roots and shoots respectively. The accumulation of Pb showed similar pattern with 40 and 8 mg $m^{-2}$ for roots and shoots of *Typha* and 15 and 6 mg $m^{-2}$ for roots and shoots of *Sparganium* sp. In another study by Ellis et al. (1994b) accumulation of heavy metals in *Typha* sp. tissues was compared to *Juncus effusus* showing the highest accumulation in *Typha* roots, especially for Cd and Zn. Both studies by Ellis et al. (1994a and 1994b) did not compare heavy metal accumulation in *Phragmites australis*, the most commonly used plant species in constructed wetlands. The species were compared in the study by Scholes et al. (1990), where *Typha* accumulated more Zn, Pb, Cr and Cd than *Phragmites,* and *Phragmites* contained higher concentrations of Cu. However, the species were sampled from two different wet detention ponds with different heavy metal loads and should thus be compared cautiously. The highest metal concentrations in both species were found in the roots, however higher Zn concentrations were found in *Typha* rhizomes than roots. Accumulation of heavy metals in the roots of different aquatic plant species is reported also by numerous other studies, e.g. Meiorin (1989), Sriyaraj and Shutes (2001), Kadlec and Wallace (2009).

Metal contents in plant tissues can vary during the year. In the study by Scholes et al. (1999), *Typha latifolia* and *Phragmites australis* were investigated. Both species contained the highest metal concentrations in the summer, followed by spring and winter and the lowest concentrations in autumn. Differences between the plant species were also observed: *Typha* contained higher concentrations of metals in the spring and summer, while in autumn and winter the concentrations were higher in *Phragmites*. This might be due to longer growing season of *Phragmites* compared to *Typha*, which enables the reed to accumulate the metals after the cattail has died off in autumn. In order to maximize the potential heavy metal uptake by plants it is advisable to include a mix of plant species into the stormwater wetland (Scholes et al., 1999). Numerous studies on plant heavy metal uptake focus on concentrations of heavy metals in plant tissues (e.g. Cardwell et al., 2002; Fritioff and Greger, 2003; Baldantoni et al., 2004); however, the plant biomass and thus the total amount of heavy metals accumulated has to be considered, when removal of heavy meals by phytoremediation is examined. The plant biomass varies significantly between the species, during the season and according to physical and chemical conditions of the environment (water, light, nutrients) (Kadlec and Wallace, 2009).

Because of relatively high treatment efficiency and flexibility, a wet pond is a BMP with a potential for being widely implemented for stormwater treatment in many countries. Literature overview indicates that wet detention ponds show efficient removal of suspended solids and associated pollutants, but the removal of dissolved and colloidal pollutants is comparatively low, since these pollutants cannot be removed by sedimentation. Hence, there is an increasing need of additional treatment of stormwater after passing wet pond treatment systems (Genc-Fuhrman et al., 2007). Wet ponds do have possibilities for complying with high water quality requirements if they are upgraded with simple and robust technologies for removal of dissolved and colloidal pollutants.

## 2.3 Upgraded wet detention ponds

Enhanced removal of dissolved and colloidal pollutants from stormwater is of special relevance in case of a sensitive receiving water body or when the stormwater is to be used as a source for drinking water. Different BMP units, which are complementary in the terms of treatment performance, can be combined. Besides coagulation, flocculation and subsequent sedimentation, microbial transformation and plant uptake, improving other removal processes can enhance the performance of wet detention ponds e.g. sorption of dissolved and colloid matter to surfaces, flocculation of fine particles and colloids and the implementation of advanced precipitation systems. In contrast to sedimentation, the mentioned processes enable higher removal of dissolved and colloidal stormwater pollutants. Dissolved and colloidal pollutants are known for its mobile nature in the aquatic environment and consequently possess the highest risk of causing adverse effects.

A key factor for deciding which unit operations to incorporate in the design of a wet detention pond is the size distribution of the pollutants, i.e. to which extent a pollutant is dissolved, associated with colloids or associated with different fractions of larger particles.

In order to improve removal of dissolved and colloidal pollutants three wet detention ponds with additional technologies for water treatment have been developed in the scope of the LIFE TREASURE project and are described in the chapter 3.1.2. In the LIFE project, a special focus was on removal of phosphorous, heavy metals and polycyclic aromatic hydrocarbons (PAH).

In the following subchapters, different technologies that can be applied to stormwater wet detention ponds in order to increase the removal of dissolved and colloidal pollutants are described.

### 2.3.1 Addition of aluminium salts to the bulk water

Aluminium salts (e.g. aluminium sulphate) form insoluble aluminium hydroxide flocks $Al(OH)_3$ in bulk water. The flocks have good settling properties and high sorption capacity for phosphate, heavy metals, organic micropollutants and algae (Al-Layla and Middlebrooks, 1975; Sorrell et al., 1980; El Samrani et al., 2008). Accordingly, these pollutants are removed by sorption to the flocks in bulk water and subsequent sedimentation in the pond. The important characteristic of alumina complexes is that they are stable under anaerobic conditions, which can appear in wet detention ponds. However, high pH values (above 8.5) that might occur at intensive photosynthesis can cause the formation of toxic aluminate ion and release off adsorbed pollutants into bulk water. If the water has low buffer capacity, it is therefore not recommended to use aluminium for pollutant control.

The addition of aluminium salts is commonly used in potable water and wastewater treatment and restoration of eutrophic lakes, where aluminium salts enable phosphorous removal from the water column and its immobilization in the sediment, which reduces the eutrophication.

Phosphorous can be precipitated from bulk water also by addition of other flocculants like calcium and iron. Calcium is usually added in the form of lime ($Ca(OH)_2$), which reacts with natural bicarbonate alkalinity and forms insoluble $CaCO_3$. The removal of P appears by precipitation of apatite ($Ca_5(PO_4)_3$) or hydroxyapatite ($Ca_5(OH)(PO_4)_3$) at relatively high pH (Kadlec and Wallace, 2009). Addition of calcium was not included in this research.

### 2.3.2 Addition of iron salts to the sediment

Ferric iron ($Fe(OH)_3$) binds phosphate and several heavy metals under aerobic conditions (Esser et al., 2004; Genc-Fuhrman et al., 2008; Kadlec and Wallace, 2009). In an aqueous environment, $Fe(OH)_3$ has the lowest solubility between pH 7 and 10 and provides sorption sites for a number of pollutants. Besides adsorption of pollutants to $Fe(OH)_3$, also insoluble precipitates with iron can be formed, e.g. $FePO_4$ and complexes with metals. Using iron to adsorb pollutants, it is crucial that the redox potential of the sediments is sufficiently high to avoid ferric iron to be reduced to ferrous iron. If ferric iron is reduced, the bound phosphate, heavy metals and other pollutants, could be released back into the bulk water phase. Furthermore, if during anaerobic conditions in the sediment sulphate reduction occurs, insoluble FeS can be produced. Iron can be added in the form of salts like iron chloride ($FeCl_3$ x $6H_2O$) (Kadlec and Wallace, 2009).

### 2.3.3 Sand filters

Stormwater wet ponds can be upgraded with sand filters at the outflow as was implemented and tested in the LIFE Treasure project. The sand filters were planted with common reed (*Phragmites* australis), and as such by their appearance and function, the sand filters correspond to subsurface flow constructed wetlands. There is an extensive literature on efficiency and performance of constructed wetlands (Kadlec and Wallace, 2009). Constructed wetlands are efficient also in elimination of different pollutants that appear in stormwater runoff. Two decades experiences on constructed wetlands operation in Denmark reported by Brix et al. (2007) showed that the systems were efficient in removal of suspended solids and organic matter. The authors also report that in order to reach appropriate elimination of nitrogen newer systems with vertical flow and recycling are used and phosphorous removal is achieved by chemical precipitation. Efficient elimination of heavy metals in constructed wetlands is reported e.g. by Lesage et al. (2007), Cheng et al. (2002). Due to their proven efficiency, sand filters planted with *Phragmites* were incorporated into the upgraded stormwater treatment ponds of the LIFE-project.

Sand filters can be of different types according to their position and water flow as follows:

- a horizontal filter is placed at the same level as the permanent water level,
- a sloping filter is placed on the banks of the pond and is submerged only at the time of high water level, and
- a vertical filter is placed in the pond and starts in the level of permanent water and goes up to the maximum water level (Vollertsen et al., 2009).

The filter capacity is affected by the hydraulic conductivity and the depth of colmation layer, which develops from particles depositing on the filter surface and can cause clogging of the filter. Compared to the filter material, the colmation layer usually has much lower hydraulic conductivity. However, the conductivity is affected by the loading of the pond/filter, the growth on the filters and the drying and mineralization during the dry periods. As stated by Vollertsen et al. (2009) the horizontal sand filter is assumed to have the deepest colmation layer, followed by the sloping filter and by the vertical filter.

### 2.3.4 Sorption filters

One of the possible technologies for upgrading existing stormwater wet ponds is an installation of sorption filters after the wet detention pond. Dissolved and colloidal pollutants as heavy metals and phosphorous are thus removed by sorption to the filter media.

When selecting a suitable material for the sorption filter, it is crucial that the selected sorption material has a high sorption capacity at the rather low pollutant concentrations in the stormwaters, which enables long-term use of the material. The sorption material should be available at suitable cost-benefit ratio. The filter should have a good hydraulic conductivity and filter clogging should be avoided. Before treatment in the sorption filters, the water needs to be passed through regular sand filters to remove most particles.

Elimination of dissolved pollutants like phosphorous and heavy metals is enabled by the characteristics of the filter materials. Filter materials that contain a lot of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) minerals are efficient in P adsorption (Brix et al., 2001) and materials containing iron or alumina such as olivine, are shown to have good sorption capacities for heavy metals (Genc-Fuhrman et al., 2007).

Different sands, calcite products and seashells were tested by Arias et al. (2001), Arias et al. (2003), Del Bubba et al. (2003), Arias, and Brix (2005). In general, the materials show good removal of phosphorous; however their use in practice for P removal from wastewater is limited by saturation and large volumes needed. E.g., a calcite filter units integrated in a constructed wetland in a study by Arias et al. (2003) showed good removal of phosphorous from municipal wastewater. However, after three months in an experimental condition the filters were saturated. The authors also pointed out that sorption is a reversible process and the release of P can be observed when the filter is loaded with lower P concentrations. Arias and Brix (2005) therefore suggest using the filters for water polishing while the majority of P should be removed by other means such as chemical precipitation in the sedimentation tank.

As mentioned sorption filters can be efficient also in removal of heavy metals. Genc-Fuhrman et al. (2007) tested 11 different sorption materials for removal of heavy metals from stormewater, namely alumina, activated bauxsol-coated sand, bark, bauxsol-coated sand, fly ash, granulated activated carbon, granulated ferric hydroxide, iron oxide-coated sand, natural zeolite, sand and spinel. Their results showed that alumina was consistently effective for all heavy metals tested which they annotate to alumina’s high surface area. Alumina surface is expected to be positively charged, thus adsorbing anion metal species, however in their experiment alumina performed equally well also with cation species indicating different mechanisms to occur, like complexation, pore diffusion and specific adsorption. Granulated ferric hydroxide also turned out to be an efficient sorbent with both negatively and positively charged groups at the surface. On the other hand, iron oxide-coated sand had moderate to poor heavy metal removal efficiency. Its average surface charge is positive, thus attracting anions like chromium. Sand and spinel ($MgAl_2O_4$) have relatively low surface area and thus low sorption was expected; however, spinel has high porosity and thus showed moderate to high heavy metal removal. From certain sorbents (activated bauxsol-coated sand, bauxsol-coated sand, fly ash, spinel) leaching of Cr was observed.

pH and heavy metal concentration have an influence on the saturation of the filter media. The saturation of the media is increasing with increasing pH and increasing initial heavy metal concentration (Genc-Fuhrman et al., 2007; Genc-Fuhrman et al., 2008). In a study of ferric hydroxide filter material Genc-Fuhrman et al. (2008) also reported that addition of humic acid reduced the heavy metal removal in the filter, possibly due to formation of stable complexes of metals and humic acids.

Besides different mineral media, also numerous natural materials have been tested as adsorbents for heavy metal removal. Somerville and Norrström (2009) tested brown seaweed and shrimp shells, which are seafood waste. Both media reduced Cu, Cd, Pb and Zn concentrations below defined limiting values. According to their findings, the main removal mechanism was likely to be the substitution with calcium, which was shown also for calcite filters in the study of Arias et al. (2003).

Filter materials for removal of phosphorous and heavy metals can increase pH in outflow water compared to raw water, which was reported for calcite filters by Arias et al. (2001) and 11 different mainly inorganic sorbents tested by Genc-Fuhrman et al. (2007).

### 2.3.5 Vegetation

The efficiency of wet detention ponds can be increased by planting suitable macrophyte vegetation. The role of plants in constructed wetlands is wide:

- Plants enhance sedimentation.

- Plant roots provide the surface for adsorption of smaller particles and colloids.
- Submerged plant parts provide the surface for growth of attached microorganisms like photosynthetic algae and bacteria. These microorganisms carry out the major pollutant transformations.
- Plants accumulate heavy metals (mainly in the roots).
- Plants take up nutrients, but elimination from the system is possible only with harvest.
- Plant roots stabilize wetland bottom and thus reduce the erosion and resuspension of bottom sediments.
- Plants release oxygen through the roots.
- Plants represent a biotope for different organisms and play an aesthetic role.

Among negative plant effects in constructed wetlands are mainly the reduced water aeration that may appear because of dense vegetation and the accumulation of dead plant material if the plants are not removed. The accumulation of dead plant material increases the accumulation of the sediment in the system and thus reduces its lifespan. Due to the negative impacts that plants can have, usually not all the wet pond area is vegetated. The control of vegetation cover can be achieved with different water depths. The majority of macrophytes live in the depths up to 0.3 m; however, some species can tolerate bigger depths, e.g. *Phragmites australis* up to 1 m.

The amount of nutrients that can be removed from the system by plant harvest depends on the nutrient stock in plant biomass at the time of harvest. The nutrient stock in the plant biomass is calculated as a product of nutrient concentration in the plant tissues and the amount of biomass at a certain area. For the amount of nutrients eliminated by harvest both the nutrient concentration in the plants and the amount of biomass on the area unit are important. However, it is know that the highest nutrient concentrations and the biggest biomass do not appear at the same time of the growing season. A caution is needed at harvest since cutting the plants during the growing season can severely affect the stand. Harvest can also be problematic in subsurface flow wetlands in cold climates since the plants during the winter insulate against freezing. On the other hand, in tropical climates the vegetation season lasts all year, therefore harvest can be performed more often and thus more nutrients removed (Vymazal, 2004).

The concentration and accumulation of nutrients and metals in plant tissues is described by the ratio between the root or shoot concentration and the concentration in the soil. The element concentration ratio of plant roots to soil is the Concentration Factor (CF) and describes phytostabilization of the element in the roots. The ratio of shoot to soil concentration is named Accumulation Coefficient (AC) and shows transport of the element from roots into aboveground tissues. The elements that are concentrated in the roots or accumulated in the shoots have CF and AC higher than one (Smical et al., 2008; Malik et al., 2010).

Different wetland plants differ significantly in metal uptake and translocation (Fritioff and Greger, 2003; Kamal et al. 2004; Weis and Weis, 2004; Read, 2008). Besides this, metal uptake by marsh plants is affected by numerous factors such as temperature, pH, light, presence of other metals in water etc. (Fritioff et al., 2005; Fritioff and Greger, 2006). Metal concentrations in stormwater vary greatly; therefore, wetland plants are subdued to high as well as to low water metal concentrations.

The uptake of metals also depends on if the element is essential to plant metabolism or not. For example Cu and Zn are essential elements and in low concentrations obligatory for normal plant functioning. They are structural and catalytical components of proteins and enzymes. Nickel is sometimes an essential element but moderate concentrations are toxic. On the other hand, Cd is not an essential element, but it is still taken up by plants; however, its uptake dynamic is different. Metal uptake is usually increasing with increasing metal concentration in the environment, but the connection is not linear (Kadlec and Wallace, 2009).

Because submerged and floating wetland plants take up nutrients and metals with their roots, stems and leaves, different authors see them as a potential and efficient phytoremediation plants. E.g., Fritioff and Greger (2006) suggest the use of *Potamogeton natans* as an efficient plant for heavy metal uptake and Nyquist and Greger (2007) report an efficient uptake of Cu and Zn by invasive *Elodea canadensis*. Nyquist and Greger (2007) also investigated the impact of initial heavy metal concentration in plant tissues on heavy metal uptake. They found that initial Zn and Cu concentration in *Elodea* tissues was not a limiting factor for uptake of these metals, while the initial Cd concentration turned out to limit the further Cd uptake.

The plants planted in a stormwater wet pond have an important role in landscape architecture and thus acceptance of the system by the local people. The aesthetic and habitat value of the plants enables the multipurpose use of the wet pond also for recreational activities, relaxation, bird watching etc.

## 2.4 Summary of the state-of-the-art

State of the art in the field of wet stormwater detention ponds reveals that wet detention ponds efficiently remove suspended solids and associated pollutants, but the removal of dissolved and colloidal pollutants is comparatively low. The removal of phosphorous, soluble heavy metals and other pollutants of 70% or less is not acceptable especially in case of a sensitive receiving water body or when the stormwater is to be used as a source for drinking water.

Additional technologies for supplementary treatment of stormwater runoff were suggested, such as sorption filters, addition of aluminium and iron salt, planted sand filters and diverse wetland vegetation with the purpose to increase elimination of soluble pollutants. These technologies are known to be efficient in the treatment of wastewaters and drinking water, however their efficiency in stormwater treatment has not been investigated until now. It is the scope of this thesis to evaluate the contribution of additional technologies to overall performance of wet stormwater detention ponds as well as to investigate the treatment processes and pollutant pathways in wet detention ponds. The accumulation of nutrients and heavy metals in the sediment and plants of wet stormwater detention ponds has been studied before, however the studies mainly focus only on sediment or only on plants, so an overview of the pollutant fate in the systems is needed. Besides this, the potential for bioaccumulation of heavy metals stored in the plants growing in stormwater detention ponds has barely been investigated. This research also focused on elimination of PAHs from stormwater in wet detention ponds and their accumulation in the sediment, which has not been studied so far.

## 2.5 Hypothesis

The research is based on the following hypotheses:

1. Wet detention ponds are efficient in reduction of suspended solids and associated pollutants from stormwater runoff. The removal of dissolved pollutants is limited.
2. The additional technologies, implemented at three wet detention ponds, will improve elimination of soluble pollutants from stormwater such us phosphorous, PAHs and heavy metals. Thus, these ponds will reach lower outflow concentrations of these pollutants compared to the investigated traditional wet detention ponds.
3. The majority of pollutants will accumulate in the sediment with the highest concentrations in the zones with the highest sedimentation, i.e. near the inlet.
4. Plants are expected to accumulate some heavy metals in the roots with minimal transport to the aboveground tissues.

# 3 MATERIALS AND METHODS

Seven stormwater treatment ponds in Denmark were investigated. Four of them were traditional wet detention ponds where the basic treatment process is sedimentation, while the other three ponds were upgraded with additional technologies to improve the removal of dissolved and colloidal pollutants.

Water, sediment and plants from the ponds were sampled and analyzed for nutrients, heavy metals and polycyclic aromatic hydrocarbons (PAH). A detailed description of the investigated systems, the sampling programme and the laboratory analyzes is given below.

## 3.1 General characteristics of the systems

### 3.1.1 Four traditional wet detention ponds

As a part of the local environmental plan, in the last years the city of Århus, Denmark, has invested in the construction and the establishment of a network of ca. 130 wet detention ponds within the city limits. The scope of a construction of 130 wet detention ponds was to control high flows and to mitigate the effect of run-off pollution. Wet detention ponds receive stormwater of different origin, namely from residential areas, highways, roads and industrial areas. The ponds were constructed as artificial water bodies with a permanent water storage volume and a fluctuating volume above it. Each pond has an inflow and outflow structure. Usually no silt trap was constructed before the inflow to the pond. Up to now, no performance assessment has been done on the stormwater wet detention ponds in Århus municipality and therefore an investigation was undertaken to estimate the heavy metal and nutrient accumulation in the sediment and plants of four selected stormwater wet detention ponds in the city. The research was carried out in the framework of this PhD thesis at Aarhus University, Denmark.

The four investigated wet detention ponds are located in the west suburbs of the city of Århus. The ponds were constructed by the municipal water works in 2003 as a part of a municipal plan to treat rainwater and to create recreational areas established with paths, information boards and to attract wildlife. The surrounding of the ponds is forested, creating a natural park-like atmosphere. The ponds are adjacent to each other and all discharge to the same stream, which flows to the nearby lake Brabrand. The four ponds were labelled A, B, C and D as shown on Figure 4. Pond D differs from other ponds in having two inflows.


**Figure 4: Areal view of the four investigated stormwater detention ponds in Århus, Denmark. Inlets are presented by circles and outlets by triangles (Google Earth, 2008).**

The runoff contribution to each one of the wet detention ponds originates from different catchments. The total catchment area draining to the four wet ponds is of about 220 ha. Pond A has a storing capacity of 7,800 $m^3$ and receives water from a catchment of approximately 28 ha from local roads and an industrial area. Pond B with a storing volume of 14,300 $m^3$ collects run-off from 109 ha from a residential area, while pond C stores 1,600 $m^3$ and receives water from 6.4 ha catchment of a combination of light industrial and a residential area. Pond D with a capacity of 16,400 $m^3$ receives runoff from 74 ha of industrial area. General characteristics of four wet detention ponds are presented in Table 5. The minimum depth of free water areas is approximately 1.2 m at the permanent water volume.

The stormwater collection and the treatment in the wet ponds operate by gravity. The wet ponds were constructed and made water tight with a layer of clay on the bottom of the ponds and a layer of sand was added on top. The ponds have inflow and outflow structures to regulate the storage and drainage of the systems so the residence time is a function of rain intensity and frequency. The ponds are designed in different shapes that consequently affect the hydraulics of the system. Ponds A and B are horseshoe shaped, while ponds C and D present oval shape (Figure 4).

**Table 5: General characteristics of the four stormwater wet detention ponds (Source: Documentation by Århus Commune).**

| Parameter | Pond A | Pond B | Pond C | Pond D |
|---|---|---|---|---|
| Annual precipitation | 661 mm | 661 mm | 661 mm | 661 mm |
| Catchment area | 28.3 ha | 109.4 ha | 6.4 ha | 74.0 ha |
| Impervious catchment area | 20.7 ha | 42.6 ha | 4.5 ha | 46.6 ha |
| Permanent volume of the pond | No data | No data | No data | No data |
| Detention volume | 7,715 $m^3$ | 14,331 $m^3$ | 1,630 $m^3$ | 16,400 $m^3$ |
| Catchment area to pond volume ratio | 367 $m^2m^{-3}$ | 76 $m^2m^{-3}$ | 39 $m^2m^{-3}$ | 45 $m^2m^{-3}$ |
| Length to width ratio | 4.7 | 6.5 | 7.3 | 11.6 |
| Max depth of detention volume | ca. 2 m | ca. 2 m | ca. 2 m | ca. 2 m |
| Max outflow from the facility | 28.3 L $s^{-1}$ | 109.4 L $s^{-1}$ | 6.4 L $s^{-1}$ | 74.0 L $s^{-1}$ |
| Overflow | every 5 years | every 5 years | every 5 years | every 5 years |

The investigated four ponds have not been planted with macrophytes during or after the construction. However, a large variety of wetland plants colonized the ponds in a natural way. On the banks of the four ponds, the emergent macrophyte broadleaved cattail (*Typha latifolia*) was dominant; in pond D, also patches of common reed (*Phragmites australis*) were present. In the group of floating macrophytes, islands of floating pondweed (*Potamogeton natans*) had developed in ponds A, B and D. Pond C was densely vegetated by submerged small pondweed (*Potamogeton pusillus*) and the entire bottom of pond B was covered by Canadian and western waterweeds *Elodea canadensis* and *Elodea nuttallii*, both invasive species in Europe.

### 3.1.2 Wet detention ponds in the scope of LIFE project

In 2007, three full-scale stormwater treatment systems were established as part of a European LIFE project TREASURE in the cities of Århus, Silkeborg and Odense, Denmark. The scope of the project was to implement and demonstrate new technologies for efficient removal of stormwater pollutants especially colloidal and soluble pollutants like phosphorous and heavy metals and organic micropollutants. In order to remove these pollutants ponds are equipped with filtration and adsorption units as described below.

The wet detention ponds were designed and engineered to meet the particular needs imposed by the morphology of their respective catchments, the quality of the drained water from the catchment and the environmental demands set by the local authorities where the sites are located. The wet detention ponds are artificial water bodies but designed like natural and recreational elements attractive to people as well as to wildlife. Since the concentration and the nature of pollutants washed from the catchment are different, the three sites have different design, structural and operational features, which are presented in Table 6.

**Table 6. General characteristics of the three stormwater wet detention ponds (Source: LIFE Treasure documentation).**

| Parameter | Odense | Århus | Silkeborg |
|---|---|---|---|
| Annual precipitation | 657 mm | 661 mm | 719 mm |
| Catchment area | 27.4 ha | 57.4 ha | 21.5 ha |
| Impervious catchment area | 11.4 ha | 25.8 ha | 8.8 ha |
| Permanent volume of the pond | 1,990 $m^3$ | 6,900 $m^3$ | 2,680 $m^3$ |
| Detention volume | 1,300 $m^3$ | 1,400 $m^3$ | 3,230 $m^3$ |
| Catchment area to pond volume ratio | 138 $m^2\ m^{-3}$ | 83 $m^2\ m^{-3}$ | 80 $m^2\ m^{-3}$ |
| Length to width ratio | 4.5 | 2.5 | 5 |
| Max depth of detention volume | 1.45 m | 1.50 m | 1.40 m |
| Max outflow from the facility | 0.025 $m^3\ s^{-1}$ | 0.110 $m^3\ s^{-1}$ | 0.033 $m^3\ s^{-1}$ |
| Area of horizontal sand filter | 100 $m^2$ | 400 $m^2$ | 180 $m^2$ |
| Length of sloping sand filter* | 30 m | 65 m | 30 m |
| Length of vertical sand filter** | 6.3 m | 12.6 m | 6.3 m |
| Number of annual overflows | 5 | 4 | 4 |

*The slope of the sand filter was 1:5 and stretched to the maximum water level of the retention volume
**The height of the sand filter was to the maximum water level of the detention volume

Each of the three ponds consists of a sand trap at the inflow, a pond with wetland vegetation, sand filters planted with *Phragmites australis* at the outflow, and different additional technologies for sorption of dissolved and colloidal pollutants. Common reed at the sand filters counteracts erosion and maintains the hydraulic conductivity of the sand filters by its deep growing root system. The schemes of the three ponds are presented in Figure 5. The systems were fully equipped with on-line monitoring equipment as well as automatic samplers.

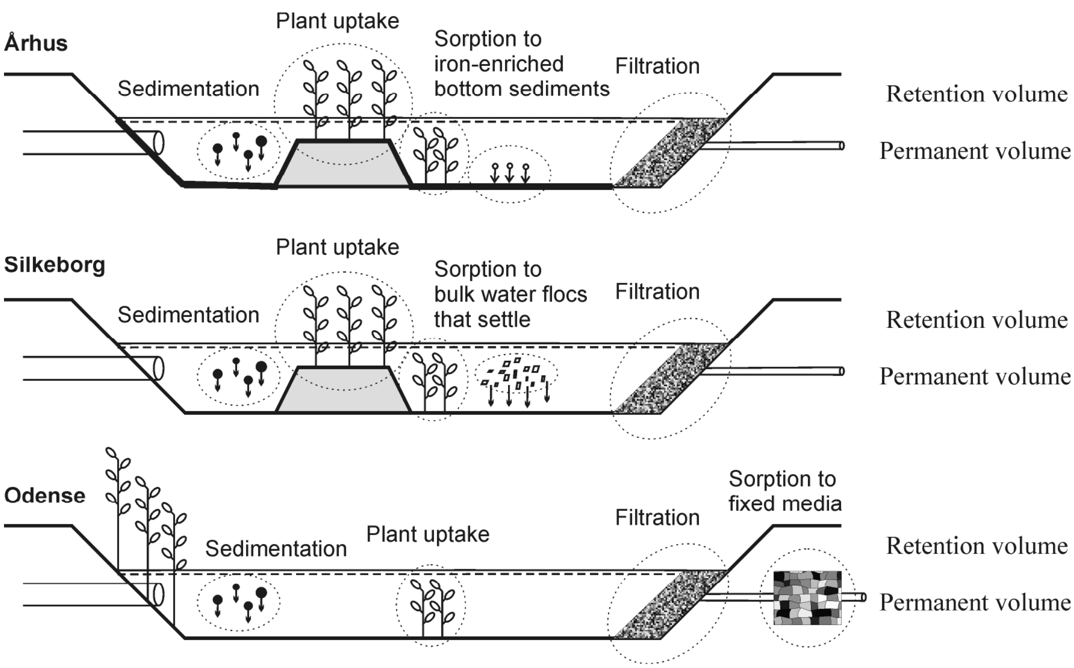


**Figure 5: Schemes of the design, main treatment processes and additional technologies implemented in the three wet detention ponds constructed in the scope of LIFE Treasure project (Source: LIFE Treasure documentation).**

#### 3.1.2.1 Århus facility

The facility in Århus treats run-off waters collected from urban catchment with a total surface of ca. 57 ha, where 50% of the area is considered impermeable. The collected waters from the catchment are treated in the new facility and later discharged to a local sensitive lake (Lake Brabrand). The facility was built adjacent and parallel to the receiving lake, in a residential neighbourhood and is included in a recreational area with bird observation towers, bicycle and walk paths (Figure 6).

The preliminary hydrological studies of the catchment showed an average yearly precipitation of around 660 mm and an estimated run-off flow of around 130,000 $m^3$ $y^{-1}$. The preliminary water quality analyses showed that the pollutant load is not especially high since 80% of the stormwaters collected come from multi-story housing buildings and the remaining 20% is water washed from roads and highway. The wastewater characterization from the catchment showed consistent presence of TSS, organic matter, nitrogen, phosphorous, and some heavy metals, among them, Pb, Zn, Cd and Cu.

**Figure 6: The positioning and surrounding of the wet detention pond in Århus (Source: LIFE Treasure documentation).**

The inlet to the pond is located at the southeast end of the pond (right side on the Figure 6) and the outlet is at the opposite end. This layout enables efficient replacement of water during run-off events and minimizes potential dead volumes. The system was made impermeable with a layer of clay. The permanent water volume of the pond is 6,900 $m^3$ and detention volume is 1,400 $m^3$. At the outlet horizontal, vertical and sloping sand filters with different filtering capacities have been constructed. The horizontal filter (400 $m^2$) is permanently submerged, while sloping and vertical filter are submerged only during rain events. Sloping filter was constructed on the banks in the length of 65 m and three vertical filters (2x$\Phi$2000 mm, 1x$\Phi$1000 mm) were positioned into the horizontal filter. The scheme of the filters is shown in Figure 7 and their positioning in the pond in Figure 8. To evaluate the effect of the filters, the system is equipped with on-line measurements.

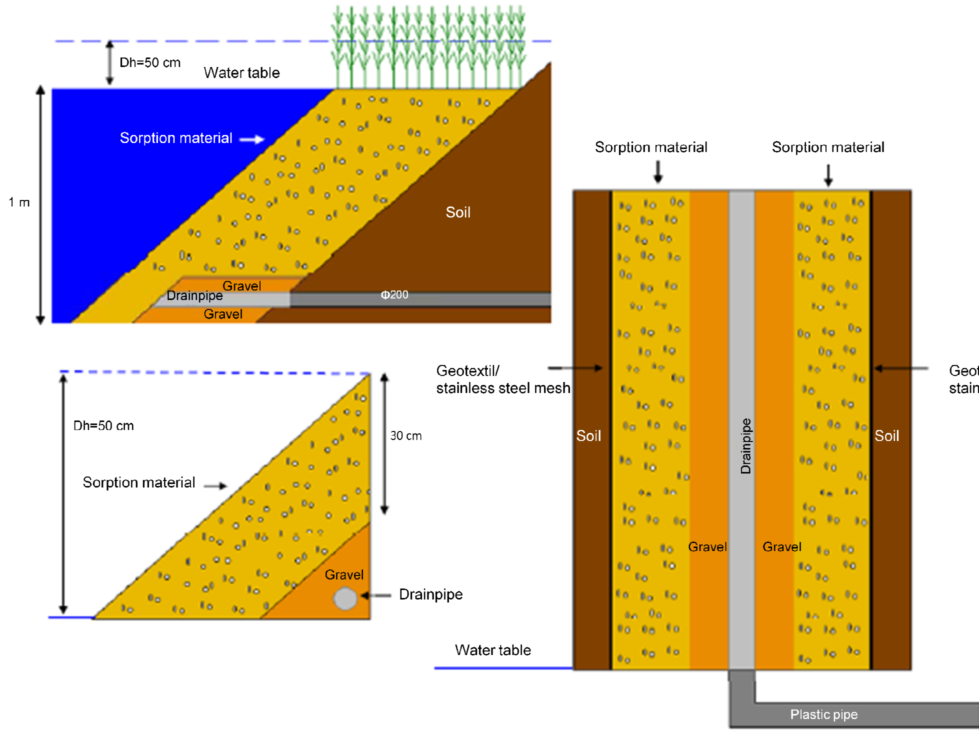


**Figure 7: Scheme of the sand filters at the outflow (Source: LIFE Treasure documentation).**

The wet detention pond in Århus was taken into operation in January 2008. The additional technology to enhance the removal of soluble and colloidal pollutants implemented in Århus pond was the addition of iron salts to the sediment. A total of 3,000 kg of iron chloride/sulphate solution (PIX 118 from Kemira Water Danmark A/S) was added to the pond in April 2009. The acidic solution contained 116 g $Fe^{3+}$ $kg^{-1}$. In order to achieve even distribution of iron salts onto the pond's bottom, pond water was pumped from the pond and mixed with product pumped from the product container. The mixture was then applied to the pond through a pipe floating on the pond's surface and repeatedly dragged along the pond.

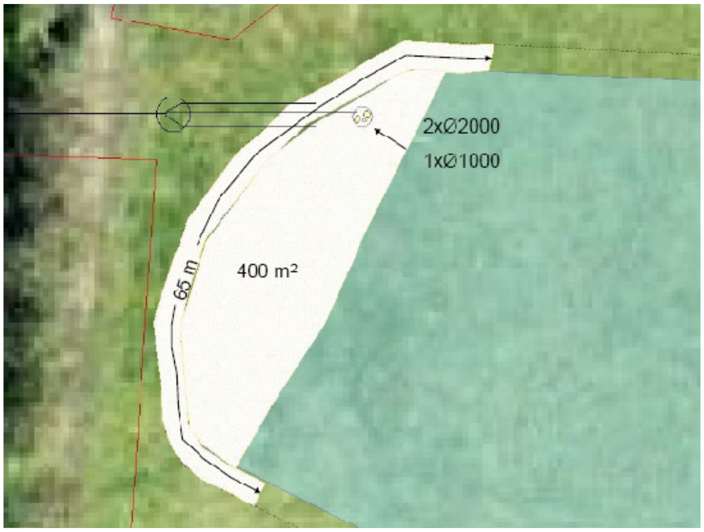


**Figure 8: Horizontal, vertical and sloping filters at the outflow from Århus facility (Source: LIFE Treasure documentation).**

Planting of the wet pond in Århus was designed according to the plant species found in a nearby Brabrand lake and their distribution in the lake. The islands of *Scirpus lacustris* and *Nympaea alba*/*Nuphar luteum* are typical for the lake and were mimicked in the pond. The horizontal and sloping sand filters at the outflow were planted with *Phragmites australis*. Altogether 2,600 plants were planted. The planting of the pond is shown on Figure 9.


**Figure 9: Planting plan for the wet detention pond at Århus (Source: LIFE Treasure documentation).**

#### 3.1.2.2 Odense facility

The facility is located in industrial area in the outskirts of the city of Odense, Denmark (Figure 10). The system receives runoff water collected from light industry catchment with a surface of 27.4 ha (impermeable area of 11.4 ha). The average annual precipitation is of around 660 mm and an estimated runoff flow of 55,500 $m^3$.

**Figure 10: The positioning of the wet detention pond in Odense located in an industrial area (Source: LIFE Treasure documentation).**

Preliminary stormwater characterization from the catchment at Odense showed a consistent presence of TSS, organic matter, nitrogen, phosphorous, heavy metals, among them, Pb, Zn, Cd and Cu, and PAHs. The pollutant load from the catchment is considered high due to pollutants originating solely from an industrial area. Therefore, the facility was designed to demonstrate the efficiency of the treatment concept for strongly polluted runoff, and the capacity of the treatment units are designed for high pollutant loads.

The inflow into the pond is constructed at the west end of the pond and the outflow at the northeast. Treated water is directed to a nearby stream Odense Å, which flows into a sensitive natural wetland (dashed red at the Figure 11). The permanent volume of the pond is 1,990 $m^3$ and the detention volume is 1,300 $m^3$. The pond bottom was made impermeable with a 30 cm thick layer of clay. At the outflow from the pond horizontal, vertical and sloping filter were constructed, as shown on Figure 7. The horizontal filter covered 100 $m^2$ and the sloping filter was constructed on the bank of the pond in the length of 30 m. Horizontal and sloping filter are planted with common reed. Four vertical filters (4xΦ500 mm) were constructed in the free water area of the pond. Vertical and sloping filters are submerged only at the time of higher water levels and horizontal filter is positioned in the level of permanent water level. A closer look at the sand and sorption filters, which represent the additional technology for removal of soluble and colloidal pollutants implemented in the Odense wet pond, is presented in Figure 12. The sorption filters were filled in December 2007, and since then the system has been operational.

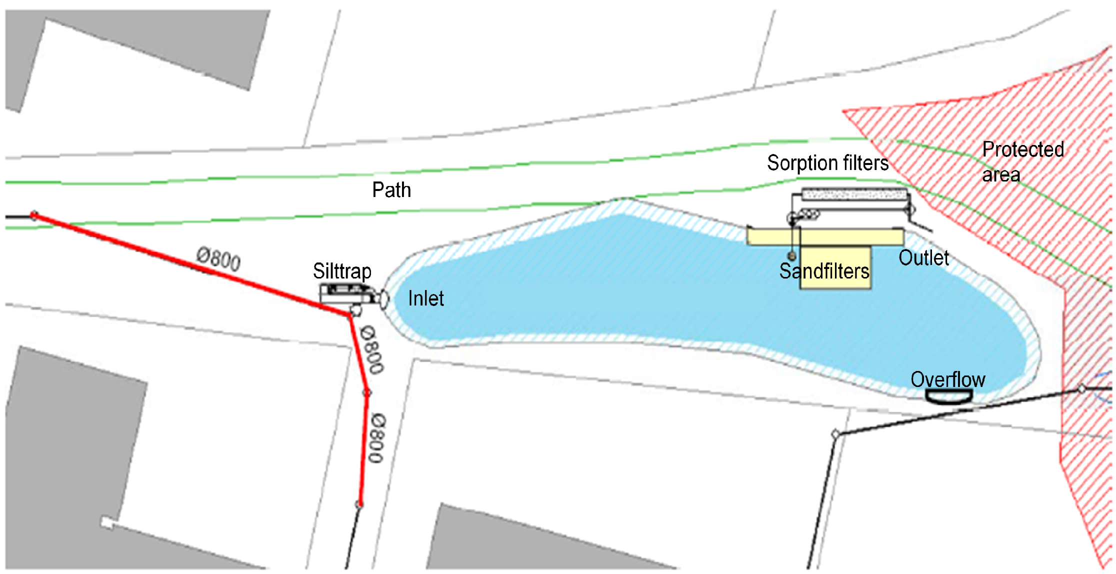


**Figure 11: Positioning of the inflow, outflow and overflow at the wet detention pond at Odense and a nearby protected wetland area (Source: LIFE Treasure documentation).**

After an initial polishing in the sand filter the treated water trickles through the fixed media filters. The initial filtration step is crucial to avoid clogging of the sorption filter that would reduce its hydraulic capacity of the system. The fixed media filter comprises of a large main filter and three smaller filters. The larger filter is filled with Oyta Shells type OYTA 0 provided by Oytaco Ltd. Denmark. The material is a natural product obtained from fossil oyster shells. The size of the grains is 0.5-2 mm and they consist of 96% of $CaCO_3$ and $MgCO_3$. Ca content is 38% (Vollertsen et al., 2009). The filter has a rectangular shape with an area of 24 $m^2$ and a volume of 55 $m^3$. It operates by gravity. The smaller filters are test filters; they have circular shape, surface area of 1.23 $m^2$ and a volume of 2.5 $m^3$. The first filter is filled with Oyta Shells, second with granulated olivine (Filterstil 2749 provided by North Cape Minerals, Norway) and the third filter is filled with 0.5 $m^3$ of Oyta Shells at the bottom, followed by 0.5 $m^3$ of iron hydroxide coated olivine (Filtersil TOC, North Cape Minerals, Norway) and 1.5 $m^3$ Oytha Shells on the top. The three testing filters operate by pumps, which enables constant water flow through the media.

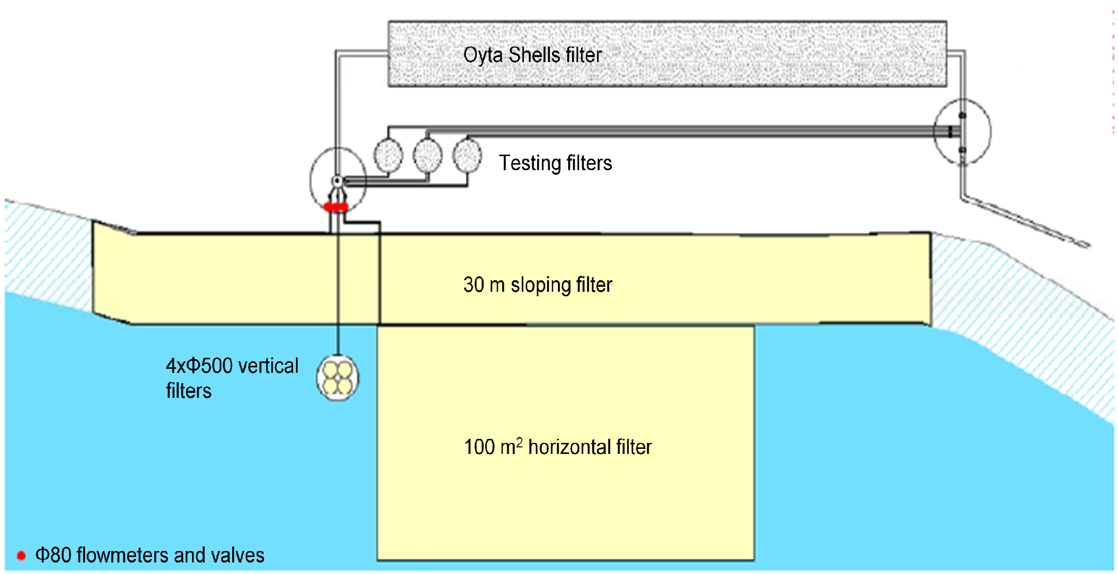


**Figure 12: Horizontal, sloping and vertical sand filter in the facility at Odense, followed by four sorption filters (Source: LIFE Treasure documentation).**

The system was planted with selected plant species, which included plants that should help counteract clogging of the sand filter, namely common reed (*Phragmites australis*). Other species were selected mainly for aesthetic reasons but also had the potential to improve the removal of pollutants. They were planted along the edges and within the wet pond. The plant species selected for the site included *Phragmites australis* (planted on the sand filters and part of a bank), *Typha latifolia*, *Rumex hydrolapathum*, *Typha angustifolia*, *Ranunculus lingua*, *Typha minima*, *Iris pseaudacorus*, *Sagittaria sagittifolia*, *Caltha palustris*, *Alisma lanceolatum* and *Nymphea alba*/*Nuphar luteum*. The scheme and planting plan of the pond is presented in Figure 13.

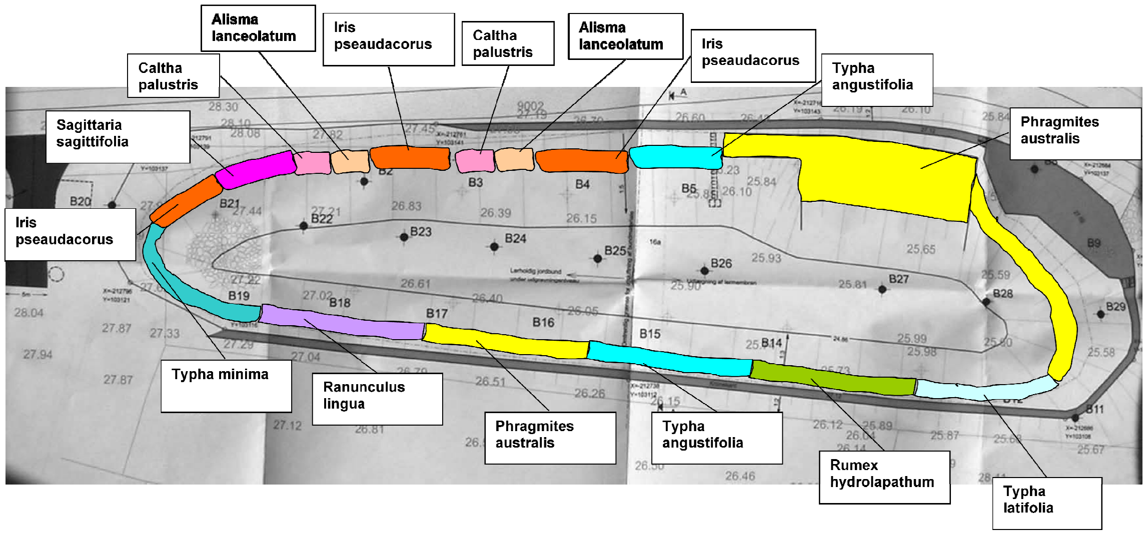


**Figure 13. A planting plan of the wet detention pond in Odense (Source: LIFE Treasure documentation).**

3.1.2.3 Silkeborg facility

The facility is located in an urban park stretching into the city of Silkeborg, Denmark, and receives runoff from a catchment with a surface of 22 ha where ca. 9 ha are considered impermeable. Approximately one third of the runoff water originates from local housing area and the remainder run off is collected from a highway (Figure 14). The pollutant load on the catchment is considered average due to the mix of traffic on the highway and the low pollutant loads from the residential area. The preliminary stormwater characterization from the catchment showed consistent presence of TSS, organic matter, nitrogen, phosphorous, and some heavy metals, (Pb, Zn, Cd and Cu) and PAHs. The facility was built to test and demonstrate the efficiency of the treatment concept for averagely polluted stormwater runoff, and the capacity of the treatment units to handle for average pollutant loads.

The inlet to the pond is located at the north-west end of the pond (top end of the pond in Figure 14) and the outlet is at the opposite end. The pond has 2,680 $m^3$ of permanent water volume and 3,230 $m^3$ of the detention volume. This pond has been fitted with two gravel barriers perpendicular to the water flow. The barriers are planted with *Phragmites australis* and are meant to increase the sedimentation capacity and thus improve the water treatment. Common reed is planted also on the sand filter at the outflow of the pond. As in Århus and Odense also in the pond at Silkeborg three types of sand filters were designed, namely horizontal, sloping and vertical filters. Once the water is treated, it is discharged to Søholt spring. The design of the pond is shown in Figure 15. The system was put in operation in autumn 2008.

**Figure 14: The positioning of the wet detention pond at Silkeborg in an urban park by residential area and close to the highway (Source: LIFE Treasure documentation).**


**Figure 15: The design of the pond in Silkeborg with two perpendicular barriers and three types of sand filters at the outflow (Source: LIFE Treasure documentation).**

The additional technology implemented at the system in Silkeborg is a flow proportional injection of aluminium hydroxides (alumin_10 from Remondis Production GmbH; the product contained 155 g $Al^{3+}$ $kg^{-1}$ in an alkaline solution) at the inflow to promote the formation of aluminium hydroxide flocks with high sorption capacity for soluble pollutants such as phosphorous. The flocks have good settling properties, which are enhanced by two flow perpendicular barriers in the pond. Besides this, the sand filters at the outflow prevent suspended particles to be discharged from the pond.

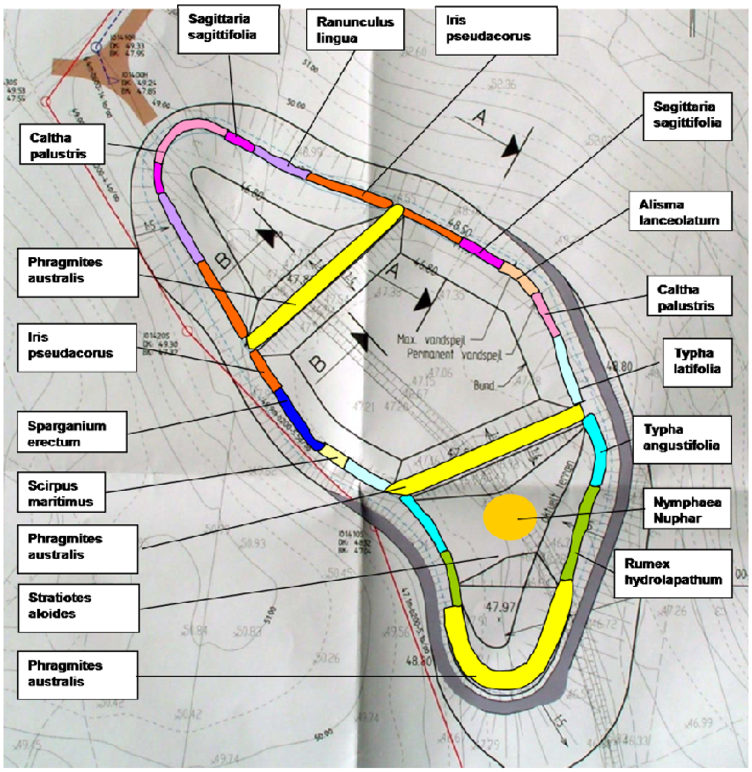


**Figure 16: A scheme of the planting plan in the wet detention pond at Silkeborg (Source: LIFE Treasure documentation).**

The wet detention pond was planted with specific plants to improve the physical appearance and enhance the removal of pollutants. About 3,700 plants were planted along the edges and along the baffles in the basin. The plant species selected for the site included *Caltha palustris, Sagittaria sagittifolia, Ranunculus lingua, Iris pseaudacorus, Alisma lanceolatum, Typha latifolia, Typha angustifolia, Rumex hydrolapathum, Phragmites australis, Stratiotes* *aloides, Scirpus maritimus, Sparganium erectum, and Nymphaea alba/Nuphar luteum* (Figure 16).

## 3.2 Sampling and analyses

### 3.2.1 Classical wet detention ponds

The sampling at the four classical wet detention ponds was carried out in the second half of 2008. Water was sampled in four campaigns, while sediment and plant samples were sampled in one campaign.

#### 3.2.1.1 Water

Grab water samples were taken at the inlet and outlet of each pond. Acid washed 1.5 L plastic bottles were used. Samples were transported, kept and analyzed following standard methods (APHA, 2005). Water samples were analyzed for suspended solids, ammonia, nitrite and nitrate nitrogen, orthophosphate, total phosphorous and metals.

Metals (Na, Ca, Fe, Zn, Cd, Ni, Cr and Cu) were measured by inductive coupled plasma – optical emission spectrometry ICP-OES. Prior measurement the samples were filtrated and 1 mL of HCl (1:1) was added to each 100 mL of a sample.

Besides stated parameters, also PAHs were analysed. In this study, the 16 PAH compounds that have been identified and selected as priority pollutants by U.S. EPA were monitored. Samples for PAHs were taken at the inlet, middle and outlet of each pond using 2 L acid washed glass bottles. After sampling, the samples were immediately transported to the laboratory where liquid-liquid extraction of PAHs with dichloromethane was carried out. In order to avoid contamination with PAHs from plastic materials the samples for PAHs analyses must be handled only by glass material. All glass material used for extraction and analyse of PAHs (amber vials, evaporatory flasks, glass Pasteur pipettes) was muffled for at least 4 hours at 400 °C before use to assure needed cleanliness.

Liquid-liquid extraction was carried out from 200 mL of the sample with 20 mL of dichloromethane. Prior the extraction 25 µL surrogates (napthalene-d8, (99%), anthracene-d10 (98%), pyrene-d10 (98%) and benzo(a)pyrene-d12 (98%)) were added to the samples. Extracts were filtered through sodium sulphate in order to remove surplus water. Sodium sulphate was activated at 400 °C for 4 hours and maintained activated at 100 °C until use. The extraction procedure was repeated three times with each sample. Samples were then concentrated using nitrogen gas to 1 mL, placed in an amber glass vial and concentrate further to 0.25 mL. Internal standard was added to concentrated samples which were then stored at -18 °C until use on gas chromatography-mass spectrometry GC-MS (Zhimadzu GC 2010). Internal standard represented a PAH mixture containing naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene at 10 mg/l in cyclohexane (from Dr. Ehrenstorfer, Augsburg, Germany).

#### 3.2.1.2 Sediment

Sediment samples for nutrient and metal analyses were taken from all the wet ponds by drilling cores. In the ponds A, C and D cores were taken along the water flow and in pond B in six transversal transects. Water depth was measured at each sampling site and GPS coordinates were taken. In each core, sediment layers were measured and separated as individual samples. Sediment samples were analyzed for water content, phosphorous, iron, manganese, calcium, sodium, potassium, aluminium, lead, zinc, cadmium, nickel, chromium, and copper.

In order to analyze metals in the sediment, samples were dried at 105 °C until constant weight. Dried samples were ground in a mortar and dried once again. Approximately 250 mg of material was digested using 4 ml $HNO_3$ (69% v/v) and 2 ml $H_2O_2$ in a microwave oven (Anton Paar, Multiwave 3000) for one hour. After digestion, samples were diluted to 50 mL and analyzed for metals by inductive coupled plasma – optical emission spectrometry (ICP-OES).

Sediments from the four ponds were sampled to analyse PAHs. Three samples from inlet, middle and outlet were sampled with an aluminium grader. Samples were wrapped in an aluminium foil and transported to the laboratory, where they were immediately subdued to freeze-drying. PAHs were extracted from approximately 2 g of freeze-dried sample using dichloromethane. Prior the extraction surrogates were added to the samples as described at water PAH analyses. Solid-liquid extraction was carried out using ultrasonic bath (15 min) followed by centrifugation (5,000 rpm for 10 min). The supernatant was removed through sodium sulphate filter as described at water PAHs analyses. The extraction procedure was repeated three times with each sample. Samples were then concentrated using nitrogen gas to a bit more than 1 mL. 1 mL of the sample was filtrated through deactivated alumina in order to remove colour. Aluminium oxide used for the filter was activated at 400 °C for 4 hours and maintained activated at 100 °C until use. Before filtering the sample, 2 mL of dichloromethane was passed through the filter. After filtering the sample, filter was eluted with 12 mL of ethyl acetate. Samples were then concentrated using nitrogen gas to 1 mL, placed in an amber glass vial and concentrate further to 0.25 mL. Internal standard as described at water PAHs analyses was added to concentrated samples which were then stored in a freezer until use on GC-MS.

#### 3.2.1.3 Plants

Plants were sampled at the inlet, middle and outlet of each pond and analyzed for P, Fe, Mn, Ca, Na, K, Al, Pb, Zn, Cd, Ni, Cr and Cu. At each sampling site, three individuals of the most representative species of emergent, floating and submerged macrophyte species were sampled. Bigger plants were separated into plant tissues in order to evaluate the content of metals in different plant parts. Plant samples were transferred to the laboratory in plastic bags and immediately washed under tab water, cut into small pieces and dried at 80 °C to constant weight. Dried samples were milled and dried again. Approximately 250 mg of dried material was digested with nitric acid in a microwave and analysed by ICP-OES as described in chapter 3.2.1.2.

### 3.2.2 Upgraded wet detention ponds

#### 3.2.2.1 Water

Besides grab water samples at the inflow, middle and outflow of each pond, the sampling program also included continuous flow measurements and flow or time proportional sampling. Parameters measured continuously include inlet and outlet flow, water level, water pH, temperature, dissolved oxygen, and water turbidity. Flow or time proportional sampling was carried out by automatic samplers installed at the inflow and outflow and after the sand filters of each pond. The following parameters were measured: total suspended solids, total nitrogen, orthophosphate, total phosphorous, oil and fat, volatile suspended solids, chloride, alkalinity, chemical oxygen demand, Fe, Al, Pb, Cd, Cr, Cu, Hg, Ni, Zn and PAHs.

Water quality parameters were measured according to Standard methods (APHA, 2005). Heavy metals and PAHs were analyzed as described in chapter 3.2.1.1.

#### 3.2.2.2 Sediment

Sediment samples were taken in three transects (inlet, middle and outlet) in each pond with an aluminium grader in autumn 2008 and summer 2009. Samples were collected in plastic cups and analyzed for organic content and metals (phosphorous, iron, manganese, calcium, sodium, potassium, aluminium, lead, zinc, cadmium, nickel, chromium, and copper) as described in chapter 3.2.1.2. Sediment was sampled also for PAH analyzes. These samples were collected in aluminium foil and analyzed as described in Chapter 3.2.1.2.

#### 3.2.2.3 Plants

All plant species were sampled according to the planting plan at each site in summer 2009. If possible, three replicates were taken for each species. Bigger plants were separated into plant tissues in order to evaluate the content of metals in different plant parts. Plant samples were analyzed for P, Fe, Mn, Ca, Na, K, Al, Pb, Zn, Cd, Ni, Cr and Cu as described in Chapter 3.2.1.3.

### 3.2.3 Statistical analyzes

Data were tested for variance homogeneity (Levene's test) and transformed by logarithm or square root when necessary. Differences in levels by different factors were identified by analyzes of variance (ANOVA). Bonfferoni test was used to identify the significant difference between the levels at the 5% probability level. The software program Statgraphics Plus 4.1 (StatPoint, Inc., USA) was used.

In the four classical wet detention ponds the differences in sediment nutrient and metal concentration between the ponds, between different locations in each pond (inlet, middle, and outlet) and between different sediment depth layers were identified by one-way ANOVA.

The differences in nutrient and metal concentrations in the sediment between the three upgraded wet detention ponds, between the locations in the ponds and between the two sampling years were identified by one-way ANOVA.

The differences in ∑PAH concentrations between the three upgraded wet detention ponds and between the locations in each pond were identified by one way-ANOVA.

One-way ANOVA analyzes was used also to compare nutrient and metal concentrations in different plant tissues, whole plants and sediment in all investigated ponds.

# 4 RESULTS

## 4.1 Water

### 4.1.1 General water quality parameters

#### 4.1.1.1 General water quality in classical wet detention ponds

Results of water quality analyzes are presented in Table 7. In general, during our study inflow concentrations of measured parameters were similar between the ponds and do not show differences due to different land use in the catchments. All investigated ponds were efficient in reduction of TSS and total P. Inflow TSS concentrations were similar in ponds A, B and C, while in the pond D they show greater variability due to two different inflows into the pond. Outflow TSS concentrations were similar in ponds B, C and D, (from 2.5±1.5 to 4.0±1.5 mg $L^{-1}$) but higher in pond A (13±4 mg $L^{-1}$). Inflow and outflow total P concentrations were similar in all the wet ponds, around 0.2 and 0.05 mg $L^{-1}$ for inflow and outflow, respectively. Removal of $PO_4$-P and $NH_4$-N was not evident in any of the ponds except for removal of $NH_4$-N in pond B where $NH_4$-N was reduced from 0.35±0.14 mg $L^{-1}$ at the inflow to 0.09±0.008 mg $L^{-1}$ at the outflow. Nitrite and nitrate concentrations in the four systems were consistently low and close to the detection limit.

**Table 7: Average water quality parameters in mg $L^{-1}$ (± 1 standard deviation) in samples from the classical stormwater treatment ponds (n = 4 for inlets and 3 for outlets).**

| | Pond A | | Pond B | | Pond C | | Pond D | |
|---|---|---|---|---|---|---|---|---|
| Parameter | Inflow | Outflow | Inflow | Outflow | Inflow | Outflow | Inflow | Outflow |
| TSS | 33±8 | 13±4 | 27±17 | 3.3±0.1 | 32±21 | 4.0±2.5 | 35±79 | 2.5±1.5 |
| $PO_4$-P | 0.020±0.004 | 0.02±0.01 | 0.05±0.02 | 0.03±0.02 | 0.11±0.10 | 0.01±0.01 | 0.03±0.03 | 0.02±0.01 |
| Tot P | 0.22±0.07 | 0.09±0.05 | 0.18±0.10 | 0.039±0.003 | 0.24±0.10 | 0.044±0.001 | 0.18±0.16 | 0.06±0.01 |
| $NH_4$-N | 0.35±0.15 | 0.18±0.06 | 0.35±0.14 | 0.09±0.01 | 0.28±0.16 | 0.14±0.05 | 0.59±0.79 | 0.23±0.07 |
| Na | 11±3 | 12±2 | 11±4 | 9.7±0.5 | 9.8±3.8 | 9.2±0.8 | 8.0±2.4 | 7.6±0.4 |
| Ca | 50±13 | 66±9 | 30±10 | 31±4 | 27±11 | 36±5 | 42±19 | 48±6 |
| Fe | 0.15±0.04 | 0.14±0.03 | 0.17±0.04 | 0.16±0.02 | 0.15±0.06 | 0.14±0.06 | 0.25±0.08 | 0.20±0.02 |

#### 4.1.1.2 General water quality in upgraded wet detention ponds

Results of water quality analyses at the inlet, pond water, after sand filter and in Odense also after sorption filter are given in Table 8. The results show that the water quality in the three ponds is as expected for urban stormwater runoff. All ponds showed efficient removal of TSS – the inflow concentrations were significantly higher compared to the basin concentrations in the ponds at Århus and Odense. TSS concentrations did not differ significantly between the basin water and samples taken after the sand filter; however, the sorption filter in Odense showed significant reduction of TSS compared to the basin water and the outflow from the sand filter. Total nitrogen and phosphorous concentrations and COD decreased through all three ponds. The reduction took place in the pond water and in most cases, there was no marked difference between the pond water and the outflow from the sand filters. Removal of ortho-P was observed in the Århus and Odense systems. The removal of ortho-P was significant for the basin and the sorption filter.

**Table 8: Average water quality parameters in mg $L^{-1}$ (± 1 standard deviation) in samples from the stormwater treatment systems in Århus (n = 21 or 22), Silkeborg (n = 13 or 14) and Odense (n = 22 to 29). Different superscript letters within rows for a system indicate significant differences at the 5% probability level.**

| | | TSS | TN | ortho-P | TP | Oils/fats | COD | Al | Fe |
|---|---|---|---|---|---|---|---|---|---|
| Århus | Inflow | $53±37^{b}$ | $2.3±1.1^{b}$ | $0.13±0.12^{b}$ | $0.28±0.16^{b}$ | 1.3±0.78 | $101±50^{b}$ | - | $1.7±1.1^{b}$ |
| | Basin | $8.3±6.6^{a}$ | $0.83±0.42^{a}$ | $0.01±0.02^{a}$ | $0.07±0.07^{a}$ | 0.90±1.3 | $57±38^{ab}$ | - | $0.26±0.23^{a}$ |
| | Outlet | $5.1±3.0^{a}$ | $0.68±0.26^{a}$ | $0.02±0.02^{a}$ | $0.14±0.10^{a}$ | 0.16±0.17 | $26±13^{a}$ | - | $1.47±0.88^{a}$ |
| Silkeborg | Inflow | 37±33 | $2.4±3.0^{b}$ | 0.10±0.27 | 0.22±0.36 | <0.10 | - | $785±802^{b}$ | - |
| | Basin | 5.3±4.5 | $1.6±1.6^{b}$ | 0.00±0.00 | 0.03±0.01 | 0.98±0.50 | $45±1.2^{b}$ | $148±143^{a}$ | - |
| | Outlet | 1.9±2.1 | $0.48±0.21^{a}$ | 0.01±0.01 | 0.02±0.01 | 0.14±0.20 | $8.8±0.58^{a}$ | $268±294^{a}$ | - |
| Odense | Inflow | $48±43^{c}$ | 3.2±1.7 | $0.13±0.16^{c}$ | 0.31±0.22 | $1.7±1.4^{c}$ | $42±6.1^{b}$ | - | - |
| | Basin | $17±9.9^{b}$ | 2.2±0.74 | $0.04±0.06^{b}$ | 0.15±0.08 | $0.31±0.35^{b}$ | $22±5.0^{a}$ | - | - |
| | After sand filter | $15±17^{b}$ | 1.3±0.83 | $0.04±0.05^{b}$ | 0.18±0.17 | $0.17±0.15^{ab}$ | $15±10^{a}$ | - | - |
| | After sorption filter | $4.0±4.1^{a}$ | 1.1±1.6 | $0.01±0.01^{a}$ | 0.03±0.02 | $0.13±0.15^{a}$ | $10±6.3^{a}$ | - | - |

The efficiencies in removal of pollutants in the three systems before and after the application of the additional technologies are compared in Table 9. In the Odense pond, the additional technology in the form of adsorption filters was in operation since the beginning of the pond operation. Hence, the efficiency shown in Table 9 is the efficiency of the pond and sand filters, while the efficiency after the additional technology represents the performance of whole system including the adsorption filters. In Århus, the average removal efficiency of all pollutants (except oils and fats) increased after the application of iron salts to the pond bottom. The highest difference on average removal efficiency before and after the addition of iron salts was observed for TP (30±57% and 63±17%, respectively). This increase is probably largely caused by removal of organic P and orthophosphate. The latter had higher and more consistent removal efficiency after the addition of iron salts. In Silkeborg, the addition of aluminium salts at the inflow increased the removal efficiency of TSS, while there was no marked difference in removal of TN and TP, and a decrease in the efficiency of ortho-P removal. No change in the efficiencies of TN and TP removal and a decrease in ortho-P removal can be misleading, since the concentrations of these pollutants were very low, e.g. the concentration of ortho-P at the inflow was only 7±7 μg $L^{-1}$ and at the outflow 6±6 μg $L^{-1}$ during the time of aluminium salts addition. The system at Odense shows higher average removal efficiencies for all investigated pollutants when the sorption filters were included in the system; however, the variation was still high. Comparing the three additional technologies, the system at Silkeborg with the addition of aluminium salts had the highest removal of TSS and the system at Odense with sorption filters had the highest removal of TP. The removal of TN was similar in all three systems, while the efficiency in ortho-P removal is hard to compare because of the low inflow concentrations to the Silkeborg pond.

**Table 9: Efficiencies in pollutants removal before and after application of additional treatment technologies at the stormwater treatment systems at Århus, Silkeborg and Odense.**

| System | TSS | | TN | | Ortho-P | | TP | | Oil/fats | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Before | After | Before | After | Before | After | Before | After | Before | After |
| Århus | 85±11% | 90±7% | 69±15% | 70±13% | 72±38% | 86±8% | 30±57% | 63±17% | 88±10% | 87±12% |
| Silkeborg | 85±11% | 99±1% | 76±10% | 71±4% | 58±47 | -93±260% | 80±20% | 80±17% | - | - |
| Odense | 43±53% | 73±72% | 62±19% | 70±40% | 51±95% | 69±34% | 8±108 | 91±6% | 85±17 | 90±13% |

Inflow to the three systems in L $s^{-1}$ is shown in Figures 17, 18 and 19. The inflow water was sampled during 22 precipitation events at Århus, 14 at Silkeborg and 29 at Odense through all monitoring period. The precipitation was more intense and frequent during summer months; especially summer in 2008 was a rather wet period. It is known that the intensity and period of stormwater runoff and intermediate dry periods affects the quality of inflow water. However, due to oceanic climate, there are no longer dry periods and less build up of sediments in drainage system. Therefore, the difference in inflow concentrations of water quality parameters in general did not differ markedly between wetter and dryer parts of the year. The exemption was turbidity, which was higher during summer months.

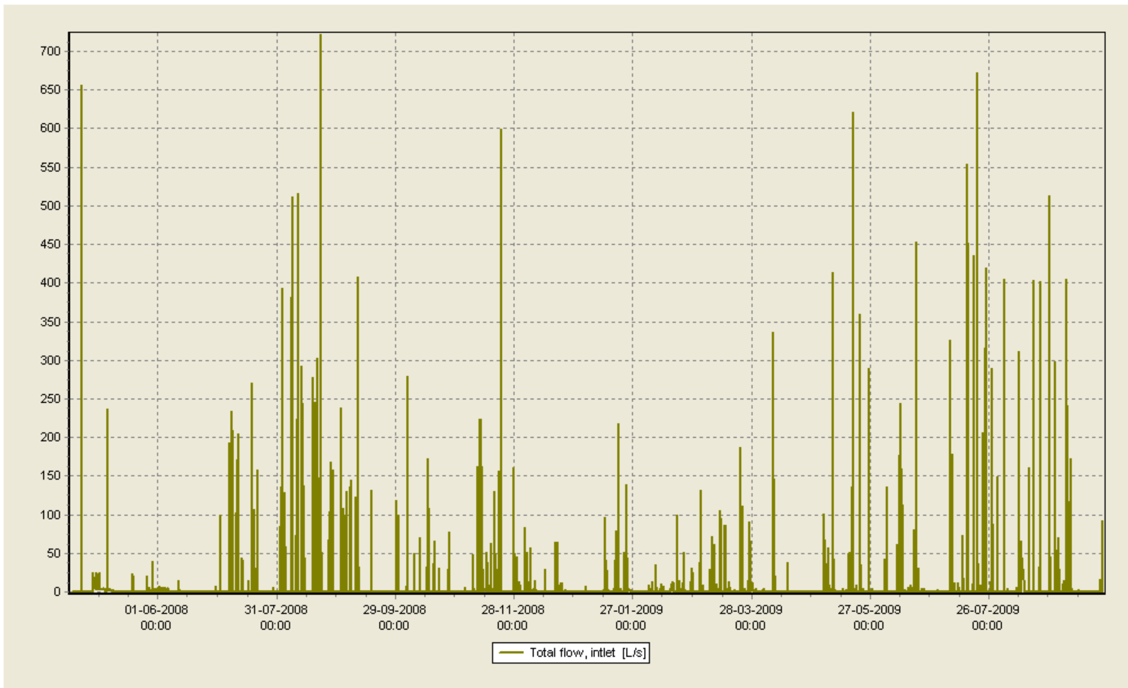


**Figure 17: Flow into the facility at Århus (Source: LIFE TREASURE, Final report).**

The pH, temperature, dissolved oxygen concentration and turbidity were measured on line in all three investigated ponds. The probes were installed on the supporting structure in the pond approximately half a meter below water surface and measured the parameters every minute. The monthly averages and standard deviation of the measurements of turbidity, pH, temperature and dissolved oxygen in Århus, Odense and Silkeborg are presented in Figures 20, 21 and 22, respectively. In the pond at Odense on the 1st July 2009, the support for measuring probes had tilted and the probes were dug into the sediment. The support and probes were put back on place and to function at the end of August. The data from this period are therefore not reliable. From Figure 21 a major drop in pH and dissolved oxygen can be seen in these months.

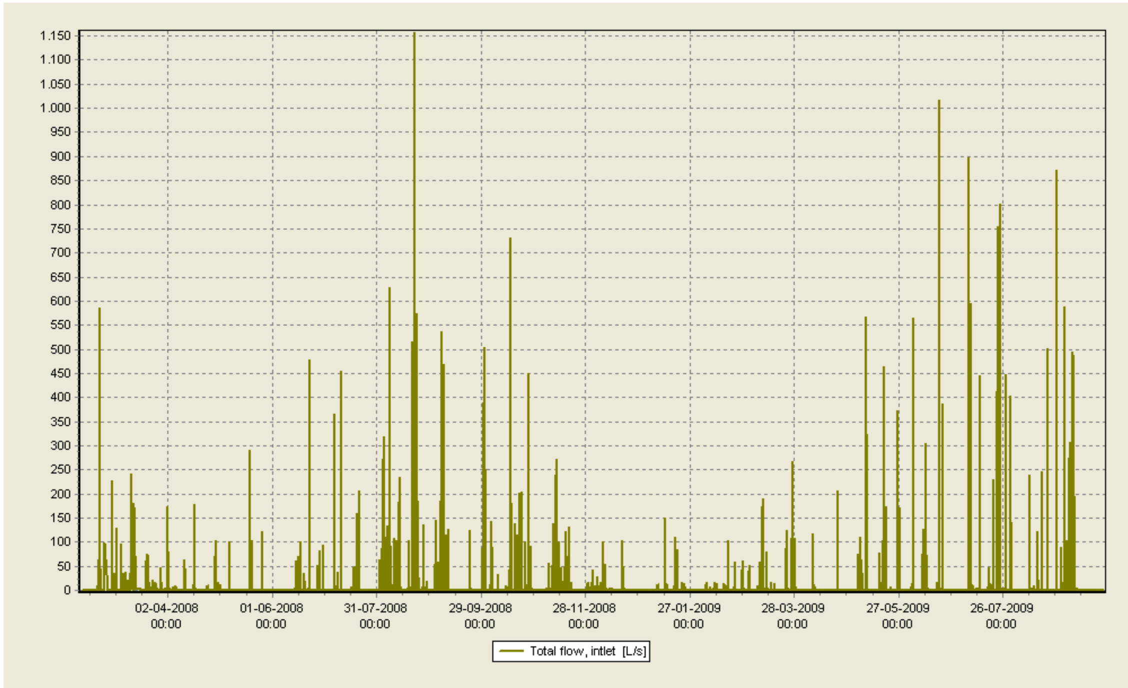


**Figure 18: Flow into the facility at Odense (Source: LIFE TREASURE, Final report).**

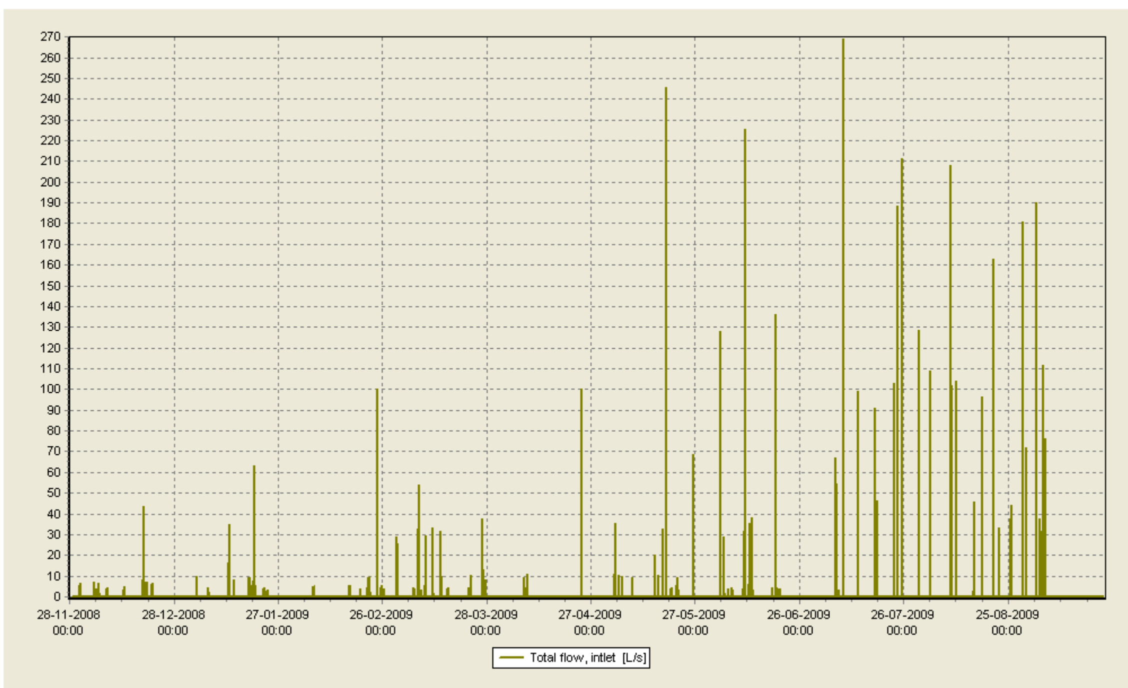


**Figure 19: Flow into the facility at Silkeborg (Source: LIFE TREASURE, Final report).**

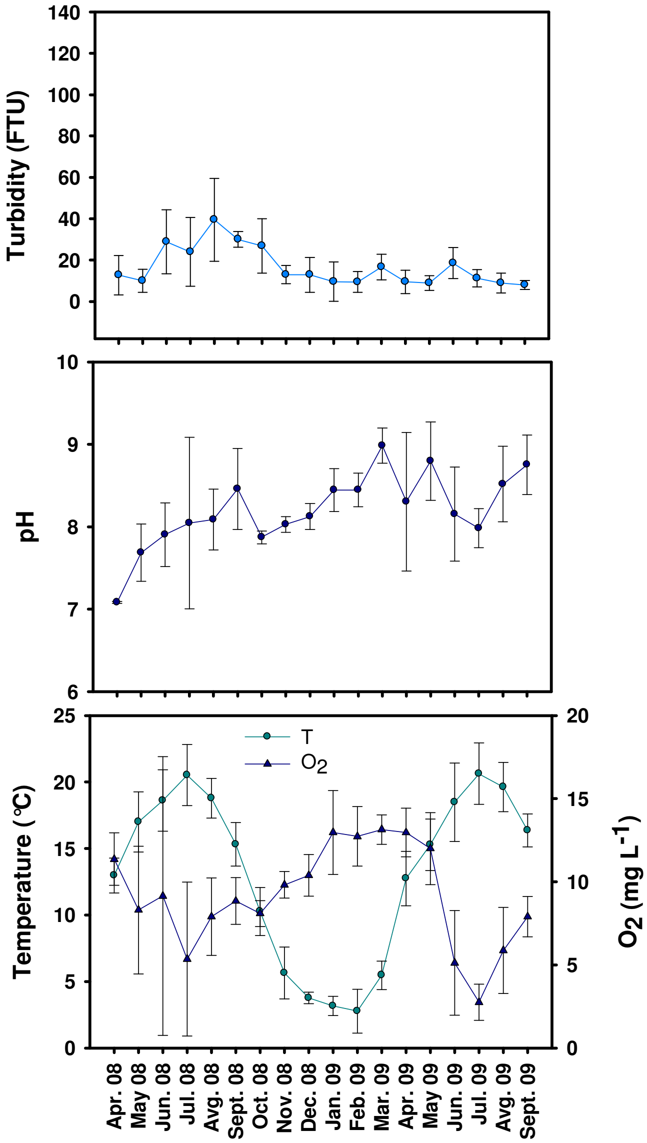


**Figure 20: Turbidity, pH, temperature and dissolved oxygen concentration in the pond water in the stormwater treatment system at Århus. Monthly averages and standard deviations are given.**

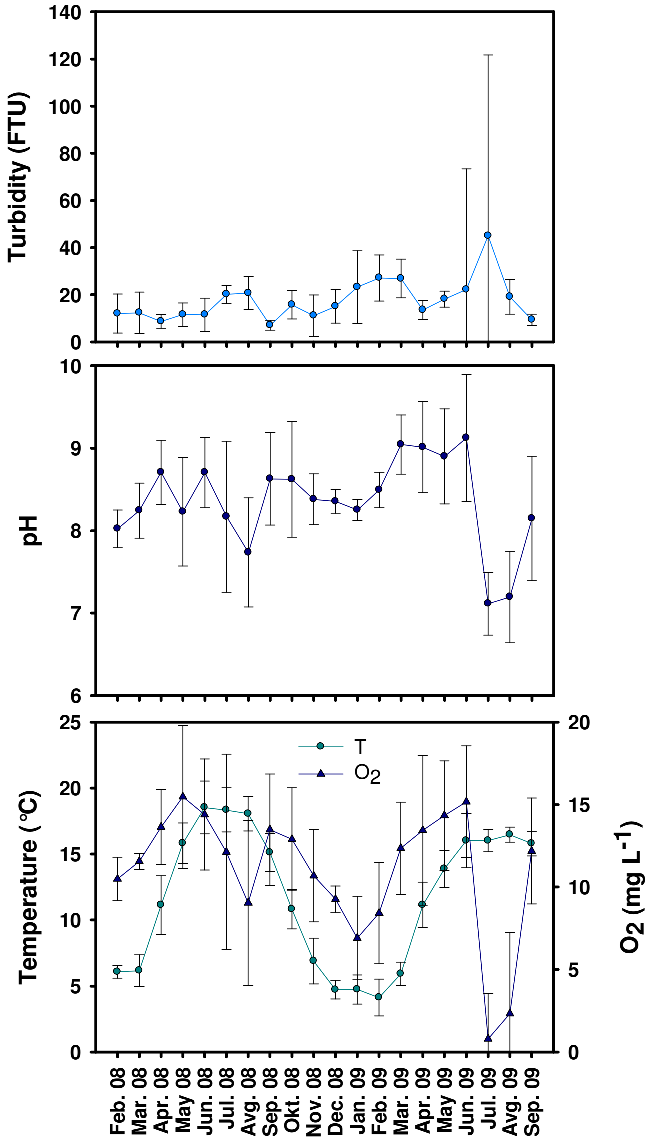


**Figure 21: Turbidity, pH, temperature and dissolved oxygen concentration in the pond water in the stormwater treatment system at Odense. Monthly averages and standard deviations are given.**

Monthly average pH varied more in the warm half of the year, while in winter months the day-night oscillations were lower in all investigated ponds. In Odense pond, average pH values were always higher than 8, except in August 2008 and the two months in 2009 when the probes were dug into the sediment. In Århus and Silkeborg, the pH was lower in the first few months of operation (below 8) and increased afterwards (above 8). The addition of iron and aluminium salts to Århus and Silkeborg ponds, respectively, did not affect monthly average pH.

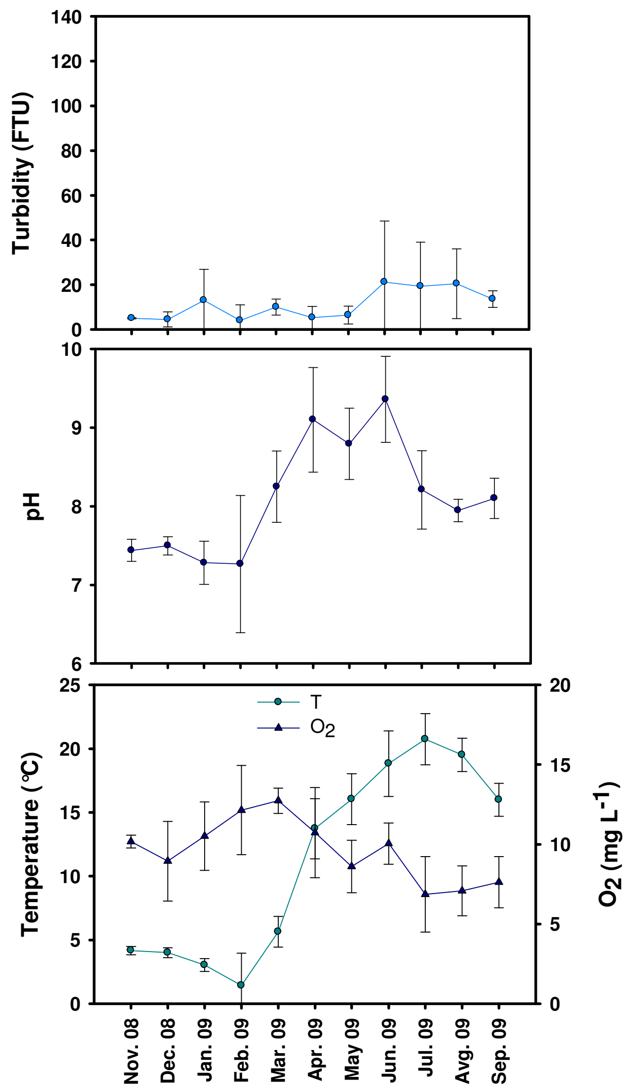


**Figure 22: Turbidity, pH, temperature and dissolved oxygen concentration in the pond water in the stormwater treatment system at Silkeborg. Monthly averages and standard deviations are given.**

Turbidity varied according to stormwater inflow: inflow event caused a rapid increase in turbidity in the ponds. Monthly averages of turbidity show seasonal dynamic with higher turbidity in summer months compared to the winter months in all three investigated ponds. Higher turbidity during summer is caused by more intensive and frequent precipitation in that period, but also higher primary production in the ponds.

Concentration of dissolved oxygen showed seasonal dynamic with lower concentrations and higher variability during summer and higher concentrations and lower variability during winter, which was evident for the ponds in Århus and Silkeborg. This is due to oxygen concentration in pond water is inversely proportioned to the water temperature; however it is also correlated with algal photosynthetic activity and wind velocity (mixing), which were not measured. In Århus the lowest concentrations were measured in July in both years, namely 5.3±4.6 and 2.8±1.1 mg $L^{-1}$ for 2008 and 2009, respectively. High standard deviation in July 2008 indicates a high diurnal variation in oxygen concentration, caused by intensive primary production. In 2009, the addition of iron salts to the sediment decreased primary production in the pond, resulting in lower variation in oxygen concentrations. In Odense, pond average oxygen concentrations in the summer months were higher compared to Århus and Silkeborg, and show a decrease in winter months. As mentioned before the results from July and August 2009 should not be evaluated.

### 4.1.2 Heavy metals in water

#### 4.1.2.1 Heavy metals in the water of classical wet detention ponds

Results of heavy metal analyze in the inflow and outflow water of four classical wet detention ponds are shown in Table 10. Pond C received higher Zn concentrations compared to the other three ponds indicating different catchment characteristics. Ni was below detection limit in ponds A and B and Cr in ponds B and C. Cd concentrations in pond A and at the inflow of pond B were higher than US EPA criteria 0.25 µg $L^{-1}$ (Appendix B). Increase in Cd concentrations was detected through the pond A and a reduction of Cd in pond B. Inflow Cu concentrations were similar in all investigated ponds. Average outflow Cu concentration was lower compared to inflow concentration in all ponds except in pond A.

**Table 10: Average heavy metals concentrations in μg $L^{-1}$ (± 1 standard deviation) in samples from the classical stormwater treatment ponds (n = 4 for inlets and 3 for outlets).**

| | Pond A | | Pond B | | Pond C | | Pond D | |
|---|---|---|---|---|---|---|---|---|
| Parameter | Inflow | Outflow | Inflow | Outflow | Inflow | Outflow | Inflow | Outflow |
| Zn | 48±41 | 33±9 | 40±22 | 21±13 | 116±93 | 38±22 | 51±49 | 22±19 |
| Cd | 0.62±1.19 | 1.62±0.85 | 0.52±0.99 | 0.16±0.23 | <0.05 | <0.05 | 0.06±0.10 | <0.05 |
| Ni | <1.0 | <1.0 | <1.0 | <1.0 | 1.2±1.4 | <1.0 | <1.0 | 1.2±1.2 |
| Cr | 0.90±1.29 | 2.0±1.5 | <0.50 | <0.50 | <0.50 | <0.50 | 0.76±1.49 | <0.50 |
| Cu | 3.7±4.0 | 3.7±3.0 | 3.1±2.0 | 1.28±0.25 | 2.9±2.8 | 1.3±1.5 | 4.2±6.1 | 1.02±0.89 |

#### 4.1.2.2 Heavy metals in the water of upgraded wet detention ponds

Results of heavy metal analyses in inflow, pond and outflow water in the systems at Århus, Silkeborg and Odense are presented in Table 11. Average and standard deviation for complete monitoring period are given. Inflow of dissolved heavy metal concentrations varied between the ponds, with Odense pond receiving higher concentrations of Pb, Cu, Ni and Zn. Average copper inlet concentrations were 451, 19 and 15 mg $L^{-1}$, and zinc 433, 181 and 114 mg $L^{-1}$ for Odense, Århus and Silkeborg, respectively. Inflow of Ni concentration in Odense's pond is around three times higher if compared to the other two ponds. There was a reduction of Pb, Cd, Cr, Cu and Zn through all the systems. In all the systems, concentrations in the pond water were lower compared to the inlet, indicating that most of the metal reduction occurs in the open water part of the system. There was no reduction of Pb, Cd, Cr and Cu through the sand filters at Århus and Silkeborg systems, possibly due to already low heavy metal concentrations in the pond water. However, sand filters in all three systems showed marked reduction of Zn. Hg concentrations were consistent through the ponds at all sites. Ni concentrations varied greatly: in Århus pond, Ni concentration was higher in bulk water and in Silkeborg at the outflow.

A comparison in removal efficiencies before and after the application of additional treatment technologies is shown in Table 12. Addition of iron salts to the bottom of Århus pond did not increase the removal of heavy metals: all calculated average removal efficiencies were lower after the iron addition except the removal of Cu and Zn, which increased slightly. In contrast to that, in Silkeborg average removal efficiencies for majority of heavy metals raised after the addition of aluminium salts at the inflow. Application of sorption filters to the system at

Odense increased the removal of Cu, while the average removal efficiencies of other heavy metals remained in the same range. Heavy metal removal efficiency in Odense pond was in general higher than in the other two ponds.

**Table 11: Average heavy metals concentrations in µg $L^{-1}$ (± 1 standard deviation) in samples from the stormwater treatment systems in Århus (n = 25), Silkeborg (n = 13 or 14) and Odense (n = 22 to 29). Different superscript letters within rows for a system indicate significant differences at the 5% probability level.**

| | Århus | | | Silkeborg | | | Odense | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Inflow | Basin | Outlet | Inflow | Basin | Outlet | Inflow | Basin | After sand filter | After sorption filter |
| Pb | 4.7±2.9 | 0.88±0.83 | 0.39±0.44 | 5.4±4.0$^{c}$ | 2.4±1.4$^{b}$ | 0.84±0.82$^{a}$ | 24±28 | 6.7±4.6 | 0.44±0.31 | 0.57±1.21 |
| Cd | 0.07±0.05 | 0.03±0.02 | 0.04±0.03 | 0.07±0.06 | 0.03±0.00 | 0.03±0.01 | 0.11±0.07$^{b}$ | 0.06±0.04$^{a}$ | 0.05±0.03$^{a}$ | 0.04±0.03$^{a}$ |
| Cr | 4.3±2.6$^{b}$ | 0.67±0.56$^{a}$ | 0.74±2.14$^{a}$ | 2.6±2.1$^{b}$ | 0.70±0.59$^{a}$ | 1.0±0.8$^{a}$ | 5.5±3.7$^{c}$ | 1.2±0.88$^{b}$ | 0.47±0.27$^{a}$ | 0.52±0.48$^{a}$ |
| Cu | 19±11$^{c}$ | 5.8±5.5$^{b}$ | 2.1±2.7$^{a}$ | 15±6$^{b}$ | 8.0±8.1$^{a}$ | 4.3±4.5$^{a}$ | 451±757 | 197±213 | 25±20 | 4.3±6.7 |
| Hg | 0.21±0.81 | 0.04±0.03 | 0.09±0.15 | 1.3±4.4 | 0.07±0.07 | 0.03±0.01 | 0.09±0.19$^{a}$ | 0.05±0.08$^{a}$ | 0.06±0.11$^{a}$ | 0.05±0.06$^{a}$ |
| Ni | 6.8±5.2$^{a}$ | 31±21$^{b}$ | 8.5±10.4$^{a}$ | 10±5 | 2.1±1.9 | 60±86 | 28±39 | 12±12 | 5.5±3.8 | 5.1±8.2 |
| Zn | 181±77 | 71±50 | 16±15 | 114±27 | 79±48 | 21±14 | 433±488$^{c}$ | 268±317$^{c}$ | 28±36$^{b}$ | 4.7±4.2$^{a}$ |

**Table 12: Heavy metal removal efficiency before and after application of additional treatment technologies at the stormwater treatment systems at Århus, Silkeborg and Odense pond.**

| | | Århus | Silkeborg | Odense |
|---|---|---|---|---|
| Pb | Before | 92±5% | 78±15% | 94±6% |
| | After | 80±22% | 85±16% | 94±8% |
| Cd | Before | 34±63% | 40±39% | 29±69% |
| | After | -60±228% | 31±36% | 26±96% |
| Cr | Before | 89±7% | -9±99% | 83±14% |
| | After | 65±75% | 77±18% | 82±24% |
| Cu | Before | 62±124% | 63±31% | 79±22% |
| | After | 68±62% | 83±12% | 95±8% |
| Hg | Before | -62±231% | 26±38% | -38±116% |
| | After | -188±455% | 53±43% | -22±112% |
| Ni | Before | -219±563% | -596±696% | 43±49% |
| | After | -114±250% | -385±382% | -21±355% |
| Zn | Before | 90±8% | 83±14% | 92±8 |
| | After | 92±7% | 79±1679% | 97±5% |

### 4.1.3 Polycyclic aromatic hydrocarbons in water

#### 4.1.3.1 PAHs in water samples from classical wet detention ponds

In classical wet detention ponds inflow, middle and outflow water for PAH analyses was sampled in one sampling campaign, hence we have no measurement of variability in concentration levels, and the analytical results only show concentrations at the time of sampling. The results are shown in Table 13. The LMW naphthalene and phenanthrene and four-ringed pyrene were detected in higher concentrations compared to other PAHs in all ponds, while other lightweight PAHs were below detection limit. The four-ringed benzo(a)anthracene and five-ringed chrysene, benzo(b)fluoranthene and dibenzo(a,h)anthracene were below detection limit in all samples. The ∑PAHs varied between 30 and 119 ng $L^{-1}$ but concentrations did not decrease consistently from inlet to outlet.

**Table 13: PAHs concentrations (ng $L^{-1}$) in the water at different locations in the four classical wet detention ponds.**

| | Pond A | | | Pond B | | | Pond C | | | Pond D | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | In | Mid | Out | In | Mid | Out | In | Mid | Out | In | Mid | Out |
| Naphthalene | 22 | 12 | 16 | <10 | 16 | 11 | 10 | <10 | <10 | 37 | 14 | 13 |
| Acenaphthylene | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Acenaphthene | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Fluorene | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Phenanthrene | 16 | 22 | 36 | <10 | 13 | 15 | <10 | <10 | <10 | 22 | 80 | 19 |
| Anthracene | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Fluoranthene | <10 | <10 | 15 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Pyrene | 22 | 19 | 23 | 15 | <10 | <10 | 14 | <10 | 11 | 20 | 15 | <10 |
| Benzo(a)anthracene | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Chrysene/triphenylene | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Benzo(b)fluoranthene | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Benzo(k)fluoranthene | <10 | <10 | <10 | <10 | 10 | <10 | 19 | <10 | <10 | <10 | <10 | <10 |
| Benzo(a)pyrene | <10 | <10 | <10 | 13 | <10 | <10 | 23 | <10 | <10 | <10 | <10 | <10 |
| Indeno(1,2,3-cd)pyrene | 20 | <10 | <10 | 13 | 12 | 12 | 18 | 13 | 13 | <10 | <10 | <10 |
| Dibenzo(a,h)anthracene | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Benzo(g,h,i)perylene | 19 | <10 | 18 | <10 | <10 | <10 | <10 | 12 | <10 | <10 | <10 | <10 |
| ∑PAH (16EPA) | 115 | 68 | 116 | 63 | 53 | 48 | 101 | 58 | 30 | 96 | 119 | 31 |

#### 4.1.3.2 Upgraded wet detention ponds

In upgraded wet detention ponds, inflow, pond water, outflow water after sand filter and in Odense also after the sorption filter were sampled. The results are shown in Table 14.

**Table 14: Average (±1 standard deviation) PAHs concentrations (ng $L^{-1}$) in the water at different locations in the wet detention ponds at Århus, Silkeborg and Odense.**

| | Århus | | | Silkeborg | | | Odense | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Inflow (n=16) | Pond (n=23) | Sand filter (n=19) | Inflow (n=4) | Pond (n=13) | Sand filter (n=11) | Inflow (n=17) | Pond (n=25) | Sand filter (n=20) | Sorption filter (n=18) |
| Naphthalene | <10 | <10 | <10 | <10 | 14±15 | <10 | <10 | <10 | <10 | <10 |
| Acenaphthylene | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Acenaphthene | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Fluorene | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Phenanthrene | 16±23 | <10 | <10 | 10±11 | <10 | <10 | 16±35 | <10 | <10 | <10 |
| Anthracene | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Fluoranthene | 25±39 | <10 | <10 | 11±13 | <10 | <10 | 28±53 | <10 | <10 | <10 |
| Pyrene | 31±56 | <10 | <10 | 14±13 | <10 | <10 | 37±75 | <10 | <10 | <10 |
| Benz(a)anthracene | <10 | <10 | <10 | <10 | <10 | <10 | 14±19 | <10 | <10 | <10 |
| Chrysene/triphenylene | 17±48 | <10 | <10 | <10 | <10 | <10 | 23±50 | <10 | <10 | <10 |
| Benz(b+j+k)fluoranthene | 48±91 | <10 | <10 | <10 | <10 | <10 | 43±88 | <10 | <10 | <10 |
| Benzo(a)pyrene | 15±29 | <10 | <10 | <10 | <10 | <10 | 17±27 | <10 | <10 | <10 |
| Indeno(1,2,3-cd)pyrene | 13±34 | <10 | <10 | 13±26 | <10 | <10 | 21±34 | <10 | <10 | <10 |
| Dibenzo(a,h)anthracene | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Benzo(g,h,i)perylene | 44±56 | <10 | <10 | <10 | <10 | <10 | 17±102 | <10 | <10 | <10 |
| ∑PAH (16EPA) | 179±403 | <10 | <10 | <10 | 16±43 | <10 | 358±479 | <10 | <10 | <10 |

In the wet detention ponds at Århus, Odense and Silkeborg, average PAHs concentrations were above detection limit only in the water sampled at the inflow, except in Silkeborg, where average naphthalene concentration was above the detection limit in water from the middle pond. In the outflow from the systems (after the sand and/or sorption filters) as well as in the pond water itself, the average PAHs concentrations were below the detection limits. The heavy molecular weight (4-6 ring) PAHs prevailed in the inflows; however a three-ringed phenanthrene was also above the detection limit. Based on raw data, all 16 PAHs were detected in concentrations above the detection limit at least at one sampling date in the systems at Århus and Odense, while at Silkeborg 11 PAHs had concentrations higher than the detection limits. The high standard deviations of the measured PAH concentrations indicate that PAH concentrations in the stormwater, as expected, fluctuate greatly. The highest diversity in PAH species and PAH concentrations were found in the Århus system, which receives stormwater mainly from residential areas. The system at Odense, which receives runoff from an industrial area, had higher average ∑PAH concentrations, while PAH levels were low in the Silkeborg system.

## 4.2 Sediment

The sediment cores taken in the four traditional wet detention ponds varied in stratification and layers' depths. In pond A, ten sediment cores were taken along the water flow as presented in Figure 23. Stratification in an upper organic layer, a sand layer and a clay layer in the bottom was not evident in any of the samples, except one. In contrast, pond B showed distinctive layers in most cases. The top layer was a dark, decomposing, loosely structured mostly organic material, the second layer had a sandy appearance and the third layer was the sealing clay. In pond B, 31 samples were taken in six transects which are shown in Figure 23. The stratification was most evident in the first two transects, where all the cores were clearly stratified into three layers. In the fourth and fifth transect only 60% of samples were stratified and in the last transect only a quarter. Cores from the second half of the pond were stratified mostly in a sand layer and clay – no organic layer was present. The thickness of the organic layer decreased through the pond, from approximately 5 cm at the inlet to 2 cm in the third transect. In pond C, five sediment cores were taken (Figure 23); they were stratified into a sand layer and a clay layer; no evident organic layer was presented. In pond D, ten cores were taken (Figure 23), five of them were stratified into an organic and a sand layer. Organic matter was also present in some of the unstratified cores in a mixture with sand.

The water content was measured in the soil samples. In most samples with stratified layers, the organic layer had a higher water content compared to the sand and the clay layer, as expected. In pond B, the organic layer contained on average 70% of water, and the sand and clay layers only 20%. The difference was not so apparent in pond D, where the organic layer on average contained 40% of water and the sand layer 30%. In some samples in pond D, the organic matter and sand were mixed.

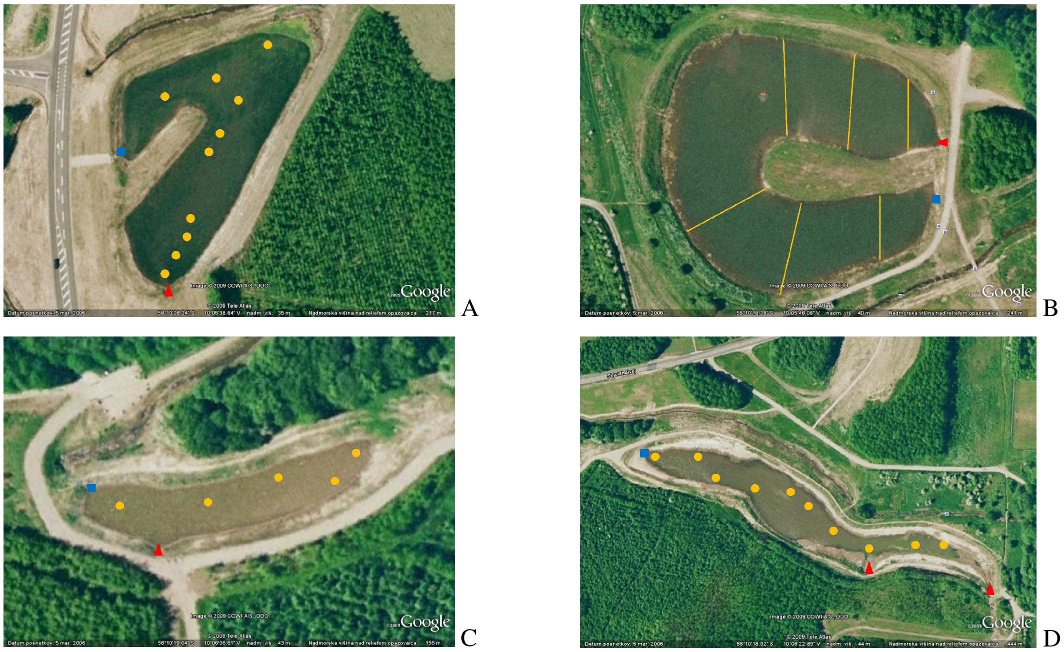


**Figure 23: Sediment sampling sites (marked with orange dots) in four classical detention ponds. Inlets are marked with red triangles and outlets with blue squares (Google Earth, 2010).**

In the three upgraded wet detention ponds, sediment was mostly not clearly stratified, therefore sediment was sampled with aluminium grader and no layers were investigated. Sediments were sampled in transects through the ponds. At each transect three samples were taken. Besides nutrients, metals and PAHs, the organic content was also analyzed (Table 15). There were no significant differences in organic content through the ponds at Århus and Odense, while in Silkeborg there was a significant decrease from the inlet to the outlet.

**Table 15: Organic content (%) in the sediments at wet detention ponds at Århus, Odense and Silkeborg. Average and standard deviation are given.**

| Location | Århus | Odense | Silkeborg |
|---|---|---|---|
| in | 7.9±3.9 | 18±10 | 9.1±4.2[c] |
| mid | 8.5±2.8 | 12±2.5 | 2.1±0.7[b] |
| out | 6.9±2.1 | 8.9±2.8 | 0.9±0.3[a] |

### 4.2.1 Nutrients and metals

#### 4.2.1.1 Nutrients and metals in the sediment of classical wet detention ponds

The results of the sediment nutrient and metal analyses indicate that nutrients and metals are present in different concentrations, decreasing in the following order: Ca>Fe>Al>K>P>Mn>Na for macroelements and Zn>Cr>Ni>Cu>Pb>Cd for heavy metals, respectively (Table 16 and Table 17). There were no significant differences in macroelements and heavy metal concentrations in the sediment between the ponds. A comparison of measured concentrations with the concentrations in the sediments of natural wetlands showed that the concentrations in the investigated stormwater ponds were higher than the ones reported for natural wetland (Mays and Edwards, 2001) (Table 16 and Table 17) for all metals except Pb.

**Table 16: Average macroelement concentrations in mg $g^{-1}$ DW (± 1 standard deviation) in sediment samples from the four classical wet detention ponds and sediment of natural wetlands (NAT) reported by Mays and Edwards (2001).**

| System | P | Fe | Mn | Ca | Na | K | Al |
|---|---|---|---|---|---|---|---|
| A (n=11) | 0.83±0.26 | 12±5 | 0.31±0.18 | 51±44 | 0.05±0.07 | 2.8±1.6 | 12±5 |
| B (n=60) | 0.98±0.43 | 13±6 | 0.34±0.18 | 43±38 | 0.20±0.29 | 3.0±1.3 | 11±5 |
| C (n=9) | 0.76±0.27 | 11±3 | 0.18±0.06 | 41±23 | 0.10 ±0.12 | 3.4±1.2 | 9.4±3.8 |
| D (n=15) | 0.46±0.38 | 9.7±2.3 | 0.25±0.12 | 36±17 | 0.14±0.06 | 2.5±0.8 | 8.2±2.2 |
| NAT* | - | 0.37 | 0.056 | - | - | - | 0.233 |

*Data for natural wetland reported by Mays and Edwards, 2001

Average Na concentration was lower in pond A compared to the other ponds, but the difference was not significant. Pond B had higher Pb, Zn and Cu concentrations. Average Pb concentration in pond B was 5.1±10.9 µg $g^{-1}$ DW, while in ponds A and D the concentrations were 1.3±2.6 and 2.2±3.9 µg $g^{-1}$ DW, respectively. Pb was below the detection limit in pond C. The average Zn concentration was three-times higher in pond B compared to ponds A and C and two-times higher compared to pond D. In addition, Cu concentration in pond B was two to three-times higher compared to the other ponds; however, as mentioned, these differences were not significant. In our study, despite that it was detected in water, Cd was not detected in any of the investigated sediment samples. Heavy metal concentrations in the investigated ponds were generally below the values reported to be typical for unpolluted sediments (Kadlec and Knight, 1996) (Table 17) with an exception of Zn concentration in pond B, which is three-times higher.

**Table 17: Average heavy metal concentrations in µg $g^{-1}$ DW (± 1 standard deviation) in soil samples from the four classical wet detention ponds, sediment of natural wetlands (NAT) reported by Mays and Edwards (2001) and unpolluted sediment (u.s.) reported by Kadlec and Knight (1996).**

| System | Pb | Zn | Cd | Ni | Cr | Cu |
|---|---|---|---|---|---|---|
| A (n=11) | 1.3±2.6 | 53±29 | <2.3 | 12±5 | 18±7 | 9.2±5.5 |
| B (n=60) | 5.1±10.9 | 150±214 | <2.3 | 12±5 | 22±11 | 19±27 |
| C (n=9) | <0.5 | 47±28 | <2.3 | 11±3 | 18±5 | 6.2±2.5 |
| D (n=15) | 2.2±3.9 | 72±73 | <2.3 | 12±4 | 17±7 | 9.9±8.8 |
| NAT* | 2.1 | 2.9 | - | 0.73 | 0.53 | 1.13 |
| u.s.** | 4-40 | 23-50 | 0.1-2.0 | 2-23 | 7-71 | 4-20 |

*Data for natural wetland reported by Mays and Edwards, 2001
**Unpolluted sediment (Kadlec and Knight, 1996)

In the sediment cores with clear stratification, the highest concentrations of heavy metals were detected in the top layers, as expected. The top layer (layer a) was usually rich in organic material; however, in some cases it was sandy. Layer a had the highest water content (on average 53%), followed by layer b with 23% and layer c with 16%. Nutrients and metals concentrations in the sediment layers and the core samples (when not stratified) are presented in Table 18. Analysis of variance showed significantly higher P concentration in layer a compared to layer b and core samples. Fe, Mn, Ca, K and Al concentrations were similar between the layers, while Na concentration was again significantly higher in layer a. Average Pb concentration was approximately ten-times higher in layer a compared to layer b, but the difference was not significant. Lead was not detected in layer c and in non-stratified samples. Also average concentrations of other heavy metals were higher in layer a (e.g. Zn concentration was approximately nine-times higher compared to layer b and c) but the difference was significant only for Ni.

**Table 18: Average nutrient and metal concentrations (± 1 standard deviation) in sediment layers (a, b, c) and core samples (when not stratified) from four classical wet detention ponds.**

| Layer | P | Fe | Mn | Ca | Na | K | Al | Pb | Zn | Ni | Cr | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | mg $g^{-1}$ DW | | | | | | | µg $g^{-1}$ DW | | | | |
| a (n=32) | 1.2±0.5[b] | 13±5 | 0.37±0.18 | 37±19 | 0.27±0.33[b] | 3.2±1.3 | 13±5 | 10±13 | 270±240 | 14±5[b] | 26±11 | 34±32 |
| b (n=32) | 0.74±0.15[a] | 12±6 | 0.27±0.19 | 44±41 | 0.06±0.08[a] | 2.8±1.2 | 12±6 | <0.5 | 34±10 | 11±4[ab] | 17±7 | 5.6±2.3 |
| c (n=7) | 0.82±0.10[ab] | 11±4 | 0.31±0.17 | 52±57 | 0.11±0.18[ab] | 2.5±1.4 | 10±6 | <0.5 | 29±12 | 10±5[ab] | 15±7 | 5±4 |
| core (n=24) | 0.82±0.25[a] | 12±4 | 0.29±0.12 | 44±35 | 0.06±0.07[a] | 2.9±1.2 | 12±4 | <0.5 | 42±18 | 12±4[a] | 18±6 | 7±3 |

Macronutrients concentrations in individual layers of ponds B, C and D are presented in Figure 24. Only one core was stratified in pond A, therefore results cannot be presented this way. In ponds B and D average P, Fe, Mn, Na, K, Al concentrations were higher in layer a compared to layers b and c, but concentrations of Ca were higher in layers b and c, due to the sandy nature of these layers. In contrast, in pond C the concentrations of all macronutrients were higher in layer b (Figure 24).

Figure 25 presents average heavy metal concentrations for the individual sediment layers in ponds B, C and D. Accumulation of heavy metals in the top sediment layer was most evident in ponds B and D, while in pond C average Ni, Cr and Cu concentrations are higher in layer b. For pond B analyses of variance showed significantly higher concentrations of Ni and Cr in layer a compared to layers b and c. The data for Pb, Zn and Cu were not distributed normally; therefore, ANOVA was not carried out.

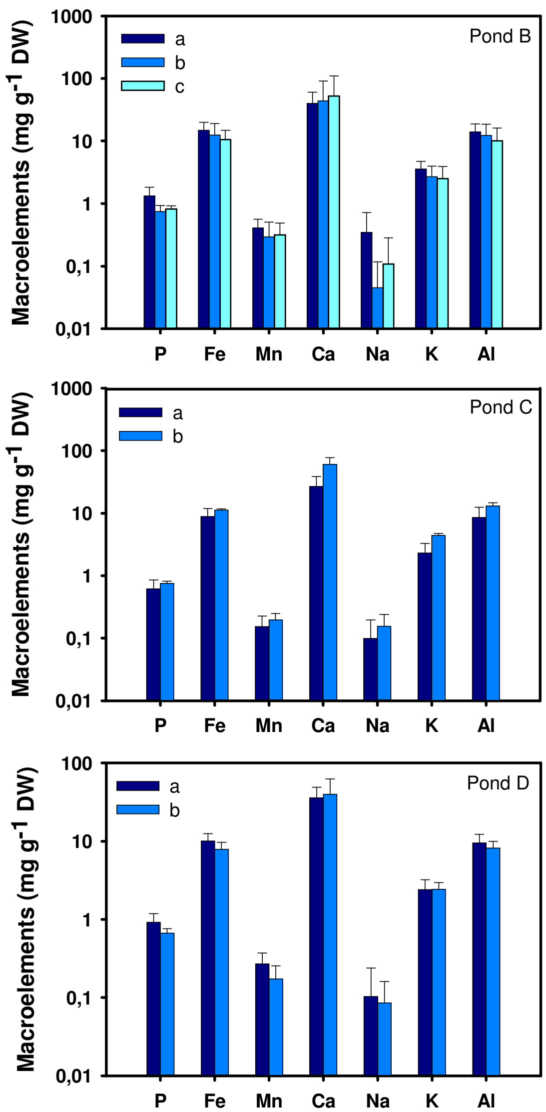


**Figure 24: Average macroelement concentrations in different soil layers (referred as a, b and c) in classical wet detention ponds B, C and D.**

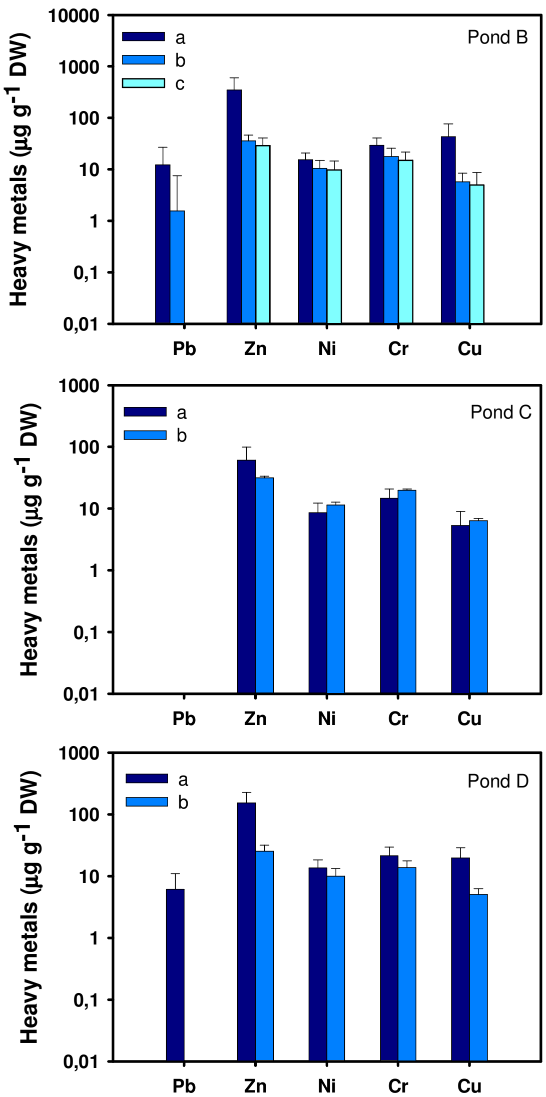


**Figure 25: Average heavy metal concentrations in different soil layers (referred as a, b and c) in classical wet detention ponds B, C and D.**

In order to analyze the differences in metal concentration through each pond scatter plots of nutrients and metals concentrations in layer a or core samples (where not stratified) against the distance from the inlet were drawn and regression tests were carried out (Figures from 26 to 33). Results should be interpreted cautiously since the length of the ponds and the water flow differ greatly from pond to pond. Pond D has the longest waterway (approx. 380 m), followed by pond B (approx. 290 m). In pond A, the water way is approx. 180 m long and in pond C 120 m. In pond C, it is hard to estimate the real waterway only by measuring the length from the inlet to outlet, since the inlet and outlet are constructed close to each other creating a large dead volume to the right side of the inlet. In this case, also the dead volume part of the pond was estimated as a water path towards the outlet.

Macroelement concentration did not show a significant linear relationship with the distance from the inlet in ponds C and D (Figure 28 and Figure 29). In pond A, there was a significant ($P < 0.05$) increase of Ca through the pond, however the correlation was weak and the coefficient of correlation low. No other significant correlations were detected in pond A (Figure 26).

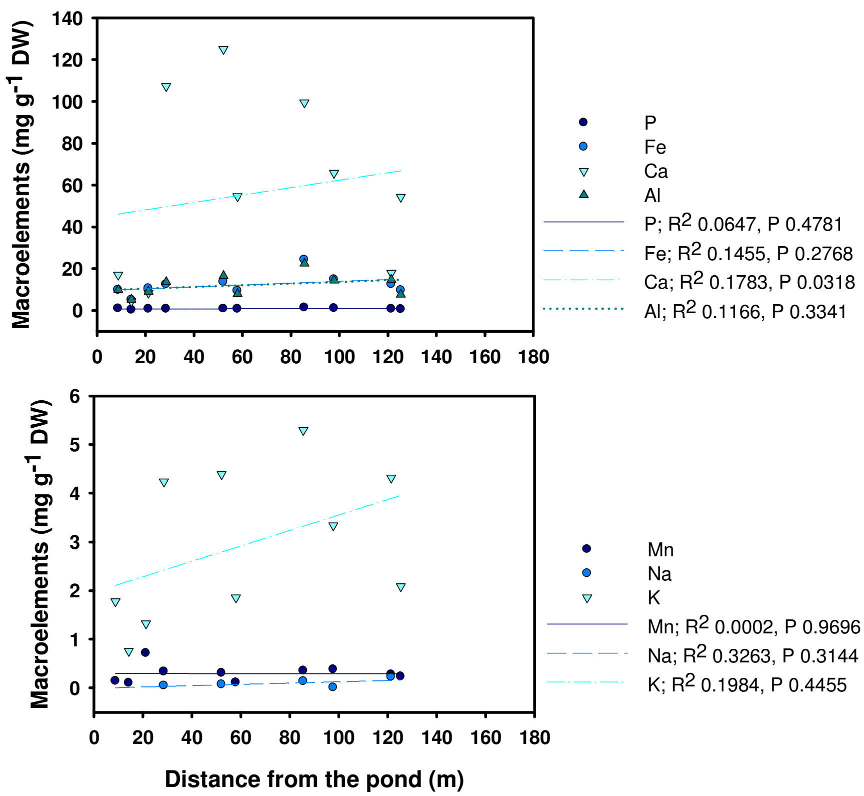


**Figure 26: Changes of P, Fe, Ca, Al (top) and Mn, Na, K (bottom) concentrations through pond A. Linear regression lines with coefficients of determination ($R^2$) and P values are given for each nutrient.**

In pond B (Figure 27), there was a significant ($P < 0.05$) but weak correlation between P concentration in the sediment and the distance from the inlet. P concentration decreased from 1.7 mg $g^{-1}$ DW at the first 30 m of the pond to 0.7 mg $g^{-1}$ DW at a distance of 200 m from the inlet. Ca concentrations decreased through the pond, but the variation between the samples remained large. Na concentrations decreased from 0.30 at the inlet to 0.10 at the outlet, showing a very weak but significant correlation.

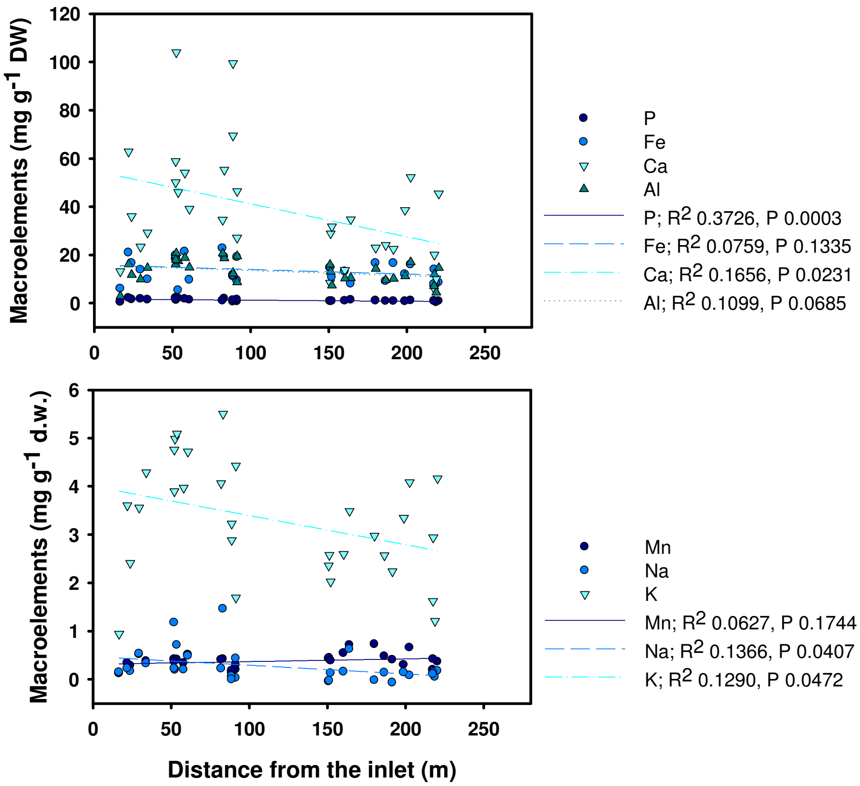


**Figure 27: Changes of P, Fe, Ca, Al (top) and Mn, Na, K (bottom) concentrations through pond B. Linear regression lines with coefficients of determination ($R^2$) and P values are given for each nutrient.**

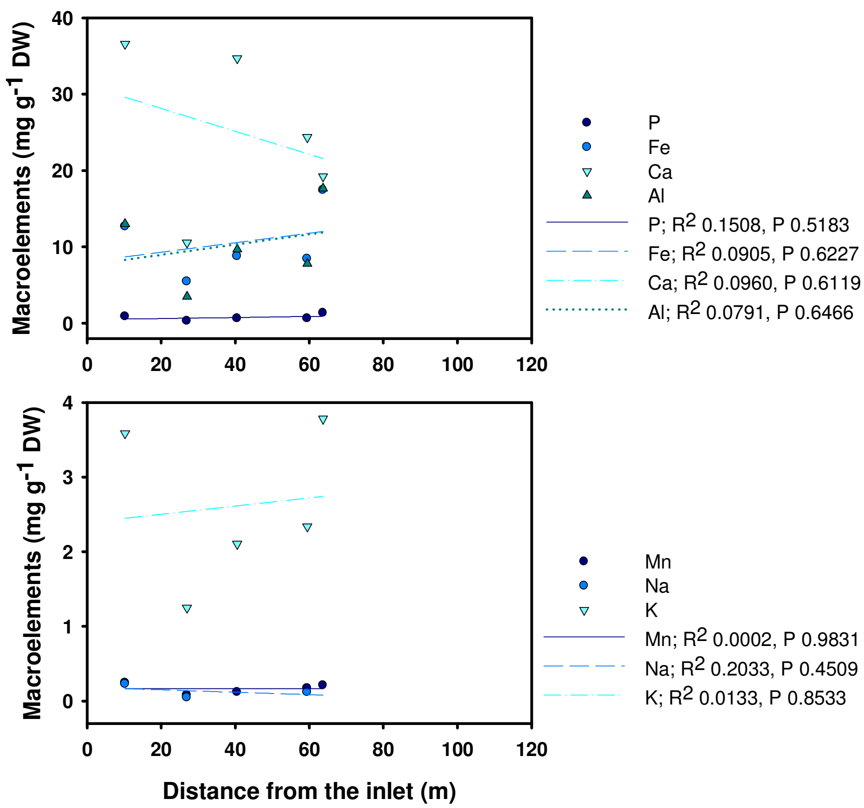


**Figure 28: Changes of P, Fe, Ca, Al (top) and Mn, Na, K (bottom) concentrations through pond C. Linear regression lines with coefficients of determination ($R^2$) and P values are given for each nutrient.**

There was no significant linear relationship between heavy metal concentration and the distance from the inlet in any of the investigated ponds, except in pond B (Figures from 30 to 33). However, some different patterns of heavy metal distribution between the investigated ponds can be seen. In pond A, there was a higher Zn, Cr, Ni and Cu concentration at a distance of 80 to 100 m from the inlet in the part where the pond is shaped as a meander. In pond A, Pb was detected only in one sample, therefore regression test for Pb could not be carried out.

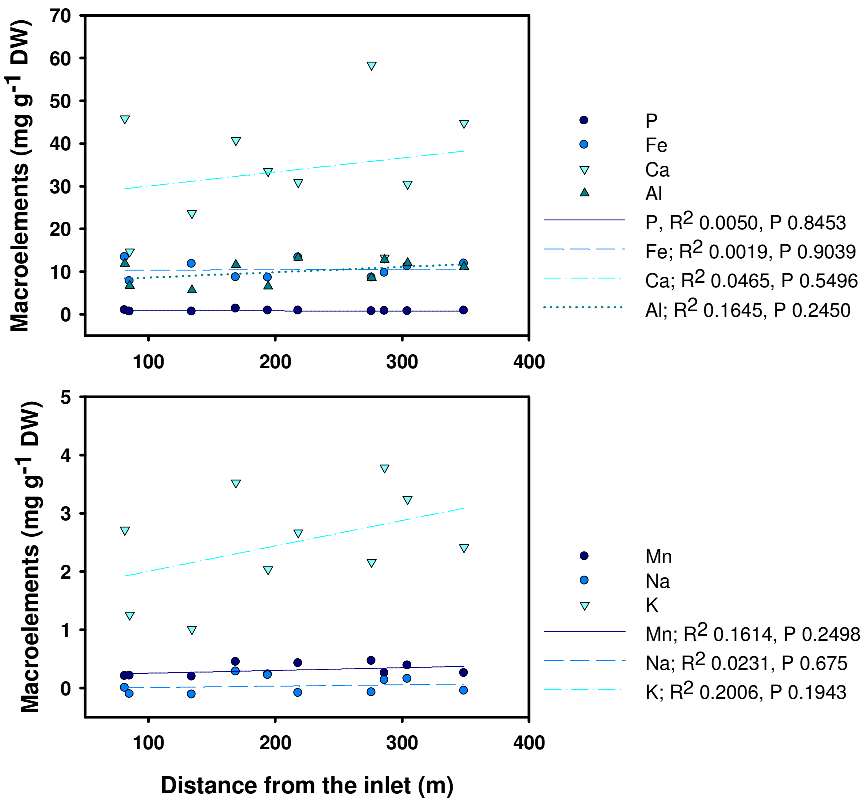


**Figure 29: Changes of P, Fe, Ca, Al (top) and Mn, Na, K (bottom) concentrations through pond D. Linear regression lines with coefficients of determination ($R^2$) and P values are given for each nutrient.**

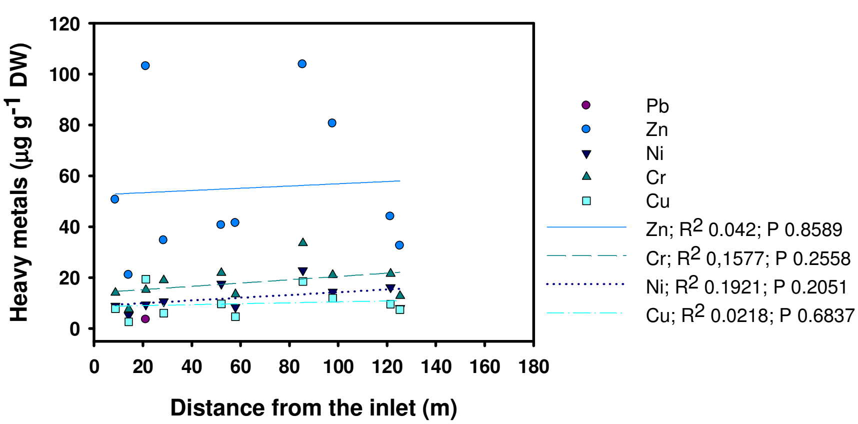


**Figure 30: Changes of heavy metals' concentrations through pond A. Linear regression lines with coefficients of determination ($R^2$) and P values are given for each metal.**

In pond B there was a significant decrease in heavy metal concentration in the sediment through the pond (Figure 31). A regression was highly significant for Zn and Cu ($P < 0.0001$). Concentrations decreased from approximately 600 and 75 µg $g^{-1}$ DW at the first 30 m, to 35 and 5 µg $g^{-1}$ DW at a distance of 200 m from the inlet, for Zn and Cu, respectively. Reduction of Cr and Ni was also significant ($P < 0.05$), but the correlation was weaker. The concentrations decreased from 35 and 20 µg $g^{-1}$ DW at 30 m to 15 and 10 at 200 m, for Cr and Ni, respectively. Pb was detected only in the first half of the pond.

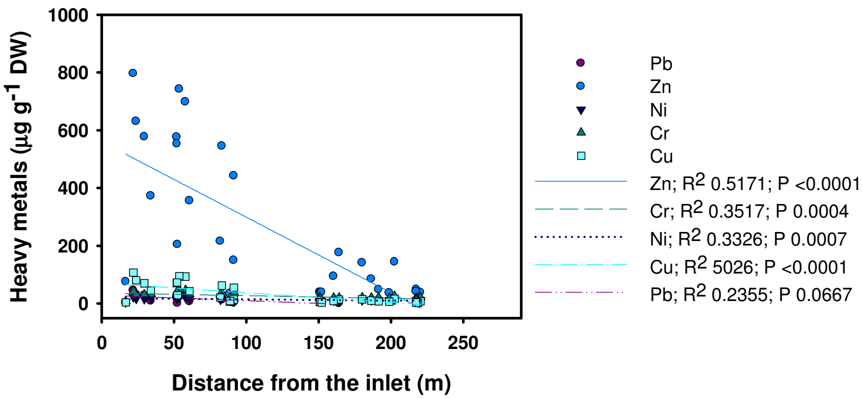


**Figure 31: Changes of heavy metals' concentrations through pond B. Linear regression lines with coefficients of determination ($R^2$) and P values are given for each metal.**

As mentioned, pond C was designed with a large dead volume to the right from the inflow. Samples with a greater distance from the inlet therefore also have a greater distance from the outlet. A regression test in this case is of less relevance since only a smaller part of water goes through the »dead edge« of the pond. As seen from Figure 32, sample nearest to the inlet (and outlet) has higher metal concentrations compared to the other samples, but no significant regressions were detected.

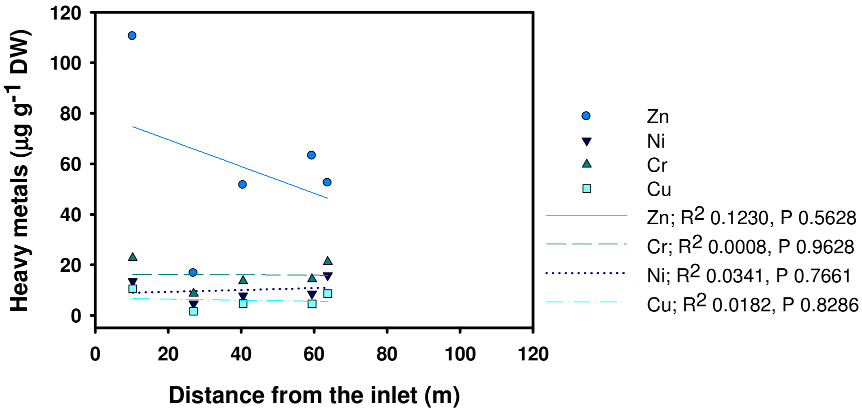


**Figure 32: Changes of heavy metals' concentrations through pond C. Linear regression lines with coefficients of determination ($R^2$) and P values are given for each metal.**

Also in pond D there was no significant reduction in heavy metal concentrations in layer a and core sediment samples through the pond although a negative trend for Zn concentration can be seen (Figure 33). Higher Zn, Cu, Pb concentrations were detected in the half of the pond closer to the inlet compared do the half of the pond closer to the outlet.

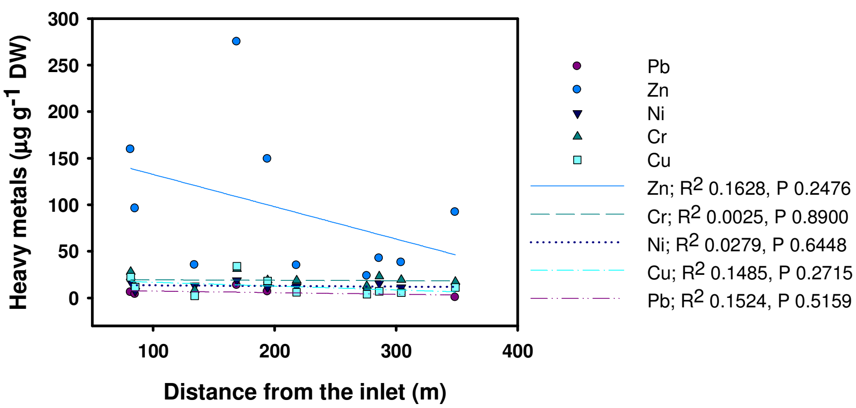


**Figure 33: Changes of heavy metals' concentrations through pond D. Linear regression lines with coefficients of determination ($R^2$) and P values are given for each metal.**

4.2.1.2 Nutrients and metals in the sediment of upgraded wet detention ponds

Concentrations of nutrients and metals in sediments sampled through each pond are shown in Table 19. Averages and standard deviations of nutrients and metals in autumn 2008 and summer 2009 are presented separately for Århus, Odense and Silkeborg in tables 20, 21 and

22 respectively. The sediment in the investigated ponds had higher concentrations of iron, calcium and aluminium compared to the other elements; due to these metals are main constituents of the earth crust.

The results of heavy metal analyses in the sediment show that metals are present in varying concentrations and decrease in the following order Zn>Cu(Cr)>Cr(Cu)>Ni>Pb in Århus and Silkeborg, while the composition of heavy metals in Odense pond is different: Cu>Zn>Pb>Cr>Ni (Table 19). Although, Cd was frequently detected in the water, it was not detected in the sediment in any of the investigated ponds.

**Table 19: Average nutrient and metal concentrations and organic content (O.c.) (± 1 standard deviation) in sediment samples from the stormwater treatment systems at Århus (n = 8 or 9), Odense (n = 5, 6 or 9) and Silkeborg (n = 6 or 9). Different superscript letters within rows for a system indicate significant differences at the 5% probability level.**

| | | Århus | | | Odense | | | Silkeborg | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Unit | Inlet | Middle | Outlet | Inlet | Middle | Outlet | Inlet | Middle | Outlet |
| P | mg g$^{-1}$ DW | 1.5±0.56 | 1.8±0.32 | 1.7±0.38 | 0.09±0.10 | 0.32±0.80 | 0.60±0.53 | 1.7±0.65$^{c}$ | 0.67±0.15$^{b}$ | 0.36±0.11$^{a}$ |
| Fe | mg g$^{-1}$ DW | 18±5.2$^{a}$ | 24±2.8$^{b}$ | 22±4.8$^{ab}$ | 22±1.7$^{a}$ | 28±3.7$^{b}$ | 23±4.0$^{ab}$ | 23±7.1$^{b}$ | 16±2.3$^{b}$ | 10±3.6$^{a}$ |
| Mn | mg g$^{-1}$ DW | 0.41±0.10 | 0.42±0.14 | 0.37±0.06 | 0.41±0.07 | 0.40±0.05 | 0.45±0.16 | 0.78±0.39$^{c}$ | 0.44±0.11$^{b}$ | 0.21±0.06$^{a}$ |
| Ca | mg g$^{-1}$ DW | 38±17 | 44±20 | 35±12 | 32±8.6 | 28±5.0 | 26±1.6 | 7.9±4.2 | 3.8±1.7 | 5.0±3.7 |
| Na | mg g$^{-1}$ DW | 0.39±0.24 | 0.32±0.09 | 0.36±0.16 | 0.47±0.18 | 0.40±0.11 | 0.30±0.06 | 0.52±0.19$^{b}$ | 0.19±0.05$^{a}$ | 0.13±0.06$^{a}$ |
| K | mg g$^{-1}$ DW | 4.1±1.7 | 5.1±1.9 | 4.5±1.5 | 3.4±0.53 | 3.8±0.27 | 3.3±0.42 | 4.5±1.5$^{b}$ | 3.2±0.58$^{ab}$ | 2.2±0.92$^{a}$ |
| Al | mg g$^{-1}$ DW | 21±8.6 | 36±17 | 25±11 | 23±7.8 | 30±9.1 | 24±9.7 | 32±10$^{b}$ | 23±6.3$^{ab}$ | 14±6.0$^{a}$ |
| Pb | μg g$^{-1}$ DW | 10±11 | 10±13 | 6.4±8.5 | 220±88$^{b}$ | 198±92$^{b}$ | 83±38$^{a}$ | 22±12 | <2 | <2 |
| Zn | μg g$^{-1}$ DW | 234±96 | 240±78 | 190±68 | 1361±538$^{b}$ | 1051±372$^{ab}$ | 760±22$^{a}$ | 378±172$^{c}$ | 82±31$^{b}$ | 26±9.5$^{a}$ |
| Ni | μg g$^{-1}$ DW | 19±6.7 | 23±4.2 | 19±4.7 | 42±12$^{b}$ | 31±6.9$^{a}$ | 22±4.7$^{a}$ | 29±10$^{b}$ | 16±2.8$^{a}$ | 10±4.1$^{a}$ |
| Cr | μg g$^{-1}$ DW | 38±17 | 43±14 | 35±11 | 80±34$^{b}$ | 62±20$^{ab}$ | 39±7.3$^{a}$ | 44±16 | 26±4.4 | 17±6.6 |
| Cu | μg g$^{-1}$ DW | 133±202 | 171±263 | 129±171 | 3293±1018$^{b}$ | 3137±1185$^{b}$ | 1625±642$^{a}$ | 45±34$^{b}$ | 6.3±5.8$^{a}$ | 4.4±2.2$^{a}$ |
| O.c. | % of DW | 7.9±3.9 | 8.5±2.8 | 6.9±2.1 | 18.3±10.2 | 11.8±2.5 | 8.9±2.8 | 9.1±4.2$^{c}$ | 2.1±0.7$^{b}$ | 0.9±0.3$^{a}$ |

Comparison of macroelement concentrations between the ponds (Table 19) showed that the pond at Århus had significantly higher P concentration in the sediment compared to Odense and Silkeborg and the pond at Silkeborg has significantly higher P concentration compared to Odense. Sediment at the Silkeborg pond contained significantly lower Fe concentration compared to the other two ponds and significantly lower K concentration compared to the Århus pond. Ca concentrations in the Århus pond were higher, but not statistically significant, compared to Silkeborg and Odense.

Comparing heavy metal accumulation between the ponds (Table 19), the pond at Odense contained markedly higher concentrations of Pb, Zn, Ni, Cr and Cu than the ponds in Århus and Silkeborg. These heavy metals were up to two orders of magnitudes higher in the pond at Odense (Cu between 1,600 and 3,300 µg $g^{-1}$ DW) compared to the other two ponds (Cu from 130 to 170 µg $g^{-1}$ DW in Århus and up to 40 µg $g^{-1}$ DW in Silkeborg). This corresponds to the higher concentrations of heavy metals in the inflow water to the Odense pond. The system at Odense also had higher average organic content in the sediment compared to the sediment from the ponds at Århus and Silkeborg. There was no marked difference in the heavy metal concentrations between Århus and Silkeborg, except Cr, which was higher in the sediment at the Århus pond.

There was usually no significant decrease in macroelements through the ponds at Århus and Odense, however there was a significant decrease in P, Fe, Mn, Na, K and Al along the pond at Silkeborg (Table 19), probably due to perpendicular sand dikes and favourable length to width ratio that enhance sedimentation. The pond at Århus contained significantly higher Fe concentration in the middle of the pond compared to the inlet, which might be the consequence of the addition of iron salts to the middle of the pond.

The concentrations of heavy metals were generally higher in the accumulated sediments at the inlet compared to the sediments at the outlet indicating an effective sedimentation of suspended solids once water comes into the system. In the pond at Silkeborg and Odense average Pb, Zn, Ni, Cr and Cu concentrations were in most cases significantly higher at the inlet. In the pond at Silkeborg Pb was detected only at the inlet (22 µg $g^{-1}$ DW), while in Odense it decreased from 220 to 83 µg $g^{-1}$ DW through the pond. Zn concentration decreased from 378 to 26 µg $g^{-1}$ DW and from 1361 to 760 µg $g^{-1}$ DW and Ni from 29 to 10 µg $g^{-1}$ DW and from 42 to 22 µg $g^{-1}$ DW for Silkeborg and Odense, respectively. Cr concentrations were reduced from 44 to 17 µg $g^{-1}$ DW and 80 to 39 µg $g^{-1}$ DW; Cu concentrations were reduced from 45 to 4 µg $g^{-1}$ DW and 3293 to 1625 µg $g^{-1}$ DW for Silkeborg and Odense, respectively. In the pond at Århus, there was no significant difference on average concentrations of heavy metals through the pond indicating an even distribution of heavy metals in the pond.

A comparison of nutrients and metals concentrations in the sediment in the pond at Århus between the two years of sampling is presented in Table 20. Despite the addition of iron salts in the second year of operation, no significant difference was observed in sediment iron and phosphorous concentrations between these years.

**Table 20: Average nutrients and metals concentrations (± 1 standard deviation) in sediment samples from the stormwater treatment system in Århus at the inlet (In), middle of the pond (Mid) and outlet (Out) in 2008 and 2009.**

| | Unit | IN 2008 (n=3) | IN 2009 (n=6) | MID 2008 (n=6) | MID 2009 (n=3) | OUT 2008 (n=3) | OUT 2009 (n=5) |
|---|---|---|---|---|---|---|---|
| P | mg $g^{-1}$ DW | 1.5±0.2 | 1.5±0.70 | 1.9±0.20 | 1.6±0.48 | 1.5±0.36 | 1.9±0.36 |
| Fe | mg $g^{-1}$ DW | 15±4.6 | 19±5.2 | 24±3.3 | 23±1.6 | 19±5.9 | 24±0.41 |
| Mn | mg $g^{-1}$ DW | 0.37±0.10 | 0.43±0.11 | 0.39±0.03 | 0.48±0.27 | 0.36±0.05 | 0.37±0.09 |
| Ca | mg $g^{-1}$ DW | 39±20 | 38±18 | 56±8.5 | 18±2.2 | 41±13 | 31±4.5 |
| Na | mg $g^{-1}$ DW | 0.29±0.06 | 0.44±0.28 | 0.38±0.06 | 0.22±0.02 | 0.35±0.07 | 0.37±0.01 |
| K | mg $g^{-1}$ DW | 3.7±1.6 | 4.3±1.8 | 6.2±0.96 | 2.8±0.62 | 5.2±1.3 | 4.0±0.17 |
| Al | mg $g^{-1}$ DW | 26±11 | 18±7.0 | 46±7.3 | 15±3.0 | 36±7.9 | 18±1.1 |
| Pb | µg $g^{-1}$ DW | 4.9±5.1 | 13±13 | 3.7±3.0 | 24±17 | 1.8±1.4 | 9.2±10 |
| Zn | µg $g^{-1}$ DW | 173±57 | 264±100 | 207±54 | 306±86 | 160±60 | 208±9.8 |
| Ni | µg $g^{-1}$ DW | 15±4.8 | 21±7.0 | 24±3.4 | 20±4.6 | 19±5.4 | 19±0.59 |
| Cr | µg $g^{-1}$ DW | 34±4.8 | 40±21 | 51±9.3 | 27±2.2 | 40±12 | 33±2.3 |
| Cu | µg $g^{-1}$ DW | 15±2.4 | 192±230 | 30±14 | 453±310 | 18±14 | 195±2.7 |

Phosphorous in the sediment of Århus pond was relatively constant through the pond in both years, ranging from 1.5 to 1.9 mg $g^{-1}$ DW. In addition, Mn concentrations were constant with around 0.37 mg $g^{-1}$ DW in 2008 and slightly higher in 2009. Ca, K and Al concentrations were lower in the second year of operation compared to the first year; however, the difference was statistically significant only for the middle of the pond. Ca concentrations ranged from 39 to 56 mg $g^{-1}$ DW in 2008 and from 18 to 38 mg $g^{-1}$ DW in 2009. K concentrations ranged from 3.7 to 6.2 mg $g^{-1}$ DW and from 2.8 to 4.3 mg $g^{-1}$ DW, for 2008 and 2009 respectively. In the first year of operation Al concentrations ranged from 26 to 46 mg $g^{-1}$ DW (the concentration was significantly higher in the middle of the pond compared to the inlet) while in the second year this difference was not obvious. In 2009, Al concentrations ranged between 15 and 18 mg $g^{-1}$ DW. Na concentrations did not show a consistent difference between the years and locations in the pond; the concentrations ranged from 0.22 to 0.44 mg $g^{-1}$ DW.

Comparison of the first and second year of operation showed a significant increase of Cu concentrations at the inlet, middle and outlet of the Århus pond (Table 20). In the first year concentrations were 15, 30 and 18 µg $g^{-1}$ DW and in the second year 192, 453 and 195 µg $g^{-1}$ DW for inlet, middle and outlet respectively. A significant increase in Cu concentration in the second year was also evident at the inlet in Silkeborg (Table 22), indicating Cu accumulation through time. In the second year of operation Cu concentrations in Århus increased for 10 to 15-times compared to the first year. The increase at the inlet at Silkeborg was lower, namely four-times (from 18 to 72 µg $g^{-1}$ DW). No significant increase was detected for other heavy metals concentrations in either of the ponds. However, the average concentrations were often higher in the second year.

Pb in the sediment in the Århus pond ranged from 1.8 to 4.9 µg $g^{-1}$ DW in the first year and increased to 9.2 to 24 µg $g^{-1}$ DW in the second. An increase in Zn concentration was also evident, however not significant: from 160 to 207 µg $g^{-1}$ DW in the first year, to 208 to 306 µg $g^{-1}$ DW in the second. Average Ni and Cr concentrations did not show consistent differences neither by locations nor by years and ranged from 15 to 24 µg $g^{-1}$ DW and from 33 to 51 µg $g^{-1}$ DW for Ni and Cr respectively.

A comparison of nutrients and metals concentrations in the pond at Odense between the first and the second year of operation (Table 21) shows that Al concentrations were significantly higher in the first year with 30, 36, 32 mg $g^{-1}$ DW, compared to the second year with 17, 19 and 16 mg $g^{-1}$ DW for inlet, middle and outlet respectively. In the first year of operation P concentrations were relatively low, namely from 0.03 in the middle of the pond to 0.19 mg $g^{-1}$ DW at the outlet. In the second year P concentrations were higher and tended to increase through the pond reaching concentrations close to 1.0 mg $g^{-1}$ DW in the middle and outlet, but the difference was not statistically significant. Fe, Ca and K concentrations were consistent in both years and all locations, ranging from 21 to 29, 26 to 36 and 3.3 to 3.8 mg $g^{-1}$ DW for Fe, Ca and K respectively. Mn concentrations were higher in the first year of operation (0.43 to 0.56 mg $g^{-1}$ DW) compared to the second year (0.34 to 0.39 mg $g^{-1}$ DW) but similar in different locations of the pond in both years. Na concentrations were higher in 2008 and decreased along the water flow from 0.59 at the inlet to 0.33 at the outlet while in 2009 the concentrations were lower (from 0.28 to 0.35 mg $g^{-1}$ DW) and consistent through the pond.

**Table 21: Average nutrients and metals concentrations (± 1 standard deviation) in sediment samples from the stormwater treatment system in Odense at the inlet (In), middle of the pond (Mid) and outlet (Out) in 2008 and 2009.**

| | | IN | | MID | | OUT | |
|---|---|---|---|---|---|---|---|
| | Unit | 2008 (n=3) | 2009 (n=3) | 2008 (n=6) | 2009 (n=3) | 2008 (n=3) | 2009 (n=3) |
| P | mg $g^{-1}$ DW | 0.06±0.09 | 0.13±0.11 | 0.03±0.05 | 0.89±1.4 | 0.19±0.26 | 0.87±0.50 |
| Fe | mg $g^{-1}$ DW | 21±2.2 | 23±0.39 | 29±1.0 | 25±6.3 | 23±4.9 | 23±4.5 |
| Mn | mg $g^{-1}$ DW | 0.44±0.03 | 0.39±0.11 | 0.43±0.05 | 0.35±0.03 | 0.56±0.16 | 0.34±0.01 |
| Ca | mg $g^{-1}$ DW | 36±11 | 28±3.2 | 28±5.2 | 29±5.6 | 26±2.3 | 26±1.1 |
| Na | mg $g^{-1}$ DW | 0.59±0.16 | 0.35±0.12 | 0.44±0.10 | 0.31±0.05 | 0.33±0.08 | 0.28±0.02 |
| K | mg $g^{-1}$ DW | 3.5±0.13 | 3.4±0.82 | 3.8±0.32 | 3.8±0.17 | 3.3±0.65 | 3.3±0.11 |
| Al | mg $g^{-1}$ DW | 30±1.7 | 17±3.5 | 36±3.0 | 19±1.2 | 32±6.1 | 16±1.5 |
| Pb | µg $g^{-1}$ DW | 285±63 | 155±52 | 246±65 | 101±45 | 97±53 | 69±15 |
| Zn | µg $g^{-1}$ DW | 1700±409 | 1022±458 | 1168±348 | 815±358 | 865±285 | 654±79 |
| Ni | µg $g^{-1}$ DW | 42±13 | 42±14 | 31±7.0 | 29±8.2 | 20±5.6 | 24±3.7 |
| Cr | µg $g^{-1}$ DW | 98±39 | 64±20 | 70±19 | 45±10 | 41±10 | 37±3.3 |
| Cu | µg $g^{-1}$ DW | 3968±642 | 2619±902 | 3736±805 | 1939±875 | 1835±929 | 1416±195 |

At Odense Pb concentration in the middle of the pond was significantly higher in the first year of operation (246 µg $g^{-1}$ DW) compared to the second year (101 µg $g^{-1}$ DW). Also at the inlet and outlet, Pb concentration was higher in 2008 compared to 2009, but the difference was not significant. Zn concentrations in 2008 ranged between 865 and 1700 µg $g^{-1}$ DW and were lower in 2009, namely from 654 to 1,022 µg $g^{-1}$ DW. Also Cr and Cu concentrations were lower in 2009, but not statistically significantly. Cr ranged from 41 to 98 µg $g^{-1}$ DW and from 37 to 64 µg $g^{-1}$ DW, and Cu from 1,835 to 3,968 µg $g^{-1}$ DW and from 1,416 to 2,619 µg $g^{-1}$ DW, for the first and second year respectively. Ni concentrations were consistent through the years and ranged between 20 and 42 µg $g^{-1}$ DW

In the pond at Silkeborg concentrations of P, Fe, Mn, Na, K and Al decreased significantly through the pond. This was evident for the first and second year of operation (Table 22) as well as for the average from both years. P concentrations decreased through the pond from 1.2 to 0.35 and from 2.1 to 0.36 mg $g^{-1}$ DW for 2008 and 2009 respectively.

In Silkeborg Pb was detected only at the inlet in both sampling years and increased from 16 µg $g^{-1}$ DW in the first year to 27 µg $g^{-1}$ DW in the second, however as mentioned the difference was not statistically significant. Average Zn, Ni and Cr concentrations were also higher in the second year of operation and increased from 22-285, 8.7-22 and 15-34 µg $g^{-1}$

DW in 2008 to 31-472, 12-36 and 20-53 µg $g^{-1}$ DW in 2009 for Zn, Ni and Cr respectively (Table 22).

**Table 22: Average nutrients and metals concentrations (± 1 standard deviation) in sediment samples from the stormwater treatment system in Silkeborg at the inlet (In), middle of the pond (Mid) and outlet (Out) in 2008 and 2009.**

| | Unit | IN 2008 (n=3) | IN 2009 (n=3) | MID 2008 (n=6) | MID 2009 (n=3) | OUT 2008 (n=3) | OUT 2009 (n=3) |
|---|---|---|---|---|---|---|---|
| P | mg $g^{-1}$ DW | 1.2±0.40 | 2.1±0.60 | 0.64±0.12 | 0.72±0.22 | 0.35±0.16 | 0.36±0.05 |
| Fe | mg $g^{-1}$ DW | 19±7.0 | 26±6.3 | 15±2.8 | 16±1.2 | 9.2±5.1 | 11±1.9 |
| Mn | mg $g^{-1}$ DW | 1.0±0.45 | 0.55±0.12 | 0.46±0.12 | 0.38±0.07 | 0.19±0.09 | 0.24±0.01 |
| Ca | mg $g^{-1}$ DW | 9.0±6.3 | 6.9±0.50 | 3.2±0.55 | 5.0±2.6 | 6.1±5.3 | 3.9±1.8 |
| Na | mg $g^{-1}$ DW | 0.37±0.08 | 0.66±0.14 | 0.17±0.06 | 0.22±0.03 | 0.09±0.05 | 0.17±0.03 |
| K | mg $g^{-1}$ DW | 4.0±2.2 | 5.0±0.56 | 3.1±0.68 | 3.5±0.19 | 1.9±1.2 | 2.6±0.58 |
| Al | mg $g^{-1}$ DW | 33±16 | 31±4.8 | 26±6.2 | 18±1.3 | 15±8.8 | 12±2.6 |
| Pb | µg $g^{-1}$ DW | 16±7.4 | 27±14 | <2.0 | <2.0 | <2.0 | <2.0 |
| Zn | µg $g^{-1}$ DW | 285±114 | 472±187 | 79±36 | 89±23 | 22±12 | 31±4.3 |
| Ni | µg $g^{-1}$ DW | 22±7.6 | 36±7.9 | 15±3.0 | 18±1.5 | 8.7±5.2 | 12±2.8 |
| Cr | µg $g^{-1}$ DW | 34±15 | 53±11 | 26±5.3 | 28±1.9 | 15±8.8 | 20±3.8 |
| Cu | µg $g^{-1}$ DW | 18±10 | 72±25 | <5.0 | 14±2.6 | <5.0 | 6.4±0.8 |

## 4.2.2 Polycyclic aromatic hydrocarbons in the sediment

### 4.2.2.1 PAHs in the sediment of four classical wet detention ponds

Sediment for PAH analyses was sampled in three transects along the four classical wet detention ponds. At the inlet, middle and outlet of each of the system three samples were taken and analyzed, except at the outlet of pond A, where only one sample was analyzed. Pond C had significantly lower PAH concentration compared to ponds A and B (Figure 34). Pond B also accumulated the highest ∑PAH concentrations compared to all other systems. In ponds A, B and D the lowest ∑PAH concentration was measured in the samples taken at the outlet, while in pond C, the lowest ∑PAH concentration was at the middle of the pond which seemed to be a hydraulicly 'dead zone' with little sedimentations.

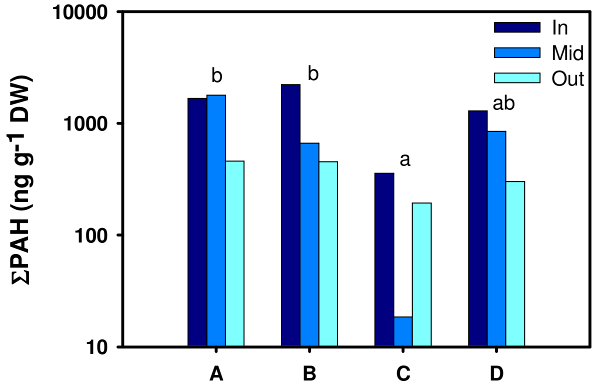


**Figure 34: Average ∑PAHs (16 PAHs recommended by U.S. EPA) in ng $g^{-1}$ DW at the inlet (In), halfway through (Mid) and at the outlet (Out) of four classical wet detention ponds (A to D). Different letters above columns indicate significant differences between the systems at the 5% probability level.**

The concentrations of individual PAHs through the four investigated ponds are presented in Table 23. Comparing PAH species fluoranthene, pyrene and chrysene prevailed above other analysed PAHs along with some other combustion-derived PAHs. In ponds A and D all investigated PAHs were above detection limit in at least one location, while in ponds B and C LMW acenaphthene and HMW dibenzo(a,h)anthracene were not detected. Besides this, LMW fluorene was not detected in pond B.

In pond A the highest concentrations at the inlet were 249±71 and 301±68 ng $g^{-1}$ DW for fluoranthene and pyrene, respectively. Average PAH concentrations in the middle of the pond were higher compared to the inlet for 11 out of 16 measured PAHs, however also for other measured PAHs the concentrations at the middle of the pond was not apparently lower. The concentrations at the outlet were lower compared to the inlet and middle with the same PAH species being dominant as at the inlet.

On the other hand in pond B concentrations of all measured PAHs decreased from the inlet to the middle of the pond and the concentrations at the outlet were similar to the concentrations at the middle of the pond. This indicates that the majority of PAH reduction appeared in the first half of the pond. Dominant PAH species at the inlet were chrysene and pyrene, followed by phenanthrene, fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene and indeno(1,2,3-c,d)pyrene (Table 23).

**Table 23: Average and standard deviation (ng g$^{-1}$ DW) of individual PAHs through four classical wet detention ponds .**

| PAH | Pond A | | | Pond B | | | Pond C | | | Pond D | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | In (n=2) | Mid (n=4) | Out (n=1) | In (n=3) | Mid (n=2) | Out (n=3) | In (n=3) | Mid (n=3) | Out (n=2) | In (n=5) | Mid (n=3) | Out (n=3) |
| NAP | 40±33 | 59±21 | 43 | 53±4 | 25±5 | 29±16 | 30±16 | 14±7 | 17±12 | 27±24 | 30±9 | 23±9 |
| ACY | 22±6 | 30±16 | 4 | 24±26 | 5±7 | 6±2 | 1±2 | <0.1 | <0.1 | 13±14 | 15±4 | <0.1 |
| ACE | <0.2 | 1.4±2.8 | 4.0 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | 7±14 | <0.2 | <0.2 |
| FL | 11±15 | 11±12 | 3 | <1 | <1 | <1 | 1±1 | <1 | <1 | 20±26 | 2±3 | <1 |
| PHE | 129±38 | 119±85 | 36 | 283±128 | 36±50 | 23±8 | 25±6 | <1 | 10±6 | 172±292 | 37±9 | <1 |
| ANT | 22±11 | 22±14 | 3 | 9±15 | <0.1 | <0.1 | <0.1 | <0.1 | 0.3±0.4 | 44±64 | 10±8 | <0.1 |
| FLU | 249±71 | 252±146 | 54 | 252±51 | 72±66 | 53±33 | 43±12 | <1 | 35±38 | 221±350 | 102±20 | 35±7 |
| PYR | 301±68 | 266±152 | 62 | 347±68 | 103±111 | 70±32 | 50±18 | <0.1 | 37±41 | 195±243 | 125±12 | 41±6 |
| BaA | 79±24 | 75±39 | 17 | 46±42 | 29±2 | 17±11 | 21±18 | <0.2 | 13±16 | 73±119 | 42±4 | 11±10 |
| CHR | 179±40 | 191±105 | 51 | 279±131 | 92±93 | 67±26 | 44±16 | <1 | 16±14 | 154±133 | 74±34 | 27±25 |
| BbF | 157±65 | 193±127 | 59 | 261±106 | 92±65 | 53±18 | 39±19 | 1±3 | 5±7 | 107±102 | 118±22 | 44±12 |
| BkF | 59±15 | 69±41 | 24 | 88±15 | 24±10 | 20±11 | 14±6 | 2±4 | 40±48 | 48±51 | 44±15 | 21±9 |
| BaP | 129±50 | 138±111 | 23 | 223±83 | 75±51 | 43±14 | 27±24 | 1±2 | 21±19 | 84±75 | 89±52 | 34±8 |
| DBA | 25±1 | 28±23 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | 14±10 | 12±9 | <1 |
| IND | 170±53 | 205±116 | 48 | 248±128 | 77±59 | 43±12 | 39±21 | <0.2 | <0.2 | 67±38 | 80±31 | 38±12 |
| BGP | 104±36 | 121±75 | 29 | 108±32 | 33±18 | 30±12 | 34±23 | <0.1 | 0.8±1.1 | 52±42 | 68±13 | 28±6 |
| $\sum$PAH | 1675±527 | 1780±1077 | 461 | 2222±603 | 663±522 | 454±187 | 357±147 | 19±11 | 194±187 | 1295±1508 | 847±155 | 301±102 |

NAP-naphthalene, ACY-acenaphthylene, ACE-acenaphthene, FL- flourene, PHE-phenanthrene, ANT- anthracene, FLU- fluoranthene, PYR-pyrene, BaA-benz[a]anthracene, CHR- chrysene, BbF-benzo[b]fluoranthene, BkF-benzo[k]fluoranthene, BaP-benzo[a]pyrene, DBA-dibenz[a,h]anthracene, BDP-benzo[ghi]perylene, IND-indeno[1,2,3-cd]pyrene.

As mentioned before, pond C had the lowest PAH concentrations compared to the other three ponds. In the middle of pond C only four PAH species were detected. Dominant PAH species at the inlet were pyrene, chrysene and fluoranthene with 50±18, 44±16 and 43±12 ng g$^{-1}$ DW, respectively (Table 23). In pond D the dominant PAH species at the inlet was fluoranthene with 221±350 ng g$^{-1}$ DW followed by pyrene (195±243 ng g$^{-1}$ DW) and phenanthrene (172±292 ng g$^{-1}$ DW). The concentrations at the middle of the pond D were similar to inlet concentrations; however, there was a decrease in most of the PAHs' concentrations at the outlet of the pond, compared to the inlet and middle.

#### 4.2.2.2 PAHs in the sediment of three upgraded wet detention ponds

Sediment was sampled for PAH analyzes in transects at the inlet, half way and outlet of the systems at Århus, Odense and Silkeborg. PAHs were found in all the samples collected from the three ponds. The system at Odense presented the highest PAHs concentrations followed by Århus and Silkeborg. The ANOVA showed a significantly lower concentration of PAHs in Silkeborg compared to other two ponds, while the difference between PAHs concentrations in Århus and Odense was not significant (Figure 35).

∑PAHs concentrations in the sediment at Århus and Odense systems did not show marked decrease through the ponds, while in Silkeborg there was a significant decrease in sediment ∑PAH concentrations (Figure 35), which is due to two flow perpendicular sand dikes constructed in this pond in order to enhance sedimentation. The concentration of average ∑PAHs in Silkeborg decreased from 262±75, 87±86 to 6±5 ng $g^{-1}$ DW, for inlet, middle and outlet, respectively (Table 24). In the pond at Århus, the highest PAHs concentrations were detected in the sediment in the middle of the pond and in the pond at Odense, higher PAHs concentrations in the middle of the pond were detected for half of the measured PAHs.

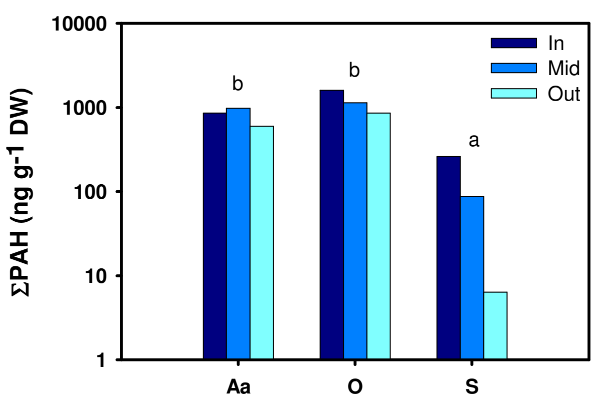


**Figure 35: Average ∑PAHs (16 PAHs recommended by U.S. EPA) in ng $g^{-1}$ DW at the inlet (In), halfway through (Mid) and at the outlet (Out) of three upgraded wet detention ponds (Aa – Århus, O – Odense, S - Silkeborg). Different letters above columns indicate significant differences between the systems at the 5% probability level.**

The results by individual PAHs through three investigated ponds are presented in Table 24. Comparing PAH species, LMW fluorene, acenaphthene and anthracene were often below detection limit in the sediment samples, which is in accordance with the results of the PAH analysis in the water. Combustion-derived PAHs like pyrene, fluoranthene and indeno(1,2,3-cd)pyrene generally occurred in higher concentrations than other PAH species.

**Table 24: Average (± 1 standard deviation) PAHs concentrations (ng $g^{-1}$ DW) in the sediment at the inlet (In), halfway through (Mid) and at the outlet (Out) of the wet detention ponds at Århus, Odense and Silkeborg.**

| PAH | Århus | | | Odense | | | Silkeborg | | |
|---|---|---|---|---|---|---|---|---|---|
| | In (n=4) | Mid (n=5) | Out (n=4) | In (n=2) | Mid (n=6) | Out (n=4) | In (n=6) | Mid (n=9) | Out (n=4) |
| NAP | 29±12 | 32±8 | 21±14 | 32±18 | 19±5 | 25±13 | 4±1 | <3 | <3 |
| ACY | 11±8 | 26±19 | 59±92 | 17±3 | 9±9 | 10±7 | 3±2 | 1±1 | 0.2±0.4 |
| ACE | <0.2 | <0.2 | 16±29 | <0.2 | 1±3 | <0.2 | <0.2 | <0.2 | <0.2 |
| FL | <1 | <1 | <1 | 18±14 | 6±10 | <1 | <1 | <1 | <1 |
| PHE | 81±98 | 47±38 | 32±29 | 111±48 | 73±41 | 40±16 | 27±12 | 9±5 | 4±3 |
| ANT | 7±5 | 7±11 | 1±1 | 16±6 | 8±9 | 1±2 | 2±2 | 1±1 | 0.1±0.2 |
| FLU | 81±29 | 111±54 | 46±12 | 217±64 | 153±59 | 117±50 | 33±13 | 12±11 | <1 |
| PYR | 91±30 | 140±53 | 69±19 | 262±106 | 199±92 | 139±58 | 37±13 | 13±12 | 1±1 |
| BaA | 29±10 | 48±16 | 15±4 | 51±20 | 47±18 | 39±14 | 9±2 | 3±3 | <0.2 |
| CHR | 59±20 | 133±74 | 65±18 | 178±71 | 149±71 | 107±58 | 30±9 | 11±11 | <1 |
| BbF | 118±88 | 125±51 | 86±18 | 159±73 | 126±65 | 101±35 | 32±11 | 13±12 | <0.1 |
| BkF | 39±29 | 43±38 | 23±23 | 53±28 | 41±14 | 34±9 | 12±4 | 5±4 | <1 |
| BaP | 90±74 | 67±30 | 32±15 | 95±68 | 90±67 | 69±38 | 19±2 | 9±10 | <0.1 |
| DBA | 19±21 | 2±4 | <1 | 80±90 | 5±12 | 8±10 | 6±10 | 1±2 | <1 |
| IND | 110±67 | 116±39 | 84±20 | 187±81 | 142±83 | 98±48 | 28±9 | 11±10 | <0.2 |
| BGP | 91±58 | 83±36 | 50±3 | 124±67 | 73±44 | 70±34 | 19±6 | 8±7 | <0.1 |
| ∑PAH | 855±515 | 982±399 | 599±203 | 1599±756 | 1143±553 | 859±370 | 262±75 | 87±86 | 6±5 |

NAP-naphthalene, ACY-acenaphthylene, ACE-acenaphthene, FL- flourene, PHE-phenanthrene, ANT- anthracene, FLU- flouranthene, PYR-pyrene, BaA-benz[a]anthracene, CHR- chrysene, BbF-benzo[b]fluoranthene, BkF-benzo[k]fluoranthene, BaP-benzo[a]pyrene, DBA-dibenz[a,h]anthracene, BDP-benzo[ghi]perylene, IND-indeno[1,2,3-cd]pyrene.

In the Århus pond, all investigated PAHs were detected except fluorene. The highest average concentrations measured at the inlet were 118±88 and 110±67 ng $g^{-1}$ DW for benzo(b)fluoranthene and indeno(1,2,3-cd)pyrene, respectively. Average PAH concentrations in the middle of the Århus pond were higher compared to the inlet and outlet for 9 out of 16 measured PAHs. In the middle of the pond pyrene, chrysene and benzo(b)fluoranthene appeared in the highest concentration, 140±53, 133±74 and 125±51 ng $g^{-1}$ DW, respectively. The concentrations at the outlet were similar or lower compared to the inlet with the same three PAHs dominant as at the inlet. Acenaphthene was detected only at the outlet of the pond.

Similar to Århus pond, also in Odense LMW acenaphthene and fluorene were not detected at all sampling sites. Like in the middle of the pond at Århus also at Odense pyrene was presented in the highest concentrations, namely at all sampling sites: 262±106, 199±92 and 139±58 ng $g^{-1}$ DW for inlet, middle and outlet, respectively. Pyrene was followed by fluoranthene. There was a decrease in concentration through the pond for majority of PAH species (Table 24).

Also at Silkeborg LMW acenaphthene and fluorene were below the detection limit at all sampling sites. At the outlet, only 4 out of 16 PAHs were above the detection limit. At the inlet pyrene was detected in the highest concentration (37±13 ng $g^{-1}$ DW) but the concentration was 2.5 and 7 times lower compared to Århus and Odense, respectively. Concentrations of all PAH species decreased through the pond (Table 24).

## 4.3 Plants

### 4.3.1 Accumulation of nutrients and metals in investigated plant species

Nutrient and metal analyses in plants sampled at the four classical and the three upgraded stormwater wet detention ponds showed different patterns in nutrient and metal accumulation between plant tissues as well as between plant species. Nutrient and metal concentrations in the shoots and roots were compared to the concentrations in the sediment for each pond. The concentration ratio of plant roots to soil is named Concentration Factor (CF) and the ratio of shoot to soil concentration is the Accumulation Coefficient (AC). The results are presented in Figures 36 and 37. The AC and CF that are higher than one, indicate accumulation of the element in the plant tissue.

Average AC and CF of macronutrients were higher than one for P, Mn, Na and K, showing an accumulation of these elements in the plant tissues. The AC and CF were below or around one for Fe, Ca and Al. Average AC was the highest for Na, followed by P indicating phytoextraction of P and Na from the sediment. *Alisma lanceolatum* accumulated markedly more P compared to other species (AC up to 44). In addition, *Caltha palustris*, *Sagittaria sagittifolia* and *Elodea nuttallii* accumulated higher P concentrations in the shoots compared to other species. *A. lanceolatum*, *C. palustris* and *Potamogeton* sp. accumulated higher concentrations of K and Mn.

The concentration of macroelements in the roots has similar pattern as accumulation of these metals in the shoots, namely with P, Mn and Na having the highest ratios to the soil. Different plant species had high variation in Na concentrations in the shoots and roots, with AC and CF from around 1 to around 170 in the shoots and 400 in the roots. More Na was stored in the roots compared to the shoots, with the highest concentrations in *Typha* sp.

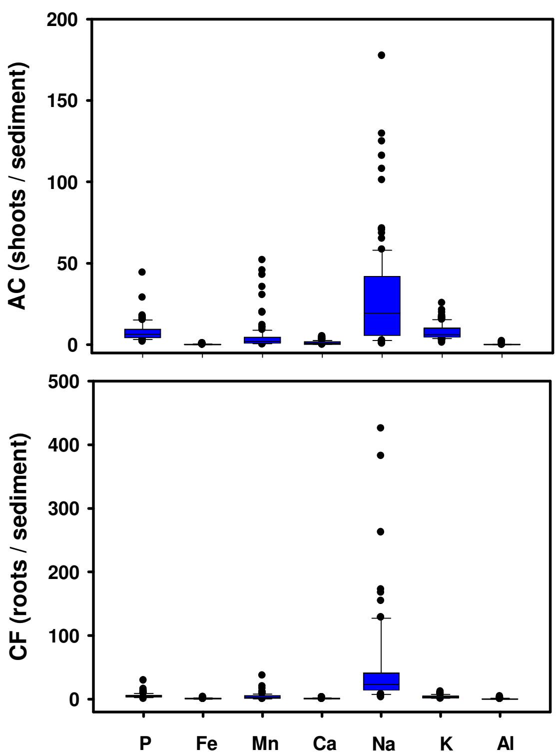


**Figure 36: Accumulation of macroelements in plants shoots (AC) and roots (CF) in relation to the sediment concentration.**

The accumulation of heavy metals in the shoots in relation to the sediment concentration is presented in Figure 37. Average ACs for all heavy metals were lower than one, meaning that there is no significant translocation of heavy metals into aboveground tissues. However, at the four classical investigated ponds, average ACs for Pb and Zn were higher than one.

*Potamogeton* sp. and *E. nuttallii* accumulated the highest concentrations of Pb and Zn, but also Cu compared to the soil. ACs were higher than one also for Zn in *S. aloides*, *S. sagittifolia* and *P. australis* and for Cu in *A. lanceolatum* and *S. sagittifolia*.

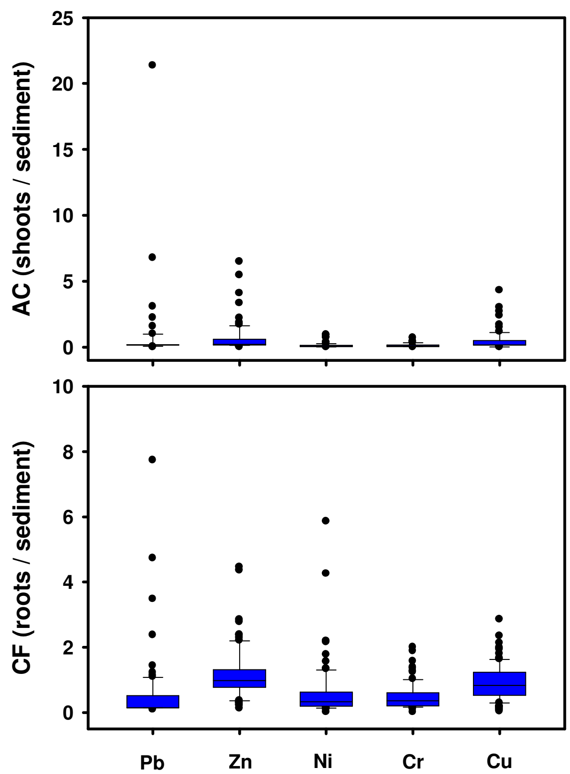


**Figure 37: Accumulation of heavy metals in shoots (AC) and roots (CF) of investigated plant species in relation to the sediment concentration.**

Concentration of heavy metals in the roots of sampled plants is presented in Figure 37. Average CFs for heavy metals in investigated plants were below one, except for Zn, indicating that there is no significant heavy metal accumulation in the roots in investigated systems. However, there is a marked difference between sampled species: certain species concentrated higher heavy metals concentrations in the roots. Species that concentrated Zn in the roots were *P. australis*, *Typha* sp., *C. palustris*, *R. lingua*, *S. maritimus* and *R. hydrolapathum*, with *Typha* and *R. hydrolapathum* having the highest CF (around 4). All these species, except *Phragmites* also had CFs for Cu higher than one, however average CF for Cu for investigated plants was below one. *Typha* sp. concentrated more Pb than other species (CF between 4 and 8), while *R. hydrolapathum* and *P. australis* concentrated more Ni (CFs between 4 and 6).

### 4.3.2 Plants at classical wet detention ponds

#### 4.3.2.1 Macroelements in macrophytes at four classical wet detention ponds

In the four classical wet detention ponds, macrophytes were sampled at the inlet, middle of the pond and at the outlet. At each sampling site the most representative emergent, submerged and floating macrophytes were sampled, however not all macrophyte types were present at each sampling site. The emergent macrophyte *Typha latifolia* (broadleaved cattail) was present at all sampling sites in all four ponds. Sampled *Typha* was divided into root, rhizome and leave tissues, while other plant species were treated as whole plants. Pond A was modestly vegetated, besides *T. latifolia* only *Potamogeton natans* (floating pondweed) was sampled at the outlet. Pond B was densely vegetated: the middle part of the pond was completely covered with invasive *Elodea canadensis* (Canadian waterweed) and at the inlet and outlet *P. natans* was present. At the inlet of the pond, also *Elodea nuttallii* (western waterweed) was found. The identification of *E. nuttallii* in pond B was the first registration of this species in Jutland peninsula, Denmark, and is an important data for an investigation of spreading of this invasive species. Ponds C and D were moderately vegetated mostly with *T. latifolia* on the banks and patches of *P. pusillus* (pond C) and *P. natans* (pond D) in the pond.

Average nutrient and metal concentrations in whole plants and plant parts were compared to the average nutrient and metal concentrations in the sediment at the inlet, middle and outlet of each pond. Macroelement concentrations in *T. latifolia* tissues and sediment are presented in Table 25.

Phosphorous concentration was significantly higher in *Typha* tissues compared to the sediment but no significant difference between the plant tissues was observed. Concentrations in different plant tissues were consistent through the ponds and between the ponds.

Iron was accumulated in the roots – the concentration in the roots was higher compared to other *Typha* tissues and sediment. Iron concentrations in plant tissues were consistent between the locations and ponds, with an exception of pond D where concentrations in leaves and roots were higher compared to the other ponds.

The concentrations of Mn were higher in roots and leaves compared to rhizomes and sediment. Manganese contents in rhizomes and roots were consistent through the ponds and between the ponds, while in leaves, the concentrations were higher in ponds B and D.

Calcium was accumulated in the roots but the concentration was higher in the sediment. The concentrations in plant tissues were consistent between the ponds and along the water flow.

Sodium concentrations differ between all plant tissues and sediment. The concentrations in the sediment were the lowest, followed by leaves, rhizomes and roots with the highest concentrations (up to 20 mg $g^{-1}$ DW). Na concentrations in the leaves were lower in ponds A and B compared to the ponds C and D. The Na concentrations in the belowground tissues were not consistent.

Similar to phosphorous, potassium was accumulated in the *Typha*, since the concentrations in all tissues were higher compared to the sediment. K concentrations in different plant parts, ponds and locations in the ponds were not consistent and varied between 4.5 and 33 mg $g^{-1}$ DW.

Aluminum concentration was significantly higher in roots and sediment compared to the rhizomes and leaves. Leaves contained significantly lower concentration compared to rhizomes. Leaves and rhizomes in pond D had higher concentrations of Al compared to the other three ponds. The concentrations in the roots varied between the ponds and locations from 6.0 to 47 mg $g^{-1}$ DW.

**Table 25: Concentrations of macroelements in mg g$^{-1}$ DW in *Typha latifolia* tissues and sediment (Sed.) at three sampling sites (In - inlet, Mid - middle and Out - outlet) along the four investigated wet detention ponds (A, B, C and D). Different letters at plant tissues and sediment indicate significant differences between them at the 5% probability level.**

| | | A | | | B | | | C | | | D | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | In | Mid | Out | In | Mid | Out | In | Mid | Out | In | Mid | Out |
| P | Leaves[b] | 6.9 | 4.2 | 6.0 | 5.9 | 6.0 | 4.5 | 6.9 | 4.4 | 5.8 | 5.0 | 3.9 | 4.5 |
| | Rhizomes[b] | 7.0 | 3.8 | 7.6 | 4.5 | 6.1 | 5.2 | 7.5 | 5.6 | 6.6 | 4.6 | 5.7 | 2.4 |
| | Roots[b] | 4.7 | 3.9 | 6.2 | 8.9 | 4.8 | 5.3 | 8.1 | 2.5 | 7.2 | 3.9 | 5.2 | 3.5 |
| | Sed.[a] | 0.72 | 0.81 | 0.62 | 1.0 | 0.91 | 0.76 | 0.62 | 0.90 | 0.82 | 0.71 | 0.81 | 0.79 |
| Fe | Leaves | 0.10 | 0.17 | 0.21 | 0.11 | 0.12 | 0.06 | 0.12 | 0.10 | 0.11 | 0.28 | 0.33 | 0.60 |
| | Rhizomes | 5.3 | 0.93 | 6.2 | 6.6 | 6.8 | 3.0 | 7.1 | 9.7 | 2.8 | 4.7 | 3.4 | 6.4 |
| | Roots | 19 | 6.5 | 19 | 13 | 20 | 27 | 10 | 9.9 | 19 | 25 | 22 | 29 |
| | Sed. | 10 | 13 | 9.7 | 10 | 15 | 11 | 9.3 | 12 | 12 | 9.4 | 9.9 | 10 |
| Mn | Leaves | 0.73 | 0.50 | 0.48 | 0.76 | 2.2 | 2.1 | 0.53 | 1.5 | 0.47 | 1.0 | 1.2 | 5.2 |
| | Rhizomes | 0.26 | 0.12 | 0.29 | 0.24 | 0.36 | 0.18 | 0.23 | 0.37 | 0.21 | 0.27 | 0.50 | 0.36 |
| | Roots | 1.2 | 2.7 | 1.3 | 1.5 | 1.4 | 2.0 | 1.1 | 0.44 | 1.1 | 0.62 | 1.5 | 1.3 |
| | Sed. | 0.35 | 0.28 | 0.23 | 0.26 | 0.41 | 0.31 | 0.13 | 0.20 | 0.24 | 0.19 | 0.29 | 0.19 |
| Ca | Leaves | 7.2 | 11 | 6.4 | 9.5 | 8.2 | 12 | 6.7 | 14 | 6.0 | 8.6 | 8.4 | 16 |
| | Rhizomes | 4.2 | 3.9 | 9.3 | 4.2 | 4.4 | 3.8 | 5.0 | 8.6 | 5.8 | 9.2 | 4.3 | 9.0 |
| | Roots | 10 | 16 | 16 | 14 | 14 | 10 | 11 | 9.8 | 11 | 15 | 7.8 | 12 |
| | Sed. | 28 | 18 | 54 | 34 | 32 | 20 | 44 | 32 | 46 | 28 | 36 | 57 |
| Na | Leaves | 8.2 | 6.0 | 5.3 | 7.9 | 5.7 | 6.0 | 3.4 | 5.5 | 5.2 | 2.1 | 4.6 | 5.4 |
| | Rhizomes | 7.7 | 7.7 | 7.7 | 12 | 8.4 | 5.5 | 7.0 | 17 | 7.7 | 4.9 | 5.2 | 9.9 |
| | Roots | 18 | 20 | 12 | 13 | 7.5 | 13 | 14 | 15 | 15 | 13 | 14 | 14 |
| | Sed. | <0.01 | 0.22 | <0.01 | 0.15 | 0.17 | 0.09 | 0.07 | 0.19 | 0.22 | 0.04 | 0.13 | <0.01 |
| K | Leaves | 12 | 24 | 21 | 16 | 14 | 12 | 19 | 10 | 19 | 17 | 12 | 8.5 |
| | Rhizomes | 18 | 18 | 29 | 12 | 21 | 16 | 19 | 9.4 | 23 | 21 | 24 | 7.5 |
| | Roots | 15 | 33 | 21 | 7.0 | 14 | 14 | 14 | 4.5 | 33 | 14 | 13 | 4.5 |
| | Sed. | 1.9 | 4.3 | 2.1 | 2.2 | 3.0 | 2.7 | 3.0 | 3.6 | 3.9 | 2.2 | 2.5 | 2.5 |
| Al | Leaves[a] | 0.41 | 0.48 | 0.88 | 0.33 | 0.25 | 0.14 | 0.34 | 0.36 | 0.35 | 0.79 | 0.95 | 1.6 |
| | Rhizomes[b] | 3.7 | 1.1 | 7.7 | 2.6 | 4.3 | 4.2 | 7.5 | 5.0 | 4.1 | 7.1 | 1.8 | 9.7 |
| | Roots[c] | 15 | 6.0 | 23 | 19 | 47 | 17 | 24 | 9.2 | 15 | 10 | 7.1 | 19 |
| | Sed.[c] | 9.7 | 15 | 7.7 | 8.1 | 14 | 11 | 10 | 13 | 12 | 8.7 | 9.2 | 11 |

Concentrations of macroelements in plant species sampled in the four classical wet detention ponds together with sediment concentrations are shown in Table 26. Phosphorous concentrations were similar in all investigated plant species (from 3.9 to 9.0 mg g$^{-1}$ DW) except *E. nuttallii* where it was approximately two-times higher (15 mg g$^{-1}$ DW). All investigated plants had higher P content compared to the sediment.

Fe concentrations were usually lower in *P. natans* compared to the other species (Table 26). While Fe was not accumulated in the plants, Mn concentrations were higher in plants compared to the sediment. In *Typha* the concentration ranged from 0.59 to 2.3 mg $g^{-1}$ DW while in *Potamogeton* species they were higher, namely up to 14 mg $g^{-1}$ DW in *P. natans* and 6.4 mg $g^{-1}$ DW in *P. pusillus*. Mn concentration in *E. canadensis* was similar to concentrations in *Typha* while Mn concentration in *E. nuttallii* was similar to Mn concentration in *P. pusillus*.

Comparing plant species, Ca concentration was the lowest in *T. latifolia*, ranging from 6.8 to 13 mg $g^{-1}$ DW. In *P. natans* the concentration was more constant and ranged from 12 to15 mg $g^{-1}$ DW; a bit higher concentration was measured in *E. nuttallii* (18 mg $g^{-1}$ DW). In *P. pusillus* the concentrations were similar to the sediment (26 - 64 mg $g^{-1}$ DW), while *E. canadensis* accumulated Ca compared to the sediment (92 mg $g^{-1}$ DW) (Table 26).

*P. natans* and *P. pusillus* contained similar Na concentrations (between 3.7 and 10 mg $g^{-1}$ DW), as well as *T. latifolia* and *E. canadensis* (between 6.6 and 11 mg $g^{-1}$ DW). Sodium content in *E. nuttallii* was higher compared to all other plant species. Investigated plant species did not accumulate Na (Table 26).

Like already described for *Typha*, also other plant species accumulated potassium in concentrations higher than the sediment. The results did not show apparent difference between the species. Concentrations ranged from 12 to 39 mg $g^{-1}$ DW.

Aluminum concentrations in *P. natans*, *P. pusillus* and *E. canadensis* were generally lower compared to *T. latifolia* and *E. nuttallii*, which had similar concentrations as sediment.

It was not possible to estimate the differences between macronutrient concentrations at different locations and different ponds, since not all species were present in all locations and all ponds.

**Table 26: Concentrations of macroelements in mg $g^{-1}$ DW in different plant species and sediment at three sampling sites (In - inlet, Mid - middle and Out - outlet) along four classical wet detention ponds (A, B, C and D) ("-" indicates that the species was not present at the sampling site).**

| | | A | | | B | | | C | | | D | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | In | Mid | Out | In | Mid | Out | In | Mid | Out | In | Mid | Out |
| P | *T. latifolia* | 6.2 | 3.9 | 6.6 | 6.4 | 5.6 | 5.0 | 7.5 | 4.2 | 6.5 | 4.5 | 5.0 | 3.5 |
| | *P. natans* | - | - | 4.2 | 9.0 | - | 3.9 | - | - | - | 8.9 | 6.6 | 5.6 |
| | *P. pusillus* | - | - | - | - | - | - | 7.0 | 7.2 | 5.7 | - | - | - |
| | *E. canadensis* | - | - | - | - | 4.2 | - | - | - | - | - | - | - |
| | *E. nuttallii* | - | - | - | 15 | - | - | - | - | - | - | - | - |
| | Sediment | 0.72 | 0.81 | 0.62 | 1.0 | 0.91 | 0.76 | 0.62 | 0.90 | 0.82 | 0.71 | 0.81 | 0.79 |
| Fe | *T. latifolia* | 8.2 | 2.5 | 8.4 | 6.5 | 8.9 | 10 | 5.8 | 6.6 | 7.4 | 10 | 8.7 | 12 |
| | *P. natans* | - | - | 0.78 | 5.8 | - | 1.1 | - | - | - | 3.2 | 4.9 | 2.3 |
| | *P. pusillus* | - | - | - | - | - | - | 7.7 | 2.2 | 5.0 | - | - | - |
| | *E. canadensis* | - | - | - | - | 4.0 | - | - | - | - | - | - | - |
| | *E. nuttallii* | - | - | - | 8.0 | - | - | - | - | - | - | - | - |
| | Sediment | 10 | 13 | 9.7 | 10 | 15 | 11 | 9.3 | 12 | 12 | 9.4 | 9.9 | 10 |
| Mn | *T. latifolia* | 0.73 | 1.1 | 0.68 | 0.84 | 1.3 | 1.4 | 0.63 | 0.75 | 0.59 | 0.64 | 1.1 | 2.3 |
| | *P. natans* | - | - | 3.7 | 1.6 | - | 6.7 | - | - | - | 11 | 14 | 12 |
| | *P. pusillus* | - | - | - | - | - | - | 5.5 | 3.5 | 6.4 | - | - | - |
| | *E. canadensis* | - | - | - | - | 1.4 | - | - | - | - | - | - | - |
| | *E. nuttallii* | - | - | - | 3.6 | - | - | - | - | - | - | - | - |
| | Sediment | 0.35 | 0.28 | 0.23 | 0.26 | 0.41 | 0.31 | 0.13 | 0.20 | 0.24 | 0.19 | 0.29 | 0.19 |
| Ca | *T. latifolia* | 7.2 | 10 | 11 | 9.2 | 8.9 | 8.6 | 7.6 | 11 | 7.4 | 11 | 6.8 | 13 |
| | *P. natans* | - | - | 14 | 13 | - | 12 | - | - | - | 15 | 13 | 14 |
| | *P. pusillus* | - | - | - | - | - | - | 26 | 54 | 64 | - | - | - |
| | *E. canadensis* | - | - | - | - | 92 | - | - | - | - | - | - | - |
| | *E. nuttallii* | - | - | - | 18 | - | - | - | - | - | - | - | - |
| | Sediment | 28 | 18 | 54 | 34 | 32 | 20 | 44 | 32 | 46 | 28 | 36 | 57 |
| Na | *T. latifolia* | 11 | 11 | 8.4 | 11 | 7.2 | 8.0 | 8.0 | 12 | 9.1 | 6.6 | 8.0 | 9.7 |
| | *P. natans* | - | - | 5.0 | 9.8 | - | 6.9 | - | - | - | 5.9 | 10 | 5.9 |
| | *P. pusillus* | - | - | - | - | - | - | 5.5 | 5.4 | 3.7 | - | - | - |
| | *E. canadensis* | - | - | - | - | 8.4 | - | - | - | - | - | - | - |
| | *E. nuttallii* | - | - | - | 17 | - | - | - | - | - | - | - | - |
| | Sediment | <0.01 | 0.22 | <0.01 | 0.15 | 0.17 | 0.09 | 0.07 | 0.19 | 0.22 | 0.04 | 0.13 | <0.01 |
| K | *T. latifolia* | 15 | 25 | 24 | 12 | 16 | 14 | 17 | 8.0 | 25 | 17 | 16 | 6.8 |
| | *P. natans* | - | - | 18 | 26 | - | 18 | - | - | - | 38 | 38 | 24 |
| | *P. pusillus* | - | - | - | - | - | - | 24 | 25 | 20 | - | - | - |
| | *E. canadensis* | - | - | - | - | 16 | - | - | - | - | - | - | - |
| | *E. nuttallii* | - | - | - | 39 | - | - | - | - | - | - | - | - |
| | Sediment | 1.9 | 4.3 | 2.1 | 2.2 | 3.0 | 2.7 | 3.0 | 3.6 | 3.9 | 2.2 | 2.5 | 2.5 |
| Al | *T. latifolia* | 6.4 | 2.6 | 10 | 7.2 | 17 | 6.9 | 11 | 4.9 | 6.3 | 6.1 | 3.3 | 10 |
| | *P. natans* | - | - | 2.0 | 10 | - | 5.2 | - | - | - | 4.2 | 4.1 | 0.76 |
| | *P. pusillus* | - | - | - | - | - | - | 1.47 | <0.01 | 1.35 | - | - | - |
| | *E. canadensis* | - | - | - | - | 2.6 | - | - | - | - | - | - | - |
| | *E. nuttallii* | - | - | - | 12 | - | - | - | - | - | - | - | - |
| | Sediment | 9.7 | 15 | 7.7 | 8.1 | 14 | 11 | 10 | 13 | 12 | 8.7 | 9.2 | 11 |

#### 4.3.2.2 Heavy metals in macrophytes at classical wet detention ponds

Heavy metal concentrations in the tissues of *T. latifolia* and the sediment are presented in Table 27. Lead was detected only in the roots in ponds A and D. In pond D, concentrations were in the same range like in the sediment and a bit higher in pond A.

**Table 27: Concentrations of heavy metals in μg $g^{-1}$ DW in *Typha latifolia* tissues and sediment at three sampling sites (In - inlet, Mid - middle and Out - outlet) along four classical wet detention ponds (A, B, C and D). Different letters at plant tissues and sediment indicate significant differences between them at the 5% probability level.**

| | | A | | | B | | | C | | | D | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | In | Mid | Out | In | Mid | Out | In | Mid | Out | In | Mid | Out |
| Pb | Leaves | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| | Rhizomes | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| | Roots | <0.5 | 4.5 | 6.2 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | 2.1 | <0.5 | <0.5 |
| | Sediment | 2.5 | <0.5 | <0.5 | 11 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | 2.6 | 2.5 | <0.5 |
| Zn | Leaves | 32 | 29 | 20 | 22 | 19 | 20 | 18 | 17 | 22 | 29 | 16 | 33 |
| | Rhizomes | 27 | 24 | 37 | 60 | 20 | 30 | 35 | 81 | 36 | 24 | 16 | 20 |
| | Roots | 117 | 126 | 147 | 212 | 129 | 133 | 205 | 134 | 87 | 97 | 72 | 71 |
| | Sediment | 48 | 44 | 32 | 206 | 108 | 38 | 33 | 49 | 71 | 77 | 69 | 59 |
| Ni | Leaves | <0.2 | 1.7 | 0.60 | 0.89 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | 0.72 | <0.2 | 0.52 |
| | Rhizomes | 0.85 | 1.2 | 2.6 | 0.65 | 0.70 | 0.84 | 1.7 | 3.3 | 0.98 | 1.9 | 0.63 | 2.3 |
| | Roots | 2.7 | 26 | 8.0 | 4.4 | 8.1 | 4.5 | 4.8 | 3.7 | 3.9 | 5.3 | 3.6 | 8.6 |
| | Sediment | 8.7 | 16 | 8.0 | 10 | 12 | 10 | 8.4 | 13 | 12 | 12 | 11 | 12 |
| Cr | Leaves[a] | <1.3 | 1.4 | 1.5 | 1.6 | 2.0 | <1.3 | <1.3 | <1.3 | <1.3 | <1.3 | <1.3 | 2.4 |
| | Rhizomes[b] | 4.1 | <1.3 | 9.9 | 2.3 | 3.4 | 3.4 | 7.1 | 6.1 | 3.4 | 3.7 | 2.0 | 4.7 |
| | Roots[c] | 8.2 | 6.0 | 11 | 13 | 35 | 8.6 | 15 | 4.9 | 7.5 | 6.8 | 5.7 | 8.6 |
| | Sediment[d] | 14 | 22 | 13 | 18 | 22 | 18 | 16 | 19 | 21 | 17 | 17 | 16 |
| Cu | Leaves | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | 10 | <0.4 | <0.4 | <0.4 |
| | Rhizomes | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 |
| | Roots | 13 | 9.7 | 13 | 12 | 16 | 22 | 8.5 | 9.4 | <0.4 | 13 | <0.4 | 6.9 |
| | Sediment | 7.8 | 9.5 | 7.4 | 26 | 13 | 5.3 | <0.4 | 6.8 | 8.5 | 11 | 9.8 | 8.2 |

Zn concentrations were higher in the roots compared to other plant parts. In pond A concentrations were approximately 2 to 5-times higher in the roots (from 117 to 147 μg $g^{-1}$ DW) compared to the sediment (from 32 to 48 μg $g^{-1}$ DW), while leaves and rhizomes had lower Zn concentrations than the sediment, indicating no transport of metal to aboveground tissues. In pond B, there was no accumulation of Zn in the roots, since the root concentrations at the inlet and middle of the pond were in the same range like in the sediment (approximately 200 and 100 µg $g^{-1}$ DW for inlet and middle, respectively). At the inlet, where sediment and root concentrations were the highest (206 and 212 µg $g^{-1}$ DW, respectively), Zn was elevated also in rhizomes (60 µg $g^{-1}$ DW). In pond C root concentrations were higher compared to the sediment and in the middle of the pond also accumulation in the rhizomes appeared. In pond D, Zn accumulation in the roots was not apparent.

Roots contained higher amount of Ni and Cr compared to leaves and rhizomes, however the concentrations in the roots were lower compared to the sediment (CF less than 1). Chromium was significantly higher in rhizomes compared to leaves, while Ni concentrations did not show significant difference. Both metals' concentrations were consistent between the ponds and locations in the ponds.

Cu concentrations in leaves and rhizomes were below the detection limit in all samples except one. There was a slight accumulation of Cu in the roots (CF = 1.1). The concentrations in the roots were consistent between the ponds as well as between different locations in the ponds.

Heavy metal concentrations in sampled plant species are presented in Table 28. In the majority of plant samples lead was below the detection limit. Detected concentrations in *P. natans* and *P. pusillus* were within the same range, while the concentration in *T. latifolia* was two-times lower and in *E. nuttallii* two-times higher compared to *Potamogeton* sp.

*Potamogeton* and *Elodea* sp. accumulated more zinc per gram of dry weight compared to *Typha*. Zn concentrations in *P. natans* in ponds B and D ranged between 89 and 329 µg $g^{-1}$ DW which in similar to *P. pusillus* in pond C (from 87 to 304 µg $g^{-1}$ DW). It is important to point out that sediment concentrations of Zn in these three ponds were different, being the highest in pond B, followed by D and C. Zn concentration in *E. canadensis* was similar to *Potamogeton* sp. (243 µg $g^{-1}$ DW), while it was much higher in *E. nuttallii*, namely 819 µg $g^{-1}$ DW.

**Table 28: Concentrations of heavy metals in µg $g^{-1}$ DW in different plant species and sediment at three sampling sites (In - inlet, Mid - middle and Out - outlet) along four classical wet detention ponds (A, B, C and D) (- indicates that the species was not present at the sampling site).**

| | | A | | | B | | | C | | | D | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | In | Mid | Out | In | Mid | Out | In | Mid | Out | In | Mid | Out |
| Pb | *T. latifolia* | <0.5 | <0.5 | 2.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| | *P. natans* | - | - | <0.5 | 5.1 | - | <0.5 | - | - | - | <0.5 | 3.4 | <0.5 |
| | *P. pusillus* | - | - | - | - | - | - | 5.3 | <0.5 | <0.5 | - | - | - |
| | *E. canadensis* | - | - | - | - | <0.5 | - | - | - | - | - | - | - |
| | *E. nuttallii* | - | - | - | 11 | - | - | - | - | - | - | - | - |
| | Sediment | 2.5 | <0.5 | <0.5 | 11 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | 2.6 | 2.5 | <0.5 |
| Zn | *T. latifolia* | 59 | 60 | 68 | 98 | 56 | 61 | 86 | 77 | 48 | 50 | 35 | 41 |
| | *P. natans* | - | - | 59 | 329 | - | 96 | - | - | - | 113 | 240 | 89 |
| | *P. pusillus* | - | - | - | - | - | - | 304 | 87 | 192 | - | - | - |
| | *E. canadensis* | - | - | - | - | 243 | - | - | - | - | - | - | - |
| | *E. nuttallii* | - | - | - | 819 | - | - | - | - | - | - | - | - |
| | Sediment | 48 | 44 | 32 | 206 | 108 | 38 | 33 | 49 | 71 | 77 | 69 | 59 |
| Ni | *T. latifolia* | 1.2 | 9.6 | 3.7 | 2.0 | 3.1 | 1.8 | 2.2 | 2.4 | 1.8 | 2.7 | 1.4 | 3.8 |
| | *P. natans* | - | - | 1.1 | 2.6 | - | 1.4 | - | - | - | 2.1 | 3.1 | 2.8 |
| | *P. pusillus* | - | - | - | - | - | - | 10 | 8.1 | 8.0 | - | - | - |
| | *E. canadensis* | - | - | - | - | 4.2 | - | - | - | - | - | - | - |
| | *E. nuttallii* | - | - | - | 11 | - | - | - | - | - | - | - | - |
| | Sediment | 8.7 | 16 | 8.0 | 10 | 12 | 10 | 8.4 | 13 | 12 | 12 | 11 | 12 |
| Cr | *T. latifolia* | 4.3 | 2.7 | 7.5 | 5.6 | 13 | 4.2 | 7.4 | 3.9 | 3.9 | 3.7 | 2.8 | 5.2 |
| | *P. natans* | - | - | 1.8 | 6.0 | - | 3.3 | - | - | - | 5.2 | 12 | 6.4 |
| | *P. pusillus* | - | - | - | - | - | - | 12 | 2.8 | 8.0 | - | - | - |
| | *E. canadensis* | - | - | - | - | 7.8 | - | - | - | - | - | - | - |
| | *E. nuttallii* | - | - | - | 9.2 | - | - | - | - | - | - | - | - |
| | Sediment | 14 | 22 | 13 | 18 | 22 | 18 | 16 | 19 | 21 | 17 | 17 | 16 |
| Cu | *T. latifolia* | 6.2 | <0.4 | 6.5 | 6.0 | 6.9 | 9.0 | <0.4 | 5.1 | 5.6 | 7.1 | <0.4 | <0.4 |
| | *P. natans* | - | - | <0.4 | 29 | - | 5.1 | - | - | - | 8.6 | 27 | 7.4 |
| | *P. pusillus* | - | - | - | - | - | - | 26 | 6.4 | 14 | - | - | - |
| | *E. canadensis* | - | - | - | - | 12 | - | - | - | - | - | - | - |
| | *E. nuttallii* | - | - | - | 57 | - | - | - | - | - | - | - | - |
| | Sediment | 7.8 | 9.5 | 7.4 | 26 | 13 | 5.3 | <0.4 | 6.8 | 8.5 | 11 | 9.8 | 8.2 |

Ni concentrations were lower compared to the sediment in *T. latifolia* and *P. natans* but in the same range in *P. pusillus* and *E. nuttallii* (from 8.0 to 11 µg $g^{-1}$ DW).

Cr concentrations were in most cases lower compared to the sediment. Concentrations ranged between 1.8 and 13 $\mu g\ g^{-1}$ DW and were not consistent between the species nor ponds or their locations.

Cu concentrations in *T. latifolia* were generally lower compared to the sediment, while in *P. natans*, *P. pusillus* and *E. nuttallii* also higher concentrations appeared (up to 75 $\mu g\ g^{-1}$ DW in *E. nuttallii*).

Cd was not detected in any of the plant samples.

### 4.3.3 Plants at upgraded wet detention ponds

In the upgraded wet detention ponds, plants were sampled according to the planting plan and analyzed for nutrients and metals. In Århus and Silkeborg, three plants of each planted species and in Odense one plant per species were sampled.

#### 4.3.3.1 Comparison of nutrient and metal content in *Phragmites australis* at the sand filters

Special attention was given to metal concentrations in *Phragmites australis* tissues at the sand filters at the outflow of each pond due to this part receives the highest hydraulic and pollutant load. The results are shown in the following figures. The concentration of each element in the plant tissues was compared to sediment concentration at each site. Besides this, average nutrient and metal concentrations in whole *Phragmites* plants were compared between the ponds.

P concentrations in the tissues of *P. australis* from the sand filters in the systems at Århus, Silkeborg and Odense compared to the corresponding sediment concentrations at each site are presented in Figure 38. There was a slight increase in plant P concentration with increasing sediment concentration. The increase was mainly caused by high P concentrations in *Phragmites* and sediment in the pond at Århus. Phosphorous concentration measured in the plants from the Århus pond was significantly higher compared to Silkeborg, which is in accordance with significantly higher P content in the sediment from Århus pond. Phosphorous concentrations in *P. australis* from Århus were also higher compared to *Phragmites* from Odense, but the difference was not statistically significant. There was no significant difference in P concentration between *Phragmites* plants in Odense and Silkeborg despite significantly higher P concentration in the sediment from Silkeborg compared to Odense. In all the systems leaves contained more phosphorous than other tissues.

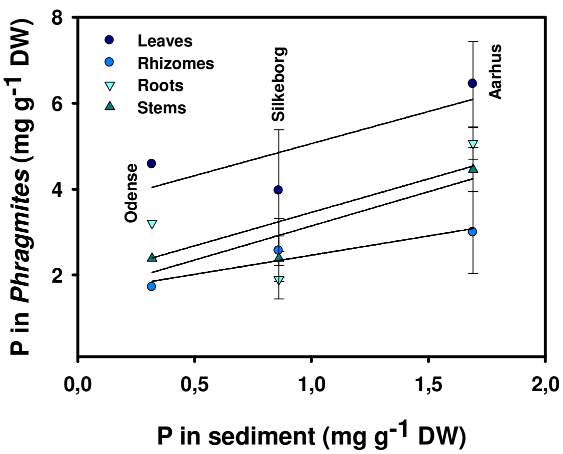


**Figure 38: Phosphorous concentrations in *P. australis* tissues compared to the concentrations in the sediment from stormwater treatment systems at Århus, Odense and Silkeborg.**

Iron concentrations in *P. australis* at the sand filters were higher in the roots compared to the rhizomes, stems and leaves in all investigated ponds. There was no correlation between root and sediment Fe concentrations. However, Fe concentrations in the roots were lower in Silkeborg (8 mg g$^{-1}$ DW) compared to Århus and Odense (21 and 22 mg g$^{-1}$ DW, respectively) which is in accordance with significantly lower Fe concentration in the sediment of Silkeborg compared to the other two ponds. However, the difference in iron concentrations in *Phragmites* from the three filters was not significant. It was expected that the plants from Århus would have higher iron concentrations due to addition of iron salts to the sediment of this pond (Figure 39).

No significant difference was observed in Mn, Ca, Na, K and Al concentrations in *P. australis* plants between the ponds. Comparing plant parts, Mn concentrations were higher in roots compared to the rhizomes, stems and leaves in all wet detention ponds. Small differences in

Mn concentration in the sediment between three wet ponds did not affect the Mn concentrations in the plants significantly (Figure 40).

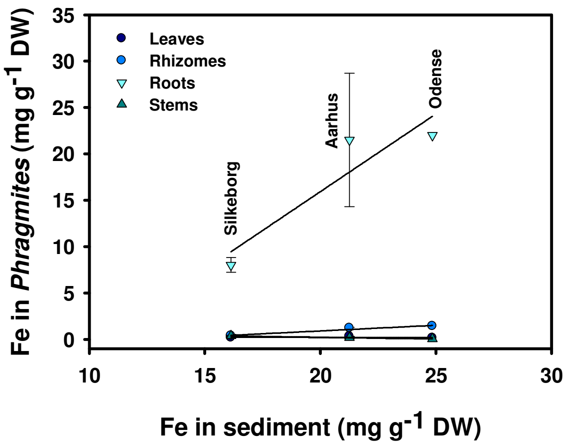


**Figure 39: Iron concentrations in *P. australis* tissues compared to the concentrations in the sediment from stormwater treatment systems at Århus, Odense and Silkeborg.**

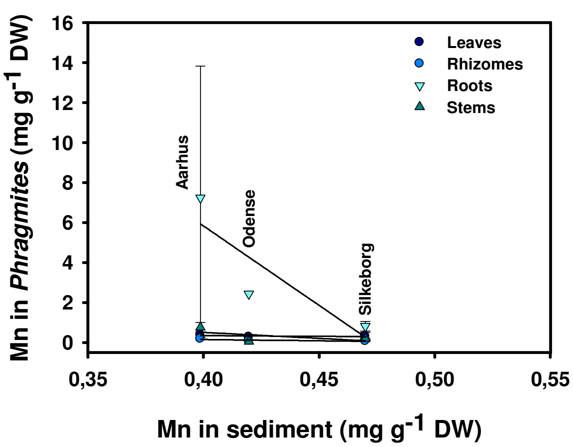


**Figure 40: Manganese concentrations in *P. australis* tissues compared to the concentrations in the sediment from stormwater treatment systems at Århus, Odense and Silkeborg.**

Ca concentrations were higher in the roots compared to the other plant parts in Odense and Århus, but not in Silkeborg, where the concentration in the sediment was the lowest. Despite Ca concentration in the sediment in Silkeborg pond was lower compared to Århus and Odense, there was no significant difference in Ca concentration in *Phragmites* plants from the three ponds (Figure 41). There was an increase in root Ca concentration with increasing sediment Ca concentration, however it was not statistically significant.

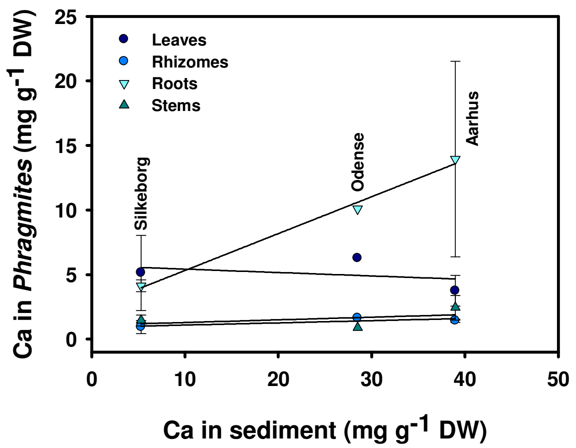


**Figure 41: Calcium concentrations in *P. australis* tissues compared to the concentrations in the sediment from stormwater treatment systems at Århus, Odense and Silkeborg.**

Sodium concentrations in *Phragmites* tissues were higher in the roots, followed by the rhizomes and stems and the lowest in the leaves. There was no significant difference in Na concentrations between the plants from three investigated wet detention ponds (Figure 42). There was no correlation between Na concentrations in the roots and in the sediments.

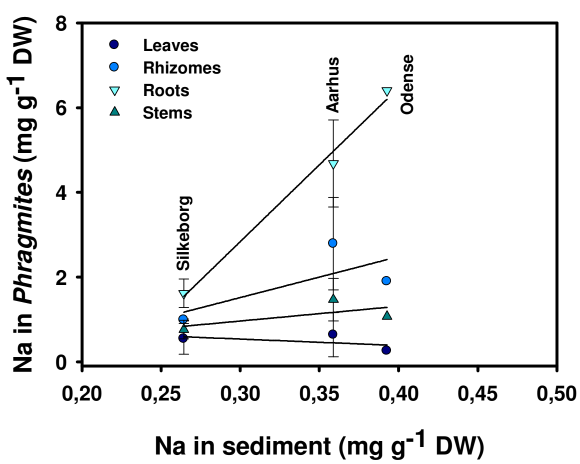


**Figure 42: Sodium concentrations in *P. australis* tissues compared to the concentrations in the sediment from stormwater treatment systems at Århus, Odense and Silkeborg.**

Potassium concentrations in reed tissues at the sand filters were higher in the aerial tissues than other plant parts. Stems sampled at Århus had the highest concentration of K (29 mg $g^{-1}$ DW) which is about twice the concentrations in stems from the other two systems. There was no significant difference in K concentration in *Phragmites* from the three wet detention ponds despite significantly lower K concentration in the sediment at Silkeborg compared to Århus (Figure 43). There was no correlation between tissue and sediment K concentration.

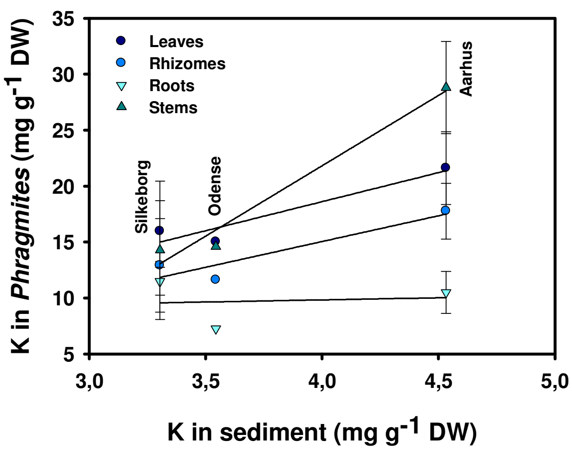


**Figure 43: Potassium concentrations in *P. australis* tissues compared to the concentrations in the sediment from stormwater treatment systems at Århus, Odense and Silkeborg.**

Aluminium concentrations were higher in roots compared to the other plant parts. As well as in the sediment also in *Phragmites*, there was no significant difference in Al concentrations between the wet detention ponds (Figure 44).

Results of heavy metal analyzes in *P. australis* from the sand filter showed higher variability between the ponds and tissues compared to macroelements. Lead was detected only in *Phragmites*' roots from Århus and Odense with more than 20-times higher concentration in Odense (not presented in a figure). This is in accordance with 20-times higher Pb concentrations in Odense sediment, compared to the sediment in Århus.

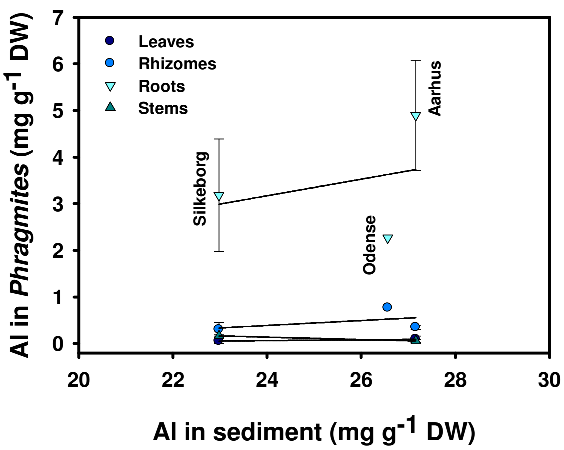


**Figure 44: Alumina concentrations in *P. australis* tissues compared to the concentrations in the sediment from stormwater treatment systems at Århus, Odense and Silkeborg.**

The Zn concentration was significantly higher (more than 15-times) in *Phragmites* from Odense compared to Silkeborg, which is in accordance with markedly higher sediment Zn concentration in Odense (Figure 45). Despite sediment Zn concentration in Odense was also significantly higher compared to Århus, there was no significant difference in Zn concentration in the reeds from the two ponds. In all wet detention ponds, Zn was accumulated in the roots, where concentrations were 4, 6 and 16-times higher compared to the leaves, for Silkeborg, Århus and Odense, respectively. Zn concentrations in the roots were 10 and 20-times higher in Odense compared to Århus and Silkeborg, respectively. Therefore, there was a strong and significant positive correlation between Zn in the roots and Zn in the sediment, but not for other tissues.

As other heavy metals, Ni was accumulated in the roots, namely with 15, 25 and 100-times higher concentrations compared to the leaves. There was no significant difference in Ni concentrations in the reeds from the three sand filters, despite significantly higher Ni concentration in the sediment in Odense compared to Århus and Silkeborg (Figure 46). However, comparing only the root concentrations, there was a correlation between the concentrations in the roots and in the sediment: the concentration of Ni in the roots was 20-times higher in Odense compared to Silkeborg and 10-times higher compared to Århus.

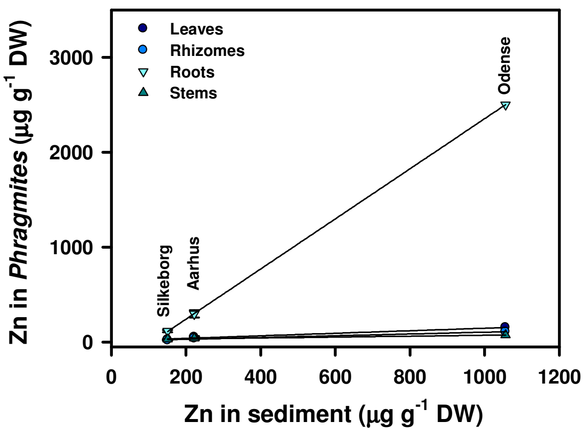


**Figure 45: Zinc concentrations in *P. australis* tissues compared to the concentrations in the sediment from stormwater treatment systems at Århus, Odense and Silkeborg.**

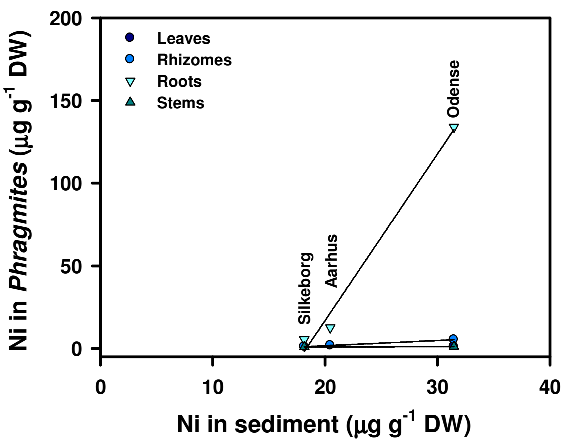


**Figure 46: Nickel concentrations in *P. australis* tissues compared to the concentrations in the sediment from stormwater treatment systems at Århus, Odense and Silkeborg**

There was no significant difference in Cr concentration between the *Phragmites* stands at the three sand filters. With increasing sediment concentration Cr concentration in the leaves and roots remained within the same range, while the concentration increased in the rhizomes from 4.5 to 20 µg $g^{-1}$ DW and shows significant positive correlation with sediment Cr concentration. With increasing sediment concentration, Cr concentration in the stems decreased from 5.0 to 0.8 µg $g^{-1}$ DW, but statistical analysis showed no correlation (Figure 47).

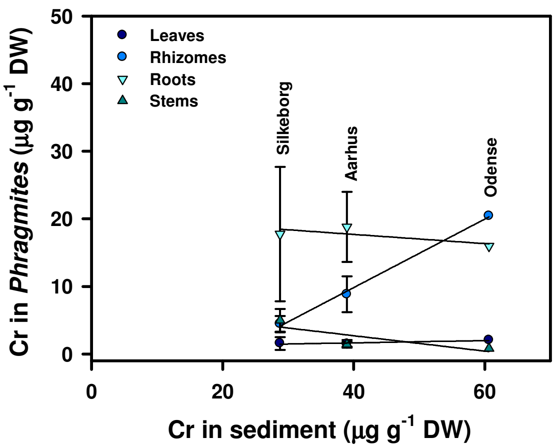


**Figure 47: Chromium concentrations in *P. australis* tissues compared to the concentrations in the sediment from stormwater treatment systems at Århus, Odense and Silkeborg.**

There was no significant difference in Cu concentration in *Phragmites* plants between the three sand filters, however Cu concentration in the roots was 115 and 125-times higher in Odense compared to Århus and Silkeborg. As other heavy metals, Cu was accumulated in the roots. It was also detected in other plant tissues in Odense and in rhizomes in Silkeborg, but not in Århus. There was a significant strong positive correlation between increasing Cu concentration in the roots and in the sediment (Figure 48).

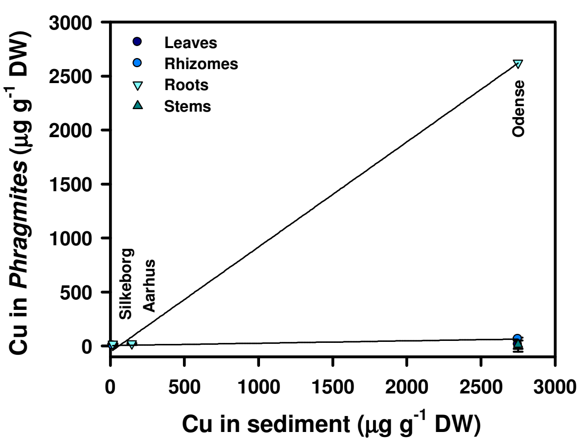


**Figure 48: Copper concentrations in *P. australis* tissues compared to the concentrations in the sediment from stormwater treatment systems at Århus, Odense and Silkeborg.**

#### 4.3.3.2 Comparison of nutrient and metal content in different plant species at Århus pond

The Århus pond was designed with three islands of wetland vegetation, namely *Scirpus lacustris* and *Nympaea alba*/*Nuphar luteum*. The water lilies did however not survive thus only *S. lacustris* was sampled. Three plants were sampled and divided on root, rhizome and leave tissues. The results are shown in Table 29 and Table 30 together with the concentrations of macroelements and heavy metals in *P. australis* from the sand filter. Element content in different tissues was compared by one-way ANOVA.

Comparing *Phragmites* and *S. lacustris* in Århus pond (Table 29), *S. lacustris* contained significantly higher P concentrations. In *S. lacustris,* P was stored mainly in the rhizomes but the difference was not significant compared to the other tissues, while in *P. australis* P was stored mainly in leaves, which had significantly higher concentrations compared to the rhizomes.

*P. australis* and *S. lacustris* did not differ significantly in the concentration of other macroelements except in K concentration, which was significantly higher in *Phragmites*, especially in stems and leaves. Comparing plant tissues of both species Fe, Mn and Al were stored mainly in the roots, which had significantly higher concentrations compared to aboveground tissues. Ca and Na in *Phragmites* were stored in the roots, but in *Scirpus* the concentrations were higher in the leaves.

**Table 29: Average macroelement concentrations (± 1 standard deviation) in mg g$^{-1}$ DW in *P. australis* and *S. lacustris* tissues from stormwater treatment pond at Århus. Different superscript letters indicate significant differences between the tissues at the 5% probability level.**

| | Tissue | P | Fe | Mn | Ca | Na | K | Al |
|---|---|---|---|---|---|---|---|---|
| *P. australis* | roots | $5.1\pm0.4^{ab}$ | $22\pm7^{c}$ | $7.2\pm7^{b}$ | $14\pm8^{b}$ | $4.7\pm1.0^{b}$ | $11\pm2^{a}$ | $4.9\pm1.2^{c}$ |
| | rhizomes | $3.0\pm0.9^{a}$ | $1.2\pm0.1^{b}$ | $0.2\pm0.1^{a}$ | $1.4\pm0.1^{a}$ | $2.8\pm1.1^{ab}$ | $18\pm3^{ab}$ | $0.3\pm0.05^{b}$ |
| | stems | $4.5\pm0.5^{ab}$ | $0.2\pm0.1^{a}$ | $0.8\pm0.2^{a}$ | $2.4\pm1.0^{a}$ | $1.5\pm0.5^{a}$ | $29\pm4^{c}$ | $0.1\pm0.04^{a}$ |
| | leaves | $6.4\pm1.0^{b}$ | $0.3\pm0.03^{a}$ | $0.4\pm0.1^{a}$ | $3.7\pm1.2^{a}$ | $0.6\pm0.5^{a}$ | $22\pm3^{bc}$ | $0.1\pm0.1^{a}$ |
| *S. lacustris* | roots | 5.8±2.7 | $23\pm12^{c}$ | $0.7\pm0.4^{ab}$ | $5.5\pm1.7^{b}$ | 5.3±1.2 | 9,5±5.7 | $4.3\pm1.0^{b}$ |
| | rhizomes | 9.7±2.7 | $3.2\pm1.8^{b}$ | $0.2\pm0.02^{a}$ | $1.8\pm0.6^{a}$ | 9±3.4 | 17±14 | $0.9\pm0.8^{a}$ |
| | leaves | 5.7±0.8 | $0.2\pm0.02^{a}$ | $1.8\pm0.9^{b}$ | $5\pm1.5^{b}$ | 11±5.6 | 18±6 | $0.1\pm0.03^{a}$ |

*P. australis* contained significantly higher concentrations of Pb, Zn and Cu compared to *Scirpus*, while *Scirpus* accumulated more Ni and Cr. Pb and Cu were detected only in the roots, while Cd was not detected in any of the species nor tissues. Zn, Ni and Cr were accumulated in the roots of both species. The concentrations were significantly higher compared to the aboveground tissues. The accumulation coefficients and concentration factors are described in the Chapter 4.3.1.

**Table 30: Average heavy metal concentrations (± 1 standard deviation) in mg $g^{-1}$ DW in *P. australis* and *S. lacustris* tissues from stormwater treatment pond at Århus. Different superscript letters indicate significant differences between the tissues at the 5% probability level.**

| | Tissue | Pb | Zn | Cd | Ni | Cr | Cu |
|---|---|---|---|---|---|---|---|
| *P. australis* | roots | 4.9±1.8 | 298±38$^{b}$ | <0.5 | 13±2$^{c}$ | 19±5.2$^{b}$ | 23±5.9 |
| | rhizomes | <2 | 40±16$^{a}$ | <0.5 | 1.8±0.8$^{b}$ | 8.8±2.7$^{b}$ | <5 |
| | stems | <2 | 39±6$^{a}$ | <0.5 | <0.5$^{a}$ | 1.4±0.3$^{a}$ | <5 |
| | leaves | <2 | 51±14$^{a}$ | <0.5 | 0.5±0.4$^{a}$ | 1.5±0.6$^{a}$ | <5 |
| *S. lacustris* | roots | <2 | 172±122 | <0.5 | 10±4.5$^{b}$ | 49±7.7$^{b}$ | 15±11 |
| | rhizomes | <2 | 51±14 | <0.5 | 6.3±6.1$^{ab}$ | 27±17$^{b}$ | <5 |
| | leaves | <2 | 28±3.4 | <0.5 | 0.6±0.6$^{a}$ | 2.7±1.1$^{a}$ | <5 |

#### 4.3.3.3 Comparison of nutrient and metal content in different plant species at Odense pond

Only one plant per planting patch was sampled in Odense pond, therefore ANOVA in elements contents between the plant species was not carried out. The results of metal concentration are presented in Table 32. The results from different patches of the same species were gathered.

The highest P concentration was detected in *A. lanceolatum* (14 mg $g^{-1}$ DW). P was mainly accumulated in the leaves, except in *Typha* sp. where the concentrations were higher in rhizomes and roots. Iron was accumulated in the roots, the concentrations were the highest in *R. hydrolapathum* and *T. minima* (33 and 35 mg $g^{-1}$ DW, respectively). Mn and Ca concentrations were higher in the roots in majority of plant species. *I. pseudacorus* and *A. lanceolatum* had higher Ca concentration, especially in *Iris* leaves.

Pb, Zn, Ni and Cu were accumulated in the roots with the highest concentrations in *R. hydrolapathum* (144; 4,700; 180 and 4,400 µg $g^{-1}$ DW for Pb, Zn, Ni and Cu, respectively).

Approximately two-times lower concentrations were detected in *P. australis* roots and three-times lower in *Typha* sp. roots. There was no significant difference in heavy metal accumulation between *P. australis* and *Typha* sp.

The pond at Odense included two *P. australis* stands. Besides the reeds at the sand filter, there was also a *Phragmites* stand on the right bank of the pond. Heavy metal concentrations in the roots from the two stands are presented in Table 31. Since the plants at the sand filter receive higher hydraulic and pollutant loads, the concentrations of all measured heavy metals are higher at the sand filter.

**Table 31: Heavy metal concentrations in *Phragmites australis* roots at the sand filter and side stand of the wet detention pond at Odense.**

| | Pb | Zn | Ni | Cr | Cu |
|---|---|---|---|---|---|
| | | | $\mu g\ g^{-1}$ DW | | |
| Sand filter | 110 | 2,500 | 130 | 16 | 2,600 |
| Side stand | 50 | 1,260 | 70 | 10 | 1,400 |

**Table 32: Average nutrient and metal concentrations (± 1 standard deviation) in plant species from stormwater treatment pond at Odense.**

| Species | Tissue | P | Fe | Mn | Ca | Na | K | Al | Pb | Zn | Cd | Ni | Cr | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | mg $g^{-1}$ DW | | | | | | | μg $g^{-1}$ DW | | |
| *A. lanceolatum* | whole plant | 14 | 14 | 0.8 | 22 | 6.9 | 55 | 1.8 | 25 | 740 | <0.5 | 35 | 29 | 580 |
| *I. pseudacorus* | bulks | 2.5±0.7 | 1.9±1.8 | 0.06±0.05 | 12±0.6 | 0.9±0.7 | 12±0.2 | 0.8±0.3 | 2.5±2.1 | 73±54 | <0.5 | 2.1±1.8 | 5.9±5.0 | 62±64 |
| | leaves | 4.3±0.2 | 0.1±0.05 | 0.2±0.2 | 22±9.4 | 1.1±0.2 | 26±7.7 | <0.005 | <2 | 18±4.2 | <0.5 | <0.5 | 1.3±0.2 | 14±4.1 |
| *P. australis* | roots | 3.0±0.3 | 18±5.9 | 1.6±1.2 | 10±0.2 | 6.3±0.1 | 9.3±2.8 | 1.8±0.6 | 82±42 | 1,880±880 | <0.5 | 101±46 | 13±3.8 | 2,000±870 |
| | rhizomes | 2.2±0.6 | 1.2±0.3 | 0.06±0.03 | 1.2±0.6 | 1.7±0.3 | 15±5.3 | 0.6±0.2 | <2 | 81±39 | <0.5 | 4.2±1.6 | 13±9.9 | 57±11 |
| | stems | 2.4±0.03 | 0.1±0.04 | 0.04±0.01 | 1.0±0.2 | 1.0±0.2 | 14±0.2 | <0.005 | <2 | 110±52 | <0.5 | 1.3±0.3 | 1.4±0.8 | 14±1.1 |
| | leaves | 4.3±0.3 | 0.2±0.02 | 0.3±0.03 | 7.3±1.4 | 0.2±0.02 | 15±0.4 | <0.005 | <2 | 115±55 | <0.5 | 1.3±0.03 | 1.6±0.6 | 14±0.8 |
| *R. lingua* | whole plant | 3.9 | 2.9 | 0.5 | 11 | 9.0 | 17 | 0.2 | 12 | 290 | <0.5 | 8.5 | 2.8 | 170 |
| *R. hydrolapathum* | roots | <0.01 | 33 | 1.5 | 18 | 2.0 | 3.1 | 3.5 | 144 | 4,700 | <0.5 | 180 | 27 | 4,400 |
| | storage roots | 3.6 | 1.4 | 0.06 | 3.2 | 2.0 | 15 | 0.03 | <2 | 100 | <0.5 | 3.2 | 1.1 | 44 |
| | leaves | 5.2 | 0.3 | 0.1 | 6.1 | 3.4 | 29 | 0.09 | <2 | 92 | <0.5 | 5.1 | 1.7 | 45 |
| *S. sagittifolia* | whole plant | 9.2 | 7.0 | 0.5 | 9.1 | 7.1 | 38 | 0.6 | 13 | 245 | <0.5 | 11 | 4.1 | 170 |
| *T. angustifolia* | roots | 3.3±1.2 | 23±2.2 | 1.0±0.03 | 15±6.6 | 12±0.1 | 13±6.5 | 2.3±0.5 | 46±9.3 | 1,130±300 | <0.5 | 49±9.5 | 12 | 1,190±390 |
| | rhizomes | 6.5±0.9 | 3.9±2.9 | 0.2±0.04 | 6.8±0.2 | 5.4±1.2 | 28±6.3 | 0.2±0.05 | <2 | 110±28 | <0.5 | 4.9±1.0 | 1.6±0.3 | 81±39 |
| | leaves | 5.3±0.3 | 0.1±0.02 | 0.5±0.2 | 6.2±0.5 | 4.1±0.03 | 19±1.3 | <0.005 | <2 | 30±5.0 | <0.5 | 2.1±0.5 | 1.3±0.9 | 11±0.27 |
| *T. latifolia* | roots | 4.5±0.7 | 22±1.0 | 0.7±0.2 | 14±1.9 | 13±0.7 | 20±1.4 | 1.7±0.1 | 49±10 | 1,080±57 | <0.5 | 46±5.0 | 12±1.5 | 1,170 |
| | rhizomes | 8.1±0.2 | 5.5±2.2 | 0.1±0.06 | 6.3±0.7 | 8.4±2.9 | 32±3.4 | 0.2±0.02 | 4.4±2.0 | 155±30 | <0.5 | 5.8±0.3 | 5.3±0.6 | 100±43 |
| | leaves | 5.4±0.2 | 0.2±0.03 | 0.6±0.06 | 9.1±0.6 | 2.9±0.4 | 27±0.5 | 0.01±0.01 | <2 | 41±8.6 | <0.5 | 3.4±0.3 | 1.0±0.4 | 19±2.4 |
| *T. minima* | roots | 9.2 | 35 | 2.1 | 17 | 18 | 17 | 2.6 | 66 | 950 | <0.5 | 33 | 16 | 810 |
| | rhizomes | 7.2 | 5.6 | 0.3 | 10 | 8.8 | 25 | 0.3 | 6.9 | 150 | <0.5 | 5.7 | 3.6 | 125 |
| | leaves | 4.4 | 0.2 | 0.6 | 14 | 4.4 | 14 | 0.02 | 5.0 | 41 | <0.5 | 2.0 | 1.5 | 59 |

#### 4.3.3.4 Comparison of nutrient and metal content in different plant species at Silkeborg pond

Results of macronutrient and heavy metal analyzes in the plants sampled in Silkeborg pond are presented in Table 33. ANOVA was used to define the differences in macronutrient and heavy metal content between different plant tissues.

Phosphorous concentrations in *C. palustris*, *I. pseudacorus*, *P. australis*, *S. erectum* was significantly higher in leaves compared to the other tissues. In *Typha* sp., P concentration was similar in the leaves and rhizomes. Compared to the other plant species, *A. lanceolatum* and leaves of *C. palustris* had the highest P concentration (13±1.0 and 12±2.5 mg $g^{-1}$ DW, respectively).

In all sampled species, Fe concentrations were (significantly) higher in the roots compared to the other plant tissues, except in *S. erectum*, where Fe was also high in the rhizomes. The concentrations in the roots varied from 4.3±2.9 in *I. pseudacorus* to 32±21 mg $g^{-1}$ DW in *S. maritimus*. Mn was mainly stored in the roots, although the difference compared to the other tissues was significant only for *P. australis* and *T. angustifolia*. However, in *R. lingua* the concentration was higher in the leaves.

Ca concentrations were mainly higher in the leaves compared to the other plant tissues, however in *I. pseudacorus*, Ca content was also high in the bulks and in *P. australis* in the roots. In addition, *S. erectum* and *T. angustifolia* had higher Ca content in the roots but in *T. minima,* the concentration was the highest in the rhizomes.

In *I. pseudacorus*, *P. australis*, *R. hydrolapathum* and *T. angustifolia* sodium was significantly higher in the roots compared to the other tissues, while in *R. lingua* and *S. erectum*, the concentration was significantly higher in the leaves. In majority of the species, K concentrations were significantly higher in the leaves than roots. In all species divided on tissues, Al was (significantly) higher in the roots, except in *T. minima* where it was also higher in the rhizomes.

In investigated plant species, lead was above the detection limit only in the roots, with an exception of *R. lingua*, where it was also above the detection limit in the rhizomes. The highest concentration was detected in *C. palustris* (4.9±3.5 μg $g^{-1}$ DW), which was planted at the inlet of the pond.

Zn, Ni, Cr and Cu accumulated in the roots of all investigated species with no significant transport to aboveground parts. The concentration of heavy metals in the roots and accumulation in aboveground tissues are described in Chapter 4.3.2.5. Zn concentration was higher in the roots compared to the other tissues in all investigated species. The highest root Zn concentration was measured in *C. palustris* (250±89 μg $g^{-1}$ DW) planted at the inflow and the lowest in *I. pseudacorus* (75±51 μg $g^{-1}$ DW).

Nickel was significantly higher in belowground tissues, except in *S. erectum*, where the difference in Ni concentration between the roots and leaves was not significantly different. The highest root Ni concentration was measured in *R. lingua* (11±2.8 μg $g^{-1}$ DW) and the lowest in *I. pseudacorus* (2.8±1.0 μg $g^{-1}$ DW).

Cr and Cu were accumulated in belowground tissues, but the difference compared to aboveground tissues was not always significant. The highest root concentration was detected in *R. lingua* (38±17 and 27±8.6 μg $g^{-1}$ DW, for Cr and Cu, respectively).

A comparison of the heavy metal concentrations between *Phragmites australis* and *Typha* sp. as the most common species used in constructed wetlands, did not show significant difference, except for Cu concentration, which was significantly higher in *Typha*.

In the Silkeborg pond, Cd was not detected in any of the plants.

**Table 33: Average nutrient and metal concentrations (± 1 standard deviation) in plant species from stormwater treatment pond at Silkeborg.**

| Species | Tissue | P | Fe | Mn | Ca | Na | K | Al | Pb | Zn | Cd | Ni | Cr | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | mg $g^{-1}$ DW | | | | | | | µg $g^{-1}$ DW | | | | | |
| *A. lanceolatum* | whole plant | 13±1.0 | 7.6±3.3 | 3.2±1.0 | 7.7±0.5 | 10±2.3 | 63±13 | 2.3±1.2 | <2 | 114±42 | <0.5 | 5.1±1.6 | 7.7±3.0 | 19±6.4 |
| *C. palustris* | roots | 4.7±1.2$^{a}$ | 23±5.9$^{b}$ | 2.0±1.8 | 12±0.6 | 6.2±5.2 | 6.6±4.5$^{a}$ | 4.7±0.9$^{b}$ | 4.9±3.5 | 250±89$^{b}$ | <0.5 | 6.2±1.5$^{b}$ | 11±1.9$^{b}$ | 25±6.0$^{b}$ |
| | leaves | 12±2.5$^{b}$ | 1.6±0.5$^{a}$ | 2.1±0.9 | 10±1.4 | 11±6.6 | 52±5.3$^{b}$ | 1.1±0.2$^{a}$ | <2 | 132±63$^{a}$ | <0.5 | 2.4±0.5$^{a}$ | 4.3±1.6$^{a}$ | 11±4.9$^{a}$ |
| *I. pseudacorus* | roots | 4.1±1.2$^{a}$ | 4.3±2.9$^{b}$ | 0.5±0.6 | 6.6±1.0$^{a}$ | 3.7±1.2$^{c}$ | 13±4.3$^{a}$ | 1.6±0.7$^{b}$ | <2 | 75±51 | <0.5 | 2.8±1.0$^{b}$ | 5.4±2.1 | 11±3.9$^{b}$ |
| | bulks | 4.0±1.7$^{a}$ | 0.9±0.5$^{a}$ | 0.2±0.1 | 10±2.6$^{b}$ | 2.5±0.8$^{b}$ | 27±12$^{b}$ | 0.6±0.5$^{a}$ | <2 | 43±13 | <0.5 | 1.9±0.7$^{ab}$ | 6.2±4.1 | 14±5.7$^{b}$ |
| | leaves | 5.7±0.9$^{b}$ | 0.6±0.3$^{a}$ | 0.6±0.3 | 12±2.8$^{b}$ | 1.6±0.2$^{a}$ | 34±6.4$^{b}$ | 0.4±0.3$^{a}$ | <2 | 28±6.6 | <0.5 | 1.3±0.6$^{a}$ | 2.1±0.9 | <5$^{a}$ |
| *P. australis* | roots | 2.4±0.5$^{a}$ | 9.8±3.2$^{c}$ | 0.7±0.2$^{c}$ | 3.2±0.9$^{b}$ | 5.1±2.3$^{c}$ | 7.0±3.3$^{a}$ | 2.1±1.0 | 3.8±2.2 | 115±31$^{b}$ | <0.5 | 4.1±1.0$^{b}$ | 11±7.3$^{b}$ | 12±6.4$^{b}$ |
| | rhizomes | 2.4±0.7$^{a}$ | 0.7±0.4$^{b}$ | 0.1±0.03$^{a}$ | 0.7±0.4$^{a}$ | 1.7±0.7$^{b}$ | 9.6±4.4$^{a}$ | 0.3±0.1 | <2 | 20±3.5$^{a}$ | <0.5 | 0.9±0.4$^{a}$ | 4.4±1.8$^{ab}$ | <5$^{a}$ |
| | stems | 2.1±0.6$^{a}$ | 0.3±0.1$^{a}$ | 0.2±0.1$^{b}$ | 1.0±0.5$^{a}$ | 1.1±0.5$^{ab}$ | 10±5.1$^{ab}$ | 0.1±0.1 | <2 | 26±7.5$^{a}$ | <0.5 | 0.6±0.4$^{a}$ | 3.9±2.9$^{a}$ | <5$^{a}$ |
| | leaves | 3.9±0.8$^{b}$ | 0.5±0.3$^{ab}$ | 0.3±0.1$^{b}$ | 3.7±1.9$^{b}$ | 0.7±0.3$^{a}$ | 15±2.4$^{b}$ | 0.1±0.1 | <2 | 25±3.9$^{a}$ | <0.5 | 0.6±0.4$^{a}$ | 2.5±2.7$^{a}$ | <5$^{a}$ |
| *R. lingua* | roots | 3.5±0.8 | 19±7$^{c}$ | 1.9±1.3 | 10±4.7$^{a}$ | 4.8±2.8$^{a}$ | 8.3±5.3$^{ab}$ | 7.8±2.1$^{b}$ | 2.0±1.6 | 153±23$^{c}$ | <0.5 | 11±2.8$^{b}$ | 38±17$^{b}$ | 27±8.6$^{b}$ |
| | rhizomes | 3.8±0.6 | 7.2±2.2$^{b}$ | 0.6±0.2 | 7.1±1.8$^{a}$ | 2.7±1.1$^{a}$ | 7.0±2.6$^{a}$ | 1.9±1.2$^{a}$ | 1.3±0.5 | 30±12$^{a}$ | <0.5 | 2.2±1.6$^{a}$ | 4.8±2.1$^{a}$ | 8.8±1.9$^{a}$ |
| | leaves | 4.7±0.6 | 1.7±0.7$^{a}$ | 3.1±0.4 | 21±3.7$^{b}$ | 9.1±1.8$^{b}$ | 15±3.2$^{b}$ | 1.4±0.7$^{a}$ | <2 | 95±31$^{b}$ | <0.5 | 2.5±1.2$^{a}$ | 4.6±2.3$^{a}$ | 9.8±3.7$^{a}$ |
| *R. hydrolapathum* | roots | 3.3±0.6 | 11±9 | 2.1±1.8 | 9,8±1.6 | 5.6±2.7$^{b}$ | 13±5.5 | 2.6±1.4$^{b}$ | <2 | 140±66 | <0.5 | 5.1±2.6$^{b}$ | 5.8±3.2$^{b}$ | 25±7.5$^{c}$ |
| | storage roots | 3.1±0.6 | 1.3 | 0.2±0.3 | 6.7±1.0 | 1.5±1.8$^{a}$ | 8.3±1.5 | 0.4±0.8$^{a}$ | <2 | 32±22 | <0.5 | 1.1±1.5$^{a}$ | 1.7±3.3$^{a}$ | 15±4.0$^{b}$ |
| | leaves | 3.0±0.2 | 0.3±0.1 | 0.7±0.2 | 18±6.9 | 2.5±0.9$^{a}$ | 17±0.7 | 0.1±0.1$^{a}$ | <2 | 18±4.3 | <0.5 | <0.5$^{a}$ | 1.0±0.5$^{ab}$ | <5$^{a}$ |
| *S. sagittifolia* | whole plant | 8.6±1.5 | 10±2.4 | 2.4±1.3 | 8.1±1.3 | 9.9±3.9 | 37±10 | 3.0±0.6 | <2 | 117±34 | <0.5 | 6.5±0.6 | 16±6.5 | 15±6.9 |
| *S. maritimus* | roots | 3.8±1.6 | 32±21$^{c}$ | 1.4±0.4 | 4.7±0.1 | 6.4±2.7 | 7.5±3.6 | 5.4±1.2$^{b}$ | 2.2±1.2 | 161±3.4$^{b}$ | <0.5 | 6.7±0.9$^{b}$ | 24±11 | 17±0,5$^{b}$ |
| | rhizomes | 4.8±1.5 | 3.4±0.6$^{b}$ | 0.5±0.2 | 2.3±0.3 | 6.6±0.9 | 17±6.5 | 0.7±0.3$^{a}$ | <2 | 29±5.3$^{a}$ | <0.5 | 4.1±3.7$^{ab}$ | 13±11 | 7.7±2.0$^{a}$ |
| | leaves | 4.7±1.4 | 0.7±0.4$^{a}$ | 0.8±0.7 | 3.2±2.2 | 9.7±2.7 | 18±6.5 | 0.4±0.3$^{a}$ | <2 | 25±8.3$^{a}$ | <0.5 | 0.9±0.6$^{a}$ | 2.0±1.1 | 6.0±3.1$^{a}$ |
| *S. erectum* | roots | 4.0±0.9$^{a}$ | 29±1.2$^{b}$ | 6.3±4.0 | 7.9±1.5$^{ab}$ | 5.2±0.9$^{a}$ | 16±7.5$^{a}$ | 3.7±0.2$^{b}$ | <2 | 138±24$^{b}$ | <0.5 | 7.7±3.9$^{b}$ | 16±7.1 | 11±3.8 |
| | rhizomes | 4.2±0.3$^{a}$ | 21±13$^{b}$ | 1.3±1.4 | 4.9±1.1$^{a}$ | 6.9±1.2$^{a}$ | 28±1.7$^{ab}$ | 0.6±0.5$^{a}$ | <2 | 35±10$^{a}$ | <0.5 | 0.6±0.5$^{a}$ | 5.8±3.0 | 5±2.2 |
| | leaves | 8.1±1.0$^{b}$ | 2±0.9$^{a}$ | 2.6±1.5 | 11±2.9$^{b}$ | 11±1.6$^{b}$ | 33±7.0$^{b}$ | 1.2±0.5$^{a}$ | <2 | 61±19$^{a}$ | <0.5 | 2.6±1.7$^{ab}$ | 3,9±2.3 | 12±2.0 |
| *S. aloides* | whole plant | 4.1 | 1.0 | 1.7 | 9.2 | 2.0 | 15 | 0.3 | <2 | 35 | <0.5 | 0.8 | 1.7 | <5 |
| *T. angustifolia* | roots | 4.2±0.7 | 15±3.9$^{c}$ | 1.9±0.9$^{c}$ | 7.4±0.4 | 9.1±3.5$^{b}$ | 25±6.8 | 4.9±3.4$^{b}$ | <2 | 156±66$^{b}$ | <0.5 | 6.4±4.5$^{b}$ | 11±6.5$^{b}$ | 19±14$^{b}$ |
| | rhizomes | 6.4±2.1 | 2.4±1.9$^{b}$ | 0.3±0.1$^{a}$ | 4.7±0.1 | 5.8±2.0$^{ab}$ | 36±15 | 0.4±0.4$^{a}$ | <2 | 22±8.8$^{a}$ | <0.5 | 1.1±0.8$^{a}$ | 3.1±2.6$^{a}$ | 6.5±2.2$^{a}$ |
| | leaves | 5.5±1.0 | 0.3±0.2$^{a}$ | 0.7±0.3$^{b}$ | 6.9±2.7 | 4.4±1.4$^{a}$ | 38±7.9 | 0.1±0.1$^{a}$ | <2 | 16±4.4$^{a}$ | <0.5 | 0.9±0.3$^{a}$ | 1.2±0.3$^{a}$ | 8.2±2.3$^{a}$ |
| *T. minima* | roots | 3.7±1.3 | 15±6.3$^{c}$ | 1.0±0.6 | 10±2.8$^{ab}$ | 9.8±4.0 | 7.4±3.2 | 3.5±4.1$^{b}$ | <2 | 165±62$^{c}$ | <0.5 | 4.8±3.6$^{b}$ | 9.9±6.2$^{b}$ | 11±4.9 |
| | rhizomes | 4.6±1.7 | 3.1±1.6$^{b}$ | 0.4±0.2 | 13±2.3$^{b}$ | 7.2±4.2 | 17±22 | 0.7±0.2$^{b}$ | <2 | 57±14$^{b}$ | <0.5 | 1.8±0.9$^{b}$ | 12±9.5$^{b}$ | 7.6±6.6 |
| | leaves | 5.0±0.9 | 0.3±0.1$^{a}$ | 0.8±0.2 | 7.6±1.2$^{a}$ | 6.9±2.0 | 30±5.2 | 0.1±0.1$^{a}$ | <2 | 24±4.7$^{a}$ | <0.5 | 0.5±0.2$^{a}$ | 2.2±1.3$^{a}$ | 5.9±2.9 |

**Table 34: Average macroelement concentrations (± 1 standard deviation) in tissues of *P. australis* from three reed stands in the pond at Silkeborg.**

| | | Barrier 1 | Barrier 2 | Sand filter |
|---|---|---|---|---|
| P | leaves | 3.8±0.59 | 4.1±0.51 | 4.0±1.4 |
| | rhizomes | 1.9±0.64 | 2.6±1.0 | 2.6±0.34 |
| | roots | 2.8±0.24 | 2.3±0.40 | 1.9±0.05 |
| | stems | 1.9±0.12 | 2.0±0.66 | 2.4±0.94 |
| Fe | leaves | 0.72±0.38 | 0.53±0.11 | 0.19±0.09 |
| | rhizomes | 0.83±0.52 | 0.93±0.27 | 0.39±0.15 |
| | roots | 12±4.3 | 8.4±0.11 | 8.0±0.80 |
| | stems | 0.23±0.08 | 0.22±0.11 | 0.39±0.05 |
| Mn | leaves | 0.33±0.17 | 0.29±0.06 | 0.31±0.19 |
| | rhizomes | 0.10±0.04 | 0.08±0.00 | 0.07±0.04 |
| | roots | 0.77±0.29 | 0.57±0.14 | 0.81±0.24 |
| | stems | 0.19±0.09 | 0.32±0.23 | 0.19±0.04 |
| Ca | leaves | 3.2±1.2 | 2.8±0.31 | 5.1±2.9 |
| | rhizomes | 0.42±0.12 | 0.76±0.22 | 0.94±0.52 |
| | roots | 2.9±0.69 | 2.8±0.83 | 4.1±0.46 |
| | stems | 0.71±0.23 | 0.83±0.16 | 1.5±0.42 |
| Na | leaves | 0.92±0.37 | 0.57±0.20 | 0.54±0.36 |
| | rhizomes | 2.1±0.31 | 2.1±0.75 | 0.99±0.02 |
| | roots | 6.4±0.35 | 6.1±1.2 | 1.62±0.34 |
| | stems | 1.6±0.31 | 0.96±0.41 | 0.76±0.22 |
| K | leaves | 14±1.6 | 16±2.5 | 16±2.7 |
| | rhizomes | 6.3±0.49 | 9.5±5.3 | 13±4.2 |
| | roots | 5.1±1.5 | 6.0±2.7 | 12±1.2 |
| | stems | 8.7±2.3 | 7.2±4.5 | 14±6.2 |
| Al | leaves | 0.11±0.14 | 0.10±0.10 | 0.05±0.05 |
| | rhizomes | 0.30±0.17 | 0.22±0.06 | 0.30±0.14 |
| | roots | 2.1±0.67 | 1.4±0.23 | 3.2±1.2 |
| | stems | 0.09±0.05 | 0.07±0.06 | 0.16±0.04 |

Besides at the sand filter at the outflow, in the Silkeborg pond reed has been planted also on two perpendicular barriers across the pond. Concentrations of nutrients and metals in different plant tissues from the three stands are presented in Table 34 and Table 35. ANOVA was used to compare element concentrations in the whole plants between different locations. Plants at the first barrier contained significantly higher concentrations of Na compared to *Phragmites* at the outflow sand filter, which corresponds to higher hydraulic, and thus pollutant load of the first perpendicular barrier. The results for K concentrations show similar pattern. Despite the addition of Al salts at the inflow to the Silkeborg pond, there was no significant difference in the Al concentrations between the three *Phragmites* stands along the pond. Comparison of heavy metals in reed's roots from the three stands in Silkeborg showed significant decrease in root Pb and Zn concentrations through the pond, while Cu content in the roots was increasing (Table 35).

**Table 35: Average heavy metal concentrations (± 1 standard deviation) in tissues of *P. australis* from three reed stands in the pond at Silkeborg.**

| | | Barrier 1 | Barrier 2 | Sand filter |
|---|---|---|---|---|
| Pb | leaves | <2 | <2 | <2 |
| | rhizomes | <2 | <2 | <2 |
| | roots | 3.8±2.2 | 3.5±0.85 | <2 |
| | stems | <2 | <2 | <2 |
| Zn | leaves | 25±3.9 | <2 | 27±4.4 |
| | rhizomes | 19±3.5 | 23±2.4 | 19±3.8 |
| | roots | 115±31 | 85±22 | 115±13 |
| | stems | 26±7.5 | 22±12 | 28±6.0 |
| Ni | leaves | 0.55±0.35 | 0.84±0.43 | <0.5 |
| | rhizomes | 0.91±0.37 | 0.93±0.57 | 1.0±0.06 |
| | roots | 4.1±1.0 | 3.7±0.98 | 5.6±0.31 |
| | stems | 0.59±0.42 | <0.5 | 0.88±0.55 |
| Cr | leaves | 2.5±2.7 | 1.7±0.26 | 1.6±0.94 |
| | rhizomes | 4.4±1.8 | 4.4±3.2 | 4.5±1.2 |
| | roots | 11±7.3 | 10±7.6 | 18±9.9 |
| | stems | 3.9±2.9 | 1.5±0.82 | 4.9±1.7 |
| Cu | leaves | <5 | <5 | <5 |
| | rhizomes | <5 | <5 | 5.3±3.0 |
| | roots | 12±6.4 | 7.4±1.4 | 21±4.4 |
| | stems | <5 | <5 | <5 |

# 5 DISCUSSION

## 5.1 Water quality improvement

### 5.1.1 Physical parameters

On line measurements of pH, temperature, dissolved oxygen concentration and turbidity in the open water of upgraded ponds showed annual oscillations of the parameters as well as variation in monthly averages. High pH and its higher variability in the summer months were probably caused by algal photosynthesis. The extraction of $CO_2$ from the water through assimilation into algal biomass at a rate faster than it can be replaced through atmospheric $CO_2$ diffusion, respiration, fermentation processes, and readjustment of carbonate equilibrium leads to an increase in pH level (Wetzel, 1983). A high impact of algal photosynthetic activity on systems' pH is due to low buffering capacity or alkalinity of the rainwater and the systems themselves in terms of their mineral structure of the soils. The growth of algae in a stormwater wet pond was reported also by Bulc and Vrhovšek (2003), who found that nutrients from the highway runoff enhanced the growth of algae, which settled at the bottom and caused an increased demand for oxygen in the basin. Besides this, Hossain et al. (2005) report a negative TSS removal (i.e. the production of TSS) in a stormwater pond during a storm event due to the dense algal growth and its wash out from the pond during the storm. This is in accordance with our findings of higher turbidity in the ponds during summer months when algal production is more intensive and precipitation more intense and frequent. Despite this, turbidity was strongly affected by larger runoff events and considerably less by small events as reported by Vollertsen et al. (2008) for the first monitoring year in the Odense pond. Except for TSS, no marked difference in inflow pollutant concentrations between wetter summer months and dryer winter months were found. However, a detailed examination of individual storm events and corresponding inflow and outflow characteristics was not carried out and is a subject of further work.

The higher pH values in the Odense pond compared to the ponds at Århus and Silkeborg can be the consequence of higher algal growth observed in this pond. Minor algal growth in Århus and Silkeborg pond could be caused by Al and Fe salts that were added to the systems with the purpose for phosphorous adsorption and removal. The addition of Al and Fe salts can have a dual effect on algal growth, namely through the reduction of phosphorous in the water which decreases algal growth as well as through direct adsorption of algae by Al flocks. The positive effect of Al addition on algae removal from a wet detention pond was reported by Al Layla and Middlebrooks (1975). The authors also investigated the effects of temperature in flocculation and consequent P and algae elimination.

The concentration of dissolved oxygen in the Århus and Silkeborg pond water was inversely proportioned to the water temperature, due to lower oxygen solubility at higher temperatures and higher oxygen uptake in summer months by biological activity. In the Odense pond, average oxygen concentrations in the summer months were higher compared to Århus and Silkeborg, due to algae bloom and intensive oxygen production during the day. The concentrations reached >20 mg $L^{-1}$, which is typical for dense algal blooms (Kadlec and Wallace, 2009). In contrast to that, dissolved oxygen concentrations in Århus and Silkeborg during summer were around 5 to 10 mg $L^{-1}$. Vollertsen et al. (2009) reported high oxygen saturation (more than 200%) during summer in the Odense pond, which was the consequence of algal growth in the free water. In the first year of operation, algae became active in March (Vollertsen et al. 2008). A decrease in $O_2$ concentration in Odense during winter might be the consequence of a degradation of algae biomass in the pond. Besides biological activity, oxygen concentration was affected also by storm events, which caused rapid decrease in oxygen concentrations and pH and increase in turbidity as mentioned before.

Oxygen concentrations in the Århus pond during summer months were low (5.3±4.6 and 2.8±1.1 mg $L^{-1}$ for 2008 and 2009, respectively), indicating a possibility of anoxic conditions at the bottom sediment and a consequent release of trapped heavy metals and phosphorous. According to Kadlec and Wallace (2009) oxygen concentrations in the pond should be around 4 mg $L^{-1}$, but not lower than 2 mg $L^{-1}$ in order to retain heavy metals and phosphorous in the sediment. In contrast to that, the study of the release of heavy metals from the sediment under different redox potentials from highly reduced to highly oxidized and neutral pH (7.5 to 8.0) by Yousef et al. (1990) showed less than a few percent release of metals. However, the decrease of pH to 5 may enhance the release of metals. In our study, the analyses of heavy metals in the Århus system showed a decreased efficiency in reduction of Pb and Cu in summer months in the pond and an increase in Ni and Zn concentrations in the pond compared to the inflow. However, the system was still efficient in heavy metal elimination, because metals were trapped in the sand filter. Low oxygen concentration in the Århus system during the summer months are probably due to microbiological degradation of organic matter.

Similar oxygen concentrations as in our study were reported also by Bulc and Vrhovšek (2003), where oxygen concentrations in the stormwater wet pond varied from 6.4 to 18.1 mg $L^{-1}$ and from 0.5 to 5.7 mg/L for inflow and outflow, respectively.

### 5.1.2 General water quality parameters

All seven investigated ponds were effective in the removal of total suspended solids (TSS) and total phosphorous (TP) indicating that the design of the ponds, water residence time, and hydraulic design were appropriate to enable sedimentation and biological removal of these pollutants. Upgraded wet detention ponds were efficient in reduction of TN, ortho-P and COD, while the four classical wet ponds in general did not show a decrease in $NH_4$-N and ortho-P. The exception was pond B, where removal of $NH_4$-N was observed: $NH_4$-N was reduced from 0.35±0.14 mg $L^{-1}$ at the inflow to 0.09±0.008 mg $L^{-1}$ at the outflow (74% removal). Compared to this, a system of constructed wetlands for stormwater treatment of natural appearance described by Meiorin (1989) showed moderate removal of $NH_4$-N (12-27%) but relatively high efficiency in ortho-P removal (53%). However, removal efficiencies during storm events and dry periods can differ significantly: Kohler et al. (2004) showed 100% removal of $NH_4$-N during storm event but no removal during dry periods. The authors suggest that little or no change in $NH_4$-N concentrations through investigated ponds is the consequence of low inflow concentrations. In the four classical wet ponds inflow $PO_4$-P and $NH_4$-N concentrations were similar or lower compared to the dry period concentrations in other studies (Kohler et al. 2004, Vollertsen et al. 2009) but still higher than background wetland concentrations, which are usually near-zero for $NH_4$-N and for ortho-P (Kadlec and Wallace, 2009). Inflow and outflow TSS, TP, TN and COD values were typical for stormwater runoff and comparable to other studies on stormwaters (e.g. Bulc and Vrhovšek, 2003).

The removal of pollutants mainly appeared in the open water part of the systems, indicating that the key mechanism of pollutants removal is sedimentation. According to this, the pollutants that appear in particulate phase settle down directly while soluble and colloidal pollutants co-precipitate with suspended matter present in stormwater or with added aluminium salts in the pond at Silkeborg.

The additional technologies implemented at the wet detention ponds at Århus, Odense and Silkeborg improved water quality in terms of general water quality parameters. The sand filters did not show further removal of pollutants, but the application of sorption filters and addition of iron salts improved the removal of all investigated pollutants except oils and fats. The addition of aluminum salts at the inflow to Silkeborg pond increased the removal of TSS, but there was no increased efficiency in elimination of other pollutants, due to low inflow concentrations.

### 5.1.3 Heavy metals in the water

In all investigated ponds Zn, concentrations were higher compared to the other metals and in the inflow to the Århus pond and in the inflow and pond water at the Odense pond exceeded the criteria for freshwater Zn concentration of 120 $\mu g\ L^{-1}$ (US EPA, 2002). Zn in stormwater is present in high concentrations due to runoff from galvanized roofs. Other measured heavy metals did not exceed freshwater criteria given by US EPA, except the concentrations of Cd in pond A and at the inlet to pond B. US EPA freshwater criteria are presented in table in Appendix B.

Similar studies on stormwater treatment report different inflow heavy metal concentrations. Ellis et al. (1994b) reported the following water concentrations in a wetland receiving stormwaters and a combined sewer outflow: 137, 8.9, 53.4 and 36.2 $\mu g\ L^{-1}$ for Zn, Cd, Cu and Pb, respectively. Hvitved-Jacobsen et al. (1994) reported a flow proportional mean value in urban run-off of 300-500, 0.5-3 and 5-40 µg $L^{-1}$ for Zn, Cd and Cu respectively; but Bulc and Vrhovšek (2003) report higher average inflow concentrations in a highway runoff of 500, 30, 230 and 130 µg $L^{-1}$ for Zn, Cd, Cu and Ni, respectively. In our study, measured Cd, Ni and Pb concentrations in the inflow water were lower compared to these studies. In the Odense pond, Zn concentrations were in the same range as reported by Hvitved-Jacobsen (1994) and Bulc and Vrhovšek (2003) and in the other investigated ponds Zn concentrations were similar to the ones reported by Ellis et al. (1994). Cu concentrations in Odense were in the same range as in the study by Bulc and Vrhovšek (2003) and in the other ponds they were comparable with Hvitved-Jacobsen (1994). Other studies on stormwater wet detention ponds (Scholes et al. 1998, Kadlec and Wallace 2009) report lower heavy metal concentrations that are more comparable to the concentrations measured at the Århus and Silkeborg wet ponds, while concentrations in the Odense pond are higher. It is also suspected that this pond receives an illegal input from a polluting industry. The difference in metal concentrations between the studies may result from different catchment characteristics, loads of the systems, and also different monitoring, which can be performed during storm events as well as during dry periods, can be time or flow-proportional or a grab sample. The highest pollutant concentrations are detected during the first flush of the rain event and depend on the length of dry season and activities in the catchment.

Upgraded wet detention ponds were efficient in removal of dissolved Zn, Cd, Cu, Cr and Pb, while classical wet detention ponds showed only occasional removal of dissolved Zn, Cd and Cu. Efficient removal of Zn, Cu, Cr and Pb in stormwater treatment wetlands was reported also by other studies, e.g. Bulc and Vrhovšek (2003) and Scholes et al. (1999). Cd removal in the study of Bulc and Vrhovšek (2003) was low and variable in the study by Scholes et al. (1999). The later reported an overall increase of Cd at the outflow for 3% according to the inflow concentration, which indicates different mobilization of Cd compared to other metals. This is similar to pond A in our study, where an increase of Cd through the pond was observed. Bulc and Vrhovšek (2003) also reported efficient removal of Ni in the stormwater treatment pond; however, in our study, efficient reduction of Ni was observed only in the Odense pond, while in the Århus and Silkeborg pond higher Ni concentrations were detected in the pond water and after the sand filter compared to the inlet. In the four classical wet detention ponds, Ni appeared in low concentrations and did not show consistent pattern between and along the ponds.

In the upgraded wet detention ponds heavy metal removal appeared mainly in the open water of the systems, indicating that the key mechanism of heavy metal removal is sedimentation. The removal of suspended solids and associated heavy metals from water column by sedimentation is reported also by Walker and Hurl (2002) and Hares and Ward (2004). Simultaneous removal of TSS and total heavy metals was studied by Hossain et al. (2005), who reported a moderate correlation between the two in a wet stormwater detention pond.

Due to co-precipitation of dissolved and colloidal pollutants with suspended particles originally presented in the stormwater as well as with added flocculants, it is hard to estimate the role of adding aluminium salts as an additional treatment technology in the system at Silkeborg. The same can be stated for enrichment of the sediment with iron salts in the system at Århus. However, at Silkeborg with the continuous addition of aluminium salts the elimination of heavy metals increased, but the addition of iron salts and application of sorption filters in general did not increase the elimination of heavy metals. However, the sorption filter at Odense showed good performance in further removal of Zn and Cu, which were still in high concentrations when water reached the sorption filters. A saturation of the media should be considered in the long term performance of such system. Despite after the addition of iron salts to the sediment at the Århus pond, there was an increased elimination of phosphorous and other pollutants, heavy metal elimination remained at the same rate. It is possible that the addition of iron salts had an instant effect on elimination of pollutants, i.e. at the time of application all iron was used and no further effect could be given. The improved elimination of general water quality parameters after the addition of iron salts would be in that case caused by other factors (e.g. sorption to organic matter). Slowly soluble forms of iron should be considered in further investigation of adding iron to stormwater ponds' sediments.

According to Tuccillo (2006) and Stenstrom and Kayhanian (2005) Zn, Cu and Ni appear in stormwater mainly in a dissolved fraction. Sand filters as an additional technology showed significant removal of Zn and in the system at Århus significant removal of Cu. Despite that, Ni elimination at the sand filters was not consistent. Sand filters can represent an important contribution of additional treatment technology towards elimination of dissolved heavy metals. As mentioned, the reduction of other pollutants at the sand filters was not detected, which may also be the consequence of efficient treatment in the open water and low pollutant concentrations entering the sand filters.

### 5.1.4 Polycyclic aromatic hydrocarbons

One sampling campaign of inflow and outflow water at the four classical wet detention ponds, show no removal of PAHs from water in these systems. In addition, less PAH species were detected in these ponds compared to the upgraded ponds. The analysis in upgraded ponds showed the influx of PAHs to the systems and the retention of them in the wetponds. All 16 PAH species were detected in the systems at Århus and Odense. According to Hwang and Foster (2006) the majority of PAHs (87%) is bound to suspended particles, thus the main removal mechanism can be sedimentation. The high degree of PAHs association with particles is caused by the low water solubility of the relevant PAHs.

In all investigated ponds high molecular weight PAHs prevailed above low molecular weight indicating pyrogenic source of these pollutants. Similar results were shown in other studies (e.g. Brown and Peake 2006, Hwang and Foster 2006). It is typical for stormwater run-off that PAHs originate from incomplete combustion of fossil fuels (i.e. pyrogenic source).

During water treatment in a wet detention pond pollutants are eliminated from the water phase. It should be noted that with these processes, some pollutants can be eliminated from the system, e.g. nitrogen via denitrification; however, other pollutants like phosphorous, metals and PAHs cannot be eliminated but are accumulated in the wetland sediment or plant tissues.

## 5.2 Accumulation in the sediment

Pollutants removed from the treated stormwater can accumulate in the sediment of a wet detention pond. The accretion of sediment in a stormwater treatment system is proportional to the flow and the TSS entering the system. The average removal of TSS from the water in the investigated systems is around 90%, meaning that these substances are trapped in the sediment, which thus accumulates with the systems age. A supplementary source of sediment is the death and decay of biological material (algae) growing in the water that settles out and increases the amount of material deposited on the bottom of the ponds.

Due to adsorption and complexation of pollutants with suspended solids, along with the accretion of the sediment, also accumulation of pollutants is expected. In the upgraded wet ponds, sediment was sampled in two consecutive seasons. However, the results showed no significant increase in heavy metal concentrations in the sediment between both sampling campaigns, except for Cu in Århus and Silkeborg. At Odense, Pb concentration in the middle of the pond was significantly higher in the first year of operation compared to the second year, which might had been caused by a re-suspension of particulate Pb from the sediment, which is in accordance also with higher Pb concentrations in the water in the second monitoring year. According to Hares and Ward (2004), who report a significant increase of heavy metal concentrations in two stormwater wet detention ponds in three years time, one additional monitoring season in our study might have showed a significant metal accumulation.

On the other hand, if sedimentation of suspended solids with adsorbed heavy metals would be the only mechanism of heavy metal removal, then the concentrations in the sediment should remain constant through the years (as it was the case in our experiment), and the amount of sediment would be the only increasing component. However, also other processes take place in a wet detention pond, such as microbial degradation of accumulated organic matter, plant uptake, volatilization etc. Therefore, in order to evaluate the accumulation of heavy metals through time, monitoring should be performed quantitatively in order to evaluate the total amount of accreted sediment with accumulated metals and in a longer time period.

Sediment accretion on the bottom of the ponds can result in sediment stratification. Due to successive sediment accumulation, stratification appears after certain time of operation. In our study the upgraded wet detention ponds did not show sediment stratification after approximately one year of operation, therefore samples were not divided by layers. On the other hand, sediment layers were more evident in classical wet ponds, which operated for around five years at the time of monitoring. However, the core stratification in the classical wet ponds differed significantly between the ponds. This difference can be attributed to the different hydraulic characteristics of the ponds, different loadings and different amount of submerged macrophyte vegetation, which is responsible for reducing hydraulic flow thus allowing greater residence time for sedimentation, filtration and bioaccumulation processes (Benoy and Kalff, 1999; Hares and Ward, 2004). In pond B, where the entire bottom was covered with *Elodea* sp., the sediment cores were mostly clearly stratified. According to Walker (2001) stratification is not significant at shallow depths and flow conditions, which might be the reason for not clear stratification in pond A (moderate flow conditions) and pond C (shallow depths).

The accumulated sediments differ from the parent soil beneath it. They are usually characterized by relatively high moisture content, a high organic matter percentage and a lower density compared to the parent soil. The accumulated sediment also contains higher nutrient and heavy metal concentrations (Yousef et al., 1994) as was find out also in our study.

### 5.2.1 Nutrients and metals in the sediment

#### 5.2.1.1 Sediment composition

The results of macroelement analyses in the sediment and sediment of the seven investigated systems indicated that the elements are present in different concentrations, namely Ca, Fe and Al prevailing above K, P, Mn and Na. In terms of heavy metals, Zn prevailed above other heavy metals and lead was the heavy metal with the lowest concentration. This nutrient and metal composition was typical of all investigated ponds except for Odense, where heavy metals appeared in the following order: Cu>Zn>Pb>Cr>Ni.

High Zn concentrations in the sediment correspond to the high Zn concentrations measured in the water. Prevalence of Zn above other heavy metals in the sediment is the consequence of high Zn loads in stormwater. Literature reports that Zn prevails in the dissolved form (Tuccillo, 2006), however some other authors found Zn mainly in the particulate form (Kadlec and Wallace, 2009). According to Kadlec and Wallace (2009) wetland sediments have the potential to contain large amounts of Zn due to chemical precipitation and cation exchange in the water. Zn was present in higher concentration compared to the other heavy metals also in the study by Scholes et al. (1998). High Pb concentrations are reported by Yousef et al. (1990) in whose study Pb concentrations were considerably higher compared to the other heavy metals concentrations. In contrast to that, in our study Pb was detected in less than half of the samples and in rather low concentrations. The difference might be caused by decreasing use of lead in the fuel, paints etc., in the past years.

Cd, which was frequently detected in water and also eliminated from it, was not detected in the sediment from any of the investigated ponds nor in any of the investigated plant species. It is likely that Cd was present mainly in the soluble form and did not tend to co-precipitate with TSS or added flocculants, thus disabling accumulation in the sediment and uptake by plants. However, in other similar studies, Cd was detected in the sediment (Ellis et al., 1994b; Sriyaraj and Shutes, 2001; Hares and Ward, 2004). In the study by Scholes et al. (1998), Cd had high mobility in a stormwater wetland and showed an even distribution through the wetland. Inflow Cd concentrations in our study were rather low and therefore it is possible that Cd settled in the sediment or taken up by plants would be below detection limit.

#### 5.2.1.2 Stratification and accumulation

Stratified sediment samples taken in the four classical wet detention ponds showed accumulation of heavy metals in the upper sediment layer. The accumulation of metals in the upper sediment layers was shown also in other studies, e.g. Yousef et al. (1990) studied metal concentrations in sediment samples from five wet detention ponds and reported a rapid decline of organic matter, nutrients and heavy metal concentrations in the core samples with depth. However, in our study a decrease in nutrient concentration through sediment layers was not so evident, since only P and Na were higher in the upper layer compared to the lower layers. Organic matter was not analysed for separate layers; however, it can be estimated through water content analyses in each layer. The results showed higher water content at the upper (organic) layer. Concentrations of heavy metals accumulated in individual sediment layers are in the same order of magnitude as in the study by Yousef et al. (1990), with the exception of Pb, which was much higher in the study by Yousef et al. (1990) due to the use of leaded gasoline in the 90's.

#### 5.2.1.3 Comparison with the sediments of natural lakes and similar studies

Much higher nutrient and metal concentrations in the sediments of the investigated wet ponds compared to natural lakes, reported by Samecka-Cymerman and Kempers (2001) indicate an accumulation of nutrients and metals from stormwater in the ponds' sediment. In our study, P concentrations were from 35 to 150-times higher; Fe concentrations were from 130 to 240-times higher; and Mn, Ca, K and Al were between 50 and 100-times higher compared to the concentrations in the sediment from natural lakes. Due to these elements are not typical stormwater pollutants, the difference can be attributed to different natural geological structure. This can also be confirmed by the aboveground concentrations of Na, K and Ca in *Phragmites* sp. growing on the sand filters, which are comparable with concentrations of these nutrients and metals in plants from natural wetlands (Kadlec and Wallace, 2009).

Comparing heavy metals concentrations, Pb concentration was approximately five-times higher in our study compared to the natural lakes in all ponds except in Odense, where Pb content was 80-times higher. Even greater differences were observed in Ni and Cu concentrations: Ni was 300 to 400 higher in all ponds except in Odense, where it was 700-times higher compared to the sediment of natural lakes; and Cu was from 76 to 10,000-times higher for Silkeborg and Odense, respectively. Zn concentrations did not show such a difference and were from 27-times higher in Silkeborg to 170-times in Odense, compared to the sediment in natural lakes reported by Samecka-Cymerman and Kempers (2001). However, reference sites from different studies differ greatly; e.g., a natural spring-fed pond treated as a background site in the study by Ellis et al. (1994b) contained much higher Cu, Pb and Zn concentrations than natural lakes reported in the study by Samecka-Cymerman and Kempers (2001). Despite this, the investigated ponds in this study still show accumulation of Zn and Cu in the sediment compared to Ellis et al. (1994b), but Pb concentrations were lower.

Considerably higher heavy metals concentrations in the sediment compared to natural stagnant water bodies are typical for stormwater wet detention ponds. Sediment heavy metal concentrations analysed in this study are in the same range as heavy metal concentrations in other similar studies (Hares and Ward, 2004; Sriyaraj and Shutes, 2001). Concentrations reported by Sriyaraj and Shutes (2001), who investigated a wetland receiving a pretreated stormwater runoff, are comparable to the sediment heavy metal concentrations in the classical wet detention ponds and the ponds at Århus and Silkeborg, but not Odense, where concentrations were 10 to 100-times higher. On the other hand, Ellis et al. (1994b), who studied wetlands receiving stormwater runoff from separate and combined sewer systems, reported on higher heavy metal concentrations compared to our and other studies. However, Zn concentrations in their study are comparable to the Zn concentrations in Odense, while Cu concentrations in Odense are still higher. Differences between the studies show a wide range of pollutant concentrations in the stormwater ponds resulting from different load of the systems and catchment characteristics.

#### 5.2.1.4 Comparison between the ponds

Comparison of macroelement concentrations in the sediment of three upgraded wet ponds showed significantly higher P concentration in the sediment from the Århus pond and significantly lower P concentration in the sediment from the Odense compared to the other two ponds, which is most likely caused by different catchment characteristics. The lawns in the urban catchment of Århus facility may enlarge the P input to the pond. The catchment from residential area and highway in Silkeborg represents lower P input and industrial catchment in Odense with limited surface of lawns has the lowest P input.

Comparing the four classical wet detention ponds, pond B had a somewhat higher P, Fe, Al and Mn concentrations in the sediment samples compared to the ponds C and D, which can be a consequence of co-precipitation of P with Fe, Al and Mn under oxic conditions in the pond, under which the insoluble P complexes accumulate in the sediment. P concentration in layer a of classical wet ponds, were similar compared to the pond at Århus. As in the ponds at Århus this is most likely the reflection of the catchment consisting mainly of individual houses with gardens that can be a source of nutrients.

Up to two orders of magnitude higher heavy metal concentrations in the sediment of Odense pond compared to the sediment in other investigated ponds corresponds to higher heavy metals concentrations in the inflow to the Odense pond. As mentioned, this pond is also not comparable to other studies from the field, indicating that the pond is receiving an inflow probably not of stormwater origin (discharge from industry).

#### 5.2.1.5 Changes in nutrient and metal concentrations through the ponds

Literature reports that usually the majority of accreted sediments accumulate in the inlet region of the wetland, which results in higher metal concentrations at the inlet (Walker and Hurl, 2002; Sriyaraj and Shutes, 2001; Hares and Ward, 2004). In contrast, lighter loadings and open water areas may foster a redistribution of suspendable material (Kadlec in Wallace, 2009). In our study, the results did not show consistent changes in nutrient and metal concentrations in the sediment through investigated ponds. However, in the pond at Silkeborg, there was a significant decrease in concentrations of all measured nutrients, metals and organic content in the sediment through the pond, with an exception of Ca and Cr. Among classical wet detention ponds, in pond B a significant decrease in all measured heavy metal concentrations and weak decrease of P and Na concentrations was found. Reduction of nutrient concentrations and organic content through the ponds at Odense and Århus was not significant. However, the wet detention pond at Odense showed significant reduction in measured heavy metals through the pond, which was not significant for the wet pond at Århus. A significant decrease in heavy metals' concentrations through the pond at Odense but not at Århus might be caused by different hydraulics of the systems; the pond at Århus has three times higher water surface area, enabling water mixing by wind and thus re-suspension of sedimented material. Among classical wet detention ponds, pond D also showed a slight decrease in Zn, Cu and Pb concentrations through the pond.

The decrease in nutrient and metal concentrations through the Silkeborg pond and pond B is the consequence of more efficient sedimentation of suspended particles and associated pollutants in these ponds. Two transversal sand dikes and favourable length to width ratio enhanced the sedimentation in the pond at Silkeborg and in pond B the sedimentation was enhanced by extensive submerged macrophyte vegetation.

### 5.2.2 Polycyclic aromatic hydrocarbons

As the majority of PAHs is known to be associated with suspended particles (Hwang and Foster, 2006), the main removal mechanism of PAHs in wet detention ponds is supposed to be sedimentation with a consecutive accumulation of PAHs in the sediment accreting on the bottom of the ponds. The results of the sediment analysis clearly showed that PAHs accumulated in the sediment; therefore, the final sediment disposal procedures may demand additional remediation techniques to safely dispose the polluted sediments in an appropriate way.

#### 5.2.2.1 Composition of PAHs in the sediment

PAHs were found in all sediment samples collected from the investigated wet ponds. In most of the ponds studied, more PAH species were detected in higher concentrations in the sediment samples than in the water. In cases when PAH species were below the detection limit in the sediment, they were usually some of the LMW PAHs (e.g. acenaphthene in ponds B, C, at Odense and Silkeborg and fluorene in pond B and at Århus). This might be because LMW PAHs are more likely to be degraded over time than HMW PAHs (Mangas et al., 1998).

PAHs that accumulated in the sediment in the highest concentrations were HMW PAHs in all investigated ponds, however in the classical ponds also some LMW were elevated. Prevalence of HMW PAHs above LMW indicate pyrogenic source of these pollutants. Similar results have been reported in other studies, e.g. Jiries et al. (2000), Brown and Peake (2006), Hwang and Foster (2006). Stormwater runoff typically contains PAHs that originate from pyrogenic sources such as incomplete combustion of fossil fuels. Combustion specific PAHs are fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(c,d)pyrene and benzo(g,h,i)perylene. Most of them, but especially pyrene and fluoranthene occurred in higher concentrations in the pond sediment as well as in the water.

#### 5.2.2.2 Comparison with other studies

In comparison with other studies (e.g. Kamalakkannan et al., 2004; Brown and Peak, 2006) the ∑PAHs in the sediment of the ponds investigated here are considerably lower. Kamalakkannan et al. (2004) report a range of ∑PAH of 38,000-65,000 ng $g^{-1}$ DW. This difference is probably caused by different age of the systems and high loadings from a highway with heavy traffic in the study of Kamalakkannan et al. (2004). Brown and Peak (2006) who investigated PAHs concentrations in the road debris and in stormwater suspended sediments from two catchments also reported higher concentrations of 16 PAHs than in our study; however, the lower limit is comparable with some of the ponds in our study. On the other hand, Jiries et al. (2000) report the same range of ∑PAHs in the study of the sediment and sludge from wastewater treatment plants as in this study. The comparison with other studies illustrates how differences in catchments characteristics can result in different pollution levels in the detention pond sediments.

#### 5.2.2.3 Comparison between the ponds

In the present study, the ∑PAHs in general did not differ markedly between the studied systems, despite the fact that the ponds received stormwaters from different catchments, had different loads and were of different age. ∑PAHs were in the same range also in the sediment from Odense pond, which otherwise differed greatly in heavy metal concentration compared to the other ponds; however, some significant difference between the ponds were still found. The lowest ∑PAH concentrations were found in the sediment from the systems at Silkeborg and pond C. The difference can be explained by differences in catchment use or more likely by the intensity of the activities in the catchment and by the ratio between the pond volume and the catchment area. The low PAHs concentrations in the system at Silkeborg can also be a consequence of relatively short period of operation (two months) for this pond as compared to the other ponds, which were in operation for 5 years (ponds A to D) and half a year (ponds at Århus and Odense). No marked difference between other ponds of different age might indicate microbial degradation of accumulated PAHs and lower accumulation of PAHs with years than expected.

Pond B accumulated somehow higher ∑PAH concentrations compared to all other systems. As mentioned before, this pond was densely vegetated with submersed *Elodea* sp. It is known that macrophyte vegetation reduces hydraulic flow thus allowing greater residence time for sedimentation, filtration and bioaccumulation processes (Benoy and Kalff, 1999; Hares and Ward, 2004), which might have also caused higher accumulation of PAHs in the system.

#### 5.2.2.4 Changes through the ponds

To our knowledge, there are no publications documenting changes in PAH concentrations in the sediment along stormwater wet detention ponds. However, because the main removal process of PAHs from stormwater is sedimentation, higher PAH concentrations are expected at the inlet region of the pond. In this study, a decrease in PAH concentration through the pond was found in the Silkeborg ponds, and to some extent in the Odense pond and ponds B and D. In pond C, the lowest ∑PAH occurred in the middle of the pond, which seemed to be a hydraulicly 'dead zone' with little water coming in there. Enhanced sedimentation by *Elodea canadensis* in pond B caused that the majority of PAH reduction in this pond appeared in the first half of the pond, while in Silkeborg there was a significant decrease in sediment ∑PAH concentrations, which is due to two flow perpendicular sand dikes constructed in this pond in order to enhance sedimentation.

∑PAHs concentrations in the sediment at Århus system did not show marked decrease through the pond. Higher PAHs concentrations were detected in the sediment in the middle of the pond compared to the sediment at the inlet. In Odense pond higher PAHs concentrations in the middle of the pond were detected for half of the measured PAHs; however ∑PAHs were still lower compared to the inlet. The difference between the ponds in spatial distribution of accumulated PAHs is probably caused by different hydraulics of the systems, different shapes of the ponds, different length to width ratio and consequent sedimentation efficiency.

## 5.3 Plant uptake

Aquatic plants in stormwater treatment ponds contribute to the reduction of hydraulic flow thus allowing greater residence time for sedimentation, filtration and bioaccumulation processes (Hares and Ward, 2004). An important constituent of upgraded wet detention ponds were also sand filters planted with *P. australis*, which is supposed to counteract clogging of the sand filters at the outflow of the ponds. Besides this, plant tissues (especially roots) contain an elevated concentration of nutrients and heavy metals, thus contributing to their elimination from the stormwater and accumulation in the pond, as shown in this study as well as reported by other authors (Scholes et al., 1998; Vardanyan and Ingole, 2006; Kadlec and Wallace, 2009).

### 5.3.1 Accumulation of nutrients and metals in different plant tissues

Comparison of nutrient and metal concentration in different tissues of wetland plants showed that heavy metals and some of the macronutrients (Fe, Al, Ca) usually appeared in significantly higher concentrations in the roots compared to the other plant tissues, which is consistent with other studies (Scholes et al., 1998; Ranieri, 2004; Vardanyan and Ingole, 2006; Sasmaz et al., 2008; Kadlec and Wallace 2009). In general, rhizomes contained lower heavy metal concentrations compared to the roots, but higher compared to the aboveground tissues. A decrease of heavy metal concentrations in an order of roots > rhizomes > leaves is reported also by Cardwell et al. (2002); however, Zn concentrations were often higher in leaves compared to rhizomes in different species, which is in consistency with Schierup and Larsen (1981), who observed a similar pattern for *P. australis*.

Restriction of metal translocation to the shoot is the strategy of metal tolerance for non-hyperaccumulators. With the restriction of metal translocation to the shoot, plants avoid the potential negative effects of high metal concentrations on the photosynthetic tissue. However, heavy metals and nutrients that are translocated to the shoot can be removed from the system through harvesting thus reducing the accumulation of heavy metals in the system. The rationality of harvesting should be considered according to mass input of heavy metals and nutrients and the percentage removed by harvesting. Due to metal concentration in aboveground parts of wetland plants may vary during the growing season and may increase significantly at the end of growing season (Bragato et al., 2006), the timing of sampling and harvesting is of a big importance and should be included in the management plant of stormwater treatment systems.

K and P are important constituents of biological macromolecules vital for plant functioning and thus appeared in higher concentrations in aboveground tissues. Occasionally leaves contained also elevated concentrations of Mn, Na and Ca. The results are similar to Meiorin (1989), who reported consistently higher uptake of Mn into *Typha* sp. leaves, namely 0.45-1.2 mg $g^{-1}$ DW, which represented 34-185% of the background sediment level. In our study; however, *Typha* sp. leaves in ponds B and D contained even higher Mn concentrations and showed greater accumulation compared to the sediment concentration (the concentrations in *Typha* leaves were 5 to 9 times higher compared to the sediment). Elevated Mn concentrations in *Typha* leaves are reported also by Sasmaz et al. (2008). Mn is important in building chloroplasts and is involved in enzyme activity for photosynthesis, which can explain higher concentrations in the leaves.

Higher Ca concentrations in the leaves of different aquatic plants are reported also by Vardanyan and Ingole (2006). Higher Ca concentrations in submerged leaves might also be the consequence of $HCO_3^-$ uptake and precipitation of Ca (which will be discussed later on), however also emergent macrophytes in our study contained higher Ca concentrations in the leaves compared to the roots. Ranieri (2004) also reports on elevated Cr concentrations in stems and leaves, due to high mobility of Cr, but this was not the case in our study. Differences between the plant species in nutrient and metal accumulation are discussed in a further chapter.

### 5.3.2 Accumulation of nutrients and metals in investigated plant species

The comparison macroelement concentrations between the plant tissues and sediment or sediment from investigated stormwater systems showed that P, K, Mn and Na had higher concentrations in plant tissues, while Ca, Al and Fe were mostly in higher concentrations in the sediment. This can be explained by P, K and Mn being and important elements in plant metabolism, while Ca, Al and Fe are the most abundant elements in earth's crust and therefore their higher concentration in sediment is expected. However, in the pond at Silkeborg Ca concentrations the plants were higher compared to the sediment. This can be explained by lower Ca concentrations in the sediment of this pond compared to all other investigated systems. Also in *P. pusillus* and *E. canadensis* from ponds B and C, Ca was in higher concentrations compared to the sediment. It is known that *Potamogeton* and *Elodea* species can utilize $HCO_3^-$ as a carbon source in water in addition to $CO_2$ (Prins et al., 1979). A by-product of bicarbonate utilization is the precipitation of Ca on the plant surface (Jones et al., 1993), which might contribute to higher Ca concentrations measured in our study.

Phosphorous is an important and limiting nutrient for primary producers and thus a problematic pollutant causing eutrophication of natural water bodies. Accumulation of P in aboveground biomass in water treatment systems is therefore important in order to evaluate the elimination of P from the systems by harvesting the macrophytes. According to literature, the phosphorous content of standing crops is not very variable, with a range of 1-5 g P $m^{-2}$, therefore the contribution of harvesting and consequently its legibility depends mostly on inlet loadings (Kadlec and Wallace, 2009). Elimination of P from water with plant uptake is more important in the case of low loads, where plant uptake can present a higher percentage of overall removal (Vymazal, 2004). Stormwater in this study had low P loads; consequently, plant harvesting could importantly contribute to P elimination from the systems. In the Odense pond, where P concentrations in the sediment were the lowest, plant consequently had the highest accumulation coefficients.

Heavy metals were mainly in higher concentration in the sediment compared to the plants and there was no significant transport of heavy metals from roots to aboveground tissues. However, the plant species at the four classical wet detention ponds accumulated Pb and Zn in the aboveground tissues in concentrations higher than in the sediment (AC > 1), because of higher accumulation of heavy metals in *Potamogeton* and *Elodea* sp. Also in the upgraded wet detention ponds plant species with submerged or floating form contained higher heavy metal concentrations compared to the sediment. Higher heavy metal concentrations in submerged or floating macrophytes can be caused by the uptake from the sediment as well as directly from water through all plant body. Fritioff and Greger (2003) therefore report that submerged plant species seem to be more efficient in elimination of heavy metals from stormwater. Moreover, in later study Fritioff and Greger (2006) found that *P. natans* uptake Zn, Cu, Cd and Pb by the leaves, stems and roots, with the highest accumulation found in the roots, and no transportation of Zn, Cu and Pb between the plant parts. The authors conclude that *P. natans* is a species of interest for use in phytoremediation, due to heavy metals are taken up directly from water by leaves and stems; there is no translocation between the roots and stems and therefore no release of metals from the sediment to the water via *P. natans*. Similar to this, Nyquist and Greger (2007) report an efficient uptake of Cu and Zn by *Elodea canadensis* at laboratory conditions and conclude that *E. canadensis* is an appropriate plant for phytoremediation of Zn and Cu. However, the biomass and thus total uptake of submerged and floating macrophytes can be lower compared to the emergent macrophytes setting the phytoremediation potential of these plants as a subject for further discussion.

In upgraded wet detention ponds, besides species with submerged or floating form, also *P. australis* had higher concentrations of Zn in aboveground parts compared to the sediment, however the AC was low. Besides that heavy metals accumulated in aboveground parts can be eliminated from the system by harvesting, they can also enter the food chain and present a threat for bioaccumulation and can have negative impact on the biota, which is not resistant to the elevated heavy metal concentrations. However, Meiorin (1989) studied bioaccumulation of heavy metals from stormwater treatment pond in the food chain, but results did not show increasing heavy metal concentrations that could be connected to the stormwater pollution. Despite certain species in this study showed certain accumulation of heavy metals in the aboveground tissues, the concentrations are still low and should not present the threat for bioaccumulation. Heavy metals that are stabilized in the root zone of macrophytes are less available to biota and thus have lower potential for bioaccumulation.

In the investigated plant species, the average concentrations of heavy metals were lower in the roots compared to the sediment. The exception was Zn, which had the highest potential for phytostabilization using investigated wetland species. Lower heavy metals in the roots compared to the sediment are in contrast to Cardwell et al. (2002), who investigated metal accumulation in different macrophytes from urban streams, and found that plant roots had higher metal concentrations than the adjacent sediments. On the other hand, Ellis et al. (1994b), who investigated heavy metal accumulation in *Typha* sp. in a wetland receiving stormwaters and a combined sewer outflow, reported a progressive decrease in measured heavy metals (Cu, Pb, Zn and Cd) from the sediment, to *Typha* root, rhizome and leaf. However, in our study, plant species generally did not accumulate heavy metals in the roots (CF < 1), but there was a marked difference between the species. Especially *Typha* sp. and *R. hydrolapathum* enabled phytostabilization of Zn. In addition, *Typha* sp. concentrated Pb in the roots, while *P. australis* and *R. hydrolapathum* stabilized Ni. Many species also had concentration factors that were higher than one for Cu. The accumulation of Pb and Zn in *Typha* roots is consistent with the study by Sasmaz et al. (2008), where concentrations of these metals but also Cd were often higher in *Typha* than in the sediment. According to Sasmaz et al. (2008) *T. latifolia* could be considered as either a bio-indicator or a bio-accumulator for sediments and water polluted by metals.

Cd was not detected in any of the plant species in the investigated ponds. However, plants can uptake Cd as reported by Scholes et al. (1999) and Cardwell et al. (2002). In contrast to that, Nyquist in Greger, (2007), who studied an uptake of Zn, Cu and Cd in *E. canadensis*, found that Cd can be released from the plants. The amount of Cd in plant tissues was found to be a limiting factor in further Cd uptake.

The contribution of plants towards elimination and accumulation of heavy metals from the stormwater tends more towards enhancing sedimentation and accumulation in the sediment rather than to the plant uptake. This was reported also by other studies, e.g. Ranieri (2004) found that less than 5% of mass load with Ni was accumulated in plant tissues in a wastewater treatment wetland. However, certain species show accumulation potential.

#### 5.3.2.1 Differences in nutrient and metal concentrations between the species

Plants analysed in this study showed different nutrient and metal concentrations, which were affected by different catchment areas as well as the different plant species. In general, macroelement concentrations in the plants were similar as reported by literature (Kadlec and Knight, 1996; Kadlec and Wallace, 2009). The exemptions were *Alisma lanceolatum*, *Caltha palustris*, which accumulated high concentrations of P and K. P was accumulated also in *Elodea nuttallii* and *Sagittaria sagittifolia*. Aluminium concentrations in the plants from the pond at Odense were in the same range as reported by Kadlec and Wallace (2009); but higher in the roots of numerous species and whole plants of *P. natans* and *E. nuttallii* from the other six ponds.

Investigated plant species differed more in heavy metal concentrations than in macroelements. The differences between the species and tissues were most evident in the Odense pond, which receives higher heavy metal load. In the pond at Silkeborg, the differences were smaller, because of few months' shorter operation time and lower loading compared to the other investigated ponds. Higher heavy metals load in the Odense pond was already found with the comparison of water and sediment results between the investigated ponds as well as with the literature. The comparison of heavy metals in species that appeared in more ponds confirms this as well. In consistency with this Nyquist and Greger (2007) as well as Fritioff and Greger (2006) found a positive linear relation between heavy metal concentration in the water and plant tissues.

The results indicate that *I. pseudacorus* accumulates the lowest heavy metal concentrations in the roots, followed by *R. lingua* and *S. sagittifolia* in the Odense pond and *S. aloides* in the Silkeborg pond. However, roots of *R. lingua* in Silkeborg contained high concentrations of Ni and Cr compared to the other species from this pond. A part of the differences between the species might also be caused by different flow patterns and the position of the species in the systems. Low uptake by *I. pseudacorus* was reported also by Ellis et al. (1994a).

In our study, the highest heavy metal concentrations were accumulated in *R. hydrolapathum* followed by *P. australis*, however in Silkeborg pond also *R. lingua* and *C. palustris* showed higher heavy metal concentrations compared to the other species. Compared to the average concentrations of Cu, Zn and Ni in the sediment from Odense, concentrations of these metals in the roots of *R. hydrolapathum* were 2, 5 and 6 times higher for Cu, Zn and Ni, respectively. In contrast, concentration factors for Pb and Cr in *Rumex* from the pond at Odense were lower than one. Due to high heavy metal accumulation, high biomass and fast reproduction, *R. hydrolapathum* has a high phytoremediation potential. Because the majority of heavy metals are stored in underground parts it does not present a threat of transferring heavy metals by the food chain; however, it is not possible to eliminate these accumulated metals from the system by harvesting.

Studies on plant uptake in stormwater wetlands mainly focus on *Typha* sp. and *Phragmites* sp. (Scholes et al., 1998; Scholes et al., 1999; Sriyaraj and Shutes, 2001) because of their widespread and proved efficiency in wastewater treatment wetlands. Scholes et al. (1998) report higher accumulation of Zn, Pb, Cr and Cd in *Typha latifolia* compared to *Phragmites australis*, whereas the concentration of Cu was higher in *Phragmites*. In contrast to that, in this study, there was no significant difference in heavy metal content between *Typha* and *Phragmites* growing in the same pond (Odense or Silkeborg), with an exception of Cu content in the Silkeborg pond, which was significantly higher in *Typha* sp. compared to *Phragmites* sp. The comparison of heavy metal concentrations in *Typha* and *Phragmites* with another study by Scholes et al. (1999) showed that Cr concentrations in both plant species and Zn in the plants from Odense were in the same range in both studies. Zn and Cu concentrations in *Phragmites* and *Typha* from Silkeborg were lower and Cu concentrations in Odense were higher. Pb concentrations were lower in both species compared to Scholes et al. (1999).

Comparison of the nutrient and metal concentrations in *Phragmites australis*, with the study by Bragato et al. (2006) on constructed wetland treating river water, in general showed lower Ni, Cu and Cr concentrations in this study, while P, K and Zn were higher. Higher P, K and Zn can be the consequence of the runoff from residential areas, where P and K originate from green plots and Zn from the roofs.

Heavy metal concentrations in *Typha* can be compared to the study by Cardwell et al. (2002), who investigated metal content in the tissues of different aquatic plants in urban streams with different load. Concentrations of heavy metals in the roots of *Typha* sp. varied according to the stream load and sediment concentration. The streams with higher loads had similar Pb and Zn concentrations in the roots as in *Typha* from Odense pond, while Cu was still higher in Odense. *Typha* roots from the pond at Silkeborg had lower Cu and Zn concentrations and similar Pb content compared to equally loaded streams. In the four classical wet ponds Cu, Pb and Zn concentrations in *Typha* roots were similar to the study.

### 5.3.3 Comparison of *Phragmites australis* at the sand filters of upgraded wet detention ponds

The results of the comparison of *Phragmites* stands from the three upgraded wet detention ponds showed different nutrient and metal accumulation in *Phragmites* between differently loaded systems. *Phragmites* sp. growing on the sand filters accumulated Fe, Mn, Ca, Na and Al in the roots, while K and P prevailed in the aboveground tissues, which was evident also for other plant species as discussed before. The concentrations of K and P in *Phragmites* tissues increased with increasing sediment K and P concentrations. The highest K and P concentrations were in sediment and plants from the pond at Århus. Phosphorous concentrations in *P. australis* at the sand filters from Silkeborg and Odense are within expected P concentrations reported in the literature for plants growing in natural environment (between 0.14% to 0.30% dry weight) (Kadlec and Wallace, 2009), while P concentration measured in the plants from Århus was higher and can be compared to P concentration in wetland plants in anthropogenic lakes reported by Samecka-Cymerman and Kempers (2001).

Stems sampled at Århus had higher concentration of K, 29 mg $g^{-1}$ DW, which was about twice the concentrations in stems from the other two systems and was comparable with K concentrations in treatment wetlands reported by Kadlec and Wallace (2009), namely 26 mg $g^{-1}$ DW.

Despite the addition of iron salts to the pond at Århus, and aluminium salts at the inflow to Silkeborg pond, there was no marked difference in the content of these metals neither in the sediment nor in *Phragmites* tissues at the sand filters between the systems. This might be due to low amount of applied salts, which is consistent also with no significant increase of iron and aluminium in the sediments of these two ponds in two consecutive sampling years.

*Phragmites* sp. at the sand filters accumulated all detected heavy metals, except Cr and Cd. Concentrations of Zn, Ni and Pb were higher compared to the sediment as discussed before and Cu concentrations in the roots were in the same range as in the sediment. In consistence with our study, Scholes et al. (1998) also reported no accumulation of Cr in the roots. Concentrations of Zn, Ni, Pb and Cu in the roots were increasing with increasing concentration of these metals in the sediment; however the concentrations in other plant tissues remained in the same range. The correlation between root and sediment concentration was strong and statistically significant for Zn and Cu. Pb was detected only in the roots from Århus and Odense. Similar to this, in the study by Cardwell et al. (2002) an increasing concentration in the plant tissues with increasing sediment concentration was clearly shown for Zn, but not for Cu or Pb.

Despite Cr was not accumulated in *Phragmites* there was a significant positive correlation between Cr concentration in the rhizomes and sediment, however the concentrations in other tissues remain in the same range with increasing sediment concentration.

Comparing heavy metal concentrations in plant tissues, similar studies of reeds report the same range of heavy metal concentrations as at Århus pond, lower compared to Odense and higher compared to Silkeborg (Scholes et al., 1998). Pb concentration in the roots of *Phragmites* in Århus are comparable to Pb concentrations in reed roots of wastewater constructed wetlands, while concentrations from Odense correspond more to stormwater treatment wetlands reported in a literature review by Kadlec and Wallace (2009) and were 20-times higher concentrations compared to Århus. Zn and Ni concentrations show similar pattern with 20-times higher concentrations in *Phragmites* roots at Odense compared to Silkeborg and 10-times higher compared to Århus. Besides Pb, Zn, and Ni; Cu concentrations in reed roots at the sand filer deviate even more, namely with 100 times higher values at Odense compared to Århus and Silkeborg.

High lead, zinc and copper concentrations in water, sediment and plants in Odense most probably originate from illegal outflow from industrial activities and not from stormwater.

### 5.3.4 Changes in metal accumulation through the ponds

Comparison of metal accumulation of same species within the same pond was carried out for two *Phragmites* stands in the pond at Odense, two perpendicular barriers and a sand filter planted with *Phragmites* in the pond at Silkeborg and for *Typha latifolia*, which was sampled along four classical wet detention ponds.

There was a significant difference in heavy metal accumulation between the reed stands in Odense and Silkeborg indicating an importance of heavy metal load on plant uptake. Despite Odense pond behaved more like a completely mixed reactor than a plug flow (Vollertsen et al., 2009), there was a significantly higher heavy metal accumulation in the sediment at the inlet compared to the outlet as discussed before. However, the side stand of *Phragmites* (positioned near the inlet) had lower heavy metal concentrations compared to the reeds at the sand filter at the outlet. This can be explained by different hydraulic loads of the location of sediment sampling, side stand and the sand filter. The side stand is exposed only to a portion of water flowing through the pond, while all water mass passes the inlet pond part (main flow) and the sand filter. *Phragmites* roots at the sand filter contained higher concentrations of all heavy metals except Cr compared to the sediment at the outflow, indicating an important contribution of plants in the removal of soluble heavy metals. Namely, at the inlet, there are a lot of suspended solids, settling down and increasing the accumulation on the bottom sediment; and at the outlet, there is less suspended solids causing low accumulation in the sediment but higher share of uptake of soluble pollutants by plants.

Plants at the first barrier in Silkeborg contained significantly higher concentrations of sodium compared to *Phragmites* at the outflow sand filter, which corresponds to elevated sodium content in the inflow water and higher hydraulic/pollutant load of the first perpendicular barrier. Despite the addition of Al salts to the inflow water in Silkeborg pond there was no significant difference in the Al concentrations between the three *Phragmites* stands along the pond. As mentioned before, the difference was significant for Al content in the sediment. There was no significant decrease in P, Fe, Mn, Na, K and Ca content in the roots, despite the sediment results showed a significantly higher concentration of these elements, except Ca at the inlet. According to heavy metals, Pb and Zn concentrations decreased significantly in the roots along Silkeborg pond, but the concentration of Cu increased. However, in the sediment the concentrations of all detected heavy metals were significantly higher at the inlet.

Despite the significant differences in nutrient and metal concentrations between *Phragmites* stands in Silkeborg and Odense, in the four classical wet detention ponds, nutrient and metal content in *T. latifolia* tissues did not show changes between the inlet, middle and outlet. This is consisted with the heavy metal concentrations in the sediment, which did not show significant changes through the ponds, except in pond B. Despite significant reduction of all detected heavy metals along pond B, there was no obvious reduction in heavy metal concentrations in *Typha* tissues in this pond. Similar to our study also Bragato et al. (2006) reported that the distance from the inlet did not affect nutrient and heavy metal concentrations in *Phragmites* shoots in an open water constructed wetland. Similar nutrient and metal concentrations in the plants from different sites indicates same growth conditions.

# 6 CONCLUSIONS

According to the results and comparison to the literature, the following conclusions important for the knowledge on stormwater treatment ponds can be withdrawn:

- Wet detention ponds are a suitable technology for stormwater runoff treatment. They are efficient in reduction of suspended solids and total phosphorous.
- Additional technologies improved elimination of soluble pollutants from stormwater:
    - Sorption filters improved the treatment performance for general water quality parameters, Zn and Cu.
    - Addition of iron salts to the bottom improved the treatment performance for general water quality parameters but did not increase the elimination of heavy metals except of Zn.
    - Addition of aluminum salts at the inflow increased the removal of TSS and heavy metals from stormwater.
    - Sand filters increased the removal of Zn and Cu.
- Addition of aluminium and iron salts enabled efficient reduction of algae bloom.
- The evaluation of the additional technologies would need further investigation in order to investigate long-term performance and cost-benefit ratio.
- Stormwater pollutants accumulated in the sediment. Sedimentation and thus accumulation of pollutants is enhanced by transversal sand dikes, extensive submerged vegetation and favourable length to width ratio of the ponds.
- PAHs were eliminated from water and accumulated in the sediment. Further research is needed in order to investigate the accumulation of PAHs with ponds' age and the role of microbial degradation in the sediment.
- Wetland plants enhanced sedimentation and accumulation of the pollutants in the sediment.
- *Typha* sp., *Phragmites australis* and *Rumex hydrolapathum* are the most appropriate species for phytoremediation of stormwater due to heavy metal accumulation in the roots and high biomass.
    - *Rumex hydrolapathum* accumulated the highest concentrations of heavy metals while accumulation was typical the lowest in *Iris pseudacorus*.

    - *Typha* sp. and *Phragmites australis* accumulated Zn, Pb and Ni in the roots in concentrations higher than the sediment.
    - Macrophytes with submerged or floating form contained higher heavy metal concentrations than the sediment, however their biomass compared to the other species is low.
- Heavy metal concentrations in the plants were correlated with concentrations of heavy metals in the water and sediment.
- P and K were accumulated in the leaves in concentrations higher compared to the sediment, therefore the macrophyte harvesting can contribute to elimination of these nutrients from the system.

# 7 SUMMARY

Seven systems for stormwater retention and treatment were investigated in terms of water quality improvement, accumulation of pollutants in the sediment and plant uptake. Four of the investigated systems were simple wet detention ponds with inflow and outflow structures and open water body. Plants vegetated the ponds by natural colonization. Three of the investigated systems were upgraded with additional technologies in order to improve stormwater treatment, especially the elimination of soluble pollutants, which were found to have lower treatment efficiencies in classical wet detention ponds. The additional technologies were sand filters planted with *Phragmites australis*, constructed at the outflow of each upgraded pond, addition of iron salts to the sediment in the pond at Århus, addition of alumina salts at the inflow to the pond at Silkeborg and application of sorption filters at the outflow from the pond at Odense.

According to water quality improvement, treatment of stormwater, however to a different extend, was confirmed for all investigated ponds, therefore confirming wet detention ponds as a suitable technology for stormwater runoff treatment. Significant differences between the investigated systems in water treatment were found. The hypothesis stating that wet detention ponds are efficient in reduction of suspended solids has been confirmed. Namely, the results showed efficient removal of suspended solids and total phosphorous in all investigated systems. The hypothesis also stated that the removal of soluble pollutants in classical wet detention ponds is limited. This has been confirmed for dissolved heavy metals and PAHs, which were not efficiently eliminated from water at four classical wet detention ponds. However, this cannot be stated for orthophosphate elimination since the inflow concentrations were too low to detect reduction.

The efficient elimination of orthophosphate, dissolved heavy metals and PAHs in the upgraded wet detention ponds is in accordance with the second hypothesis saying that additional technologies will improve elimination of soluble pollutants from stormwater. The upgraded wet detention ponds had lower outflow concentrations of Zn, Cd and PAHs compared to classical ponds; however, this cannot be stated for orthophosphate and other heavy metals.

Applied additional technologies had different effects on water treatment:

- Sorption filters improved the treatment performance for general water quality parameters, Zn and Cu.
- Addition of iron salts also improved the treatment performance for general water quality parameters but did not increase the elimination of heavy metals. The exemption was a slight increase in efficiency in Zn elimination.
- Addition of aluminum salts increased the removal of TSS and heavy metals from stormwater.
- Sand filters increased the removal of Zn and Cu.

Due to different loadings, lower number of water samples taken at the four classical wet detention ponds and because the upgraded systems were new and had higher treatment capacity, more investigation would be needed to make firm conclusion on different treatment efficiencies between the two types of systems. The contribution of sand and sorption filters to water treatment is also hard to evaluate because the majority of pollutants is eliminated from water already in the basin, so the pollutant concentrations entering the filters are too low for further elimination. The evaluation of the additional technologies would need further investigation also in order to investigate long-term performance and cost-benefit ratio.

The results of the study also showed the positive impact of reduced use of Pb in car fuel on the environment. Namely, Pb concentrations measured in our study were lower compared to older studies on stormwater systems.

In the upgraded wet detention ponds, pollutant elimination mainly took place in the open water of the ponds, indicating that the key removal mechanism is sedimentation. Stormwater pollutants accumulated in the sediment, which confirms the third hypothesis. This hypothesis also assumed that the highest pollutant concentrations will appear in the zones with the highest sedimentation (i.e. near the inlet), which cannot be verified completely. The concentrations of accumulated nutrients, heavy metals and PAHs tend to decrease through the systems but the decrease was significant only for heavy metals in the systems at Odense and Silkeborg and pond B and for PAHs and nutrients in the pond at Silkeborg. It was found that sedimentation and thus accumulation of pollutants is enhanced by transversal sand dikes, extensive submerged vegetation and favourable length to width ratio.

Concentrations of PAHs in the stormwater were highly variable. The relative concentrations of the 16 PAHs analysed differ between the systems as a consequence of differences in type of catchment area and systems load. Generally, combustion derived PAHs prevailed in water as well as in the sediment in the majority of the systems. Low molecular weight PAHs were often below detection limit in the water as well as in sediment samples. The research showed that planted wet detention ponds can efficiently remove PAHs from stormwater and retain them in the sediment suggesting that such systems are capable of protecting natural waters from pollution with PAHs. The accumulation of the PAHs in the sediment also implies that final sediment disposal procedures may demand additional remediation techniques to safely dispose the polluted sediments in an appropriate way. However, further research is needed in order to investigate the accumulation of PAHs with ponds' age and the role of microbial degradation in the sediment.

The contribution of plants towards elimination and accumulation of nutrients and heavy metals from the stormwater is mainly due to enhanced sedimentation and accumulation in the sediment and to a less extend due to the plant uptake. Ponds with less wetland vegetation (e.g. pond A) were less efficient in sediment accumulation.

A decrease in heavy metal concentrations was found in the order of sediment>roots>rhizomes>leaves. However, there was marked difference between plant species:

- Macrophytes with submerged or floating form contained higher heavy metal concentrations than the sediment. However, their use in phytoremediation is limited due to low plant biomass. Besides this, due to accumulation of heavy metals also in the stems and leaves, they can present higher risks for bioaccumulation along the food chain.

- *Typha* sp. accumulated Zn and Pb in the roots in concentrations higher than the sediment.
- *Rumex hydrolapathum* and *Phragmites australis* accumulated Zn and Ni in the roots in concentrations higher than the sediment.
- Many species also accumulated Cu in concentrations slightly higher than in the sediment.
- The lowest concentrations of heavy metals were measured in *Iris pseudacorus*, while the highest accumulation was typical for *Rumex hydrolapathum*.

*Rumex hydrolapathum* has high phytoremediation potential due to high heavy metal accumulation, high biomass and fast reproduction. The accumulated heavy metals in the underground parts do not represent a threat for consumers and accumulation in the food chain; however, it is not possible to eliminate them from the system by harvesting.

P and K were accumulated in the leaves in concentrations higher compared to the sediment, therefore the macrophyte harvesting can contribute to elimination of these nutrients from the system.

Heavy metal concentrations in the plants were correlated with concentrations of heavy metals in the water and sediment. Zn, Ni, Pb and Cu concentrations in *Phragmites* roots and Cr in *Phragmites* rhizomes were increasing with increasing sediment concentrations. However, increased sediment concentrations did not affect other plant tissues. In addition, K and P in aboveground tissues were positively correlated with K and P concentrations in the sediment. There was a significant difference in heavy metal accumulation between the reed stands growing in the same pond indicating an importance of heavy metal load on plant uptake. However, the decrease in heavy metal concentrations in the roots along the pond was not evident for all investigated systems.

Pond at Odense showed different composition of heavy metals and higher heavy metal load and accumulation compared to all other investigated ponds. The difference was found at all levels – stormwater pollutant load, sediment and plant accumulation.

Algal bloom can appear in wet detention ponds. It has a significant impact to the oxygen content and pH of the pond water, and therefore can affect the heavy metal and phosphorous accumulation in the sediment. Addition of aluminium and iron salts in Silkeborg and Århus, respectively, enabled efficient reduction of algae bloom, through elimination of phosphorous, however also adsorption of algae to aluminium flocks is possible.

Investigated systems were found to be efficient best management practice for stormwater detention and treatment. Additional technologies improved stormwater treatment, however further investigation is needed to elaborate firm conclusions on the contribution and long-term performance of applied technologies. In all investigated systems pollutants were accumulated in the sediment suggesting further research on accretion of sediment in time and development of new technologies for remediation of sediments with increased nutrient, heavy metal and PAH concentrations. Plants have an important contribution in stormwater treatment in terms of enhancing sedimentation and accumulation in the sediment as well as phytostabilization of heavy metals and uptake of phosphorous. Besides this, plants improve the aesthetic appearance of wet detention ponds and enable better public acceptance and inclusion of the systems into park and recreational areas.

# POVZETEK

Raziskave izboljšanja kvalitete vode, akumulacije onesnažil v sedimentu in rastlinski privzem so potekale na sedmih sistemih za zadrževanje in čiščenje padavinskih vod. Štirje od proučevanih sistemov so bili enostavni mokri zadrževalni bazeni z dotočnimi in odtočnimi objekti ter odprto vodno površino. Rastline so se na teh sistemih zarasle prek naravne kolonizacije. Trije od proučevanih sistemov so bili nadgrajeni z dodatnimi tehnologijami z namenom izboljšanja čiščenja padavinske vode, posebno odstranjevanja topnih onesnažil, za katere je bila ugotovljena nižja učinkovitost čiščenja v klasičnih zadrževalnih bazenih. Dodatne tehnologije so predstavljali peščeni filtri zasajeni s *Phragmites australis*, ki so bili zgrajeni na iztoku iz vsakega nadgrajenega bazena, dodatek železovih soli v sediment bazena v Århusu, dodatek aluminijevih soli na dotoku v bazen v Silkeborgu in postavitev sorbcijskih filtrov na iztoku iz bazena v Odenseju.

Glede na izboljšanje kvalitete vode je bilo, sicer v različnem obsegu, v vseh sistemih dokazano čiščenje padavinske vode, kar potrjuje mokre zadrževalne bazene kot ustrezno tehnologijo za čiščenje padavinskega odtoka. Med proučevanimi sistemi so bile ugotovljene značilne razlike v čiščenju vode. Hipoteza, ki navaja, da so mokri zadrževalni bazeni učinkoviti v zniževanju suspendiranih snovi, je bila potrjena. Rezultati so namreč pokazali učinkovito odstranjevanje suspendiranih snovi in celotnega fosforja v vseh proučevanih sistemih. Hipoteza prav tako navaja, da je odstranjevanje raztopljenih onesnažil v klasičnih mokrih zadrževalnih bazenih omejeno. Slednje je bilo potrjeno za odstranjevanje raztopljenih težkih kovin in PAH, katerih odstranjevanje iz vode v štirih klasičnih zadrževalnih bazenih ni bilo učinkovito. Po drugi strani pa to ne velja za odstranjevanje ortofosfata, saj so bile dotočne koncentracije prenizke, da bi lahko zaznali znižanje.

Učinkovito odstranjevanje ortofosfata, raztopljenih težkih kovin in PAH v nadgrajenih zadrževalnih bazenih je v soglasju z drugo hipotezo, ki navaja, da bodo dodatne tehnologije izboljšale odstranjevanje raztopljenih onesnažil iz padavinske vode. Nadgrajeni mokri zadrževalni bazeni so imeli nižje iztočne koncentracije Zn, Cd in PAH v primerjavi s klasičnimi zadrževalniki, kljub temu pa tega ne moremo trditi za ortofosfat in druge težke kovine.

Uporabljene dodatne tehnologije so različno vplivale na čiščenje vode:

- Sorbcijski filtri so izboljšali učinkovitost čiščenja splošnih parametrov kvalitete vode, Zn in Cu.
- Dodatek železovih soli je prav tako izboljšal učinkovitost čiščenja splošnih parametrov kvalitete vode, vendar ni povečal odstranjevanja težkih kovin. Izjema je bilo rahlo povečanje v učinkovitosti odstranjevanja Zn.
- Dodatek aluminijevih soli je povečal odstranjevanje suspendiranih snovi in težkih kovin iz padavinske vode.
- Peščeni filtri so povečali odstranjevanje Zn in Cu.

Da bi lahko podali končne zaključke o različnih učinkovitostih čiščenja med dvema tipoma sistemov, bi bilo potrebno opraviti več raziskav, saj so sistemi prejemali različne dotočne obremenitve, na klasičnih mokrih zadrževalnikih je bilo odvzeto manjše število vzorcev vode, poleg tega pa so bili nadgrajeni sistemi novi, zaradi česar so imeli večjo kapaciteto čiščenja. Prispevek peščenih in sorbcijskih filtrov k čiščenju vode je prav tako težko oceniti, saj se večina onesnažil odstrani iz vode že v samem bazenu, zaradi česar so koncentracije onesnažil, ki vstopajo v filtre, prenizke za nadaljnjo eliminacijo. Evalviranje dodatnih tehnologij bi zahtevalo nadaljnje raziskave tudi z namenom ugotavljanja delovanja na dolgi rok in razmerja med ceno in učinkovitostjo.

Rezultati študije so prav tako pokazali pozitiven učinek zmanjšane uporabe Pb v avtomobilskem gorivu na okolje. Koncentracije svinca merjene v naši raziskavi so bile namreč nižje v primerjavi s starejšimi raziskavami na sistemih padavinskih vod.

Odstranjevanje onesnažil je v nadgrajenih mokrih zadrževalnikih večinoma potekalo v prosti vodi, kar nakazuje, da je glavni mehanizem odstranjevanja sedimentacija. Onesnažila iz padavinske vode so se akumulirala v sedimentu, kar potrjuje tretjo hipotezo. Slednja je prav tako domnevala, da se bodo najvišje koncentracije onesnažil pojavljale v predelih z največjo sedimentacijo (t.j. v bližini dotoka), vendar tega ni bilo možno povsem potrditi. Koncentracije akumuliranih nutrientov, težkih kovin in PAH so se sicer načeloma skozi sisteme zniževale, vendar je bilo zmanjšanje značilno le za težke kovine v sistemih v Odenseju in Silkeborgu ter v bazenu B in za PAH ter nutriente v bazenu v Silkeborgu. Ugotovljeno je bilo, da sedimentacijo in posledično akumulacijo onesnažil pospešujejo peščene prečne pregrade, obsežna potopljena vegetacija in ugodno razmerje med širino in dolžino.

Koncentracije PAH v padavinski vodi so bile zelo variabilne. Relativne koncentracije 16 analiziranih PAH so se razlikovale med sistemi kot posledica razlik v tipih prispevnih področij in obremenitev sistemov. Na splošno so tako v vodi kot v sedimentu večine sistemov prevladovali PAH, ki nastanejo pri izgorevanju. PAH z nizko molekulsko težo so bili pogosto pod mejo detekcije tako v vzorcih vode kot tudi sedimenta. Raziskava je pokazala, da zasajeni mokri zadrževalni bazeni lahko učinkovito odstranjujejo PAH iz padavinske vode in jih zadržijo v sedimentu, iz česar sledi, da so ti sistemi ustrezna zaščita naravnih voda pred onesnaženjem s PAH. Akumuliranje PAH v sedimentu nakazuje tudi na možno potrebo po dodatnih remediacijskih tehnikah pri postopkih končnega deponiranja sedimenta z namenom zagotoviti varno odlaganje onesnaženih sedimentov na ustrezen način. Kljub temu pa so potrebne nadaljnje raziskave z namenom proučevanja kopičenja PAH s starostjo sistemov in vloge mikrobne razgradnje v sedimentu.

Prispevek rastlin k odstranjevanju in akumulaciji hranil in težkih kovin iz padavinske vode je predvsem v pospeševanju sedimentacije in akumulacije v sediment in v manjši meri v rastlinskem privzemu. Bazeni z manj močvirske vegetacije (npr. bazen A) so bili manj učinkoviti v akumuliranju sedimenta.

Koncentracije težkih kovin so se zmanjševale v zaporedju sediment>korenine>rizomi>listi. Kljub temu so bile ugotovljene pomembne razlike med rastlinskimi vrstami:

- Koncentracije težkih kovin v makrofitih s potopljenimi ali plavajočimi oblikami so bile višje kot v sedimentu. Kljub temu je njihova uporaba v fitoremediaciji omejena, saj imajo razmeroma majhno biomaso. Poleg tega zaradi akumulacije težkih kovin tudi v steblih in listih, lahko predstavljajo večje tveganje za bioakumulacijo v prehranjevalni verigi.

- *Typha* sp. je akumulirala Zn in Pb v koreninah v koncentracijah višjih kot v sedimentu.
- *Rumex hydrolapathum* je akumuliral Zn in Ni v koreninah v koncentracijah višjih kot v sedimentu.
- *Phragmites australis* je akumuliral Ni v koreninah v koncentracijah višjih kot v sedimentu.
- Številne vrste so akumulirale Cu v koncentracijah, ki so bile nekoliko višje kot v sedimentu.
- Najnižje koncentracije težkih kovin so bile izmerjene v *Iris pseudacorus*, medtem ko je bilo največje akumuliranje značilno za *Rumex hydrolapathum*.

Zaradi velike akumulacije težkih kovin, velike biomase in hitre reprodukcije ima *Rumex hydrolapathum* velik potencial za fitoremediacijo. Težke kovine akumulirane v podzemnih delih ne predstavljajo nevarnosti za potrošnike ter s tem akumulacije v prehranjevalni verigi, vendar pa jih ni možno odstraniti iz sistema s košnjo.

P in K sta se kopičila v listih v koncentracijah višjih kot v sediment, zato bi s košnjo makrofitov lahko prispevali k odstranjevanju teh hranil iz sistema.

Koncentracije težkih kovin v rastlinah so bile odvisne od koncentracij težkih kovin v vodi in sedimentu. Koncentracije Zn, Ni, Pb in Cu v koreninah in koncentracija Cr v rizomih *Phragmites*-a so se povečevale s povečevanjem teh koncentracij v sedimentu. V nasprotju s tem pa povečane koncentracije v sedimentu niso vplivale na druga rastlinska tkiva. Poleg tega je bila ugotovljena pozitivna korelacija tudi med koncentracijama K in P v nadzemnih delih ter koncentracijama K in P v sedimentu. Ugotovljena je bila značilna razlika v akumuliranju težkih kovin med različnimi sestoji trstičja znotraj istega bazena, kar nakazuje na pomembnost obremenitve s težkimi kovinami na rastlinski privzem. V nasprotju s tem pa upadanje koncentracije težkih kovin v koreninah vzdolž bazena ni bilo očitno v vseh proučevanih sistemih.

Bazen v Odenseju je imel drugačno sestavo težkih kovin ter večje obremenitve in akumulacijo težkih kovin v primerjavi z ostalimi proučevanimi sistemi. Razlika je bila ugotovljena na vseh nivojih – v obremenjevanju z onesnažili iz padavinske vode, sediment in akumulaciji v rastlinskih tkivih.

V mokrih zadrževalnih bazenih se lahko pojavi cvetenje alg. Slednji ima velik vpliv na vsebnost kisika in pH v vodi zadrževalnika in posledično lahko vpliva na akumuliranje težkih kovin in fosforja v sedimentu. Dodatek aluminijevih in železovih soli v Silkeborgu in Århusu je preko odstranjevanja fosforja omogočil učinkovito zmanjšanje cvetenja alg, poleg tega pa je možna tudi direktna adsorbcija alg na kosme aluminija.

Proučevani sistemi so se izkazali kot učinkovita dobra gospodarska praksa (*ang.* best management practice - BMP) za zadrževanje in čiščenje padavinskih vod. Dodatne tehnologije so izboljšale čiščenje vode, vendar so potrebne nadaljnje raziskave za dosego trdni zaključkov o prispevku in dolgoročni učinkovitosti uporabljenih tehnologij. V vseh proučevanih sistemih so se onesnažila akumulirala v sedimentu, zato bi bilo smiselno nadalje raziskati kopičenje sedimenta v času in razvoj novih tehnologij za remediacijo sedimentov s povečanimi koncentracijami hranil, težkih kovin in PAH. Rastline so imele pomemben prispevek k čiščenju padavinskih vod s pospeševanjem sedimentacije in akumuliranja v sedimentu kot tudi s fitostabilizacijo težkih kovin ter privzemom fosforja. Poleg naštetega rastline tudi izboljšajo estetski izgled mokrega zadrževalnega bazena in omogočijo boljše sprejemanje s strani javnosti ter vključevanje sistemov v parke in rekreacijske površine.

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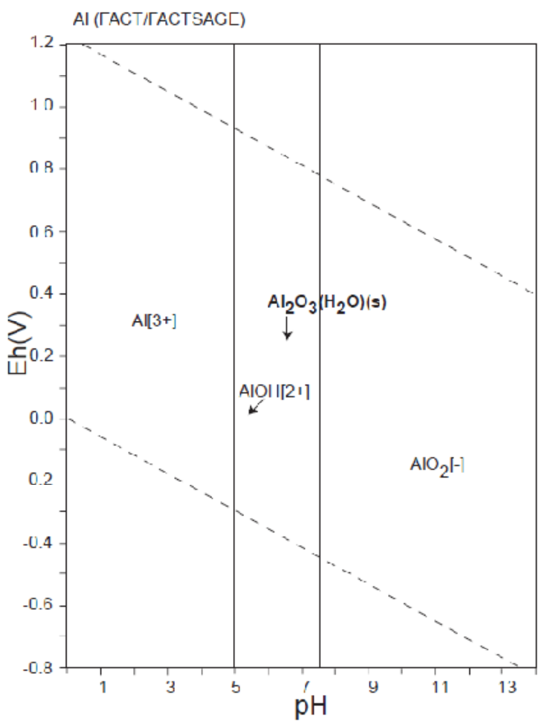
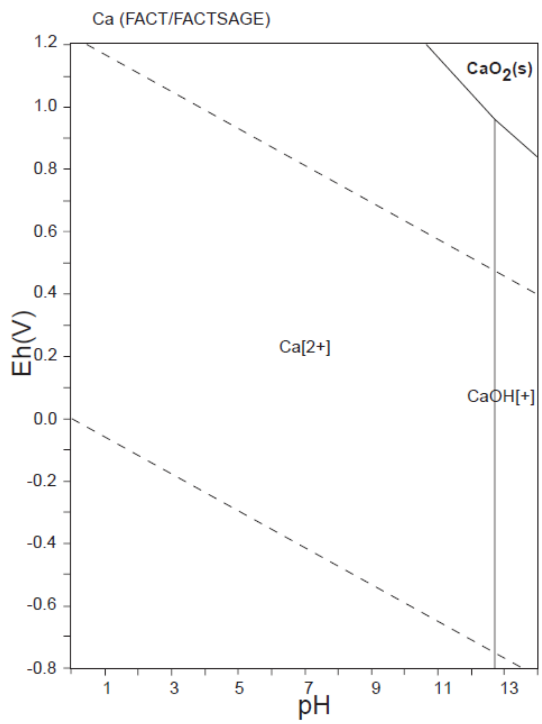
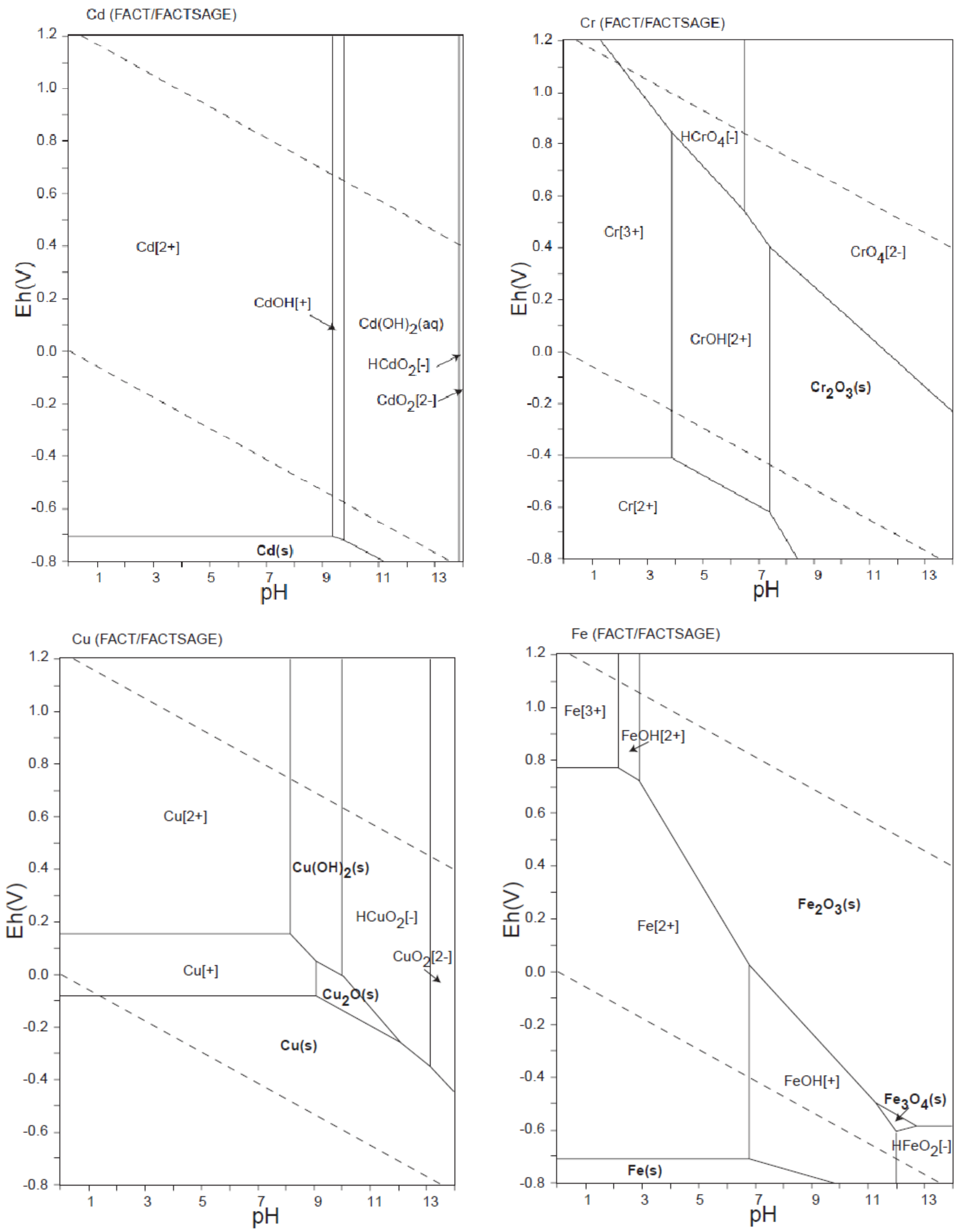
# APPENDICES

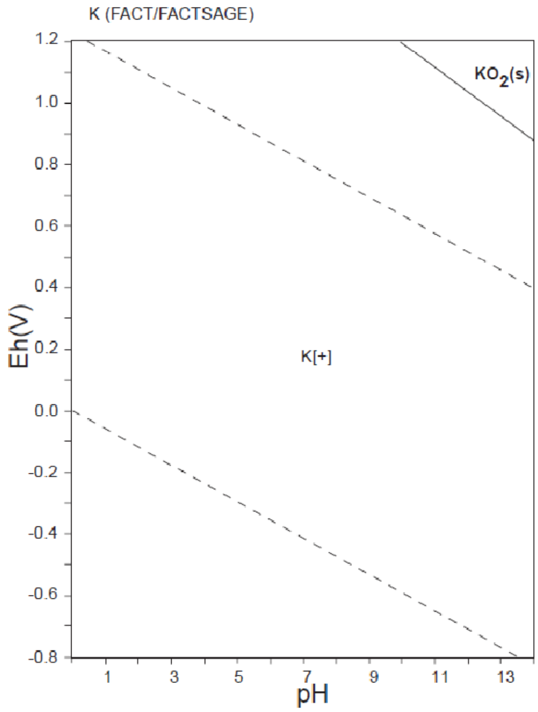
## APPENDIX A

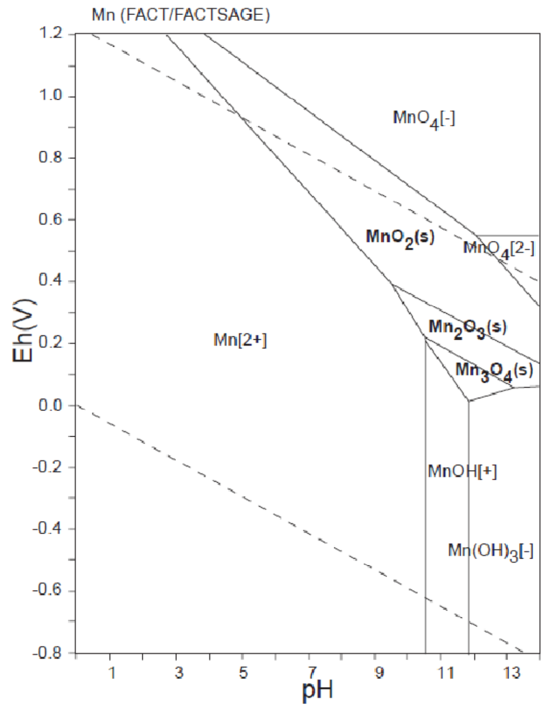
Porbaux diagrams for elements analysed in this study.

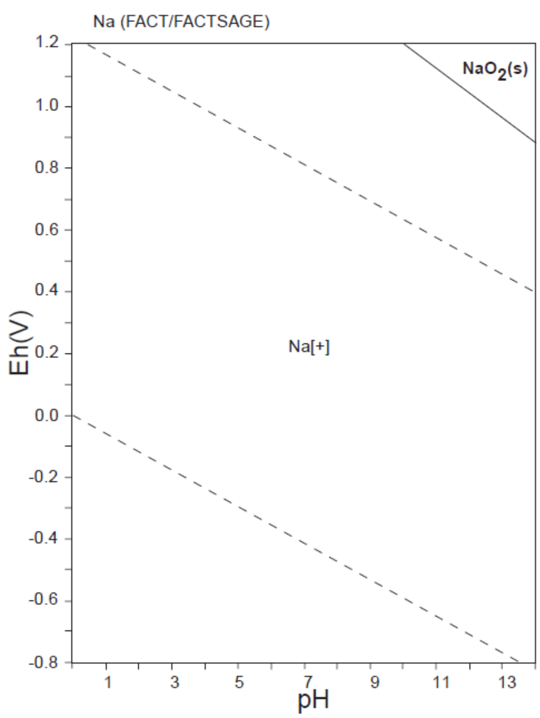


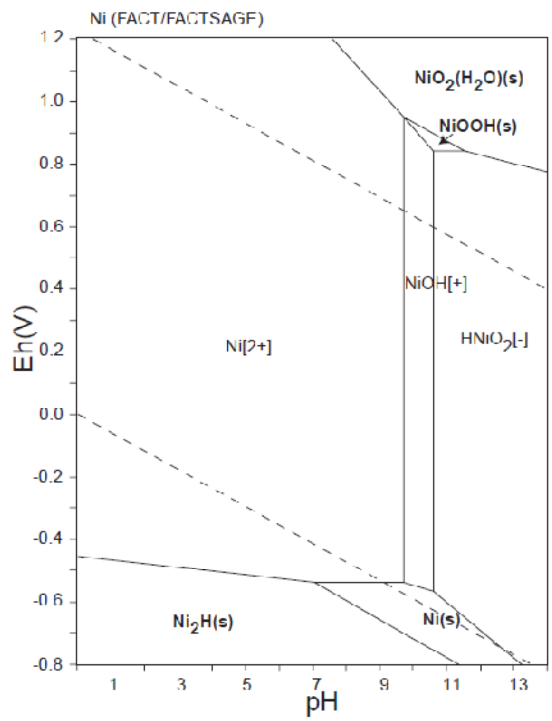



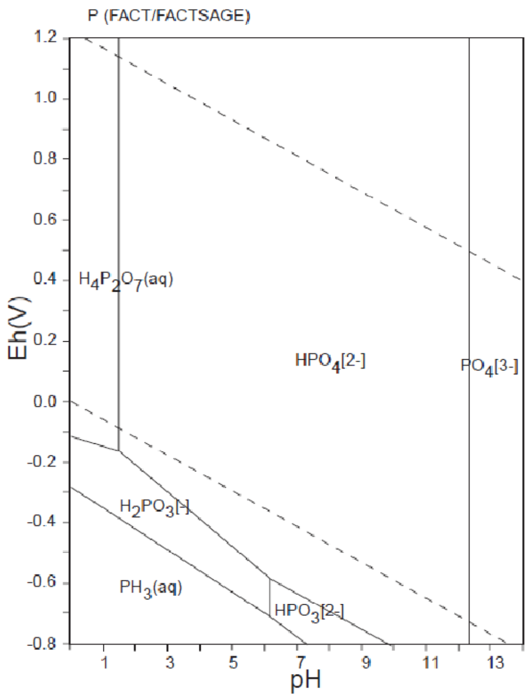

Cd (FACT/FACTSAGE)
Cd[2+]
CdOH[+]
Cd(OH)2(aq)
HCdO2[-]
CdO2[2-]
Cd(s)
Cr (FACT/FACTSAGE)
HCrO4[-]
Cr[3+]
CrO4[2-]
CrOH[2+]
Cr2O3(s)
Cr[2+]
Cu (FACT/FACTSAGE)
Cu[2+]
Cu(OH)2(s)
HCuO2[-]
CuO2[2-]
Cu[+]
Cu2O(s)
Cu(s)
Fe (FACT/FACTSAGE)
Fe[3+]
FeOH[2+]
Fe2O3(s)
Fe[2+]
FeOH[+]
Fe3O4(s)
HFeO2[-]
Fe(s)
Eh(V)
pH

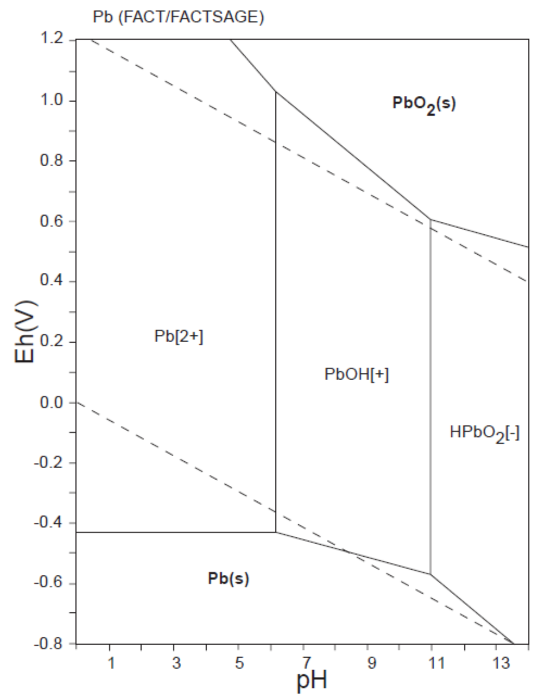

K (FACT/FACTSAGE)
$KO_2$(s)
K[+]
Eh(V)
pH

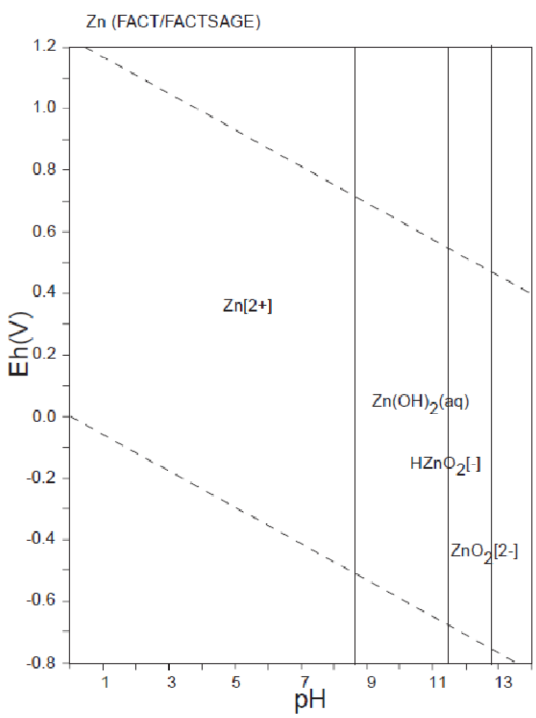

Mn (FACT/FACTSAGE)
$MnO_4$[-]
$MnO_2$(s)
$MnO_4$[2-]
$Mn_2O_3$(s)
$Mn_3O_4$(s)
Mn[2+]
MnOH[+]
$Mn(OH)_3$[-]
Eh(V)
pH


Na (FACT/FACTSAGE)
$NaO_2$(s)
Na[+]
Eh(V)
pH


Ni (FACT/FACTSAGE)
$NiO_2(H_2O)$(s)
NiOOH(s)
NiOH[+]
Ni[2+]
$HNiO_2$[-]
$Ni_2H$(s)
Ni(s)
Eh(V)
pH


P (FACT/FACTSAGE)
Eh(V)
pH
$H_4P_2O_7$(aq)
$HPO_4$[2-]
$PO_4$[3-]
$H_2PO_3$[-]
$PH_3$(aq)
$HPO_3$[2-]


Pb (FACT/FACTSAGE)
Eh(V)
pH
$PbO_2$(s)
Pb[2+]
PbOH[+]
$HPbO_2$[-]
Pb(s)


Zn (FACT/FACTSAGE)
Eh(V)
pH
Zn[2+]
$Zn(OH)_2$(aq)
$HZnO_2$[-]
$ZnO_2$[2-]

# APPENDIX B

US EPA National Recommended Water Quality Criteria.

| Heavy metal | Unit | Concentration |
|---|---|---|
| Fe | mg $L^{-1}$ | 1000 |
| Zn | µg $L^{-1}$ | 120 |
| Cd | µg $L^{-1}$ | 0,25 |
| Ni | µg $L^{-1}$ | 52 |
| Cr | µg $L^{-1}$ | 74 (Cr III) |
| Cu | - | - |

*http://www.epa.gov/waterscience/criteria/wqctable/index.html#F2