Potential impacts and treatment of stormwater runoff

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Preface

This dissertation is submitted in a partial fulfillment of the requirements for obtaining the Doctor of Philosophy (Ph.D.) degree. The dissertation consists of an extended summary and seven supporting papers. The main results of the Ph.D. study are presented in the extended summary and additional details are given in the supporting papers.

The study was carried out under the supervision of Professor Jes Vollertsen at the section of Environmental Engineering, Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Denmark. The study was completed during the period September 2007 to July 2012 and was supported by PH-Consult and The Danish Road Directorate.

There are many people to thank. First and foremost I would like to thank Jes Vollertsen for his supervision and great help as well as his big encouragement and laid back approach to everything throughout the whole Ph.D. Thanks to the whole SPW-group for good discussions both the scientific and the not so scientific. Thanks to all my changing officemates especially Diana and Elise who always have been ready to discuss everything else than work. Also thanks to Mette and all the "youngsters" at Chemistry and Environmental Engineering for making the lunch discussions unforgettable.

Finally I would like to thank Bruno, Tilde and Sine for reminding me of what is important in life and forcing me to take everything as it comes.

Aalborg, June, 2012

Tove Wium-Andersen

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English abstract

Stormwater from urban areas contains significant amounts of pollutants. Phosphorus causes, for example, algal bloom and subsequent oxygen depletion in receiving waters. Unlike many organic pollutants, heavy metals are not degraded and, therefore, accumulate, potentially causing acute or long-term toxic effects in the environment. Consequently, treatment of stormwater is often required to minimize its potential negative ecological impacts.

This study has focused on the potential toxicity of stormwater runoff, the performance of the wet detention pond as well as additional treatment of stormwater runoff in combination with wet detention ponds. The purpose of this has been to determine the impacts of stormwater runoff on the receiving waters, whether it is necessary to treat the runoff before it enters the environment and how this treatment should be applied to achieve better removal of colloidal and truly dissolved pollutants.

Three wet detention ponds serve as the backbone in the present study. They were constructed in 2007 and 2008 in the cities of Aarhus, Silkeborg an Odense, Denmark as a part of the EC funded LIFE-Treasure project. They were equipped with flow meters monitoring inlet and outlet, online sensors monitoring the pH, dissolve oxygen level, water level, temperature and turbidity in the pond basin. They all had sand filters at the outlet and all had been applied an additional treatment technology – iron enriched bottom sediment in Aarhus, aluminum addition in Silkeborg and sorption filter after the sand filter in Odense. These technologies were added to examine the removal of colloidal or truly dissolved pollutants, as these are the most bioavailable and can have detrimental impacts on the receiving waters. Furthermore, water samples were collected in the inlet, in the pond as well as in the outlet (in Odense also after the sorption filter). The water samples were subsequently analyzed for pollutants e.g. heavy metal and nutrients.

The stormwater runoff showed a wide range of toxic effects, ranging from no effects to severe effects. The toxicity varied both in time and space. Consequently, a robust, continuous and extensive treatment technology is crucial to protect the receiving water from pollutants. The performance and ecological dynamics of the wet detention ponds were examined by modeling firstly the removal of pollutants and secondly by developing a larger eutrophication model targeted wet detention ponds which gave insight in the pH, dissolved oxygen concentration and algae growth within the ponds. Change in toxicity due to aluminum addition to stormwater samples were examined in the laboratory. Furthermore, five different sorption materials were evaluated with artificial stormwater giving profound knowledge of the performance of these materials for use in future designs of sorption filters.

This study has contributed to an increased understanding of the potential impacts and treatment of stormwater runoff applying wet detention ponds and combinations with tertiary treatment. This knowledge can be applied in future design and construction of such systems.

Dansk resume (Danish abstract)

Regnvand fra befæstede arealer indeholder signifikante mængder af forurenende stoffer. For eksempel forårsager blandt andet fosfor opblomstring af alger og efterfølgende iltsvind i recipienterne. Modsat mange organiske miljøfremmede stoffer, bliver tungmetaller ikke nedbrudt men akkumuleres, hvilket kan føre til akutte eller langvarige toksiske effekter i nærmiljøet. Det vil sige, at behandling af regnvand er nødvendigt for at minimere regnvands potentielle negative indflydelse på naturen.

I dette studie har fokus været på regnvands potentielle toksicitet, våde regnvandsbassiners virkningsgrad samt supplerende behandling af regnvand i kombination med våde regnvand bassiner. Formålet med dette, har været at bestemme regnvandets indflydelse på recipienterne, hvorvidt det er nødvendigt at behandle regnvandet inden udledning til naturen samt hvorledes denne eventuelle behandling skal udføres, for at opnå bedre fjernelse af kolloider og opløste stoffer.

Tre våde regnvands bassiner udgør fundamentet for dette studie. De blev bygget i 2007 og 2008 i henholdsvis Aarhus, Silkeborg og Odense, som en del af det EC støttede LIFE-Treasure projekt. De blev udstyret med flowmetre i ind- og udløb samt online sensorer placeret i selve bassinerne til måling af pH, koncentration af opløst ilt, vandspejls niveau, temperatur og turbiditet. Alle tre bassiner er udstyret sandfilter før udløbet og alle har fået implementeret én supplerende renseteknik – jernberiget bundsediment i Aarhus, tilføjelse af aluminium i Silkeborg og sorptionfiltrering efter sandfilteret i Odense. Bassinerne var udvidet med disse teknologier for, at undersøge fjernelse af kolloider samt opløste stoffer, da disse er de mest biotilgængelige og derved kan skade recipienterne. Derudover blev der udtaget vandprøver i ind- og udløb samt efter sorptionsfilteret i Odense. Vandprøverne blev efterfølgende analyseret for forurenende stoffer bl.a. tungmetaller og næringsstoffer.

Regnvandet viste et bredt spektrum af toksicitet, fra ingen skadelige virkninger til alvorlige skadelige virkninger. Den toksiske effekt varierede både i tid og sted. Som følge heraf er en robust, kontinuert and ekstensiv behandlingsteknologi altafgørende for at beskytte naturen mod de forurenende stoffer der findes i regnvand. Det våde regnvandsbassins virkningsgrad og dynamiske processer heri blev undersøgt ved at modellere fjernelsen af forurenende stoffer samt derefter at udvikle en detaljeret eutrofieringsmodel. Denne blev udviklet specifikt til våde regnvandsbassiner og gav viden om pH, koncentration af opløst ilt samt algevækst i bassiner. Ændring af regnvand toksicitet ved tilførsel af aluminium blev undersøgt i laboratoriet. Desuden, blev fem forskellige sorptionsmaterialer evalueret ved hjælp af kunstig regnvand, hvilket gav betydelig viden omkring effektivitet og virkningsgrad af disse materialer. Viden som kan benyttes ved dimensionering af fremtidige filtre.

Dette studium har bidraget til større forståelse af regnvands potentielle indflydelse på naturen samt hvorledes regnvand kan behandles i våde regnvands bassiner med og uden supplerende renseteknikker. Denne viden vil kunne anvendes i forbindelse med dimensionering og konstruktion af fremtidige bassiner.

1 Introduction

Technologies for treatment of pollutants in wastewater from households and industries are well-established. What remains is reducing the pollutant loads introduced to surface waters by stormwater runoff from urban areas. Such runoff contains numerous pollutants in varying but significant concentrations, for example polycyclic aromatic hydrocarbons (PAHs), heavy metals, biocides, nutrients and suspended solids (Göbel et al., 2007b; NURP, 1983). The pollutants can have potential negative ecological impacts on receiving waters (Fisher et al., 1995; Marsalek et al., 1999). The negative impacts can be eutrophication, oxygen depletion and toxic effects towards flora and fauna. The pollutants originate from urban atmospheric fallout, traffic and urban constructions and installations (Marsalek et al., 1999). Knowledge about sources, pathways, loads and efficient treatment technologies are essential to be able to meet requirements for good ecological standard of the receiving water bodies.

A stormwater treatment technology that has proven robust and efficient as well as simple to implement and operate is the wet detention pond (Hvitved-Jacobsen et al., 2010). The wet detention pond allows flocculation, sedimentation, and degradation to occur, reducing the concentration of pollutants. The technology is especially efficient for pollutants in association with particles and suspended solids. However, the most bioavailable and thereby maybe the most harmful pollutants are those bound to colloids or truly dissolved.

The objective for the present study is to contribute to the knowledge about reducing this fraction of the pollutants. The focus is on stormwater treatment applying wet detention pond and combinations with additional treatment for improvement of performance. The study contributes to a better understanding of the processes in the pond. It furthermore yields tools appropriate in the design of wet detention ponds as well as technologies for additional treatment.

2 State of the art

Several well established technologies for stormwater management exist, e.g. dry ponds, wetlands, infiltration trenches and ponds, filters and swales. Furthermore, the rainwater can be handled locally e.g. by rain gardens, green roofs, filter strips and porous pavement. In the present study only the wet detention pond will be looked into.

The wet detention pond is an artificial lake with a permanent water pool designed to collect stormwater and subsequently drain it slowly, which reduces the hydraulic impacts on receiving water systems located downstream of the discharge. The stormwater is often detained for days during which the treatment processes occur. The main treatment processes are:

- Sedimentation of particulate matter and following accumulation of pollutants in the sediment.
- Plant uptake of dissolved pollutants in the pond vegetation followed by degradation and some accumulation in the sediment after death and decay of the plants.
- Adsorption of fine particles and colloids on surfaces in the pond, e.g. bottom and plants.
- Degradation of organic pollutants.

When designing and constructing a wet detention pond, three dimensions should be considered: the size of permanent volume, the size of detention volume and the depth of the pond. Several dimensioning methods exist, e.g. based on catchment area, desired pollutant removal efficiency or desired detention time (Hvitved-Jacobsen et al., 2010). Whether these methods calculate the total volume, the permanent wet volume or the detention volume are an individual estimate for each pond and mainly depend of the hydraulic restrictions connected to the receiving waters.

An important factor for a well-functioning wet detention pond is the depth of the pond. The depth of a pond affects the oxygen concentration and pH in the pond. That is, the deeper the pond the higher the risk for oxygen depletion and undesired pH values, due to poor mixing of the water column, stratification and thereby low reaeration (Herb and Stefan., 2005; Madsen et al., 2007; Hvitved-Jacobsen et al., 2010). This can lead to malodors, release of phosphorus and metals from the sediment as well as oxygen depletion and undesired pH values which again affects the receiving waters. On the other hand, the pond should not be too shallow as resuspension of the bottom sediment can occur, due to wind induced eddies (Bentzen et al., 2009). Moreover, it is the surface area of a pond and not the depth which increases the construction costs. Consequently, a new pond should be as deep as possible to keep the construction costs low and to avoid resuspension, but not so deep that oxygen depletion or diverging pH values occur.

The traditional wet detention pond often consists of at grit chamber followed by the pond itself and in the outlet maybe a water brake. This design is relatively efficient towards particulates and suspended solids and pollutants associated with these (e.g. Stanley, 1996; Petterson et al., 1999; Hossain et al., 2005; Semadeni-Davies, 2006; Vollertsen et al., 2009a). However, with respect to pollutants bound to colloids or truly dissolved, wet detention pods have rather limited effects. It is, however, these pollutants which are most mobile in the aquatic environment as well as most bioavailable, potentially contributing of the deterioration of the receiving waters (Tuccillo, 2006; Marsalek et al., 1999). These pollutants bound to colloids or truly dissolved can, generally seen, be removed from the water phase in three ways: by filtration, by sorption or by improving the flocculation and thereby the sedimentation. Sand filtration is a well know technology and is applied in treatment of drinking water, surface water and wastewater (Göbel et al., 2007a; Arias et al., 2001; Leupin and Hug, 2005). The flocculation can be improved by adding chemicals/flocculants to the water phase. Addition of flocculants has been applied in lake restoration to removed phosphorus from the water phase. Two often used flocculants are aluminum and iron. Aluminum forms stabile flocs but applied in too high concentration, aluminum itself will become toxic to the flora and fauna in the lake or pond (Cooke et al., 2005). Iron forms complexes with phosphorus which then is accumulated in the sediments, however, these complexes are vulnerable towards anaerobic conditions (Cooke et al., 2005). Sorption filters can have a wide range of sorption material and are applied for treatment of waters in a wide range of contexts (Liu et al., 2005; Garcia-Sanchez and Alvarez-Ayuso, 2002). However, pretreatment, e.g. sand filtration is necessary to avoid clogging of the sorption filter. That is, several additional treatment methods targeted colloidal or dissolved pollutants exist. However, they have only to a limited extent been applied to wet detention ponds.

Numerous studies have their focus on the stormwater itself. That is, pollutant source, first flush, concentration of pollutants versus dry period, rain intensity, catchment use, and etc. has been investigated (e.g. Göbel et al., 2007b; NURP, 1983; Marsalek et al., 1999; Sansalone and Buchberger, 1997). However, these studies have often only data from grap samples or from single rain events. Only a few studies with a continuous monitoring program of pollutant load over a long time span exist, e.g. Vollertsen et al. (2009a).

That is, there are gaps in the knowledge concerning the continuously pollutant load and ecological impacts of stormwater runoff and effluent from wet detention ponds. Moreover, chemical, biological and physical processes in wet detention ponds, as well as their long-term performance needs to be evaluated to obtain a better base for dimensioning future ponds. Also the combination of such ponds with methods for additional treatment needs investigation. The present Ph.D. dissertation contributes knowledge to these issues by the study of various fundamental processes and by the interpretation of full-scale investigations made on three wet detention ponds constructed as research facilities with the purpose of gaining knowledge on stormwater treatment.

3 Study site

In 2007 three full-scale wet detention ponds were established as part of an EC-funded LIFE project in the cities of Aarhus, Silkeborg and Odense, Denmark. All three ponds are located in green areas in connection to their catchments, serving as recreational areas. The three ponds receive stormwater runoff from three different catchment types and have different physical outlines, see Table 1. The ponds were designed for a retention time of 72 hours at a return period of 4 $year^{-1}$ and follow the recommendations of e.g. Hvitved-Jacobsen et al. (1994), Pettersson et al. (1999) and Vollertsen et al. (2007). The ponds are all planted with different green plants to enhance treatment as well as for aesthetic purposes.

Figure 1: The ponds in Odense, Aarhus and Silkeborg, respectively, approximately one year after construction.

The ponds were designed as 1.0 to 1.5 m deep traditional wet detention ponds with 1 m retention volume. First the stormwater enters a grit chamber. After the grit chamber, the stormwater enters the earthen ponds through boulders to disperse the inflow jet stream. All ponds are equipped with clay membranes. At the outlets the ponds were established with sand filters. Furthermore, the ponds were equipped with an additional experimental treatment technology to improve the removal of dissolved and colloidal contaminants e.g. phosphorus, organic micro-pollutants and heavy metals.

Precipitation in the catchments is measured by tipping bucket gauges of the Danish SVK rain gauge system, located a few kilometers from each pond. Meteorological data (radiation, air temperature, wind direction and wind speed) is measured at nearby weather stations administrated by the Danish Meteorological Institute, DMI. For further information about the study sites see articles **I**, **II**, **III**, **IV**, **VI** and **VII**.

3.1 Aarhus pond

The Aarhus pond receives runoff from an urban residential catchment, has a permanent volume of 6,900 m^3 and a detention volume of 1,400 m^3. The pond is located close to the receiving Lake Brabrand which is a part of an important recreational area in Aarhus as well as a natura 2000 habitat. Three small circular planted islands were established within the pond to improve the visual appearance as well as prevent jet streams within the pond. The experimental treatment technology tested in this pond was iron enriched bottom sediments. That is, the bottom sediments of the pond were iron-enriched by dosing iron sulfate into the water phase in order to enhance the pollutant removal capacity of the system.

The pond in Aarhus receives stormwater from a catchment of 57 ha (impermeable area of 26 ha) were 80% of the area is blocks of flats and 20% of the area is roads and highway. The estimated average runoff for the catchment is 132,000 m^3 $year^{-1}$ (Table 1).

3.2 Odense pond

The pond is located in a recreational area in the southern part of Odense, Denmark. The pond serves an industrial area and is designed as a single 1.5 m deep wet detention pond with a permanent volume of 1,990 m^3 and detention volume of 1,300 m^3. The catchment area is 27.4 ha (11.4 red ha) and the estimated runoff is 55,500 m^3 $year^{-1}$. The additional technology tested in this system was fixed-media sorption filters. The sorption filters were divided into one large filter and three smaller test filters. The water ran through the larger filter by gravitation. The three test filters were fed by intermittent pumping in order to precisely control the flow rate and pattern through the filters (Table 1).

3.3 Silkeborg pond

The wet detention pond in Silkeborg has a permanent volume of 2,680 m^3 and a detention volume of 3,230 m^3. The pond receives stormwater runoff from a residential area and a section of a highway passing through the district with a total area of 21.5 (impermeable area of 8.8 ha). The pond is divided into three sections by two planted earthen barriers. During dry weather these barriers divides the pond in three disconnected sections, during rain when the water level rises, the water passes over the barriers. The pond was equipped with a flow proportional injection system to dose aluminum salts which form aluminum hydroxide flocks that co-precipitate with phosphate and heavy metals in the pond (Table 1).

Table 1: Pond and catchment characteristics

	Unit	Aarhus	Odense	Silkeborg
Type of catchment		Residential (blocks of flats)	Light industry	Residential (detached houses) and highway
Total catchment area	ha	57.4	27.4	21.5
Impervious catchment area	ha	25.8	11.4	8.8
Precipitation	mm y^{-1}	661	657	719
Annual design runoff	m^3	131,900	55,500	49,600
Permanent volume	m^3	6,900	1,992	2,680
Detention volume	m^3	1,400	1,310	3,230
Permanent water depth	m	1.25	1.45	1.00
Length to width ratio	-	3:1	4.5:1	3 chambers of app. 1:1 each
Max. design outflow	L s^{-1}	150	25	120
Permanent pond volume per impermeable catchment area	m^3 m^{-2}	267	175	305
Total pond volume per impermeable catchment area	m^3 m^{-2}	322	290	672

3.4 Online measurements

All three wet detention ponds were equipped with flow meters to monitor inlet and outlet flows as well as *in-situ* sensors to monitor pH, temperature, dissolved oxygen, turbidity and water depth. Inlet flows were measured by a smaller and a larger full-flowing magnetic flow meter in each pond (Krone optiflux, DN 150 mm and DN 500 mm in Odense, Aarhus and DN 400 mm in Silkeborg) coupled in series and parallel to a rectangular weir, allowing accurate flow measurement from 1 L s^{-1} up to several m^3 s^{-1}. The flow meters were placed after the grit chamber to protect against silting. Sensors for online monitoring of pH (WTW SensoLyt 700 IQ), dissolved oxygen (WTW FDO 700 IQ), temperature (via pH meter) and water depth (Klay Hydrobar) were placed in the ponds. In Odense and Aarhus the sensors were in the middle of the ponds. In Silkeborg sensors were in both the middle and last sub-compartment. Readings were stored every minute.

Online measurements in Odense and Aarhus were initiated primo 2008 and terminated late September 2009. Measurement in Silkeborg was initiated November 2008 and also terminated late September 2009.

3.5 Water samples

Auto-samplers (Maxx TP IV) holding 24 one-liter plastic bottles were placed in the inlets after the grit chambers and in the middle of the basin (Odense), in the end of the basin (Aarhus), and in the last sub-compartment (Silkeborg). Furthermore, water samples were collected after the sand filters and after the sorption filter in Odense. Water samples were collected flow proportionally in the inlets and time proportionally in the ponds and after the filters. The auto-samplers were emptied every 14 days or when full. The storage on site could potentially have caused some changes in the samples, e.g., degradation of PAHs and complex binding of heavy metals, leading to underestimation of pollutant concentrations and of toxic effects. Such changes were minimized by placing the auto samplers underground in dark and cool environments. The subsamples from the auto-samplers were pooled, divided in aliquots and analyzed for total concentrations of copper, lead, zinc, cadmium, nickel, chromium, mercury, total PAH (after USEPA), suspended solids, nitrogen as well as total and dissolved phosphorus. All analysis was performed by an accredited laboratory following international or European standards. Furthermore, grab samples were taken in the ponds for determination of chlorophyll and *E-Coli*.

The water samples from Aarhus covered the time span from mid June 2008 to late September 2009. Odense covered the time span from late March 2008 to late September 2009 and Silkeborg cover the time span from mid-December 2008 to late September 2009.

4 Methodological considerations

Three different analyses/experiments campaigns have been carried out during the present Ph.D. study. Firstly, estimation of stormwater toxicity has been carried out on water samples from the ponds. Secondly, experimental test of sorption media has been carried out. Thirdly, two different stormwater pond models have been developed based on the large data set achieved by the comprehensive surveillance of the ponds.

4.1 Estimation of stormwater toxicity

Toxic effects are estimated by exposing test organisms to a potential toxic sample or compound followed by a calculation of the inhibition of the test organism. The inhibition can be growth inhibition, mobility inhibition, inhibition of reproduction, etceteras. Toxicity is expressed as a given effect concentration (EC) after a given exposure time. That is, EC_{50} and EC_{10} is the concentration giving an inhibition equal to 50% and 10% after a certain exposure time, respectively. That is, the higher toxicity of a sample the lower EC-values and vice versa. Toxicity is not an absolute estimation but a relative measurement characteristic for the applied test organism and exposure time, resulting in different EC-values for the same compound. Therefore, it is important to consider which organisms are relevant to use as test organisms for stormwater runoff. The optimal solution is to use a battery of toxicity tests to reveal the ecological impacts of a sample (Dutka, 1988).

In the present study of stormwater toxicity, samples have been taken from inlet, basin and outlet of the above described ponds except from the pond in Silkeborg. Some of the stormwater samples were added aluminum salts to examine eventual harmful or beneficial effects of this compound which later was added to the pond in Silkeborg. Furthermore, toxicity of pure dissolved heavy metals (Cd, Cu, Pb, Zn, Cr and Ni) was determined for reference purposes.

4.1.1 Applied toxicity tests

Toxicity tests were chosen on the basis the following criteria:

- The tests should be validated and comply with a standard
- An existing protocol should be available
- The applied test organism should be found naturally in water.
- The tests should use organisms on different tropic levels
- The tests should be cost-time efficient.
- The tests should be relative cheep to purchase.

These criteria led to three different tests using bacteria (*Vibrio fischeri*), algae (*Selenastrum capricornutum)* and crustaceans (*Daphnia magna*) as test organisms. All three tests are designed to measure acute toxic effects and the test organisms are distributed on different tropic levels. The first test is based on the bacteria’s capacity to emit luminescence, the second growth of algae and the last the mobility of daphnia. They were all carried out according to international standards (DS/EN ISO 11348-1, DS/EN ISO 8692, DS/EN ISO 6341). The two first tests needed alteration of the samples. All alterations are unwanted as this can affect or change the content of toxic substances, e.g. change the solubility or remove pollutants from the sample. The bacteria test, prescribe addition of NaCl as the bacteria is marine. However, the bacteria test is fast, giving the result after only 30 min. Furthermore, it is commonly used (e.g. Marsalek et al., 1999; Kay et al., 2008; Corsi et al., 2009) and easy to apply. Filtration of the samples is necessary when using the algae test as the samples have a natural content of phytoplankton which can interfere with the test results. However, the algae test uses a test organism which is indigenous to freshwater, the test is easy to carry out and no advanced equipment is needed. Furthermore, the test has low time consumption (72 h). In addition, in these two tests a large number of test individuals are introduced to each dilution of sample and thereby minimizing statistical fluctuations. That is, despite the alterations of samples the tests have other advantages and were included in the test battery. The last test using daphnia needed no alterations. However, this test uses a limited number of test individuals introducing significant statistical fluctuations. Furthermore, the daphnia should be hatched prior to test which should be initiated 72 h before initiating the toxicity test giving a total of 120 h of test time whereof 48 h are exposure time. For further details concerning specific experiments see articles **I** and **II**.

4.1.2 Data analysis

Two set of analyzing campaigns were carried out during this Ph.D. In the first study (article **I**) four stormwater runoff samples from Odense were tested with all three toxicity tests with and without aluminum addition. Data were analyzed according to the respective standards, dose-response curves (inhibition as a function of concentration of sample) were obtained and EC_{50} and EC_{10} values were estimated when possible.

In the second study (article **II**) the toxicity of 38 water samples from the ponds in Odense and Aarhus and solutions of 6 heavy metals were measured using only the algae toxicity test. This test was found to be the most sensitive and reliable during the first study. The dose-response curves were modeled by a four-parameter log-logistic function using the drc-package in R (Ritz and Streibig, 2005). EC_{50} values were calculated using the same software.

4.2 Sorption filter

To increase the understanding of low cost sorption materials with potential for usage in polishing pretreated stormwater runoff, a set of experiments were carried out in the laboratory.

4.2.1 Filter media

When designing sorption filters, it is essential that the selected filter media has a high sorption capacity at low pollutant concentration levels, characteristic of stormwater runoff and effluent from wet detention ponds. In order to reduce the required contact time, the kinetics of the sorption process must be rapid. Furthermore, the sorption material must be commercially available at an affordable price/effect ratio. A wide range of sorption materials are commercially available. However, in the present study focus was on natural occurring materials subjected to minor modification. Furthermore, low cost, high physical stability and high sorption capacity were considered important. Considering these characteristic, Limestone, Zeolite, Shell-sand and two different kinds of Olivine granules were chosen for the experiments, see article **V** for further descriptions.

4.2.2 Experimental setup

Sorption capacity, desorption and sorption kinetics of the five materials were examined. Capacity and desorption were examined by batch experiments and kinetics by column experiments. The sorbates chosen were arsenic, cadmium, chromium, copper, lead, nickel, phosphorus and zinc mixed in deionized water, imitating artificial stormwater.

Sorption capacity of the filter material was examined to obtain knowledge about the lifespan of the different materials. For each sorbent, a fixed quantum of material was placed in a fixed volume of aquatic solution containing the eight sorbates at different concentrations. The start concentrations in the aquatic solutions were chosen by initial testing and a desire to identify equilibrium conditions for water phase concentrations relevant for stormwater and effluent from wet detention ponds with sand filtration. For further details see article **V**.

Desorption of adsorbed elements was analyzed by three sequential extraction steps. Extractions were first made by pure deionized water followed by addition of NaCl and subsequently by raise of the pH. The two last steps were performed to simulate chemical changes which can occur in the water phase of wet detention ponds. NaCl is used as de-icing agent on roads, causing increased NaCl concentrations in stormwater runoff and high pH-levels can occur in detention ponds during summertime (Vollertsen et al., 2009a). For further details see article **V**.

Sorption kinetics was investigated by eight small flow-through columns operated in parallel. Residence times were varied to allow determination of sorption kinetics. The residence times were kept short to avoid equilibrium between sorbent and sorbate in the columns. Artificial stormwater was pumped from reservoirs to the water saturated columns containing the filter media. The contact time between liquid and sorbent was varied by changing the flow through the columns by adjusting the pump rate. For further details see article **V**.

4.3 Modeling pond dynamics

The detailed measuring campaign carried out on the three above described ponds resulted in a large dataset, giving a unique and robust platform for developing models and prediction tools targeted stormwater ponds.

4.3.1 Modeling pollutant removal

The removal of pollutants in the ponds was described by applying simple first order kinetics to measured concentrations of pollutants in the inlets and ponds. Model parameters were varied until the best agreement between measured and simulated pollutant concentrations in the ponds was achieved. Two different calibration procedures were applied. The first method used the average removal efficiency (that is one parameter value) as target value. The second calibration procedure used a least square method to fit the simulations to the whole of the measured time series and thereby became a more complex model. Furthermore, temperature constants (α) varying from 1.00 to 1.09 were applied to this calibration to identify a possible temperature dependency of the treatment processes. The idea was that the magnitude of α could cast light over whether the removal was mainly controlled by physically/chemically processes (α in the range of 1.03 to 1.05) or mainly by biological processes (α in the range of 1.07 to 1.09). See article **III** for further details.

4.3.2 Eutrophication model

A comprehensive model describing the processes in a wet detention pond has been developed, article **IV**. The model simulates pH and dissolved oxygen variations in a wet detention pond. These parameters are of special interest due to their role in impacts on receiving waters as well as their role in release of pollutants bound in the sediments; cf. chapter 2. Furthermore, the model predicts the growth of phytoplankton, benthic algae and macrophytes in the modeled wet detention pond. Several more or less complex eutrophication models have already been developed and described in the literature, e.g. Hipsey et al. (2006). However, these do not target wet detention ponds. Compared to natural lakes, wet detention ponds receive large loads of nutrients in highly varying concentrations. Moreover, the hydraulic load pattern and water residence time are highly variable compared to what is typical for natural lakes. And last, the wet detention ponds receive a wide range of contaminants which can be toxic to flora and fauna in the pond, which typically is not the case for natural lakes. Consequently, a targeted model was needed to simulate the eutrophication of wet detention ponds. Furthermore, a rather simple model was preferred to minimize the data requirement for calibrating and validating the model. See article **IV** for further details.

5 Discussion and perspectives

The measuring campaign revealed that the ponds in Aarhus and Odense were subject to illicit discharges. The pond in Aarhus received sporadic discharges of significant amounts of septic wastewaters, which was observed by wastewater odor at the pond inlet and confirmed by detection of *E.Coli* in the inflow. The discharges occurred irregularly, sometimes with intervals of days, sometimes with intervals of months. The source and extent hereof could, however, not be identified. The pond in Odense received sporadic discharges of significant amounts of chemical waste containing high concentrations of copper, zinc and lead. The discharges occurred approximately every half year, resulting in temporary copper concentrations above 1,000 $\mu g\ L^{-1}$ in the pond. The high loads of pollutants were both measured in the water samples and in the sediment, see articles **IV** and **VI.** The source hereof was not identified. No unexpected discharges were observed in Silkeborg, however, this pond had a permeable clay membrane in the middle compartment which had to be repaired before the measuring campaign could be initiated, giving a significant shorter data series for this pond.

The intensive measuring campaign of the three wet detention ponds revealed similar concentrations of heavy metals in stormwater runoff as reported in literature (Pitt et al., 2004; Vollertsen et al., 2009a). However, very high concentrations of copper, zinc and lead were observed in Odense and of zinc in Aarhus. Furthermore, higher concentrations of nickel were measured in the pond in Aarhus than in the inlet to that pond, properly due to release from the constructed clay membrane. Furthermore, higher nickel concentrations were measured after the sand filter than in the pond in Silkeborg, which suggest release of this heavy metal from the sand filter. The measured concentrations of PAH were similar to reported values in the literature, e.g. Vollertsen et al. (2009a); Göbel et al. (2007b). Nitrogen was found in concentrations typical for Danish stormwater runoff (2 mg L^{-3}) (Silkeborg Municipality, 2009) in the inlet to all three ponds. Concentrations of phosphorus were in Silkeborg lower than the typical values for Danish stormwater runoff (0.3-0.5 mg L^{-3} for total phosphorus and 0.1-0.3 mg L^{-3} for orthophosphate) but similar for Odense and Aarhus. For further results see article **II, VII** and Silkeborg Municipality (2009). The loads of nutrients, PAHs and heavy metals were for all three ponds very varying and behaved stochastic.

5.1 Impacts on receiving waters

The tested stormwater runoff samples in the first study (article **I**) were found to be toxic towards two of the three applied test organisms. The stormwater samples were highly toxic towards the algae, less toxic towards the crustaceans and non-toxic towards the bacteria, see article **I**. In the following only results revealed from the algae tests are commented. Furthermore, the toxicity analyses in the second study were only carried out on the algae as test organism.

The stormwater runoff in Odense revealed occasionally high toxic effects. Copper and zinc were found to be the most likely main toxicant as a relative good agreement between this pollutants and high toxicity were found, see Figure 2 and article **II**.

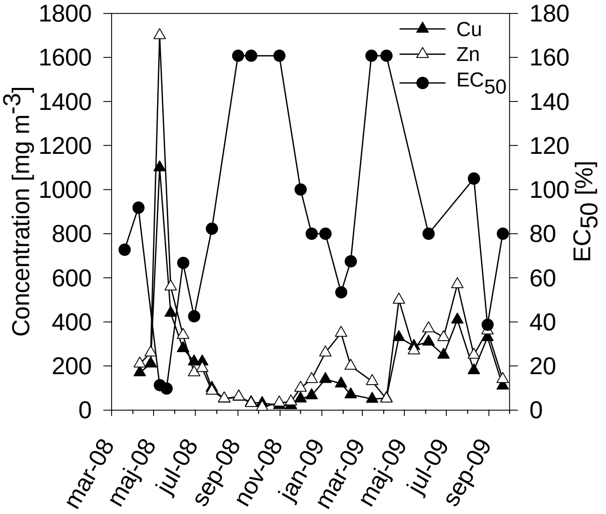

Figure 2: Toxicity and content of heavy metals in the pond water from Odense. Note that low EC$_{50}$-values correspond to high toxic effect and vice versa.

Toxicity of the pure heavy metals were also estimated which revealed that over half of the copper could be complex-bound by compounds in the stormwater, see Figure 3. The binding of copper resulted in lower toxic effects than similar concentration of pure metal in pure water would lead to. For zinc higher measured inhibitions than theoretical inhibitions were observed. That is, zinc is most likely not the main toxicant, as some of the zinc should be complex-bounded as the copper, which again should lead to even lower inhibitions for zinc. Consequently, copper were identified as the main toxicant. However, copper was most likely not the only pollutant which contributed to the observed toxic effect. The mix of pollutants present in the water could have resulted in additive effects which causes higher inhibitions than for the pure metals. For further results and discussion see article **II**.

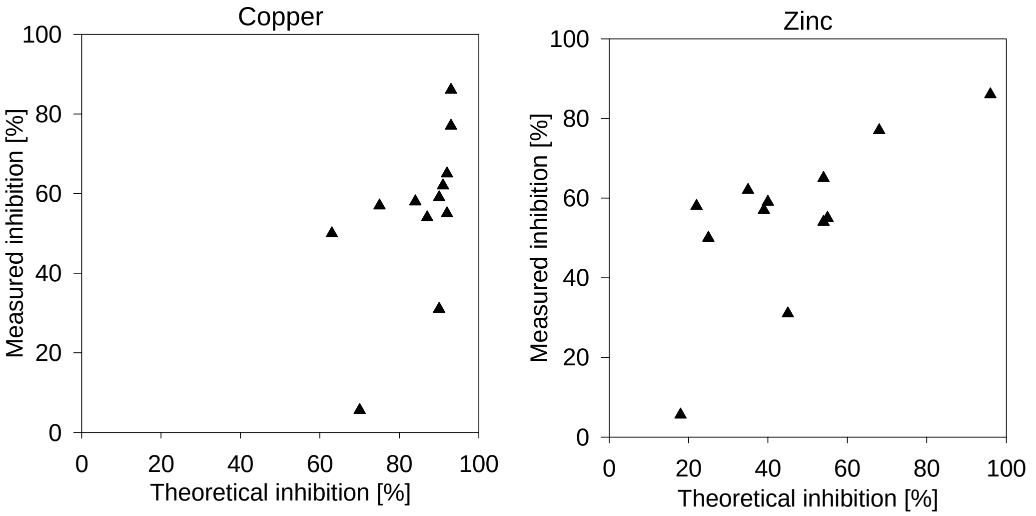

Figure 3: Measured growth inhibition of the algae (inhibition caused by undiluted pond water) and theoretical inhibition (calculated inhibition caused by the level of metal in the pond water using the dose-response-curve for the pure metal).

The stormwater runoff from Aarhus showed occasionally toxic effects. These less severe effects were properly due to the general lower levels of heavy metals in this pond. No correlation between toxic effects and individual pollutants could be identified, see article **II**.

Generally, stormwater runoff was found to be toxic, but the level of toxicity varied significantly in time and between catchments. That is, a robust and extensive technology is needed for treatment of stormwater runoff. Furthermore, the treatment should be continuously and able to reduce pollutant concentrations in an already dilute solution and occasionally remove extremely high pollutant concentration from the water. Wet detention ponds have for this purpose proven robust and appropriate.

5.2 Performance and management of ponds

Wet detention ponds buffer the hydraulic and pollutant peaks for receiving waters, furthermore, wet detention ponds have proven robust and efficient to reduce the concentration of unwanted pollutants, especially suspended solids and associated pollutants. The three studied ponds had after the sand filters removal efficiencies up to 90, 85 and 64% for chromium (Chromium had inlet concentrations around 2-5 µg L^{-1}). Removal efficiencies up to 59% for cadmium were measured in Silkeborg, despite the relative low inlet concentrations around 0.07 µg L^{-1}. For suspended solids (inlet concentration around 40-50 mg L^{-1}) a removal efficiency up to 96% was measured in Silkeborg. In Odense copper concentrations up to 3,300 µg L^{-1} were observed in the inlet, however, the highest measured concentration after the sand filters were 49 µg L^{-1} (Vollertsen, unpublished data) and an overall removal efficiency of 92% were measured after the sand filters. That is, wet detention ponds are efficient toward the low continually pollutant load but also towards the extreme, discrete and unpredictable illicit discharges which can have severe impacts on vulnerable recipients due to its acute toxicity (article **I** and **II**).

5.2.1 Aluminum addition

Despite the relative high removal efficiencies determined in the ponds and after the sand filters, low but significant pollutant concentrations are still present in the effluent. These relative low concentrations will most likely not have any acute toxic impacts on the flora and fauna in the receiving waters, however, some long term or accumulating effects can occur. Furthermore, if the receiving waters are classified as vulnerable, additional treatment of the stormwater can be crucial.

Three experimental technologies were testes in the studied ponds. However, only two of the three technologies have been addressed in the present Ph.D.-study, aluminum addition and filtration through sorption filters.

To assess the impact of aluminum on the toxic effect of stormwater runoff, aluminum was added to two runoff samples from the pond in Odense. The aluminum concentrations were ranging from 2 to 40 mg Al L^{-1}. The toxicity test using the algae as test organism showed reduced toxic effect when the aluminum concentration was 2 to 10 mg Al L^{-1} compared with the toxic effect for pure stormwater runoff, see Figure 4. That is, the aluminum may reduce the toxic effect of stormwater runoff. At concentration levels above 20 mg Al L^{-1}, aluminum itself became toxic and the toxic effect was higher than for the runoff without aluminum. This limit between beneficial and toxic effects will depend on a number of water quality parameters, such as the concentration of organic matter, phosphorous, toxic compound, pH etceteras. The most effective aluminum concentration to reduce toxic effects was in this study found to be 7 mg Al L^{-1}. However, the most cost effective aluminum concentration seemed to be 5 mg Al L^{-1} which corresponds to the interval typically applied for cost-effective phosphorous removal in lake restoration (Cooke et al., 2005). For further details see article **I**.

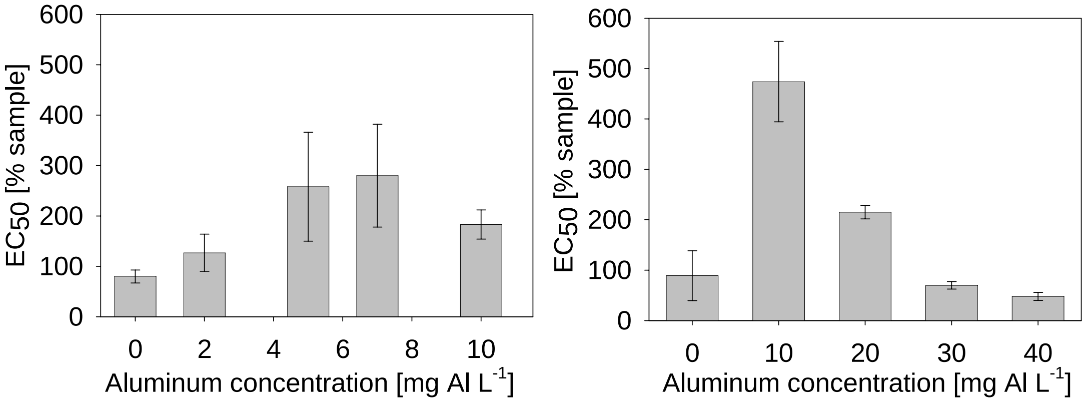

Figure 4: EC_{50} values and standard deviations for the aliquots from the two stormwater runoff samples measured with the algal test. A high EC_{50}-value is equivalent to a low toxic effect. Water samples are from the Odense pond.

The technology was, as described in chapter 3.3, implemented in the pond in Silkeborg, adding down to 5 mg Al L^{-1} stormwater in the inlet. Despite the promising indications of pollutant removal from the toxicity experiments, due to the observed decreasing toxicity, no removal of pollutants were observed when measuring total concentrations of pollutants (Silkeborg Municipality, 2009). These contradictory observations could be at result of the dissolved pollutant being removed from the water phase but not settling out, maybe due to fluffy flocks. When the pollutant is bounded to the aluminum flocks the pollutants are not bioavailable and can consequently not cause any toxic effect. However, if the flocks have not settled out the pollutants are included in the measurements of total concentrations. The addition of aluminum in the Silkeborg pond had a positive effect on chlorophyll concentration which was significantly lower than expected. That is the addition of aluminum prevented blossom of phytoplankton (Silkeborg Municipality, 2009).

5.2.2 Sorption filter

The full scale sorption filters in Odense showed high removal efficiency towards the majority of the measured pollutants. For copper, zinc, lead and orthophosphate the efficiency was over 95% and for chromium, total phosphorus, total suspended solids as well as oil and grease the efficiency was over 85%. To gain knowledge about how a future sorption filter should be designed and what materiel should be present, three laboratory scale test were carried out (capacity test, desorption test and sorption kinetics) on five different sorption materials (shell-sand, zeolite, limestone and two different olivine granulates) using artificial stormwater containing a mixture of phosphorus, arsenic, cadmium, chromium, copper, nickel, lead, and zinc at different concentrations. In the present extended summary only some data concerning copper and phosphorus are presented and only sorption capacities and kinetics are discussed. For all data see article **V.** Whether a sorbent is applicable as stormwater filter material depends first on its sorption capacity at relevant sorbate concentrations. In addition to the sorption capacity of the sorbent, desorption characteristics must be taken into account, as must physical stability and effluent pH as well as sorption kinetics.

Measured data and modeled capacity isotherms for the five sorbents are presented in Figure 5. For some combination of sorbate and sorbent, there was a strong correlation between the water-phase concentration and the mass sorbed by the solid phase. For other combinations, this correlation was weaker or even absent at the water-phase concentrations investigated.

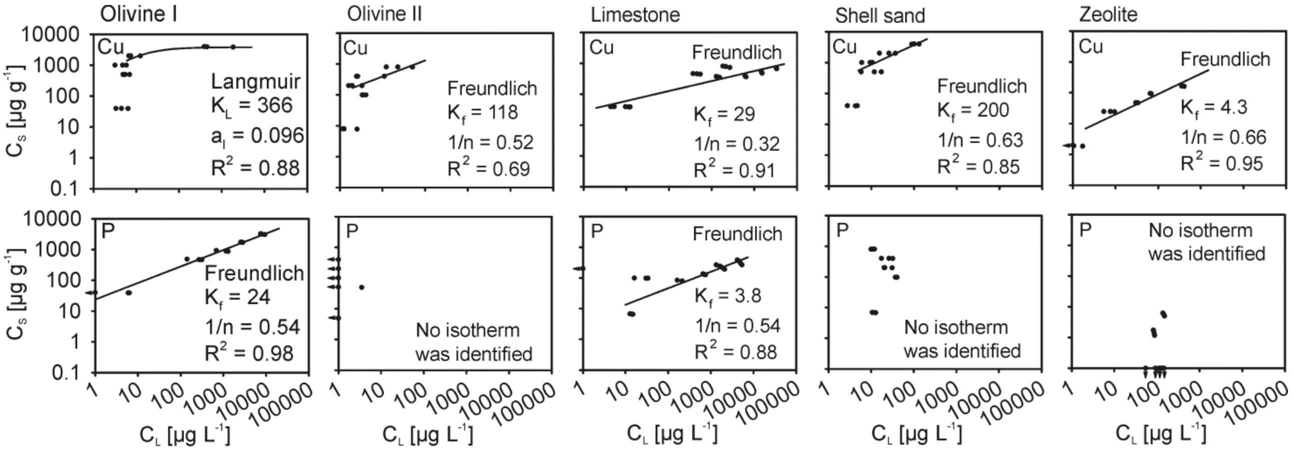

Figure 5: Measured data (circles) and modeled sorption isotherms (lines). Data points located on the axes indicate values at or below the respective values.

For most elements, a threshold water concentration could be identified, down to which sorption occurred. E.g. for sorption to olivine I for copper it was approximately 5 µg L^{-1}. A threshold value for phosphorus was not seen for olivine I but could exist somewhere at less than 1 µg L^{-1}, which was the lowest applied concentration.

The kinetic experiments revealed that the adsorption occurred in what could be seen as two steps: a rapid initial adsorption followed by a somewhat slower adsorption, see Figure 6. This finding is consistent with a two-step sorption mechanism (fast/slow) presented by Wilde and Benemann (1993) and Plazinski et al. (2009). The amount of sorbate adsorbed within the initial minutes of contact time was considerable for most sorbent/sorbate combinations. Taking all sorbent/sorbate combinations into account, the median of the removal efficiency after 1 minute of contact time was 83% and 93% after 10 minutes of contact time, for further details see article **V**. High initial removal has been reported in several other studies (e.g., Chen et al., 2010; Altun and Pehlivan, 2007).

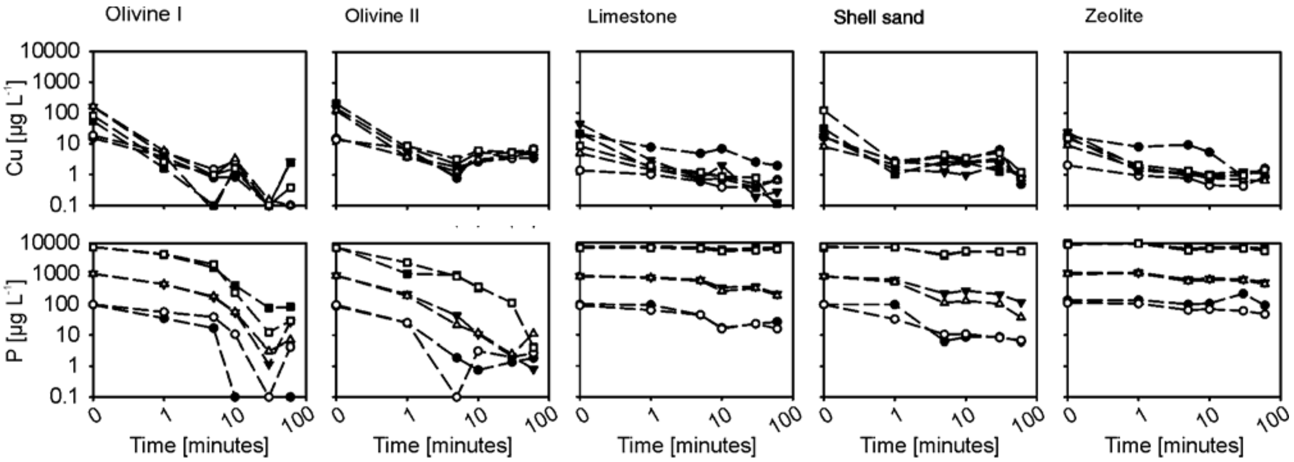

Figure 6: Measured sorption kinetics for contact times up to 60 minutes. Data points located on the axes indicate values at or below the respective values.

Applicability for Stormwater Filters. Comparing the different materials, the tested limestone had a good physical stability, it was not prone to desorption, and the pH of the effluent was unproblematic. However, it had, for a number of elements, a comparatively low sorption capacity in the relevant concentration ranges.

The other carbonatic media, shell-sand, generally had a better sorption capacity than the limestone. It was more prone to desorption but was not additionally affected by sodium chloride or increase in pH. It had a moderate physical stability and contained a large fraction of fine particles. The pH of the effluent was unproblematic. Of the tested media, the shell-sand had some of the slowest sorption kinetics. However, for nickel, cadmium, and phosphorus, the kinetics was rather fast.

The sorption capacity of the tested zeolite was comparatively poor for most tested sorbates. An exception was lead, for which the capacity was good and the determined removal rate the highest measured for all combinations of sorbent and sorbate. The zeolite tested in the present study had poor stability towards physical stress and desorbed several of the studied sorbates relatively easily.

The two olivine granulates had rather high sorption capacities and generally also the fastest sorption kinetics. Both types of olivine granulates had a moderate physical stability. The binding of the elements studied was generally strong when subjected to sodium chloride and pH increase. However, leakage of chromium from unused sorbent was observed for both types of granulates as well as reported in the literature (Forsvarsbygg, 2009). The pH of the effluent was high, potentially causing adverse effects on receiving waters.

5.3 Design and dimensioning ponds

It is necessary to have some tools or guidelines when dimensioning and designing a wet detention pond. One method is applying first order removal kinetics to a future pond using measured removal rates in exiting ponds. This will give an estimation of needed pond volume to achieve the desired effluent pollutant concentrations. The removal kinetics of the three ponds, studied in the present Ph.D.-study, has been modeled using different modeling approaches, see article **III.** The modeled removal rates are presented in Table 2. To model removal rates it was necessary to determined whether the ponds behaves as plug flow reactors or were fully mixed (see chapter 2). The sensors placed in the middle of the ponds showed mixing of water already 20 to 90 minutes after the onset of storm events. That is the changes in pH, temperature and oxygen level due to entering runoff showed that the three wet detention ponds should be characterized as fully mixed reactors and not as plug flow reactors.

Table 2: Removal rates determined for the three ponds. Skullerud is a wet detention pond in Norway which has been simulated by a similar approach (Vollertsen et al., 2007), and is included for references purposes No removal rate was estimated for nickel in Aarhus as the concentration generally was higher in the pond than in the inlet, properly due to leakage from the clay membrane.

	SS	P_{tot}	P_{sol}	N_{tot}	Pb	Cd	Cu	Zn	Cr	Hg	Ni
Odense	0.32	0.14	0.26	0.08	0.90	0.21	0.28	0.15	1.21	0.08	0.20
Aarhus	0.66	0.23	1.44	0.09	0.43	0.04	0.14	0.07	0.82	0.36	-
Silkeborg	0.13	0.36	3.73	0.01	0.03	0.02	0.03	0.04	0.02	0.02	0.27
Skullerud	0.55	0.16	0.25	0.02	0.15	0.07	0.04	0.13	-	-	-

The estimated removal rates for suspended solids, total phosphorous, total nitrogen and nickel were somewhat similar in the three ponds as well as in the Skullerud pond reported by Vollertsen et al. (2007). That is, there is some continuity in the removal of these pollutants despite differences in load and design of the four ponds. Consequently, these results can be used in future design of wet detention ponds. However, for the other seven pollutants no clear tendency for the removal rates were found and future prediction of removal of these pollutants in wet detention ponds seems difficult.

The removal rates were modeled using temperature dependencies from zero to 1.09 to reveal whether biological or chemical/physical removal processes were dominating in the ponds. Furthermore, different fitting procedures between modeled and measured data were applied. A weak tendency towards dominating biological removal processes were observed, however, further studies have to be carried out on longer data series or other ponds before a conclusion can be made. For now the model therefore should be kept as simple as possible when designing future wet detention ponds. That is, first order removal kinetics without temperature dependency of the process kinetics. For further results see article **III**.

To gain more knowledge of the biological, chemical and physical performance of wet detention ponds, an eutrophication model targeted wet detention ponds was developed. The model predicts pH, dissolved oxygen and biomass of primary producers under dynamic conditions, as these are parameters crucial for at well functioning pond, see chapter 2. For further model description see article **IV**. The model is deemed to be a potential tool for improving the design of wet detention ponds by taking the behavior of the plant ecosystem into account and has the potential to yield information on parameters critical for design. The prediction of phytoplankton is important as wet detention ponds not only serve as treatment facilities but also as recreational water bodies in the city.

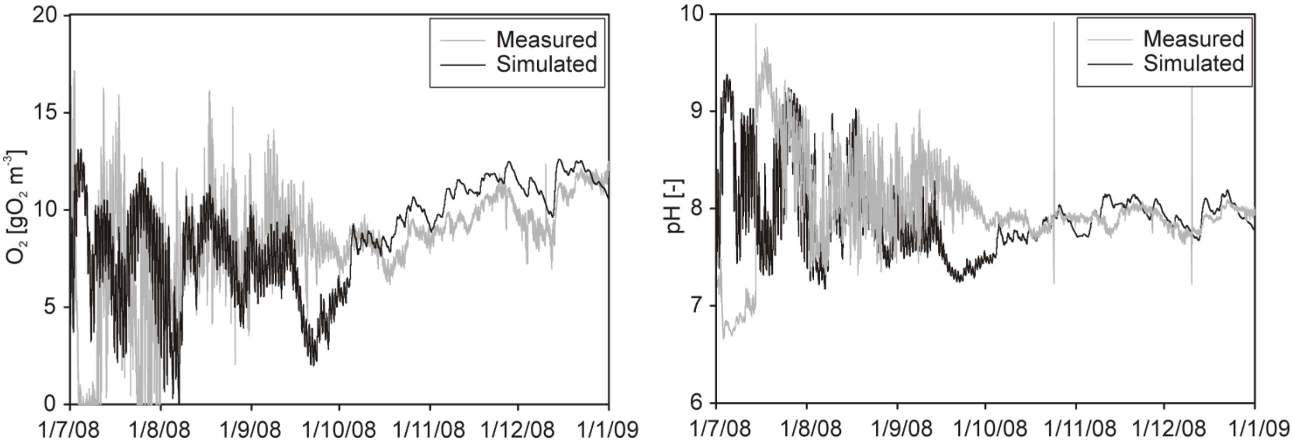

Figure 7: General calibration of the eutrophication model to the data series from the pond in Aarhus.

The eutrophication model was successfully calibrated to the data from the Aarhus pond, see Figure 7. However, validation of the model applying the calibration parameters obtained from Aarhus on the Odense pond was not satisfactory. The cause might have been differences in characteristics not captured by the model, for example difference in primary producer species, differences in runoff quality, differences in pond geometry or differences in shelter conditions. That is, to predict absolute variations in dissolved oxygen and pH a specific calibration for each pond is necessary. However, if the relative impact of, for instance, change of depth and surface area are wanted the model will give useful results, despite the deficient validation.

6 Concluding remarks

This Ph.D. study investigated the potential impacts of stormwater runoff, the performance of wet detention ponds and combinations with additional treatment. The additional treatment technologies investigated were aluminum addition to the stormwater as well as filtration and sorption of the pond effluent. Moreover, the toxicity of runoff was investigated. A better understanding of the ecological function and treatment dynamics within the pods were achieved by developing two different models. As the focus on preservation of a good ecological state of the surface waters increases, better knowledge concerning impacts of and treatment of stormwater runoff is essential. It is believed that this Ph.D. study contributes significant to the increasing pool of knowledge on stormwater runoff and wet detention ponds, and future research and practical pond construction can benefit from this.

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I **Wium-Andersen, T.**, A. H. Nielsen, T. Hvitved-Jacobsen and J. Vollertsen. (2010) *Reduction of Stormwater Runoff Toxicity by Wet Detention Ponds.* Urban Environment, Proceedings of the 9th Urban Environment Symposium. Alliance for Global Sustainability Bookseries, Springer 2010, ISBN: 978-90-481-3042-9.

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IV **Wium-Andersen, T.**, A. H. Nielsen, T. Hvitved-Jacobsen, H. Brix, C. A. Arias and J. Vollertsen (Submitted). *Modelling the eutrophication of stormwater ponds.* Ecological modelling, submitted.

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Reduction of Stormwater Runoff Toxicity by Wet Detention Ponds

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Introduction

Stormwater runoff contains a wide range of contaminants [1]. Pollutants like PAH’s, biocides, heavy metals and nutrients are often found in varying, but significant concentrations. Due to the content of various contaminants, stormwater runoff has been found to be toxic to the aquatic environment [2–4], with potential negative ecological impacts on receiving waters.

Toxic effects are estimated by exposing test organisms to the potential toxic sample or compound followed by a calculation of the inhibition of the test organism. The inhibition can be growth inhibition, mobility inhibition, inhibition of the reproduction and etceteras. Inhibition is expressed as a given effect concentration (EC) after a given exposure time. That is, EC50 is the concentration giving an inhibition equal to 50% after a certain exposure time and EC10 is the concentration giving an inhibition equal to 10% after a certain exposure time. Toxicity is not an absolute estimation but a relative measurement characteristic for the test organism applied, resulting in different EC50 values for the same compound. Therefore, it is important to consider which organisms that is relevant to use as test organisms for environmental samples such as stormwater runoff. The optimal solution is to use a battery of toxicity tests to reveal the ecological impacts of a sample [5].

To reduce the content of nutrients, organic matter and the different organic and inorganic micro pollutants, the stormwater runoff can be led through a wet detention pond where sedimentation and uptake by plants reduce the concentration of the contaminants. To improve sedimentation, a flocculent such as aluminum can be added to the water phase. It is well known that aluminum can reduce the content of phosphorous in the water phase in lakes [6], but whether aluminum addition also reduces the toxic effect of the water phase has not been identified.

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The objective of this study is to investigate how addition of aluminum affects the toxicity of stormwater runoff. The toxic effect is estimated applying three different toxicity tests. The results of the study can be applied to determine whether addition of aluminum to wet detention ponds can reduce the toxic effect of stormwater by adding similar quantities of aluminum as typically used to remove phosphorous from the water phase.

Method

Collection and Storage of Samples

Stormwater runoff samples were collected from a wet detention pond located in the southern part of Odense, Denmark. The wet detention pond is constructed as a part of the EC LIFE-treasure project [7] and is placed in a green area next to a catchment with light industry and associated roads (Fig. 1). The catchment has an area of 27.4 ha of which 11.4 ha are impervious, resulting in an estimated runoff of 55,500 m^3/year. The stormwater runoff is pretreated in a grit chamber before entering the pond. Stormwater runoff for analysis was collected from the center of the pond. The samples were collected in glass bottles over a 2 month period and stored at 5°C until analysis.

Preparation of Samples Prior to Analysis

Four samples were collected over a 2 month period, two samples in February 2008 (sample I and II) and two at the beginning of April 2008 (sample III and IV). Due to a natural content of microalgae in the samples, the samples where filtrated

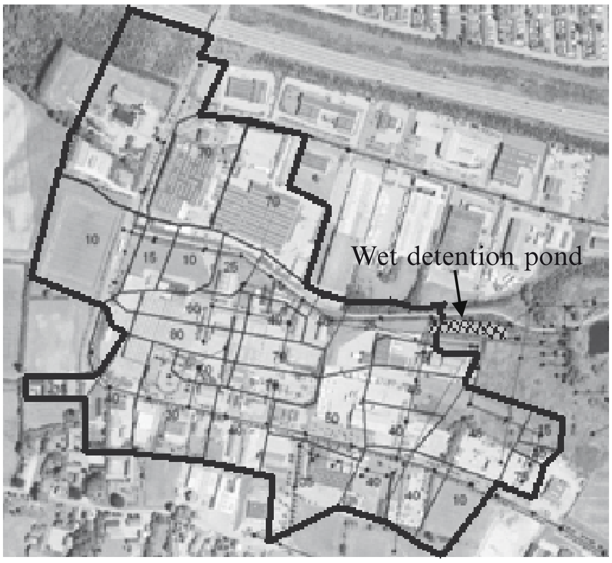

Fig. 1 Wet detention pond from where the samples were collected. The appurtenant catchment is outlined

through a 0.45 µm filter prior to toxicity tests. All four samples were analyzed for toxic effects using different toxicity tests. The last two samples were treated by aluminum addition to investigate its potential influence on the toxic effect.

The samples collected in April were divided into aliquots of 320 mL in 500 mL glass bottles. Aluminum sulfate ($Al_2(SO_4)_3$ $16H_2O$) was added to a final aluminum concentration of 0, 2, 5, 7 and 10 mg Al/L (sample III) and a concentration of 0, 10, 20, 30 and 40 mg Al/L (sample IV). The aliquots were placed on a shaker for 1 h to ensure thoroughly mixing and afterwards left to settle for 3 days at 5°C. Three days was chosen as this is the minimum hydraulic retention time for a typical Danish wet detention pond for stormwater treatment [8]. After the 3 days, the supernatant was extracted without disturbing the settled precipitate. The supernatant was tested for toxic effects by three different toxicity tests. The natural pH-value for sample III and IV prior to aluminum addition was 8.76 and 8.78, respectively. The products of the dissociation and hydration of the aluminum salt at these pH-values is mainly aluminum hydroxide ($Al(OH)_3$) and to a lesser extent aluminate ion ($Al(OH)_{4-}$). Aluminum hydroxide could be observed as visible flocks in the aliquots with an aluminum concentration equal to 5 mg Al/L and above.

Toxicity Tests

Toxicity tests were chosen on the basis the following criteria: The tests should be validated and comply with a standard; an existing protocol should be available; the tests should use organisms on different trophic levels; and the tests should be cost-time efficient. These criteria led to three different tests, using bacteria (Vibrio fischeri), algae (Selenastrum capricornutum) and crustaceans (Daphnia magna) as test organisms. Vibrio fisheri is a marine bacterium and will therefore not be found naturally in wet detention ponds. However, the test is commonly used and relative fast, giving the result after only 30 min and was on this basis included in the test battery. The last two tests use organisms which are indigenous to freshwater. All three tests are designed to measure acute toxic effects.

The test using Vibrio fisheri is based on the capacity of the bacteria to emit luminescence, meaning that the less luminescence the bacteria produce, the more stressed are the bacteria due to exposure to toxic substances. Specific volumes of the samples and different dilutions hereof were mixed with bacteria suspension (duplicate for each dilution). The luminescence was measured after 0, 5, 15 and 30 min of exposure to the sample on a M500 analyzer from SDI in the Microtox® Acute mode. Decrease in luminescence relative to a control gives an expression for the toxic effect and EC-values can be estimated. As Vibrio fischeri is a marine bacterium, the runoff samples were adjusted to a salinity of 2% prior to analysis. An advantage of this test is that for each dilution, a very large number of test individuals are applied, minimizing statistical fluctuations. The whole test was carried out according to the international standard DS/EN ISO 11348-1.

The algal test is based on growth inhibition of the algae due to toxic substances. A specific volume of an algae suspension is added to a dilution series of a sample. Triplicates were made for each dilution. The growth rate was hereafter estimated by measuring the optical density (OD) at 670 nm after an exposure time of 0, 24, 48 and 72 h. The growth rate of the algae is inhibited by toxic substances and a relative inhibition to a control can be calculated. In this study the toxicity test kit Algaltoxkit FTM, MicroBioTests Inc., was applied and the tests were carried out using 10 cm cuvettes as incubation chambers. An UVmini-1,240 spectrophotometer from Shimadzu was used to measure the OD670. Approximate 10,000 algae cells/mL were added to each cuvette at the beginning of each test, which due to the high number of individuals minimized the statistical fluctuations. The test is based on the international standard DS/EN ISO 8692.

The last test in this study applied the Crustacea Daphnia magna as test organism. The ability of the daphnia to swim is affected by toxic compounds and is therefore used as an expression of the toxic effect. The daphnia were exposed to dilutions of a sample and immobile daphnia were counted after 24 and 48 h. Twenty daphnia were exposed to each dilution of the sample, which was a much lower number of individuals than for the two other tests, resulting in larger statistical fluctuations. For each test, a control was made to ensure that the immobilization was caused by the toxic effect and not by any physical stress. In this study the toxicity test kit Daphtoxkit FTM, MicroBioTests Inc., was applied, based on the international standard DS/EN ISO 6341.

Results and Discussion

Data obtained from the four samples and the three toxicity tests were analyzed according to the respective standards. Dose-response curves were obtained and EC50 and EC10 values were estimated when possible. It was a general conclusion for the samples tested that the bacteria test was less sensitive than both the Daphtoxkit FTM and Algaltoxkit FTM. This is consistent with previous reported observations [2, 9]. The stormwater runoff had no observable effect on the luminescence readings (data not shown), indicating that the samples were non-toxic. The daphnia were only inhibited by undiluted aliquots, that is 100% stormwater runoff. Estimations of EC50 values were therefore not possible. The inhibition by 100% stormwater runoff samples was in the magnitude of 20–50% after 48 h of exposure, indicating a low toxic effect. The algal test was on the other hand much more sensitive to the toxic compounds in the runoff. Hence, calculation of EC50 values was possible, giving EC50 values in two groups: sample I and II had a low EC50 about 10% dilution (after 72 h of exposure) and sample III and IV had a relative high EC50 about 85% dilution (after 72 h of exposure). The significant difference in toxic effect may be due to a strong natural algal blossom in the wet detention pond, beginning by the end of March. This algal blossom may cause removal of toxic compounds from the water phase due to uptake by the algae and sorption at their surfaces.

When the samples were filtrated prior to analysis, all contaminants absorbed or adsorbed by the algae were removed from the sample. Even though there were large differences between the toxic effects of the samples, the samples were in general toxic to the test organisms and treatment by adding aluminum was relevant. The EC50 values obtained by the algal test (72 h exposure) and standard deviation for the different aliquots from the sample III and IV, are shown in Fig. 2.

EC50 values above 100% dilution were calculated by extrapolation of the dose-respond curve and not by concentration of the samples, for example by evaporation. As shown in Fig. 2 the toxic effect of the stormwater runoff decreased with increasing aluminum concentration up to 7 mg Al Al/L. Above 7 mg Al/L the toxic effect increased with increasing aluminum concentration. In the aliquots added 30 and 40 mg Al Al/L, the toxic effect was greater than for the pure sample. That is, aluminum reduced the toxic effect of the stormwater runoff up to a certain level. Above this level the aluminum itself became the source of the toxic effect. In Fig. 3, EC10

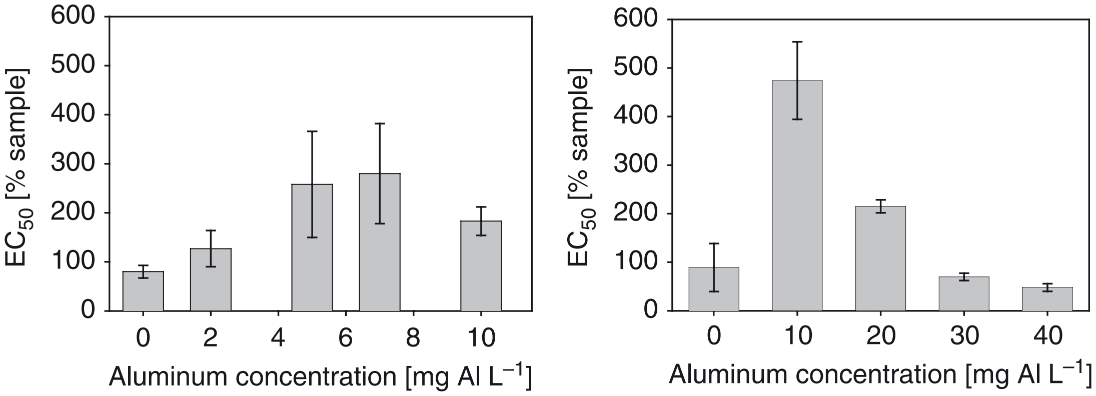

Fig. 2 EC_{50} values and standard deviations for the aliquots from sample III (*left graph*) and sample IV (*right graph*) measured with the algal test. A high EC_{50}-value is equivalent to a low toxic effect

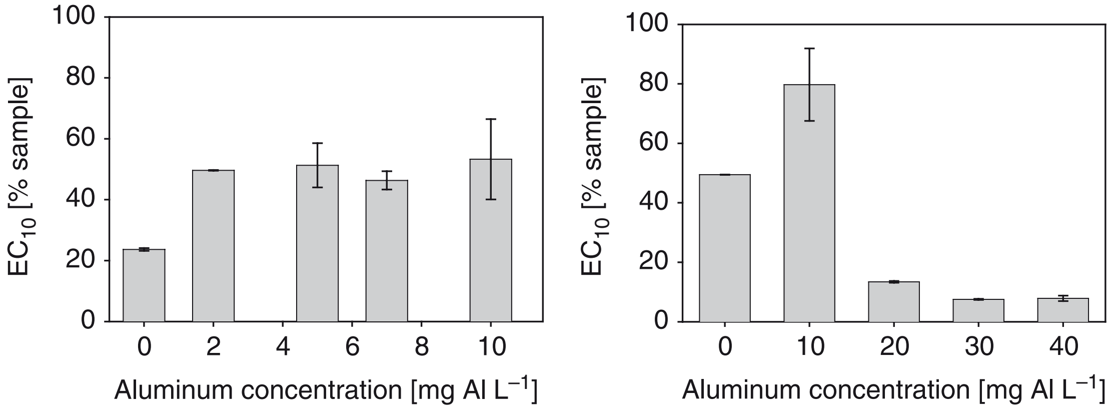

Fig. 3 EC_{10} values and standard deviations for the aliquots from sample III (*left graph*) and sample IV (*right graph*) according to the algal test. The higher the EC_{10}-values, the lower the toxic effect

values and standard deviations of the aliquots from sample III and IV are shown (72 h exposure).

The EC10 values were all below 100% and therefore estimated by interpolation. Figure 3 shows the same tendencies as Fig. 2, that is lower toxic effect for aluminum concentrations between 2 and 10 mg Al/L compared with stormwater runoff without aluminum. As shown, highest EC50 occurs at 10 mg Al Al/L. At 20 mg Al Al/L, the EC10 is lower than the EC10 for the aliquot without aluminum addition. This is not consistent with the EC50 for the same aliquot, where the EC50 is indicating that this aliquot has a lower toxic effect than the aliquot without aluminum addition. In principle, the EC10 and EC50 should show the same tendency. However, due to uncertainties in the tests and also in their interpretation, deviations from this might happen. Due to this uncertainty, it cannot be concluded whether the addition of 20 mg Al Al/L to stormwater runoff has a positive or negative effect on the toxicity. It is therefore, in order to avoid toxic effects, recommended to add not more than 10 mg Al Al/L when treating stormwater runoffs.

The tendency for the daphnia test was the same as for the algae test, that is untreated stormwater runoff had a significant toxic effect as well as runoff samples with addition of 30 and 40 mg Al Al/L; showing an inhibition at 25% and 95% in the undiluted aliquots with 30 and 40 mg Al Al/L, respectively. The other aliquots did not show any significant toxic effects. With the bacterial test, the observation of an increasing toxicity in the aliquots with 30 and 40 mg Al Al/L was not observed – most likely due to the relative poor sensitivity of the test.

The limit between beneficial and toxic effects caused by the addition of aluminum will be different at other pH-values due to the equilibrium between the speciation of the aluminum hydroxides. The equilibrium influences the solubility and flock formation and thereby the removal of toxic substances and the toxic effect of the aluminum hydroxides itself due to different speciation hereof.

At pH 8.2, EC50 for the microalgae Selenastrum capricornutum equal to 460 μg Al/L is reported [10]. The EC50 reported is low compared to the results in this study where aluminum began to show toxic effects at a concentration level of 20,000–40,000 μg Al/L. The large difference is probably due to the nature of the samples tested in this study, resulting in removal of toxic substances and phosphorus by reactions with aluminum as well as side reactions with organic matter. Because of these reactions the aluminum may become unavailable to the test organisms.

Addition of aluminum to lakes in order to obtain optimal phosphorus removal efficiency is reported in the range from 2 to 30 mg Al/L with the most cost-effective dosing between 2 and 5 mg Al/L [6, 11]. The most effective decrease in toxic effect was in this study obtained in the range from 7 to 10 mg Al/L, slightly higher than the cost-effective dose for phosphorous removal. The higher EC50 achieved with addition of 7 to 10 mg Al/L compared to the EC50 at 5 mg Al/L should be considered insignificant, taking the higher cost in consideration. The cost-effective concentration of aluminum for reduction of toxic effects is therefore around 5 mg Al/L. This correspond to a consumption of approximately 300 kg Al/year for the stormwater pond from where the samples originated.

Conclusion

The stormwater runoff analyzed in this study was found to show toxic effects according to two of the three applied toxicity tests. The stormwater was highly toxic to the algae, lesser toxic to the crustaceans and non-toxic to the bacteria – revealing that the bacteria Vibrio fisheri was the least sensitive organism and that the algae Selenastrum capricornutum was the most sensitive organism. Two stormwater runoff samples showed a high toxic effect to the algae with EC50-values at 10% dilution and two samples showed a lower toxic effect with EC50-values at 85% dilution.

To assess the impact of aluminum on the toxic effect of stormwater runoff, aluminum was added to two samples in concentrations ranging from 2 to 40 mg Al/L. The toxicity test using the algae Selenastrum capricornutum showed reduced toxic effect for aliquots with aluminum concentration from 2 to 10 mg Al/L compared with the toxic effect for pure stormwater runoff. That is, the aluminum may reduce the toxic effect in stormwater runoff. At concentration levels above 20 mg Al/L, aluminum itself becomes toxic and the toxic effect is higher than for the pure runoff. This limit between beneficial and toxic effects will depend on a number of water quality parameters, such as the concentration of organic matter, phosphorous, toxic compound, pH etceteras.

The most effective aluminum concentration to reduce toxic effects was in this study found to be 7 mg Al/L. However, the most cost effective aluminum concentration is 5 mg Al/L which corresponds to the interval typically applied for cost-effective phosphorous removal.

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II

Heavy metals, PAHs and toxicity in stormwater wet detention ponds

T. Wium-Andersen, A. H. Nielsen, T. Hvitved-Jakobsen and J. Vollertsen

ABSTRACT

Concentrations of 6 different heavy metals and total polycyclic aromatic hydrocarbons (PAHs) were determined in stormwater runoff and in the pond water of two Danish wet detention ponds. The pond water samples were analyzed for toxic effects, using the algae *Selenastrum capricornutum* as a test organism. Stormwater and pond water from a catchment with light industry showed high levels of heavy metals, especially zinc and copper. The pond water showed high toxic effects and copper were found to be the main toxicant. Additionally, a large part of the copper was suspected to be complex bound, reducing the potential toxicity of the metal. Another catchment (residential) produced stormwater and pond water with moderate concentration of heavy metals. The pond water occasionally showed toxic effects but no correlation between heavy metals and toxicity was identified. PAHs concentrations were for both catchments low and no correlations between PAH concentrations in the pond and toxicity were found.

Key words | detention ponds, heavy metals, stormwater, toxicity

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INTRODUCTION

Stormwater runoff from urban areas contains numerous pollutants in varying but significant concentrations, for example polycyclic aromatic hydrocarbons (PAHs), heavy metals, biocides, nutrients and suspended solids (Göbel *et al.* 2007). Due to the content of the various compounds, stormwater runoff has been found to be harmful to the aquatic environment, with potential negative ecological impacts on receiving waters, e.g., lakes, streams and coastal waters (Fisher *et al.* 1995; Marsalek *et al.* 1999). The negative impacts can be eutrophication, oxygen depletion and toxic effects towards flora and fauna. To reduce the content of pollutants, the stormwater runoff can be treated in, for example, a wet detention pond where sedimentation and uptake by plants reduce the concentration of the contaminants.

The pollutants in stormwater runoff originate from three overall sources: natural background due to decomposition of minerals; human activity (roads, buildings); and illicit discharges (Marsalek *et al.* 2006). Which pollutant is found and in what concentration depends on the catchment's land use. In the literature, it is generally accepted that pollution of the aquatic environment caused by stormwater runoff is related primarily to heavy metals and PAHs (Ellis *et al.* 1987; Marsalek *et al.* 2006). PAHs and heavy metals in stormwater are found to have both acute and chronic toxic effects towards aquatic flora and fauna (Marsalek *et al.* 1999). Toxicity of heavy metals depends on physical and chemical conditions (e.g. pH, redox, complexing ligands and ion strength) as the mobility and bioavailability of the metals are affected by these conditions (Ure & Davidson 2002). PAHs have generally a relatively low solubility and high affinity towards organic carbon (Simon & Sobieraj 2006). That is, PAHs are often found attached to settable particles (Marsalek *et al.* 1999), and therefore mainly found in the sediment and not the water phase of wet detention ponds.

Several studies have measured toxicity of stormwater runoff; many of them examine the toxicity of sediment in ponds, lakes or streams receiving stormwater runoff. The sediments are often found to be highly toxic as pollutants settle and accumulate in the sediments (Boxall & Maltby 1997; Grapentine *et al.* 2008; Karlsson *et al.* 2010). This concentration of pollutants in pond sediments often causes high sediment toxicity even though the pond receives stormwater with low bulk water toxicity. However, the potentially most harmful and bioavailable pollutants are not the particle-bound pollutants of pond sediments but

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those which are suspended as colloids or dissolved in the water phase (Vollertsen *et al.* 2009a). The lack of concentration makes determination of stormwater toxicity somewhat more difficult compared to determining pond sediment toxicity. Stormwater toxicity does furthermore vary significantly in time as the water phase toxicity depends on variables like first flush, dry period since last rain event and precipitation in the individual rain events (Marsalek *et al.* 1999).

The objective of this paper is to investigate the load of heavy metals and PAHs in stormwater from two Danish catchments and to investigate correlations between individual pollutants in the water samples and toxic effects towards aquatic organisms. The focus will be on heavy metals and PAHs, as these pollutants are recognized as potentially harmful.

METHODS

Sampling sites

Samples of stormwater runoff were collected from two wet detention ponds located in Odense and Aarhus, Denmark. The ponds were constructed as a part of the EC LIFE-Treasure project (Vollertsen *et al.* 2009a). Both ponds are located in green areas in connection to their catchments. The pond in Odense receives stormwater from a catchment of 27 ha (impermeable area of 11 ha) containing light industry and associated roads. The pond in Aarhus receives stormwater from a catchment of 57 ha (impermeable area of 26 ha) were 80% of the area is blocks of flats and 20% of the area is roads and highway. The estimated average annual runoffs for the two catchments are 55,500 and 132,000 m^3 $year^{-1}$ respectively.

Inflows to the two ponds are monitored by full-flowing magnetic flow meters (Krohne Optiflux 2000) coupled in series and an overflow weir coupled in parallel hereto, allowing accurate flow measurement from 1 L s^{-1} up to several m^3 s^{-1}. In order to protect the flow metering devices, the stormwater was discharged through a grit chamber before entering the ponds. Water samples were collected flow proportionally in the inlet to the basins and after the grid chamber. In the pond, the samples were collected time proportionally. All samples were collected by auto samplers equipped with plastic containers. The auto samplers were emptied when full and at least every 14 days. The storage on site could potentially have caused some changes in the samples, e.g., degradation of PAHs and complex binding of heavy metals, leading to underestimation of PAH concentrations and of toxic effects. Such changes were minimized by placing the auto samplers underground in dark and cool environments. The subsamples from the auto samplers were pooled and afterwards divided in aliquots for estimation of harmful effects and determination of chemical compounds. The samples from Odense cover the time span from late March 2008 to late September 2009 and the samples from Aarhus cover the time span from mid June 2008 to mid March 2009.

Handling and analysis of samples

Metal and PAH analysis were performed by an accredited laboratory following ISO standard 17294 and ISO standard 78/2. Pond water samples from the basin and stormwater runoff samples from the inlet in Odense and Aarhus were analyzed for total concentrations of copper, lead, zinc, cadmium, nickel, chromium, mercury and total PAH (after USEPA), see Table 1 for number of samples. The chemical analyses were a part of a larger measuring campaign and due to the large number of samples only analyses of total concentrations was economically feasible. When a sample's content of an element was below the detection limit, half of the detection limit was used in the calculations. This was the case for 1% of the samples regarding zinc and nickel, 5% for copper, 11% for lead, 14% for chrome, 52% for cadmium, 81% regarding mercury and 48% for total PAH.

To estimate the harmful effect to aquatic organisms, measurement of the toxicity has been carried out. In this study an algal toxicity test which is based on growth inhibition of the algae *Selenastrum capricornutum* due to toxic substances, has been used and the toxicity test kit Algaltoxkit F™, MicroBio Tests Inc., was applied. This algal toxicity

Table 1 | Number of pooled stormwater runoff samples and pooled pond water samples analyzed for heavy metals, PAHs and toxicity

Odense					**Aarhus**				
Stormwater runoff		**Pond water**			**Stormwater runoff**		**Pond water**		
Heavy metals	**PAHs**	**Heavy metals**	**PAHs**	**Toxicity**	**Heavy metals**	**PAHs**	**Heavy metals**	**PAHs**	**Toxicity**
24	16	29	23	25	25	15	25	18	13

Toxicity of stormwater runoff was not determined.

test was chosen as it is validated and complies with a standard; an existing protocol is available (DS/EN ISO 8692); the test organism is found naturally in fresh water and the test is cost-time efficient. The test is designed to estimate the acute toxicity of a sample and not the mutagenic or carcinogenic effect of a sample. When working with toxicity, it is important to consider that the result will vary with the applied test organism and exposure time. That is, a sample will not be equally toxic to different test organism and will show higher toxicity when longer exposure time has been used.

Toxicity of samples. The toxicology test used in this study followed the DS/EN ISO 8692 standard using the micro algae *Selenastrum capricornutum* as test organism and an exposure time of 72 h. Pond water samples were, before determination of the toxic effect, filtrated through a 0.45 μm filter to remove natural contents of microalgae which else would have invalidated the tests. This filtration might have removed some of the toxic content, resulting in some underestimation of the toxic effect when comparing the result with the total pollutant concentrations. After filtration a specific volume of the test algae in suspension was added to a dilution series of the sample. The samples were diluted with an algal growth medium. Triplicates were made for each dilution, and 10 cm plastic cuvettes were used as incubation chambers. The cuvettes were shaken every 24 h to ensure exchange of O_2 and CO_2. The growth rate was thereafter estimated by measuring the optical density at 670 nm (UVmini-1240, Shimadzu) after an exposure time of 72 h. The growth rate of the algae was inhibited by toxic substances present in the sample and a relative inhibition to the control was calculated. That is, toxic effects in this study refer to the test organism *Selenastrum capricornutum*. Other test organisms e.g. bacteria, daphnia, etc., would have revealed other toxicity results.

The dose-response-curves (inhibition as a function of concentration of sample) were modeled by a four-parameter log-logistic function using the drc-package in R (Ritz & Streibig 2005). The result was an EC_{50}-value [with the unit % pond water runoff]. EC_{50} is the concentration of sample which causes a growth inhibition of 50% and is used to compare the toxicity of the different samples. That is, the higher toxicity the lower EC_{50}-value and *vice versa*. For 12 out of the total 25 samples from Odense and 9 out of 13 from Aarhus, it was not possible to estimate an EC_{50}-value due to lack of toxic effect (flat dose-response-curve) or due to a clear but relative low toxic effect (less than 50% inhibition for the undiluted sample). For these samples visual inspection of the dose-response-curves were made. If the dose-response-curve did not show any toxic effect the sample was given the highest measured EC_{50}-value from that pond and if a weak toxic effect was observed an EC_{50}-value of 80% was assigned. Four of the samples from Odense showed highly variable growth inhibitions for the triplicates and neither visual nor mathematical analyses of the dose-response-curves were possible. These four samples were rejected and the data are not shown.

Toxicity of heavy metals

EC_{50}-values for selected pure metal salts were determined for reference purposes. Solutions with $Cd(NO_3)_2$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Zn(NO_3)_2$, $Cr(NO_3)_2$ and $Ni(NO_3)_2$ were made with demineralized water. The toxicity of Hg was not determined. Dilution series were made for each metal suspension, using an algal growth medium to ensure optimal growth conditions for the algae. The metal solutions were tested for toxicity applying the same procedure as for the pond water samples. The same anion (nitrate salts) were used for all metals so that the potential influence of the anion on the result could be neglected.

RESULTS AND DISCUSSION

Chemical analyses

The heavy metals measured in this study are copper, zinc, lead, nickel, chromium, cadmium and mercury. Concentrations and range of heavy metals in stormwater runoff and pond water from this study are shown in Table 2 and compared to some literature values in Table 3.

Except for nickel the metal levels in the pond water were higher in Odense higher than in Aarhus. The source of the high concentrations of especially copper in the Odense pond has not yet been identified, but the pattern looks like occasional illicit point discharges. The median concentrations in the pond water were generally lower than the concentrations in the runoff entering the ponds showing that the ponds were operating well concerning their function as treatment facilities. The only exception is nickel in the Aarhus pond where nickel was higher in the pond water than in the stormwater runoff. This could be explained by nickel leaching from the clay membrane to the pond.

All metal concentrations in the stormwater runoff in Odense were higher than the literature values from Skullerud, Norway (Vollertsen *et al.* 2009b) particularly for

Table 2 | Concentrations of heavy metals in the inlets and ponds in Odense and Aarhus (range in brackets)

	Odense		**Aarhus**	
	Stormwater runoff*	**Pond water**	**Stormwater runoff***	**Pond water**
Cu	155 (17–3,300)	140 (21–1,100)	21 (<1–31)	3.1 (<1–73)
Pb	18.5 (2.2–110)	5.6 (1.1–18)	4.8 (1.3–11)	<0.5 (<0.5–38)
Zn	290 (82–2,100)	200 (14–1,700)	210 (88–350)	44 (15–320)
Cd	0.096 (<0.05–0.28)	0.059 (<0.05–0.17)	0.071 (<0.05–0.23)	<0.05 (<0.05–0.59)
Ni	13.5 (1.9–150)	8.2 (<1–46)	8.2 (1.6–25)	23 (6.4–39)
Cr	5.15 (0.9–14)	1.0 (<0.5–4.2)	3.4 (1.1–8)	<0.5 (<0.5–47)
Hg	<0.05 (<0.05–0.79)	<0.05 (<0.05–0.37)	<0.05 (<0.05–4.1)	<0.05 (<0.05–0.16)

Data marked with an asterisk are flow-weighted average concentrations others are median concentrations. All concentrations are in mg m^{-3}.

Table 3 | Concentrations of heavy metals in stormwater runoff and pond water found in the literature

	Skullerud, Norway		**NSQD, USA**	
	Stormwater runoff highway*	**Pond water highway***	**Stormwater runoff residential**	**Stormwater runoff industrial**
Cu	86	36	12	22
Pb	17.1	4.1	12	25
Zn	272	78	73	210
Cd	0.21	0.08	0.5	2
Ni			5.4	16
Cr			4.6	14
Hg			3	0.2

Skullerud data are from a pond in Norway, receiving stormwater runoff from a highway (Vollertsen *et al*. 2009b). NSQD (The National Stormwater Quality Database) are median concentration in stormwater runoff from numerous catchments in the USA with the written usage (Pitt *et al*. 2004). Data marked with an asterisk are flow-weighted average concentrations others are median concentrations. All concentrations are in mg m^{-3}.

copper. On the other hand, all concentrations in the stormwater runoff in Aarhus were lower than in Skullerud. The pond water metal concentrations are either comparable (lead and cadmium) or significantly higher (copper and zinc) than the literature data from the pond in Skullerud. In Aarhus the concentrations in the pond water were generally lower than in Skullerud. The two data sets from National Stormwater Quality Database (NSQD) (now known as the International Best Management Practices (BMP) Database) showed large differences between residential and industrial catchments. The Aarhus catchment consists mainly of residential areas and can be compared with the data from the residential catchment in NSQD. Only the copper and zinc concentrations were significantly higher in the stormwater runoff in Aarhus than the typically values for residential catchments reported in NSQD. The concentrations of zinc and copper correspond to the concentrations in the industrial catchments. The catchment in Odense consists mainly of light industry. Metal concentrations in the stormwater runoff from Odense were comparable with the data from the industrial catchments reported in NSQD. However the concentration of copper and zinc were significantly higher in Odense than in NSQD.

For both Odense and Aarhus the summarized concentrations of PAHs in the pond water were low (Table 4) and generally were the individually PAH concentrations below the detection limits. The median concentrations were approximately a factor 5 higher in the stormwater runoff than in the pond water. In other words, the low concentrations in the pond water were due to sedimentation of the PAHs.

The levels of PAHs for both stormwater runoff and pond water were comparable to data from Skullerud (Vollertsen *et al*. 2009b).

Toxicity of pure metals

The initial tests with pure metals showed that the test organism *Selenastrum capricornutum* was highly sensitive towards copper, moderately sensitive towards zinc,

Table 4 | Concentrations of total PAH in the inlets and in the ponds in Odense and Aarhus (range in brackets) and corresponding literature data

	Odense		**Aarhus**		**Skullerud**	
	Stormwater runoff*	**Pond water**	**Stormwater runoff***	**Pond water**	**Stormwater runoff***	**Pond water***
Total PAH	0.25 (<0.01–1.5)	0.047 (<0.01–2.1)	0.35 (<0.01–1.3)	0.059 (<0.01–0.22)	0.43	0.05

Data marked with an asterisk are flow-weighted average concentrations, the others are median concentrations. The data from Skullerud are based on the sum of 4-PAH and are samples of stormwater runoff from a highway in Norway (Vollertsen *et al*. 2009b). All concentrations are in mg m^{-3}.
*Median concentrations

Table 5 | Determined EC_{50}-values for pure metal salts and calculated standard deviations

	Cu $(NO_3)_2$	Pb $(NO_3)_2$	Zn $(NO_3)_2$	Cd $(NO_3)_2$	Ni $(NO_3)_2$	Cr $(NO_3)_2$
EC_{50} [mg m^{-3}]	39	3181	97	107	188	103
Std. Error	3.8	944	79	8.3	40	21

cadmium and chromium and had a low sensitivity towards lead (Table 5).

The concentrations of lead, cadmium, chromium and nickel in the Odense pond water (Table 2) were low compared to the estimated EC_{50}-values for pure metal and have probably not lead to any toxic effects (Table 5). Copper and zinc in the Odense pond water were, on the other hand, found in relatively high concentrations compared to their toxicity. Their median concentrations were respectively 3.6 and 2.1 times higher than their EC_{50}-values and could potentially have caused high toxic effects. Medians of the metal concentrations in the Aarhus pond water were all below the corresponding EC_{50}-values. However, the maximum concentrations of copper and zinc were 1.9 and 3.3 times higher than the EC_{50}-values and could therefore potentially have caused toxic effects. Nickel had a maximum concentration which corresponded to half of the measured EC_{50}-value, which potentially could cause weak toxic effects.

The toxicity of pure PAHs was not determined due to the very low concentrations of PAHs found in the samples. Focus was therefore chosen to be on heavy metals, which were found in much higher concentrations. The low concentrations of PAHs could have lead to low toxic effects but are most likely surpassed by the toxic effect caused by the heavy metals.

Toxicity of samples from Odense

Except for one measurement in August 2008 the summarized concentrations of PAHs were low and typically below detection limit (Figure 1).

There was no correlation between PAH concentrations in the pond and the water phase toxicity. Therefore the observed toxic effect most likely did not origin from the pond water content of PAHs.

Concentrations of copper, zinc, lead and nickel in the pond water in the Odense pond tended to correlate. That is, the concentrations peaked at the same time (Figure 2). As mentioned in the introduction, the heavy metals can originate from many different sources. However, the high correlation indicates that the metals in Odense originate from the same source.

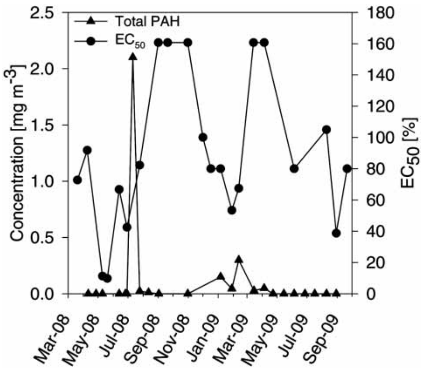

Figure 1 | Toxicity of the pond water towards the algae *Selenastrum capricornutum* and summarized concentration of PAHs in the pond water. Note that low EC_{50}-values correspond to high toxic effect and *vice versa*.

Nickel occurred in two relative large peaks shortly after the 7th of March 2009. At the same time the concentrations of the copper, zinc and lead increased as well, however not to the same degree. Additionally, chromium peaked just before the 12th of February 2009, which did not correlate with other metals. The concentrations of cadmium and mercury were generally very low and often below detection limits.

The toxicity of the stormwater towards the algae *Selenastrum capricornutum* and the concentration of copper as well as zinc correlated well (nonlinear) for the pond water from Odense (Figure 2). When the concentration of the two heavy metals increased the EC_{50}-value decreased i.e. the toxicity increased and *vice versa*. Nickel, chromium and mercury showed some peaks in concentration which did not lead to any increase in toxicity, i.e., despite the large increase in relative concentrations, the concentrations were still too low to cause any toxic effect. On the contrary, decreases in the EC_{50}-value were observed on dates with no increases in lead and cadmium concentration; i.e., lead and cadmium seemed not to cause any acute toxic effects. Taken together, this indicates that the toxicity of the pond water from Odense was caused by the relative high concentrations of zinc and copper.

The correlation between individual heavy metals and pond water toxicity is illustrated in Figure 3. The data illustrates how the toxic effect of the pond water correlates with the relative high levels of zinc and copper. The relationship could be described as linear with a threshold or simple linear if the two points to the right hand side of the graph are regarded as outliers. No correlation was observed between the others metals and toxicity. Whether the main

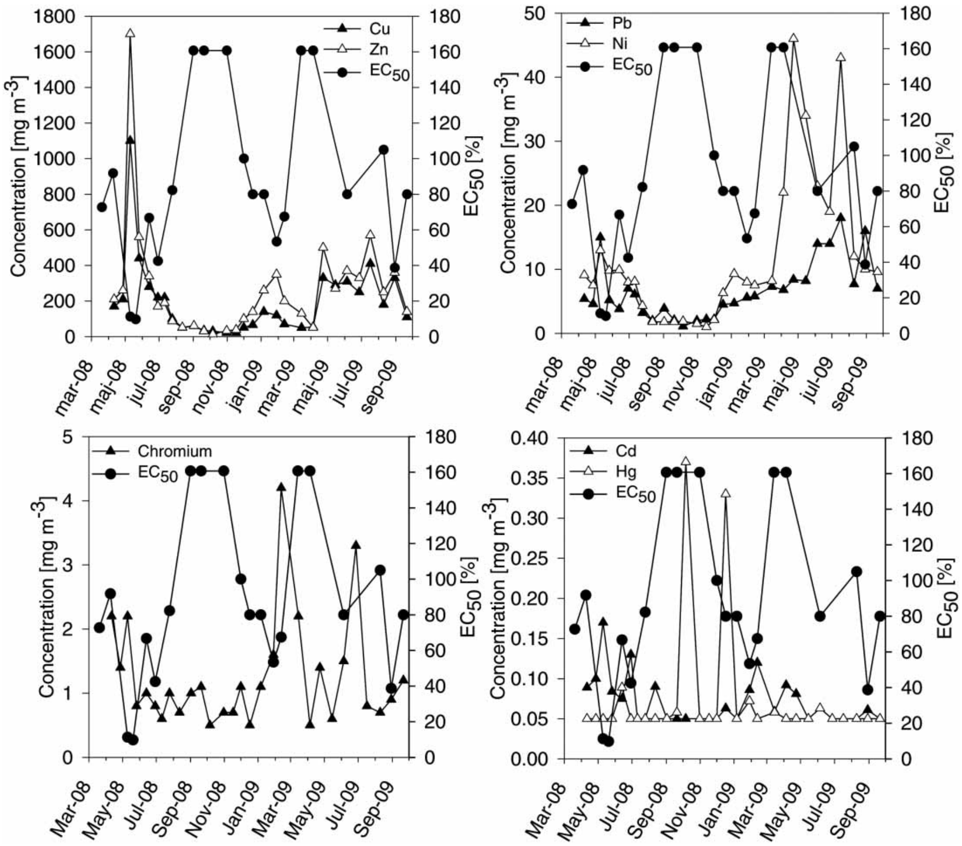

Figure 2 | Toxicity and content of heavy metals in the pond water from Odense. Note that low EC_{50}-values correspond to high toxic effect and *vice versa*.

toxicant is zinc or copper is not conclusive as there is a strong linear correlation ($r^2 = 0.94$) between the concentrations of the two metals.

If one of the heavy metals zinc or copper were the sole source to the toxic effects, the growth inhibition of the undiluted sample (100% pond water) and the theoretical inhibition, calculated using the dose-response-curve for the pure metal and the measured total concentration of heavy metal, should correlate. This measured inhibition and theoretical inhibition for copper and zinc are shown at Figure 4.

For copper the theoretical inhibitions are higher than the measured. That is, the potential toxic effect of the copper present was not expressed. As mentioned in the introduction, the toxicity of metals is lowered if complex binders are present in a sample, which most likely is the case with naturally samples as pond water. In other words, the toxicity of copper in the pond water samples are lowered because some of the metals are bound and therefore not bioavailable. In this study only the total concentrations of heavy metals were measured, resulting in more pronounced difference between measured and theoretical inhibition. For zinc higher measured inhibitions than theoretical inhibitions were observed. That is, the pond water showed higher toxic effect than what the zinc concentration could potentially cause. In addition, when over half of the copper was complex bound, some of the zinc also should be bound, which again should lead to even lower inhibitions for zinc. In other words, zinc is most likely not the main toxicant. Despite these observations, copper is most likely not the only pollutant which contributed to the observed toxic effects. The mix of pollutants found in the pond water could have resulted in additive effects which causes higher inhibitions than for the pure metals.

Toxicity of samples from Aarhus

Generally low concentrations of PAHs were observed in the pond water from Aarhus and there was little correlation between PAH concentrations and toxicity (Figure 5).

The two peaks in toxicity cannot be explained by PAHs as no corresponding peaks in concentration of PAHs were observed.

Except for the first measurements of metal concentrations in the Aarhus pond (Figure 6) the heavy metal

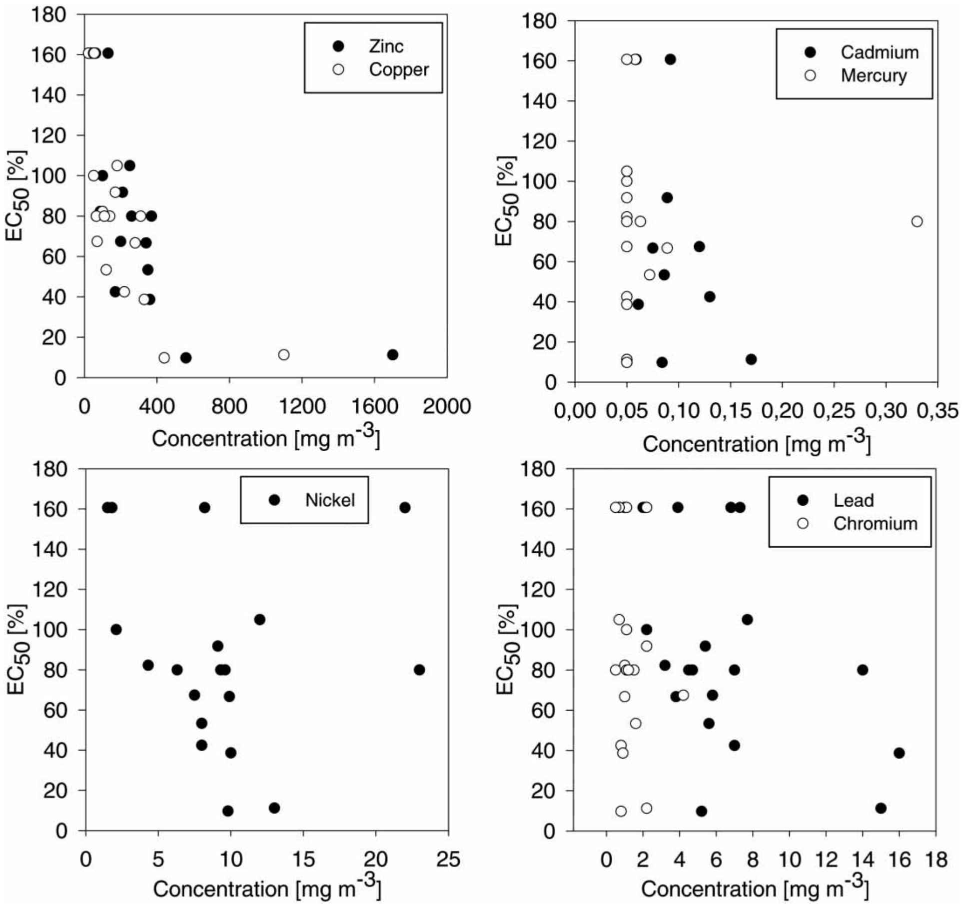

Figure 3 | Correlation between toxicity and heavy metal concentration in pond water samples from Odense.

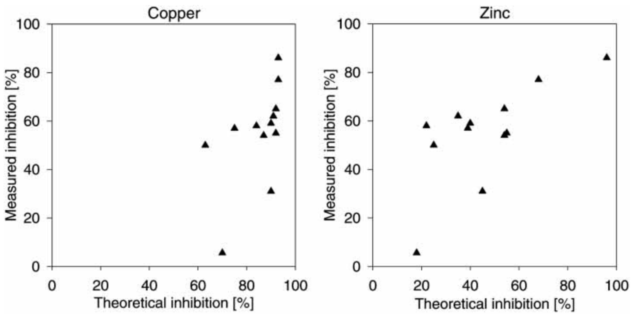

Figure 4 | Measured growth inhibition of the algae (inhibition caused by undiluted pond water) and theoretical inhibition (calculated inhibition caused by the level of metal in the pond water using the dose-response-curve for the pure metal).

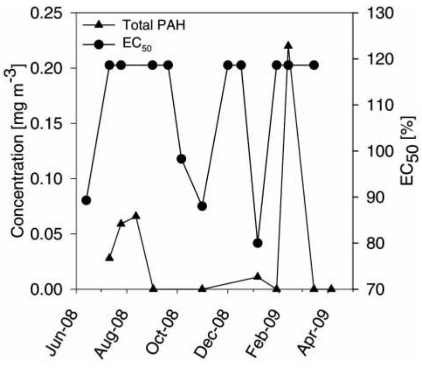

Figure 5 | Toxicity towards the algae *Selenastrum capricornutum* and summarized concentration of PAHs in the pond water. Note that low EC_{50}-values correspond to high toxic effect and *vice versa*.

concentrations in the pond water in Aarhus were generally low compared to the pond water in Odense. These initial high concentrations were most likely caused by contamination during the construction of the pond. Before the second sample was collected, the concentration levels had normalized. Except for zinc and nickel the metal concentrations were often below or very close to the detection level. Nickel was the only metal found in concentrations higher than in the Odense pond, but despite the higher level the concentrations were still below the estimated EC_{50}-value for nickel.

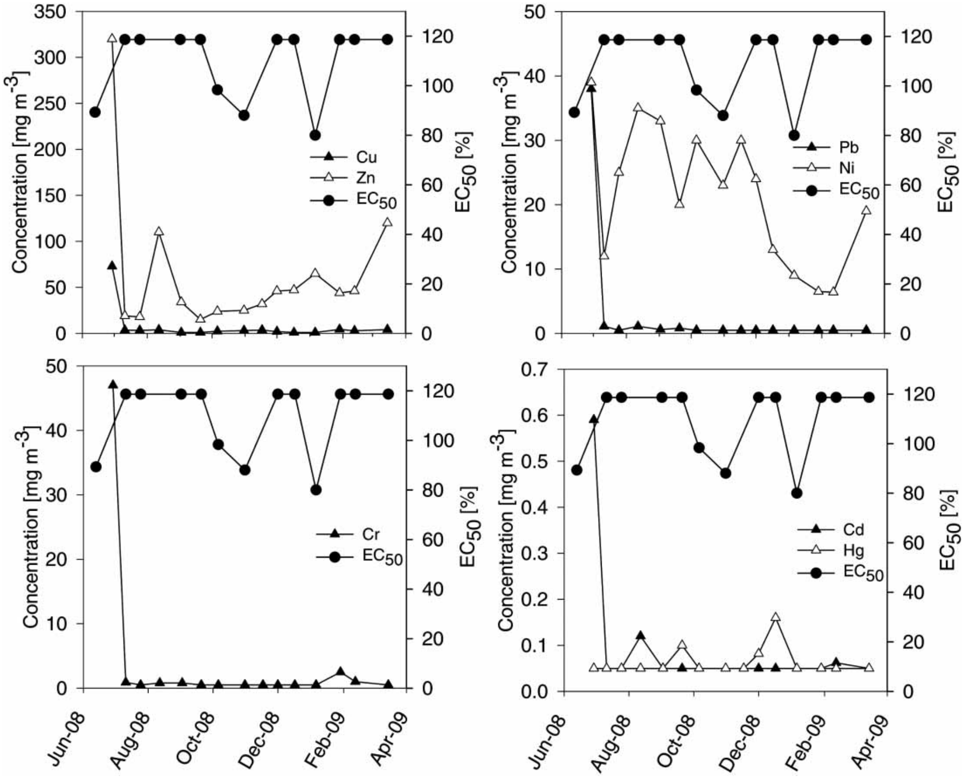

Figure 6 | Toxicity towards the algae *Selenastrum capricornutum* and content of heavy metals in the pond water samples from Aarhus. Note that low EC_{50}-values correspond to high toxic effect and *vice versa*.

It is seen from Figure 6, that pond water toxicity peaked in three of the samples. The initially low EC_{50}--value can potentially be explained by the initially high concentrations of metals. The two other peaks cannot be explained by peaks in any of the seven measured heavy metals. For the pond water of Aarhus, the good correlation seen for pond water in Odense between some of the heavy metals and toxicity could not be observed.

The Odense catchment with a relative high pollutant load showed high toxicity. The main toxicant was most likely copper which was found in high concentrations. The other catchment, Aarhus with lower pollutant load, showed lower toxic effects. A clear main toxicant was not identified. The finding of a specific main toxicant in Odense is a result of the extraordinary high copper concentrations. Generally it is probably hard to identify one main pollutant which causes toxic effects in pond water and pond water toxicity must typically be contributed to additive effects of the pollutants present. The investigations indicate that stormwater with rather typical pollutant content can exhibit some toxic effects on aquatic organisms, but that undesirable behavior like illicit discharges can cause more pronounced effects. Which sources play the greater role on a larger scale is, however, unknown and the quantification hereof a goal for future research.

CONCLUSION

An industrial catchment showed high levels of heavy metals, especially copper and zinc. The level of PAHs was moderate. The high levels of heavy metal caused occasionally high toxic effects towards the used test organism the algae *Selenastrum capricornutum*. The high concentrations of copper were found to be the most likely main toxicant. Some of the copper could be complex bound; resulting in lower toxic effects than similar concentrations of pure metals in pure water would lead to. A residential catchment showed generally lower loads of heavy metals but similar concentrations of PAHs. The pond water from this catchment occasionally showed toxic effects. There were no correlations between toxic effects and individual pollutants for this catchment. Generally, stormwater runoff in a wet detention pond is found to be toxic, but the level of toxicity varies significantly in time and between catchments.

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III

Modeling nutrient and pollutant removal in three wet detention ponds

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Abstract

Three wet detention ponds receiving stormwater runoff and located in Århus, Silkeborg and Odense, Denmark were studied. The ponds were continuously monitored by measuring turbidity, temperature, pH, oxygen level and water level in the ponds as well as inflow and outflow. Water samples were collected from the inlets and from the downstream end of the ponds and analyzed for suspended solids, total and soluble phosphorous, nitrogen and seven heavy metals. Performance of the ponds was modeled by routing the measured flow though the ponds and simulating pollutant removal by 1st order kinetics with and without temperature adjustment.

Introduction

Stormwater contains a large range of pollutants, e.g. suspended solids, nutrients, heavy metals, pesticides and poly aromatic hydrocarbons (PAHs) [1]. Nutrients can lead to eutrophication and following oxygen depletion in the receiving waters. Furthermore, heavy metals, PAHs and other micopollutants can have toxic effects on flora and fauna in the receiving waters [2,3]. That is, treatment of stormwater is from time to time necessary before leading it back to the environment. An obstacle for stormwater runoff treatment is that hydraulic and pollutant loads are intermittent and highly variable over time. The facility must furthermore be robust and maintenance-free and treat runoff at low pollutant concentrations to even lower concentrations. Wet detention ponds have proven efficient performance in this context and are commonly chosen for treatment of stormwater runoff.

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The performance of a wet detention pond depends on numerous factors such as pond geometry and hydraulic retention time. The retention time of a pollutant – being it a dissolved component or a particle – is affected by the size, depth and length to width ratio of the pond as they influence the mixing and flow patterns [4]. The pollutant removal rate is affected by factors like temperature, which influence on the biological processes but also on the viscosity of the water and thereby the sedimentation of particles.

As a part of the EC-founded LIFE-treasure project three wet detentions ponds were constructed in 2007 and 2008 in the cities of Silkeborg, Århus and Odense, Denmark [5]. An aim of that project was to investigate the performance of wet detentions ponds in Denmark by caring out an intensive monitoring campaign of flow, pollutant load as well as removal together with monitoring the physical and chemical state in the ponds.

The objective of this study is to determine whether removal rates for different pollutants are alike in the three ponds. Furthermore it is investigated whether the rates are affected by temperature. Mixing in the wet detention ponds is investigated to determine the degree to which the ponds in this context can be viewed as fully mixed or following a plug flow principle.

Methods

Site and pond characteristics

The three ponds receive stormwater runoff from three different catchment types and have different physical outlines (Table 1). Precipitation is measured by tipping bucket gauges of the Danish SVK rain gauge system, located a few kilometers from each pond. All three ponds were designed as recommended by e.g. [4,6,7], that is, they were designed to have a retention time of 72 hours with a return period of 4 year^{-1}.

First the stormwater enters a grid chamber. After the grid chamber, the stormwater enters the earthen ponds with boulders to disperse the inflow jet stream. All ponds are equipped with clay membranes. The pond in Århus has three small circular islands with plants in the middle of the pond, to disperse jet streams. In Silkeborg the pond is equipped with two planted earthen barriers, during dry weather dividing the pond in three disconnected sections. The pond in Odense has no additional jet stream management. Schematic drawings of the ponds are presented in Figure 1.

Table 1. Pond and catchment characteristics.

Type of catchment	Odense	Århus	Silkeborg
	Light industry	Residential (blocks of flats)	Residential (detached houses) and highway
Total catchment area [ha]	27.4	57.4	21.5
Impervious catchment area [ha]	11.4	25.8	8.8
Permanent wet volume [m^3]	1,990	6,900	2,680
Retention volume [m^3]	1,992	1,400	3,230
Permanent water depth, max [m]	1.45	1.25	1.00
Length to width ratio	4.5: 1	3:1	3 chambers of app. 1:1 each
Precipitation [mm y-1]	657	661	719
Annual runoff [m3]	55,500	131,900	49,600

On-line measurements

Inlet flows were measured by a smaller and a larger full-flowing magnetic flow meter in each pond (Krone optiflux, DN 150 mm and DN 500 mm in Odense, Århus and DN 400 mm in Silkeborg) coupled in series and parallel to a rectangular weir. The accuracy of the measurement was better than 1% for inflows between app. 3 L s^{-1} and app. 1 m^3 s^{-1}. At flows over app. 1 m^3 s^{-1} the weir begins to convey some of the flow. The flow over the weir is estimated by the water level in the grid camber.

Fig. 1. Schematic drawings of the three ponds, top: Odense; bottom left: Århus; bottom right: Silkeborg.

Sensors for online monitoring of pH (WTW SensoLyt 700 IQ), dissolved oxygen (WTW FDO 700 IQ), temperature (via pH meter) and water depth (Klay Hydrobar) were placed in the ponds. In Odense and Århus the sensors were in the middle of the ponds. In Silkeborg sensors were in both the middle and last sub-compartment. Readings were stored every minute.

Stormwater sampling

Auto-samplers equipped with plastic containers were placed in the inlets after the grid chambers and in the middle of the basin (Odense), in the end of the basin (Århus), and in the last sub-compartment (Silkeborg). Water samples were collected flow proportionally in the inlet and time proportionally in the basins. The auto-samplers were emptied when full or every 14 days. The auto-samplers were placed underground, i.e. dark and cold to minimize changes of the samples during the storage on site. The subsamples from the auto-samplers were pooled and analyzed for total concentrations of copper, lead, zinc, cadmium, nickel, chromium, mercury, total PAH (after USEPA), suspended solids and nitrogen as well as total and dissolved phosphorus. All analyses were performed by an accredited laboratory following ISO 17294m, manual MK2260-GC/MS, DS/EN 872, DS/EN I 6878aut, manual SM17 udg 4500 and DS/EN I 11905 auto. The water samples from Odense cover the time span from mid April 2008 to late September 2009. Århus cover the time span from mid June 2008 to late September 2009 and Silkeborg cover the time span from mid December 2008 to late September 2009.

Wet pond modeling

The water balance in the ponds consists of measured inflow, volume of water in the pond and outflow. Evaporation from and precipitation on the pond surface are neglected as these are minor compared to inflow and outflow. Exfiltration from and infiltration to the pond through the wetted perimeter are set to zero as all three ponds were equipped with an impermeable clay membrane. Some groundwater infiltration was visually observed during wet periods but deemed inconsequential. The volume of water in the pond is calculated continuously with a 1-minute time resolution, corresponding to the frequency of the flow and water level readings.

Removal of a pollutant is simulated simultaneous with the water balance by simple 1st order kinetics with and without temperature adjustment (Arrhenius equation, see eq. 1 and 2). The true removal of pollutants from the water phase in wet detentions ponds are a complex mixture of chemical, physical and biological processes e.g. flocculation, bacterial degradation, adsorption, absorption, resuspension of sediments and sedimentation which again are affected by for example particle characteristics and water viscosity. That is, simple kinetics such as 1st order kinetics has its limitations when simulating removal of pollutants in wet detention ponds [8,9], but they were chosen as the detailed processes and boundary conditions are not well defined or understood [10].

$$\frac{dC}{dt} = -kC \tag{1}$$

$$\frac{dC}{dt} = -k\alpha^{20-T}C \tag{2}$$

C is the concentration of a pollutant	[g m^{-3}]
k is the removal rate	[g m^{-3} day^{-1}]
α is the temperature dependency constant	[-]

Inputs to the model are the measured temperature, inflow and concentration of pollutants in the inlet and in the pond. The model simulates the pollutants in the pond using inlet pollutant loads and 1st order kinetic for pollutant removal. The model is coded in Pascal and iterates the removal rate until a best fit between simulated and measured pollutants in the pond is achieved. Two different fitting procedures were used. First the average mass of pollutants discharged from the pond was fitted to the measured pollutant discharge. That is, the model was fitted to one value, namely the average removal of the whole measuring campaign. Next a least square method was applied to continuously simulate the pollutant removal.

Results and discussion

Mixing of the water phase in the ponds

Examples of online measurements and measured inflow are shown for Odense in Figure 2, for Århus in Figure 3 and for Silkeborg in Figure 4.

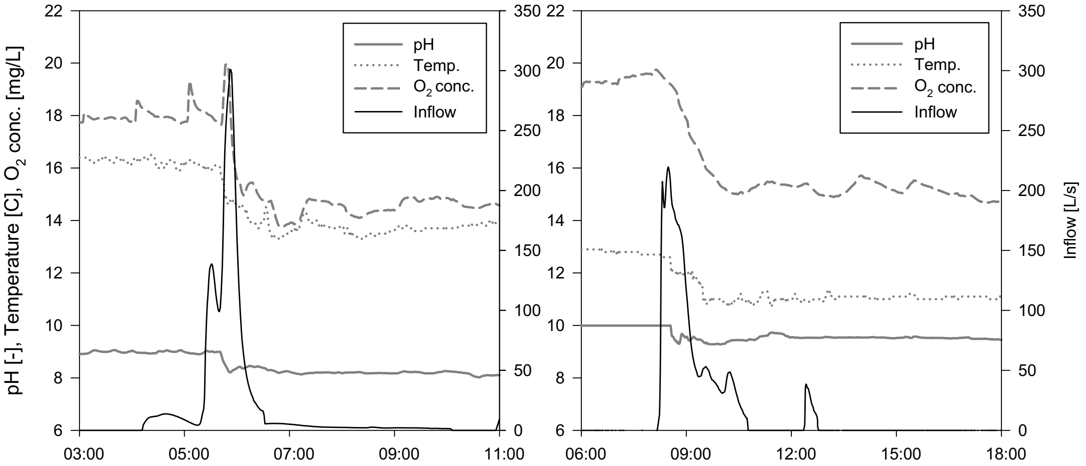

Fig. 2. The influence of runoff events on pH, temperature and oxygen level in the pond in Odense. Right graph: 19-05-2008, left graph: 22-04-2009.

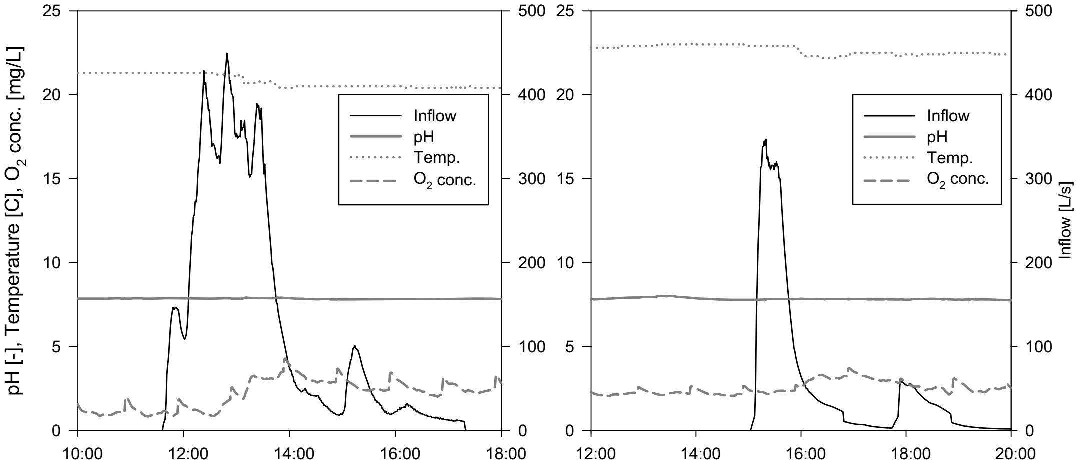

Fig. 3. The influence of runoff events on, temperature and oxygen level in the pond in Århus. Right graph: 18-07-2009, left graph: 06-07-2009.

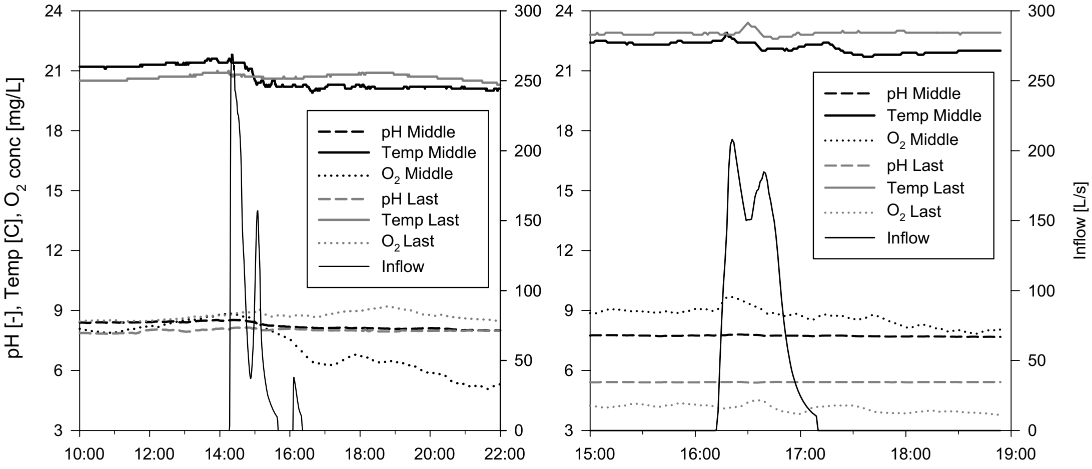

Fig. 4. The influence of runoff events on pH, temperature and oxygen level in the pond in Silkeborg. There are two sets of sensors: in the middle compartment and in the last compartment. Right graph: 08-07-2009, left graph: 08-08-2009.

For the pond in Odense, runoff events caused quick and clear responses in pH, temperature and oxygen levels. After typically 20 minutes the parameters became affected. In the examples of Figure 3, oxygen declined with app. 4 mg L^{-1}, temperature with app. 2˚C and pH with 1 unit.

In the pond in Århus, the response is comparatively smaller and slower than the pond in Odense. In the example of Figure 4, pH is not affected, the oxygen level increases with app. 2 mg L^{-1} (graph to the left) and 1 mg L^{-1} (graph to the right). The temperature declines with app. 1˚C in both examples. The responses occur within 1.5 hours from the start of the event.

In Silkeborg the response to a runoff event is evident in the middle compartment but not in the last compartment. In the example of Figure 5 (graph to the left), temperature in the middle compartment declines with approximately 2˚C, the oxygen level declines fast with 2 mg L^{-1} and continuous to decline. For the event depicted in the graph to the right, the temperature declines a bit and becomes unstable, the oxygen level first increases with 1 mg L^{-1} and thereafter begins to decline. This increase in oxygen level is also seen in the last sub-compartment app. 20 minutes later. The pH is not affected in any of the cases. The responses to the events are seen within approximately 30 minutes in the middle compartment.

As these observations show, the mixing in the ponds is quick compared to the rate with which pollutants typically are removed in wet detention ponds [4]. The ponds are therefore simulated as one fully mixed box and not as a set of boxes.

Fit of models

Each pond has been modeled six times. Once by the procedure of fitting to the average removal efficiency only and without temperature correction (ARE). And five times with the more complex fitting procedure using a least square method (LSM) and with a temperature dependency constant, α, ranging from 1.00 to 1.09. An α of one corresponds to no temperature dependency. An α of 1.03 – 1.05 emulates sedimentation as the dominating removal process as such α-value follows the temperature dependency of water viscosity. When α is in the range of 1.07 – 1.09, biological processes are indicated as being dominant. For each of the six models the error between measured and simulated values was determined by equation 3. The errors were standardized so they can be compared across the different pollutants and ponds, despite differences in pollutant loads and dataset size.

$$\sum \frac{\left(\frac{\mathit{Modeled}\ C-\mathit{Measured}\ C^{2}}{\Sigma \mathit{Measured}\ C}\right)}{\mathit{Number\ of\ measurements}} = \mathit{Error} \tag{3}$$

It was not possible to model the removal of nickel for the pond in Århus as the concentrations of nickel were higher in the pond than in the inlet – properly caused by internal released from e.g. the clay membrane. Modeling the removal of zinc in the pond in Silkeborg was only possible with ARE as LSM went unstable, probably due to the limited number of data. All determined errors are shown in Figure 5.

The smallest errors, that is, the best fit, for the pond in Århus were achieved using ARE for 6 out of 10 pollutants. The other 4 pollutants had the smallest error by LSM with temperature correction α = 1.07. Looking at the total error (all errors for each pollutant added together) the best fit was achieved using LSM without temperature correction, that is α = 1.00.

In the pond in Odense the best fit was found for 5 out of 11 pollutants when using ARE. The other 6 pollutants achieve the best fit with LSM. One pollutant had the smallest error whit α = 1.00, another pollutant had the smallest error with α = 1.07 and the last 4 pollutants had the smallest error with α = 1.09. The total error was smallest using ARE.

In Silkeborg the picture was more blurry. Four out of the 10 pollutants had the best fit using ARE. The last 6 pollutants had the best fit using LSM with different α-values. Three pollutants without temperature correction, α = 1.00, one pollutant with α = 1.03, one with α = 1.05 and one pollutant with α = 1.07. The smallest total error was achieved by using ARE. It was tested whether better fits were achieved using three fully mixed boxes in the model instead of one fully mixed box (i.e. simulating the 3 compartments as 3 boxes), but no tendencies were found for the individual pollutants. However, the total error using ARE with three boxes were 28 % lower than the total error using one box.

For many of the pollutants in Odense and Århus relative good fits were achieved with LSM and an α–value of 1.07 – 1.09, indicating that biological removal was dominating. However, the overall tendency for all three ponds was that the best fit was achieved using ARE, indicating a random temperature dependency. The stochastic behavior of both pond input and removal processes probably overruled the detailed processes like temperature dependency. This independency of temperature was also found in [11]. It was therefore concluded that at the data-level available and with the current knowledge of processes, it is not feasible to simulate detailed removal processes and that only average removal should be modeled.

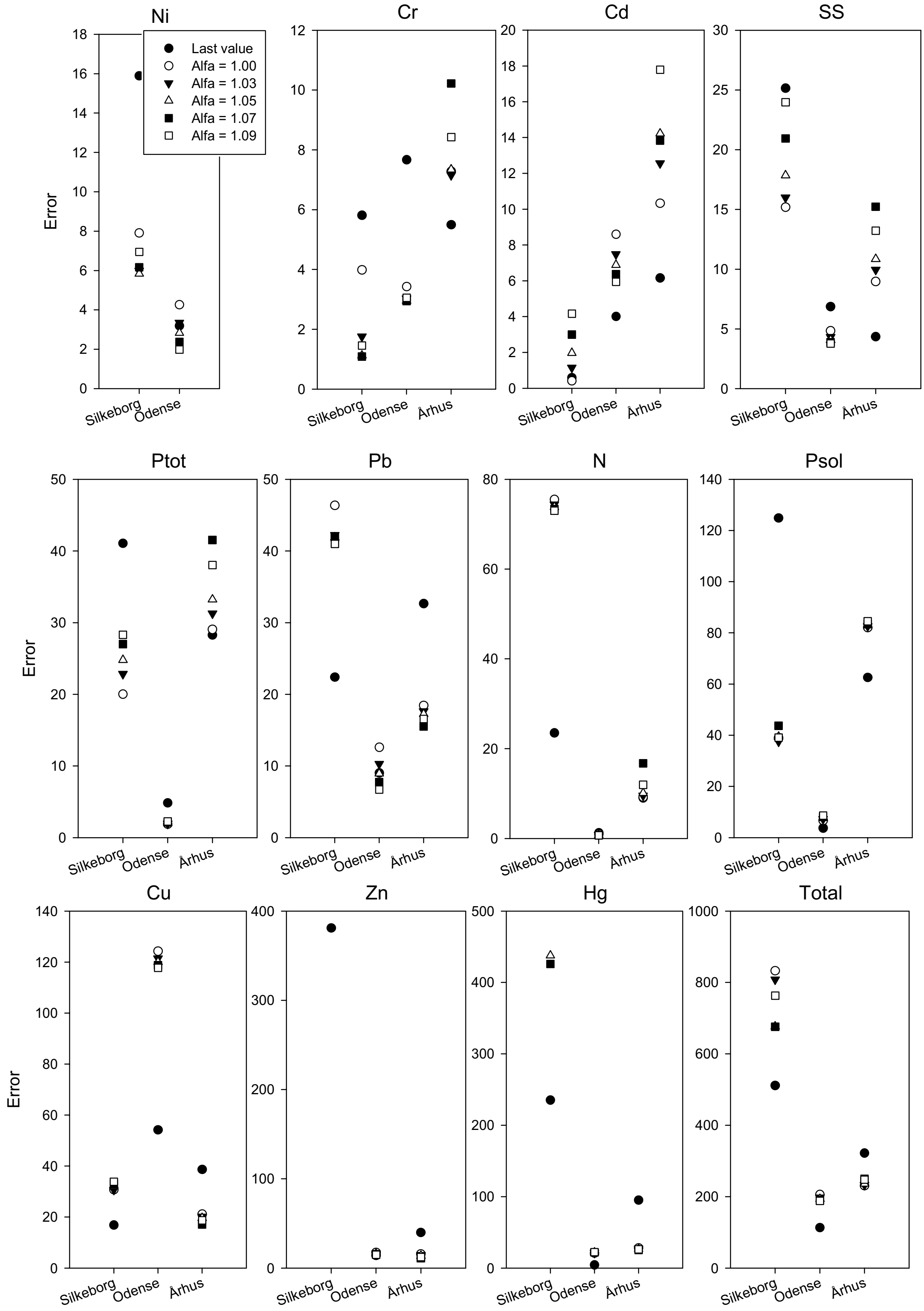

Fig. 5. Error between model and measured data for each pollutant and the total error (sum of the error for each pollutant). The error is calculated for ARE and LSM with α-values from 1.00 to 1.09.

Removal rates

For each model a set of removal rates were found, one for each pollutant. The actual value of a removal rate depends on the model by which it is determined, i.e. which α–value was applied. The rates found for each pollutant differ between ponds but are generally of the same magnitude except for a few pollutants, e.g. dissolved phosphorous in Silkeborg. The removal rates for dissolved phosphorous in Silkeborg ranged from 0.48 to 23.26 when using one box in the models. The rates got significantly lower when using 3 boxes, which was expected [12], but did not give a better fit. In Table 2 the simulated removal rates are shown. The rates for all 11 pollutants in the three ponds were determined by ARE which had the lowest total error. Furthermore, removal rates determined by a similar approach for a wet detention pond in Skullerud, Norway [7] are shown for comparison.

Table 2 shows relative similar removal rates across the four ponds for total phosphorous and total nitrogen. For the rest of the pollutants quite fluctuating removal rates were found, illustrating a general uncertainty in predicting pollutant removal in wet detention ponds.

Table 2. Removal rates determined using ARE. Skullerud is a wet detention pond in Norway which has been simulated by a similar approach [7].

	SS	Ptot	Psol	Ntot	Pb	Cd	Cu	Zn	Cr	Hg	Ni
Odense	0.32	0.14	0.26	0.08	0.90	0.21	0.28	0.15	1.21	0.08	0.20
Århus	0.66	0.23	1.44	0.09	0.43	0.04	0.14	0.07	0.82	0.36	-
Silkeborg	0.13	0.36	3.73	0.01	0.03	0.02	0.03	0.04	0.02	0.02	0.27
Skullerud	1.9	0.12	0.14	0.02	0.65	0.14	0.10	0.52	-	-	-

Conclusion

Changes in pond pH, temperature and oxygen level due to runoff entering the ponds showed that the three wet detention ponds studied should be characterized as fully mixed reactors and not as plug flow reactors. Sensors placed in the middle of the ponds showed mixing of water already 20 to 90 minutes after the onset of storm events.

Two different simulation procedures as well as a range of temperature dependencies were applied in the models describing the wet detention ponds. Generally, the simplest simulation procedure without temperature adjustment gave the best fit to measured data. However, for some pollutants a more complex method with temperature dependencies corresponding to biological degradation being the dominant pollutant removal processes gave the best result. It was concluded that more knowledge of the individual processes is needed before more complex models should be applied; so far only modeling of the average removal seems feasible.

The removal rates for total phosphorous and total nitrogen were somewhat similar in the three ponds studied as well as in a pond reported in literature. For the other 9 pollutants no clear tendency for the removal rates were found and future prediction of removal of these pollutants in wet detention ponds seems difficult.

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IV

Modeling the eutrophication of stormwater ponds

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Nomenclature

A	Surface area per unit volume	m^{-1}
A_{pb}	Bottom area of the pond	m^2
BA	Benthic algae including epiphytes	$gC\ m^{-3}$
$b_{D,BA}$	Decay rate of *BA*	s^{-1}
$b_{D,MP}$	Decay rate of *MP*	s^{-1}
$b_{D,PP}$	Decay rate of *PP*	s^{-1}
D	Molecular diffusivity of a given gas	$m^2\ s^{-1}$
h_i	Predicted value in the base case at the given time step *i*	-
I	Light intensity in the water column	$J\ m^{-2}\ s^{-1}$
I_0	Light intensity at the pond surface	$J\ m^{-2}\ s^{-1}$
K_{DIC}	Half-saturation constant for S_{DIC}	$gC\ m^{-3}$
K_I	Half-saturation constant for I	$J\ m^{-2}\ s^{-1}$
$K_{L,O2}$	Air-water mass transfer coefficient of O_2	$m\ s^{-1}$
$K_{L,CO2}$	Air-water mass transfer coefficient of CO_2	$m\ s^{-1}$
K_N	Half-saturation constant for S_N	$gN\ m^{-3}$
K_{O2}	Half saturation constant for S_{O2}	$gO_2\ m^{-3}$
K_P	Half-saturation constants for S_P	$gP\ m^{-3}$
$k_{R,BA}$	Respiration rate of *BA*	s^{-1}
$k_{R,MP}$	Respiration rate of *MP*	s^{-1}
$k_{R,PP}$	Respiration rate of *PP*	s^{-1}
MP	Macrophytes	$gC\ m^{-3}$
P	Base case parameter value	-
pH_{inhib}	Bell-shaped function varying between zero and one, with optimum at pH equal to 7.5	-
PP	Phytoplankton	$gC\ m^{-3}$
R_{SOD}	Sediment oxygen demand rate constant	$gO_2\ m^{-2}\ s^{-1}$
$Sc_{O2/DIC}$	Schmidt number (v/D) for S_{O2} and S_{DIC}, respectively	-
S_{CS}	CO_2 saturation concentration	$gC\ m^{-3}$
S_{DIC}	Dissolved inorganic carbon	$gC\ m^{-3}$
S_i	Normalised sensitivity index at time step i	-
S_N	Dissolved nitrogen	$gP\ m^{-3}$
S_{O2}	Dissolved oxygen	$gO_2\ m^{-3}$
S_{CO2}	Concentration of dissolved CO_2	$gC\ m^{-3}$
S_{OS}	Dissolved oxygen saturation concentration	$gO_2\ m^{-3}$

S_P	Dissolved phosphorus	gP m^{-3}
switch	Function between zero and one preventing extinction of the primary producers during winter	-
T	Water temperature	°C
U_{10}	Wind speed 10 m above ground (10-minutes average speed)	m s^{-1}
V_p	Volume of the pond	m^3
X_{BA}	Biomass of primary producers *BA*	gC m^{-3}
X_{MP}	Biomass of primary producers *MP*	gC m^{-3}
X_{PP}	Biomass of primary producers *PP*	gC m^{-3}
$Y_{C:C}$	C taken up or released when consuming or producing CO_2 (always 1)	gC gC^{-1}
$Y_{C:O2}$	C produced per O_2 consumed by sediment oxygen uptake	gC gO_2^{-1}
$Y_{N:C}$	N produced per C in biomass produced by photosynthesis or by respiration	gN gC^{-1}
$Y_{N:O2}$	N produced per O_2 consumed by sediment oxygen uptake	gP gO_2^{-1}
$Y_{O2:C}$	O_2 produced per C in biomass produced by photosynthesis or by respiration	gO_2 gC^{-1}
$Y_{P:C}$	P produced per C in biomass produced by photosynthesis or by respiration	gP gC^{-1}
$Y_{P:O2}$	P produced per O_2 consumed by sediment oxygen uptake	gP gO_2^{-1}
Z	Water depth	m
A	Attenuation coefficient for fresh water	m^{-1}
B	Attenuation coefficient for phytoplankton	m^2 g^{-1}
Γ	Ratio between N or P taken up from the sediment to N or P taken up from the water phase (zero for *PP* and *BA*; between zero and one for *MP*)	-
θ_{grd}	Temperature constant for growth, respiration and decay of *PP*, *BA* and *MP*	-
θ_{SOD}	Temperature constant for the sediment oxygen demand	-
θ_{wg}	Temperature constant for the water/liquid mass transfer	-
$\mu_{max,BA}$	Maximum specific growth rate of *BA*	d^{-1}
$\mu_{max,MP}$	Maximum specific growth rate of *MP*	d^{-1}
μ_{maxPP}	Maximum specific growth rate of *PP*	d^{-1}
N	Kinematic viscosity of water	m^2 s^{-1}
ρ_a	Air density	g m^{-3}
ρ_w	Water density	g m^{-3}
$\lvert\Delta h_i\rvert$	Absolute difference in predicted value between the base case (calibration) and sensitivity case (±30%) at the given time step i	-
$\lvert\Delta P\rvert$	Absolute change in parameter value	-

Abstract

A model, targeting eutrophication of stormwater detention ponds was developed and applied to simulate pH, dissolved oxygen and the development of algae and plant biomass divided into three groups, phytoplankton, benthic algae and macrophytes. Two large data sets from an intensive monitoring campaign of two Danish stormwater ponds were used to calibrate and validate the model. One general calibration covering 6 consecutive months together with two additional short-term calibrations during summer (31 days) and winter (56 days) were carried out applying the data series from one of the ponds. The calibrations showed a good agreement between measured and modeled data considering the time spans. When validated on the second pond, significant disagreement was found for the summer validation while the winter validation was acceptable. The cause might have been differences in characteristics not captured by the model, for example difference in primary producer species, differences in runoff quality, differences in pond geometry or differences in shelter conditions. It was concluded that a different calibration targeted at the second pond was required to achieve a proper simulation of pH and dissolved oxygen during the growth season.

Keywords Eutrophication, Stormwater, Wet detention pond, pH, Dissolved oxygen

1 Introduction

Stormwater runoff from roads and urban surfaces often contribute to the deterioration of the aquatic environment. Runoff contains a wide range of contaminants in varying concentrations (NURP, 1983). Among these contaminants are heavy metals, suspended solids, nutrients, and organic micro-pollutants like PAH's and biocides. If discharged without prior treatment, the pollutants can have detrimental impacts on the flora and fauna of surface waters. Therefore treatment is often required to protect the receiving aquatic environment. Due to the nature of stormwater runoff, treatment facilities must be robust and capable of handling an intermittent runoff pattern as well as a wide range of pollutant concentrations. One treatment technology which has proven robust and efficient in managing both flows and pollutants loads from stormwater runoff is the wet detention pond. A wet detention pond is an artificial lake with a permanent pool of water designed to detain stormwater runoff. While detained, the quality of the stormwater is improved by sedimentation, adsorption, chemical precipitation, and biodegradation – hereby mitigating the negative impacts on the receiving waters.

The specific load of nutrients to a wet detention pond can be significant and, like in a natural lake, can cause eutrophication of the pond (Mitsch and Reeder, 1991; Gelbrecht *et al.*, 2005). In natural lakes the resulting algal bloom will lead to high water turbidity, high pH and periods of low dissolved oxygen concentration due to decomposition of dead algae (Torno *et al.*, 1985). With respect to wet detention ponds, this process has not been studied in details but could potentially lead to low dissolved oxygen concentrations in the pond. Upon discharge, such water has detrimental impacts on the receiving water fauna and flora (Magaud *et al.*, 1997). Low dissolved oxygen concentrations in the pond could furthermore lead to anaerobic conditions at the pond bottom, resulting in malodors and lowered redox conditions in the sediments. The latter can cause release of phosphorus and heavy metals previously immobilized in the pond sediments (Wong and Yang, 1997). The algal biomass in a pond also influences the removal of pollutants, as the algal biomass absorbs pollutants, which thereby are removed from the free water phase (Mehta and Gaur, 2005).

To predict the dissolved oxygen concentration in a stormwater pond, it is necessary to simulate the growth and decay of the flora, together with a number of related processes. In other words, it is necessary to set up an eutrophication model of the system. Several eutrophication models have been developed for fresh waters and marine waters; for example the CAEDYM model, which is developed for lakes and reservoirs (Hipsey *et al.*, 2006). However, a stormwater pond differs from a natural lake in several ways (Hvitved-Jacobsen *et al.*, 2010):

- Hydraulic load pattern and residence time: In contrast to natural lakes, stormwater ponds only receive input during runoff events. I.e. the inflow pattern to a wet pond is characterized by periods of no inflow, interrupted by short periods of high inflow rates. Furthermore, in many ponds the outlet is restricted, resulting in large fluctuations in water volume and water level. Due to the high variability of the inflow pattern, the residence time of the water also varies significantly.
- Nutrient load and load pattern: The nutrient load varies with the variation in inflow rate, causing larger temporal load variation for stormwater ponds compared to natural lakes.
- Contaminants: The contaminants in stormwater runoff can be toxic to the aquatic flora and fauna, while it is typically not the case for the inflow to natural lakes.

For these reasons, a targeted model is needed for simulation of eutrophication in stormwater ponds. Additionally, a rather simple model is preferred to minimize the data requirement for calibrating and validating the model.

The objective of this study is to develop an eutrophication model targeted at stormwater ponds. The model shall predict pH, dissolved oxygen and biomass of primary producers under dynamic conditions, to yield better understanding of the biological, chemical and physical performance of such ponds. The model is calibrated and validated on data from two wet detention ponds with equipment for continuous monitoring of flow, water levels, turbidity, pH, dissolved oxygen, temperature, as well as measured pollutant loads and discharges.

2 Methodology

2.1 Study site

The studied ponds were constructed as part of an EC-funded LIFE project in the cities of Odense and Aarhus, Denmark. The two ponds receive stormwater runoff from catchments of different land use and have different physical characteristics, Table 1. The ponds consist of one compartment without sediment forebay. The ponds were designed for a retention time of 72 hours at a return period of 4 year^{-1} and follow the recommendations of e.g. Hvitved-Jacobsen *et al.* (1994), Pettersson *et al.* (1999) and Vollertsen *et al.* (2007).

The ponds were monitored for inlet and outlet flows as well as pollutant loads. Water levels and water quality parameters were monitored by online sensors in the ponds. Pollutants were measured by automatic sampling. Details on online sensors and sampling for the pond in Odense are found in Vollertsen *et al.* (2009). The pond in Aarhus was similarly equipped. Meteorological data (radiation, air temperature, wind direction and wind speed) were measured at nearby weather stations administrated by Danish Meteorological Institute, DMI.

The measuring campaign revealed that both ponds were subjected to illicit discharges. The pond in Aarhus received sporadic discharges of septic wastewaters, which was observed by wastewater odor at the pond inlet and confirmed by detection of *E.Coli* in the inflow. The discharges occurred irregularly, sometimes with intervals of days, sometimes with intervals of months. However, the source and extent hereof could, not be identified. The pond in Odense received sporadic discharges of chemical waste with high concentrations of copper, zinc and lead. The discharges occurred approximately every half year, resulting in temporary copper concentrations above 1,000 µg L^{-1} in the pond. The source hereof was not identified

2.2 Data series

Online sensors placed in the middle of the ponds monitored the pH (WTW SensoLyt 700 IQ), temperature (via pH meter), turbidity (WTW VisoTurb 700), dissolved oxygen level (WTW FDO 700 IQ) and water depth (Klay Hydrobar) and measurements were logged every minute. The data series have been adjusted for sensor drift and recalibrations.

Inlet flows were monitored using two magnetic flow meters, one small and a larger full-flowing in each pond (Krone optiflux, DN 150 mm and DN 500 mm in both ponds). The flow meters were coupled in series together with a rectangular weir coupled in parallel with the two flow meters. The flow over the weir was estimated by the water level in the grid chambers, placed upstream for the inlets of the ponds.

Auto-samplers were placed at the inlets of the ponds after the grid chambers. Additionally, an auto-sampler was placed at the middle of the pond in Odense and at the end of the pond in Aarhus. Flow proportional water samples were collected in the inlets and time proportional in the ponds. The auto-samplers were emptied every 14 days or when full. The auto-samplers were equipped with plastic containers and placed underground, i.e. dark and cold to minimized changes of the samples during storage.

The subsamples from the auto-samplers were pooled and analyzed for total concentrations of copper, lead, zinc, cadmium, nickel, chromium, mercury, total PAH (after USEPA), suspended solids, nitrogen as well as total and dissolved phosphorus. All analysis were performed by an accredited laboratory, following international or European standards (ISO 17294m, manual MK2260-GC/MS, DS/EN 872, DS/EN I 6878aut, manual SM17 udg. 4500 and DS/EN I 11905 auto). Furthermore, grab samples were taken from the ponds for determination of chlorophyll (analyzed after DS/EN 2201). The water samples from Odense covered the time span from mid April 2008 to late September 2009. The samples from Aarhus covered the time span from mid June 2008 to late September 2009. In April 2, 2009, iron salts were added to the sediment in the pond in Aarhus in order to enhance pollutant removal. Furthermore, both ponds became ice-cover in January and February, 2009. Therefore, monitoring data obtained after January 1st was not used for modeling purposes.

This surveillance of the ponds has resulted in a large dataset, giving a unique and robust platform for calibrating and validating a model predicting pH and oxygen levels in the stormwater ponds.

2.3 Model outline

An eutrophication model targeted at stormwater ponds (Figure 1) was developed based on eutrophication models for freshwater systems as described by Hamilton and Schladow (1997) and Jørgensen and Bendoricchio (2001). The model is relatively simple and calculates growth of primary producers subdivided into phytoplankton (*PP*), benthic algae including epiphytes (*BA*) and macrophytes (*MP*) as well as concentrations of dissolved oxygen, CO_2, N and P. Calculated changes in dissolved inorganic carbon (DIC) constituted, together with the pH and the DIC of the incoming stormwater, the basis for calculation of pH. These modeled pH and O_2 concentrations were compared to measured data for the purpose of calibrating the model.

A pond was in the model described as one completely mixed compartment. The mixing of the water in both ponds has been studied by Wium-Andersen *et al.* (2012) by analyzing the time passing from inflow events to response in online measurements (turbidity, pH, temperature and oxygen). The response times were found to be between 0.5 to 2 hours and it was concluded that, during a runoff event, the ponds became completely mixed within hours. For a similar pond and using an inert tracer, Madsen *et al.* (2007) found that between events the studied pond at most became completely mixed within a day. Compared to the time scale of the biological processes, and considering that the ponds are shallow, it therefore seemed appropriate to use only one completely mixed compartment for simulation.

To simulate the light penetration into the pond, the water column was within each time step divided in layers of 0.1 m, simulating plant and algae growth in each layer. After completion of all process simulations of one time step, the water column was again completely mixed prior to simulation of the next time step.

2.3.1 Boundary conditions

In the model, water only entered or left the ponds through the inlet and the outlet, that is, precipitation on the pond surface, evaporation, exfiltration and infiltration was considered negligible.

Inflow to the model was determined by the measured inflow time series. This inflow was simulated as having a fixed pH and a temperature equal to the measured air temperature. The water was assumed saturated with O_2 and CO_2 at the respective temperature and pH. DIC of the inflow was calculated from the CO_2 content, pH and temperature assuming equilibrium conditions. The concentrations of nitrogen and phosphorus in the inflow were set to the measured data series. For nitrogen, only the total concentration had been measured, whereas it was the dissolved fraction that was applied in the model. The dissolved part was assumed to be a fixed fraction of the measured total concentration, namely 0.4.

The outflow was simulated as a short pipe connected to a water brake. In other words, up to a certain cut-off level, the outflow increased as a constant multiplied by the square root of the water depth. An overflow became active at high water levels in the pond. The outflow carried dissolved phosphorus, dissolved nitrogen, suspended algae, dissolved oxygen and DIC out of the pond, corresponding to the concentrations in the pond at that time step.

Energy entered the model as radiation through the surface of the ponds. The input radiation was determined by the measured time series of meteorological data. Absorption and dispersion causes radiation to decline through the water column. The radiation penetrating the water column (*I*), or better, the light intensity at a given depth, was in the model described by equation *a* (Jørgensen and Bendoricchio, 2001).

$$I = I_0 e^{-(\alpha + \beta X_{PP})z} \qquad (a)$$

The parameters in this and the following equations are explained in the nomenclature.

O_2 and CO_2 entered and left the modeled pond over the water surface due to gas/liquid mass transfer (reaeration), where the driving force was the difference between the saturation concentration and the actual (modeled) concentration. However, the gas/liquid mass transfer is also highly influenced by wind, and several equations describing this interaction have been proposed (Ro and Hunt, 2006; Ro *et al.*, 2007; Wanninkhof, 1992). In the present study equation *b* was applied (Ro and Hunt, 2006). This equation was chosen over others due to the high influence of the wind speed (in the power of 1.81), as high influence of wind speed on dissolved oxygen and pH was observed by inspecting the measured data series.

$$K_L = 170.6\,\mathrm{Sc}_{O_2/DIC}^{-0.5} U_{10}^{1.81} \left(\frac{\rho_a}{\rho_W} \right)^{0.5} \theta_{wg}^{T-20} \qquad (b)$$

2.3.2 Primary producers

Primary producers were subdivided into three groups: *PP* (phytoplankton), *MP* (rooted macrophytes) and *BA* (benthic algae including epiphytes). The different behavior of these groups was modeled by different growth, decay and respirations kinetics. Furthermore, macrophytes were modeled as capable of taking up a fixed ratio of their nutrients directly from the sediment. The two other groups of primary producers were modeled to assimilate nutrients from the water phase only. Additionally, only phytoplankton was washed out from the pond by the discharged water. *PP* and *MP* performed photosynthesis in the entire water column, whereas the *BA* only existed in the bottom layer.

Growth of primary producers and thereby biomass performing photosynthesis was described by equation *c*, where *X* and μv_{max} represent the parameters for *BA*, *MP* and *PP*, respectively.

$$\mu_{max}\frac{I}{I+K_I}\left(\gamma+\frac{(1-\gamma)S_N}{S_{N+}K_N}\right)\left(\gamma+\frac{(1-\gamma)S_P}{S_P+K_P}\right)\frac{S_{DIC}}{S_{DIC}+K_{DIC}}X\,\theta_{grd}^{T-20}pH_{inhib} \qquad (c)$$

It is well known that within these three groups of primary producers, maximum growth rates, half saturation constants, light dependencies, and nutrient requirements are, among others, highly diverse (Jørgensen *et al.*, 1991; Carpenter and Lodge, 1986; Sand-Jensen and Borum, 1991; Schladow and Hamilton, 1997). However, as the development and abundance of different species in the ponds had not been studied, only these three groups were chosen and no consideration was given to individual species.

The respiration and decay of the primary producers was described by equations *d* and *e*, respectively. *X* , k_R and b_D represent the parameters for *BA*, *MP* and *PP*, respectively.

$$k_R\theta_{grd}^{T-20}X\ pH_{inhib}\ switch \qquad (d)$$

$$b_D\theta_{grd}^{T-20}X\ switch \qquad (e)$$

2.3.3 Dissolved oxygen

Oxygen was produced by photosynthesis (*c*) and used by respiration (*d*) and by mineralization of the sediment. The latter process, the sediment oxygen demand (SOD) was described by equation *f*. The flux of oxygen into the sediment was assumed instantaneously, that is, no diffuse boundary layer and sediment diffusion processes were explicitly included in the model.

$$R_{SOD}\theta_{SOD}^{T-20}\frac{S_{O_2}}{S_{O_2}+K_{O_2}}\frac{A_{pb}}{V_p}pH_{inhib} \qquad (f)$$

Moreover, oxygen enters or leaves the system by gas/liquid mass transfer (reaeration) across the pond surface, equation *g*.

$$K_{L,O_2}a\left(S_{O_S}-S_{O_2}\right) \qquad (g)$$

2.3.4 Inorganic carbon

Inorganic carbon was assimilated by photosynthesis (*c*) and produced by respiration (*d*) and by mineralization of sediment (*f*). Furthermore, CO_2 was exchanged over the pond surface by gas/liquid mass transfer, equation *h*.

$$K_{L,CO_2} a\left(S_{C_S} - S_{CO_2}\right) \tag{h}$$

2.3.5 pH

The pH of the water was calculated from the DIC assuming that only carbonate species affect the total alkalinity of the water. This assumption is justified when other species that may affect the alkalinity are present in low concentrations compared to DIC. In the ponds, pH was almost always above 7. Assuming CO_2-equilibrium between water and atmosphere at a pH of 7 yields a corresponding DIC concentration of 67 µmole L^{-1}. A main candidate for another compound affecting the alkalinity in stormwater ponds is phosphate. In the water phase of the ponds phosphate was typically below 0.1 mg L^{-1} (3 µmole L^{-1}), i.e. the concentration of DIC at equilibrium was typically significantly higher than the concentration of phosphate. Similarly conditions exist for other compounds such as ammonia, or organic acids, which also could potentially affect the alkalinity.

2.3.6 Nutrients

Phosphorus and nitrogen were assimilated during photosynthesis and produced during respiration and mineralization of the sediment. The assimilation and production were modeled as a fixed ratio to the assimilation and production of inorganic carbon, respectively.

2.3.7 Process matrix

A process matrix is a systematic arrangement of stoichiometry and process kinetics, which is routinely applied when communicating models of activated sludge, anaerobic sludge digesters, and transformations in sewer networks (e.g. Henze *et al.*, 1987; Hvitved-Jacobsen, 2001; Nielsen *et al.*, 2006). This arrangement is adapted to the present study, as it gives a ready and clear overview of processes and compounds included in the model, Table 2. In the matrix, each row represents a process (e.g. growth of primary producers) and each column represents a model component (e.g. phytoplankton biomass (X_{PP})). The matrix of processes and components is multiplied by the process rates described in the previous text and stated in the column furthest to the right.

2.4 Calibration

The model was calibrated by systematic adjustment of the parameters. Each parameter was changed within ranges found in literature (Table 3), one at a time. This procedure was repeated until the calibration was satisfactory. The best agreement between modeled and simulated time series of pH and dissolved oxygen was determined by visual comparison. This approach was chosen instead of minimizing the numerical simulation error, for example in terms of the minimum numerical distance between measured and simulated values of pH and dissolved oxygen, because different aspects of the time series were assigned different weights. For example, was it at the same time attempted to obtain a good simulation of diurnal variations and of variations covering the time-scale of weeks and months. A numerical fitting method would in such case not give better simulation results per se.

2.5 Sensitivity analysis

A sensitivity analysis was carried out to evaluate the response of the model to input parameter uncertainty. Several methods for sensitivity analysis exist (e.g. Jørgensen and Bendoricchio, 2001; Spitz and Moreno, 1996; Brito and Newton, 2011). In the present study the method presented by Brito and Newton (2011) was applied. In this method, each parameter, one at a time, was changed by ±30% with base in its value obtained by the calibration. Sensitivity indexes were calculated by applying equation *i*.

$$S_i = \frac{|\Delta h_i| / h_i}{|\Delta P| / P} \qquad (i)$$

For each state variable and for each parameter, the mean of *S* has been calculated over three days of model output.

3 Result and discussion

The period from July 1, 2008 to January 1, 2009 was chosen for calibration and validation of the model. During this period the pond in Aarhus received a total inflow of 49,830 m^3 corresponding to a mean hydraulic residence time in the pond of 25 days. The accumulated nutrient load was 93 kg total-N, 14.5 kg total-P and 6.3 kg ortho-P. The pond in Odense received 44,490 m^3 corresponding to a mean hydraulic residence time of 8.3 days. The accumulated nutrient load was 123 kg total-N, 15.3 kg total-P and 8.2 kg ortho-P. Comparing the actual received water volumes to the design values (Table 1), it is seen that the pond in Aarhus received less runoff than expected in the design, while the pond in Odense received more than it was designed for. This resulted in a significant difference in hydraulic retention times of the two ponds. Furthermore, the pond in Aarhus received slightly less nutrients compared to the pond in Odense.

The data series from the on-line sensors in the two ponds were of high quality and revealed much information about the dynamics in the stormwater ponds. Fluctuations in pH, dissolved oxygen as well as temperature were significant, both over the year but also over single days (Figure 2, 3, 4 and 5). For example, the pond temperature in both Aarhus and Odense fluctuated with 1-2°C over a dry weather summer day, while the dissolved oxygen concentration fluctuated with as much as 6-9 gO_2 m^{-3} and the pH with up to 1 unit. Moreover, the pond in Odense was from time to time highly supersaturated and during prolonged periods, the dissolved oxygen concentration was above 20 mg L^{-1} – the detection limit of the applied O_2 sensors. The pH in the ponds was generally high with annual average values around 7.5 to 8. Lower and higher values occurred, and pH ranged from below 7 to above 10 (the latter being the detection limit of the applied pH sensor). The variability in dissolved oxygen and pH was generally higher in Odense compared to Aarhus, Figure 2.

3.1 Calibration

The calibration of the model was carried out on 6 consecutive months of the data series from Aarhus, with equal focus on pH and dissolved oxygen. Literature values and ranges for all 28 input variables are shown in Table 3.

It was not possible to identify studies that quantified the growth, respiration and decay of relevant freshwater benthic algae. Furthermore, it was no possible to find studies that quantified the ratio of nutrient uptake for macrophytes. However, several publications address algae and plant dynamics in eutrophic lakes and they reveal mechanisms describing interactions between such groups of primary producers (Sand-Jensen and Borum, 1991; Carpenter and Lodge, 1986; Barko and Smart, 1981; Madsen and Cedergreen, 2002; Xie *et al.*, 2005). Based on this literature it was chosen to assign the same values to parameters quantifying respiration and decay of *BA* and of *PP*. The growth rate of *BA* was chosen slightly lower than that of *PP*. For *MP*, the ratio between uptake of phosphorus and nitrogen from the water column and from the sediment depends both on plant species, on concentration of nutrients in the water column and on the age of the plants. For the simulations it was assumed that *MP* took up 50% of their phosphorus and nitrogen from the sediment (Mulderij *et al.*, 2007) which gave them a significant advantage when nutrient limitations occurred in the water column. Literature values together with the values applied for calibrating the model are shown in Table 3.

It was possible to calibrate the model to at dataset covering 6 months, making use of parameter values within the range reported in the referred literature (Table 3). $\mu_{max,PP}$ was during the calibration identified as one of the most important parameters for a good agreement between model and measurements. While the value for this parameter was within the range of reported literature values, it was, however, in the high end of that range. This could be interpreted as an indication of good conditions for growth of phytoplankton in the pond. This assumption is consistent with visual inspections of the pond during summer, which revealed high concentrations of phytoplankton. Furthermore, the average chlorophyll concentration in the Odense pond in the period from beginning of May to end of August 2009 was on average 288 µg L^{-1} (determined on 11 samples equally distributed over this period). During calibration, K_I was observed to be the half saturation constant having the most influence on the simulations. K_I was found mainly to control the shift in the goodness of the simulation when going from summer to winter. That is, the shift from the summer period that had large diurnal fluctuations in dissolved oxygen and pH, to the winter period that had significantly smaller fluctuations. K_I does so by determining the minimum intensity of light needed for growth (eq. *c*). R_{SOD} and $k_{R,BA}$, $k_{R,MP}$ and $k_{R,PP}$ are the main parameters determining the consumption of O_2. $k_{R,BA}$, $k_{R,MP}$ and $k_{R,PP}$ were observed to be of most importance during summer when the content of algae was high, while R_{SOD} was important all year round. The calibrated value for R_{SOD} was in the lower end of the range reported in the referred literature (Table 3). It can be explained by the pond being rather new. Its construction was completed only a few months prior to the start of the data collection, limiting the quantity of organic matter accumulated as sediment at the bottom of the pond.

Figure 3 shows the modeled and measured concentrations of dissolved oxygen and pH from mid-summer to mid-winter. Despite the long time span and high resolution of measured data there is a good overall agreement between modeled and measured data series. However, during some days, short-term variations in dissolved oxygen of several mg L^{-1} were seen on the time scale of minutes to a few hours. The same was observed for pH, where short-term variations from time to time were up to one pH-unit. These variations could not be simulated and are believed to be sensor artifacts due to growth and particle deposition on the sensor membranes.

In general, the model could reproduce the large dissolved oxygen and pH fluctuations measured during summer as well as the smaller fluctuations measured during winter, Figure 3. Furthermore, the model simulates the low dissolved oxygen concentrations measured around mid-July and the beginning of August. However, towards the end of September quite low levels of dissolved oxygen and pH were modeled but not seen in the measured data series. Relative low wind speeds measured during this period were identified as the cause hereof. That is, the model consumption of dissolved oxygen due to respiration and to SOD was larger than the O_2 supplied by reaeration. This lead to low dissolved oxygen concentration and a low stripping of CO_2, the latter then lead to a low pH. Moreover, during summer some rather large fluctuations in dissolved oxygen were observed together with some comparatively small fluctuations in pH. As processes affecting dissolved oxygen and pH were strongly linked (Table 2), it was problematic to reproduce this pattern. The best calibration to reproduce this pattern lead to problems in reproducing the comparatively low dissolved oxygen concentrations observed during winter. Therefore, two additional calibrations were carried out: one for summer (August 2008, 31 days) and one for winter (November/December 2008, 56 days), Figure 4 and 5.

3.1.1 Summer calibration

To achieve better agreement between model simulations and measurements during summer, the respiration of PP and BA were increased and the SOD lowered, Table 3. The calibrated model could not simulate the high concentrations of dissolved oxygen observed during daylight without producing too large diurnal pH fluctuations. That is, the calibrated model was a compromise between optimal simulation of dissolved oxygen and pH, Figure 4. However, there was a high degree of agreement between measured and modeled dissolved oxygen levels during night time. Furthermore, there was good agreement between measured and modeled pH. However, the simulated levels during night time were slightly on the low side. Overall, the model could be brought in reasonable agreement with the measured data during the calibration period.

3.1.2 Winter calibration

The overall pattern of both dissolved oxygen and pH during winter was well simulated, Figure 5. The winter calibrations clearly showed the high sensitivity of the model towards the wind speed, causing the original choice of equation *b* as the model for the gas/liquid mass transfer. The high dependency on wind speed caused a rapid mass transfer of modeled CO_2 and O_2 when wind speed increased. As the dissolved oxygen concentration in the pond typically was several mg L^{-1} below saturation, and the pond at the same time was supersaturated with CO_2, the corresponding mass transfers caused fluctuations in dissolved oxygen and pH. This is well illustrated by, for example, the period December 13-15 where strong winds caused significant increases in dissolved oxygen as well as pH. To achieve the rather low dissolved oxygen concentrations observed during winter, it was necessary to increase the value of R_{SOD} during winter compared to summer. The contrary would seem more logical as bacterial activity decreases during winter due to low temperature. However, the oxygen utilization of the pond sediment was probably not as much limited by temperature as by the availability of organic matter. In other words, the SOD should be less dependent on temperature. It is not well understood why the SOD increased in winter but could be related to the observation that the Aarhus pond received illegal discharges of septic wastewaters or that the pond has got older and more organic matter has accumulated at the bottom. In the model, an Arrhenius term (equation *f*) was applied in the calculation of the SOD, which probably caused the need to increase the value of R_{SOD}.

3.2 Sensitivity analysis

A sensitivity analysis was carried out for all input parameters included in the calibration. The analysis was carried out with respect to both dissolved oxygen and pH. Figure 6 and 7 show the 15 most influential parameters determined by the analysis. The most influential parameters identified in the sensitivity analysis were pH_{runoff}, the three temperature constants and $\mu_{max,PP}$. These parameters all had a substantial influence on the daily fluctuation of dissolved oxygen and pH, together with the general level of pH (pH_{runoff}). The least influential parameters were the three decay rates.

3.3 Validation

Validation was carried out on the Odense pond applying the model parameters obtained from the summer and winter calibration on the Aarhus pond (Table 3). The input to the model was the measured flow, water quality and climate data from Odense, and the simulations were compared with measurements of the corresponding pH and dissolved oxygen, Figure 8 and 9. The simulations were done on the same time period as for the calibrations, e.g. August and November/December 2008.

From Figure 8 it is clear that the validation yielded poor agreement between modeled and measured summer data. The fluctuations of pH and O_2 in the Odense pond were significantly larger than those measured in the Aarhus pond, and the model was not capable of reproducing these by applying the parameter values obtained in the calibration on the Aarhus pond. However, except for the first seven days, the simulated and measured levels varied together in time. That is, when the measured data increased the simulated also increased, however, not to the same extent.

For the winter validation, the pH of the runoff entering the pond (pH_{runoff}) was changed from 8.4 to 8.0, due to a generally lower pH level in the Odense pond. The high levels of pH and dissolved oxygen observed during the first seven days of this month could not be simulated, Figure 9. No obvious explanation for these rather high levels could be identified. The validation for the rest of the month was, however, reasonable when it came to the general level of pH and dissolved oxygen. However, modeled pH as well as modeled dissolved oxygen fluctuated more than the measured values. The cause was identified as being the models sensitivity towards wind speed, Figure 6 and 7.

While the validation of the model was acceptable for winter conditions, it was not convincing for summer conditions when the activity of the primary producers was high. However, it was possible to calibrate the model to the Odense pond applying another set of parameters (results not shown). This observation might well hold true for other ponds also, and it is deemed probable that a dedicated calibration would be needed for each pond the model is applied to. Differences in calibration parameters could be caused by numerous factors, examples of such being variations in physical pond characteristics such as water depths and geometry, variations in wind sheltering, or different composition of the stormwater with respect to compounds inhibiting biological processes. The latter was a known problem for the pond in Odense where illicit discharges of heavy metals occurred sporadically. Yet, none of these factors were explicitly included in the model as their influence could not be quantified. Another explanation could be the significant difference in loads of water and nutrients on the two ponds. The hydraulic load on the Odense pond was three times larger than the hydraulic load on the Aarhus pond, and the nutrient load was approximately 4 times larger. This might have selected for different species of primary producers in the two ponds, and hence for different growth characteristics.

3.4 Application of the model

Regardless of a high nutrient load on the ponds, no significant oxygen depletion or harmful high pH were observed. This could be explained by the, compared to natural lakes, high exchange rate of water in the stormwater ponds, causing the phytoplankton to be washed out before it caused, for example, significant oxygen depletion. This explanation was supported by the simulated algae biomass in the pond in Aarhus, Figure 10. Here it is seen that the *PP* biomass decreased when stormwater runoff was introduced to the pond, i.e. when exchange of water took place. In primo August a period of heavy rain occurred, halving the *PP* biomass within a few days. Furthermore, as early as mid-October, the *PP* biomass had become insignificant due to a combination of low growth rates caused by decreased solar radiation and washout caused by increased runoff. This washout of *PP* then gave the *MP* and *BA* biomass an opportunity for a bloom. The *MP* and *BA* achieved its maximum biomass as late as the beginning of October. In absolute terms, this biomass maximum was, however, still rather low compared to the biomass maximum achieved by the bloom of *PP*.

The simulated maximum in *PP* biomass was approximately 12 gC m^{-3}, Figure 10. Assuming a carbon to chlorophyll ratio of 50 mgC mgChl^{-1} (Jørgensen *et al.*, 1991), the simulated PP corresponded to 240 µgChl L^{-3}. In the following summer (2009), the chlorophyll concentration in the Aarhus pond was measured and on average found to 288 µg L^{-3}. Even though these simulated and measured chlorophyll concentrations correspond to two different growth seasons, the agreement in magnitude is deemed to support the simulation results.

Besides explaining observations made on primary producers in stormwater ponds, the developed model has potential as a planning and design tool for new stormwater ponds. Even though the model is far from perfect, as the validation on the Odense pond clearly showed, it is in principle capable of predicting how different load patterns and land uses affect the presence of primary producers. It is also capable of assessing the sensitivity of primary producer growth on pond geometry. It can for example answer questions on how an increased or decreased water depth affects dissolved oxygen and pH in the pond. The deeper the pond, the less the footprint and hence, the less the land cost of the pond. Today, stormwater ponds are seldom designed deeper than 1.5 m as engineers want to avoid low dissolved oxygen (Hvitved-Jacobsen *et al.*, 2010). It is probably a rather conservative choice and water depths could in many situations be increased, leading to decreased investment costs. Similarly, other design characteristics could be assessed by applying the model, for example the effect of outlet flow restriction or the effect of compartmentalizing the pond.

4 Conclusion

The model could be successfully calibrated to a Danish stormwater pond. However, validation of the model applying the calibration parameter set on another pond was not satisfactory. The cause might have been differences in characteristics not captured by the model, for example difference in primary producer species, differences in runoff quality, differences in pond geometry or differences in shelter conditions.

The model showed that the intermittent flow pattern and comparative short hydraulic residence times strongly affected the presence of different groups of primary producers. For example, the phytoplankton washed out from the pond in the late summer, resulting in a bloom of macrophytes and benthic algae in the late autumn.

The model is deemed a potential tool for improving the design of stormwater ponds by taking the behavior of the plant ecosystem into account. It has the potential to yield information on parameters critical for design, for example levels of pH and dissolved oxygen. Also the prediction of phytoplankton is an issue as stormwater ponds not only serve as treatment facilities but also as recreational water bodies in the city.

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Table 1: Pond and catchment characteristics

	Unit	Odense	Aarhus
Type of catchment		Light industry	Residential (blocks of flats)
Total catchment area	ha	27.4	57.4
Impervious catchment area	ha	11.4	25.8
Permanent wet volume	m^3	1,990	6,900
Retention volume	m^3	1,992	1,400
Permanent water depth, max	m	1.45	1.25
Length to width ratio	-	4.5 : 1	3:1
Average precipitation	mm y^{-1}	657	661
Annual design runoff	m^3	55,500	131,900

Table 2: Matrix formulation of the stormwater pond eutrophication model

	X_{PP}	X_{BA}	X_{MP}	S_{O2}	S_{Psol}	S_{Nsol}	S_{DIC}	Process Rate
Growth of *PP*	*1*			$Y_{O2:C}$	$-Y_{P:C}$	$-Y_{N:C}$	$-Y_{C:C}$	Equation *c*
Respiration of *PP*	*-1*			$-Y_{O2:C}$	$Y_{P:C}$	$Y_{N:C}$	$Y_{C:C}$	Equation *d*
Decay of *PP*	*-1*							Equation *e*
Growth of *BA*		*1*		$Y_{O2:C}$	$-Y_{P:C}$	$-Y_{N:C}$	$-Y_{C:C}$	Equation *c*
Respiration of *BA*		*-1*		$-Y_{O2:C}$	$Y_{P:C}$	$Y_{N:C}$	$Y_{C:C}$	Equation *d*
Decay of *BA*		*-1*						Equation *e*
Growth of *MP*			*1*	$Y_{O2:C}$	$-Y_{P:C}$	$-Y_{N:C}$	$-Y_{C:C}$	Equation *c*
Respiration of *MP*			*-1*	$-Y_{O2:C}$	$Y_{P:C}$	$Y_{N:C}$	$Y_{C:C}$	Equation *d*
Decay of *MP*			*-1*					Equation *e*
Sediment oxygen demand				*-1*	$Y_{P:O2}$	$Y_{N:O2}$	$Y_{C:O2}$	Equation *f*
Gas/liquid mass transfer, oxygen				*+1*				Equation *g*
Gas/liquid mass transfer, CO_2							*+1*	Equation *h*

Table 3: Literature values and ranges of input parameters together with the values applied for the calibration and sensitivity analysis. Note that parameter units might differ from the nomenclature

Parameter	Unit	Literature values and ranges	Applied value		
			General	Modifications from general calibration	
				Summer	Winter
$b_{D,BA}$	d^{-1}		0.001		
$b_{D,MP}$	d^{-1}	0.001[c]	0.001		
$b_{D,PP}$	d^{-1}	0.001-0.125[e], 0.88[i]	0.001		
K_{DIC}	$gC\ m^{-3}$	0.83-5.3[g], 0.36-9[h]	5.3		
K_I	$J\ m^{-2}\ s^{-1}$	4.8-18.1[b], 7.2[d], 6.7[f], 35.7[f], 35.4[l], 2.2[l]	11.1		
K_N	$mgN\ m^{-3}$	25[d], 1.4-980[c], 0-500[e], 47[l]	2.5		
K_{O2}	$gO_2\ m^{-3}$		0.5		
K_P	$mgP\ m^{-3}$	1.4[a], 5.9[a], 0.5[b], 0.2-1500[c], 3[d], 1-30[e], 11[l]	6		
$k_{R,BA}$	d^{-1}		0.8	0.92	
$k_{R,MP}$	d^{-1}	0.018[c]	0.018		
$k_{R,PP}$	d^{-1}	0.03-0.92[c], 0.001-0.171[e], 0.08-0.1[m]	0.8	0.92	
$pH_{optimum}$	-	6.31-6.84[n], <6.5[o], 8[p]	6.7		
pH_{runoff}	-	7.37-8.07[q], 4.5-10.1[r]	8.4		
R_{SOD}	$gO_2\ m^{-2}\ d^{-1}$	0.02-50[c]	1.7	1.6	2.8
$Y_{C:O2}$	$gC\ gO_2^{-1}$	2.67-4.21[k], 3.1[c]	0.375		
$Y_{N:C}$	$gN\ gC^{-1}$	0.25[d], 0.18[k], 0.15[l]	0.18		
$Y_{N:O2}$	$gN\ gO_2^{-1}$		0.068		
$Y_{O2:C}$	$gO_2\ gC^{-1}$	2.67-4.21[k]	2.67		
$Y_{P:C}$	$gP\ gC^{-1}$	0.025[d], 0.008[j], 0.019[j] 0.024[k]	0.024		
$Y_{P:O2}$	$gP\ gO_2^{-1}$		0.015		
α	m^{-1}	0.2[d], 0.03-15.1[e]	0.4		
β	$m^2\ g^{-1}$		0.3		
γ	-		0.5		
θ_{grd}	-	1.02-1.14[c], 1.066[m]	1.09		
θ_{SOD}	-	1.045[c]	1.045		
θ_{wg}		1.024[s]	1.024		
$\mu_{max,BA}$	d^{-1}		5.1		
$\mu_{max,MP}$	d^{-1}	0.08-0.2[c]	0.17		
$\mu_{max,PP}$	d^{-1}	0.5[d],0.1-11[b], 1.3-3.63[e], 2.90[f], 0.1-5.65[m]	5.6		

[a] Holm and Armstrong (1981). [b] Auer and Forrer (1998). [c] Asaeda and Van Bon (1997) and references therein. [d] Mulderij *et al.* (2007) and references therein. [e] Hamilton and Schladow (1997) and references therein. [f] Storey *et al.* (1993). [g] Caperon and Smith (1978). [h] Clark and Flynn (2000). [i] Brun *et al.* (2001). [j] Thingstad *et al.* (1996). [k] Fraga *et al.* (1998). [l] Jørgensen *et al.* (1991) (average of relevant values). [m] Jørgensen *et al.* (1991). [n] Mayo (1997). [o] Necchi and Zucchi (2001). [p] Graham *et al.* (1996). [q] Dierberg *et al.* (2002). [r] Kayhanian *et al.* (2007). [s] Hvitved-Jacobsen (2001).

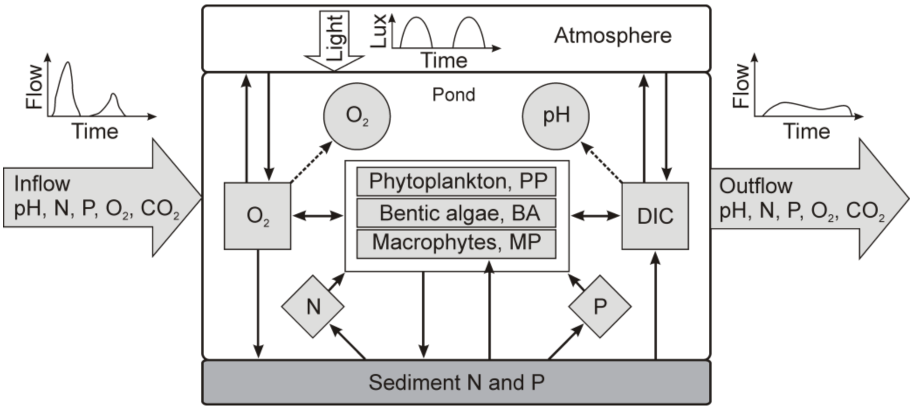

Figure 1: Schematic diagram of the eutrophication model. Wide arrows indicate interactions with the surrounding environment (water and energy). Narrow arrows indicate transformations and gain or losses of chemical compounds and diamonds are sub-parameters used to calculate the main parameters shown in the squares, which were again compared to measurements by the sensors indicated as circles.

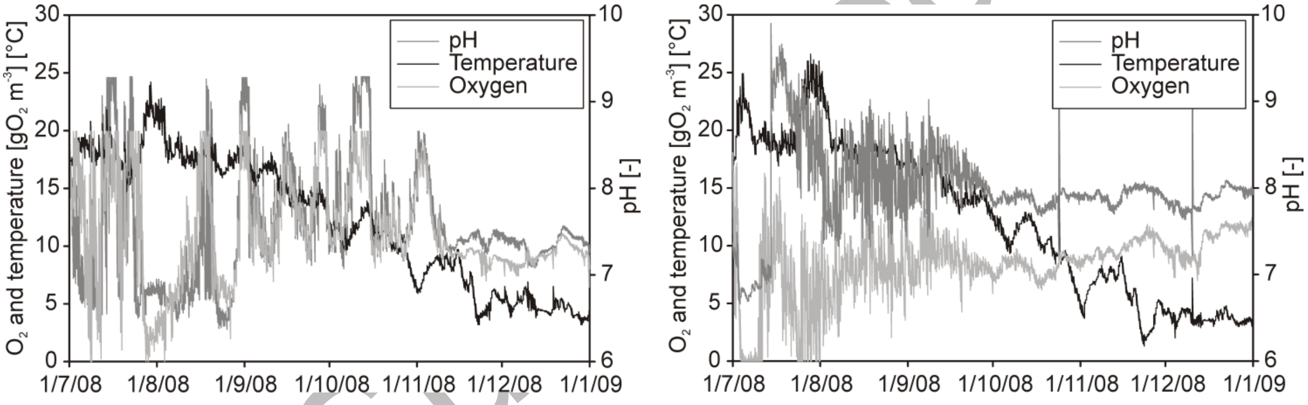

Figure 2: Temperature, dissolved oxygen and pH in the two stormwater ponds. Aarhus to the left and Odense to the right.

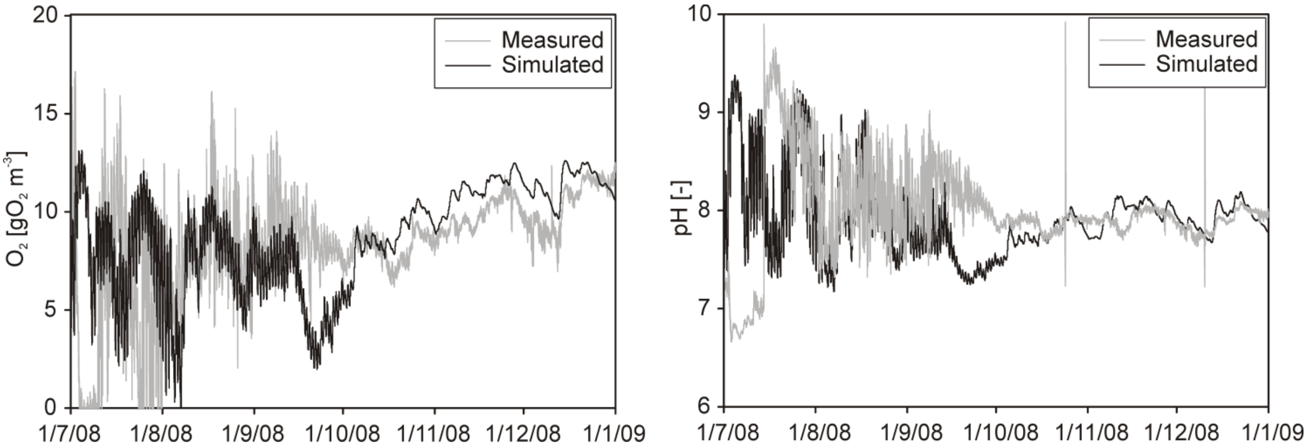

Figure 3: General calibration of the eutrophication model to the data series from the pond in Aarhus.

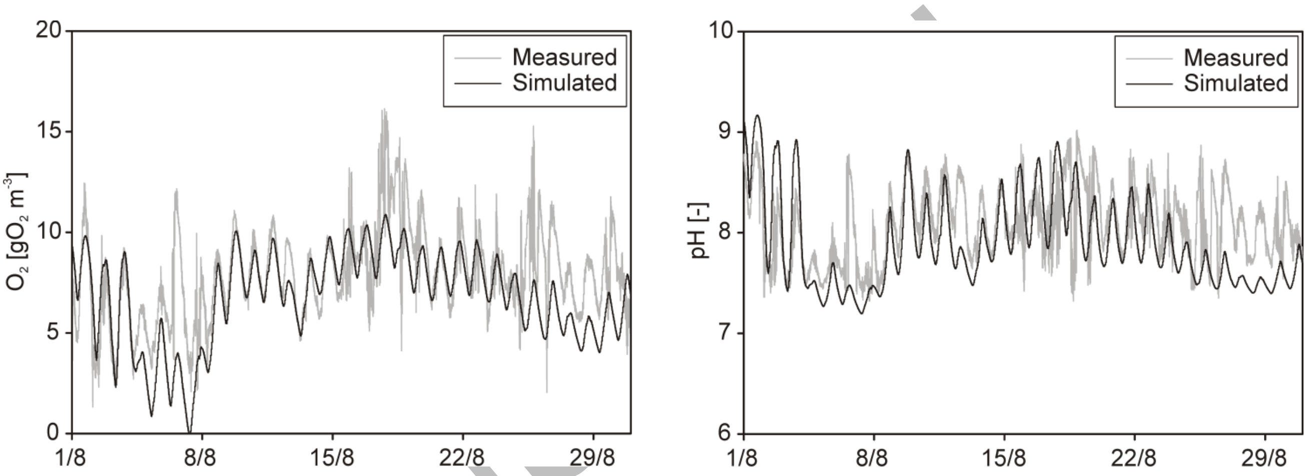

Figure 4: Summer calibration of the eutrophication model to the data series from the Aarhus pond.

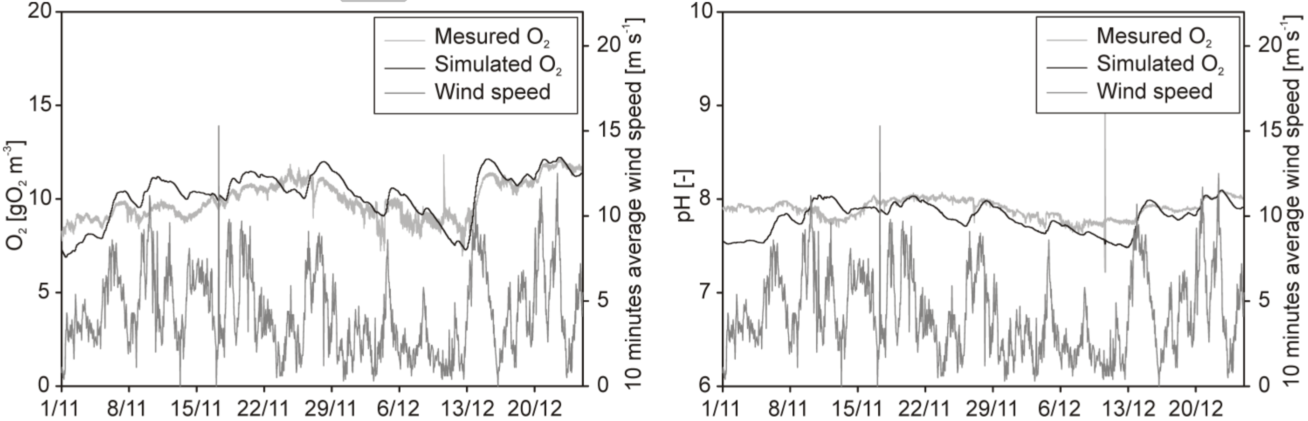

Figure 5: Winter calibration of the eutrophication model to the data series from the Aarhus pond as well as the corresponding average wind speed.

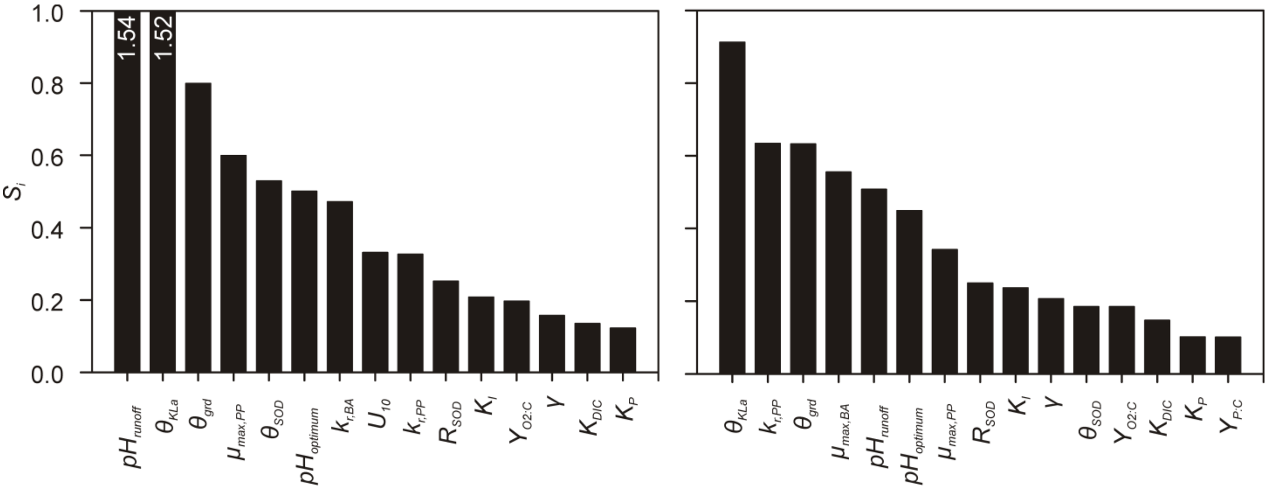

Figure 6: Sensitivity analysis with dissolved oxygen as output parameter. To the left the input parameter has been reduced by 30% and to the right raised by 30%.

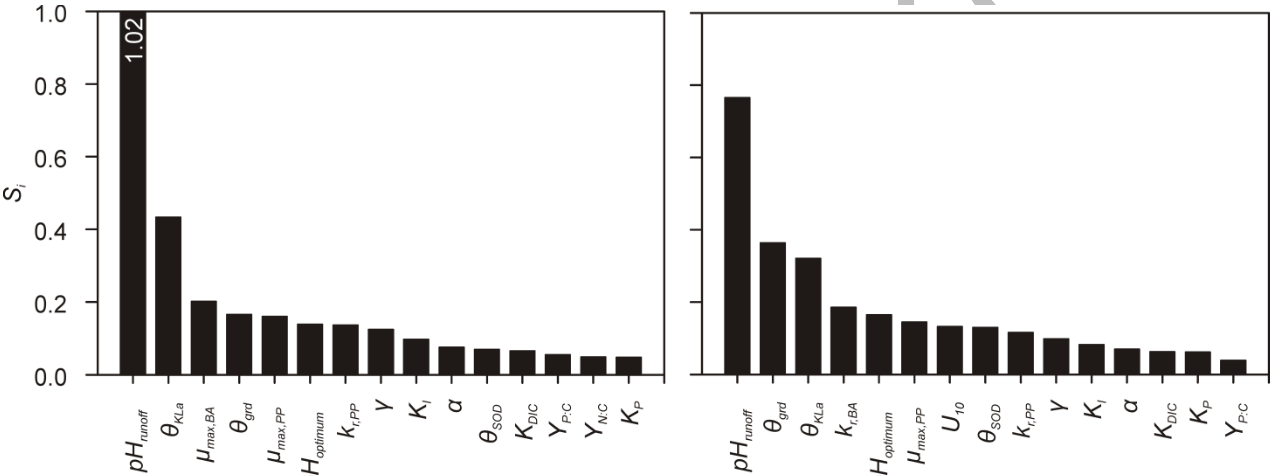

Figure 7: Sensitivity analysis with pH as output parameter. To the left the input parameter has been reduced by 30% and to the right raised by 30%.

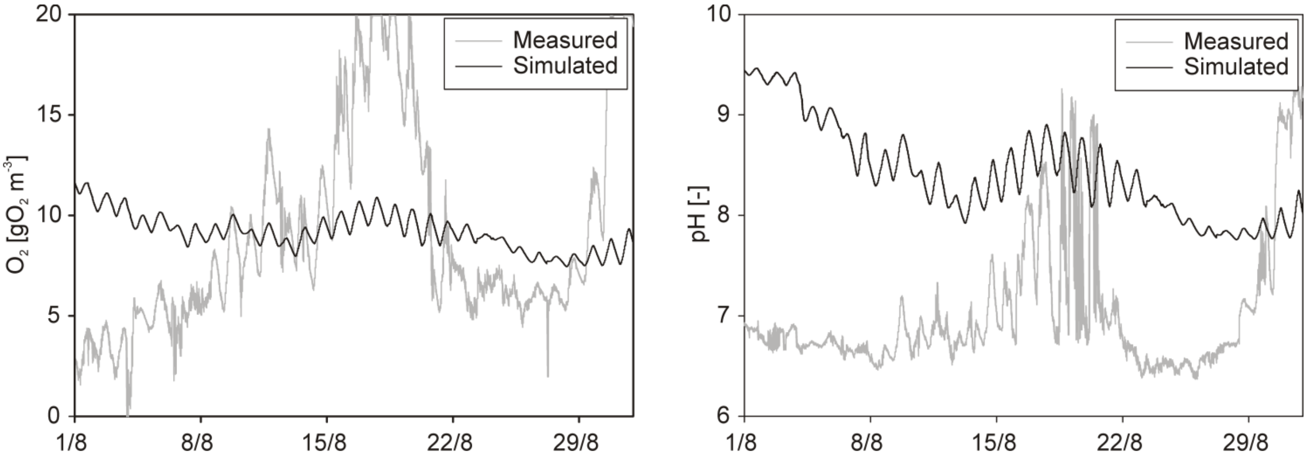

Figure 8: Validation of the summer-calibrated model using input data from the pond in Odense.

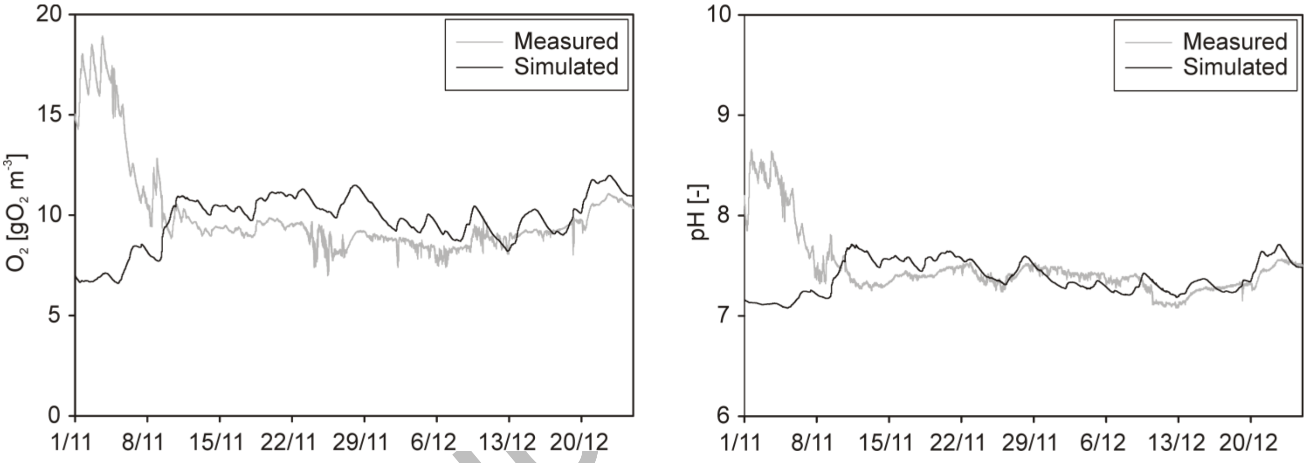

Figure 9: Validation of the winter-calibrated model using input data from the pond in Odense.

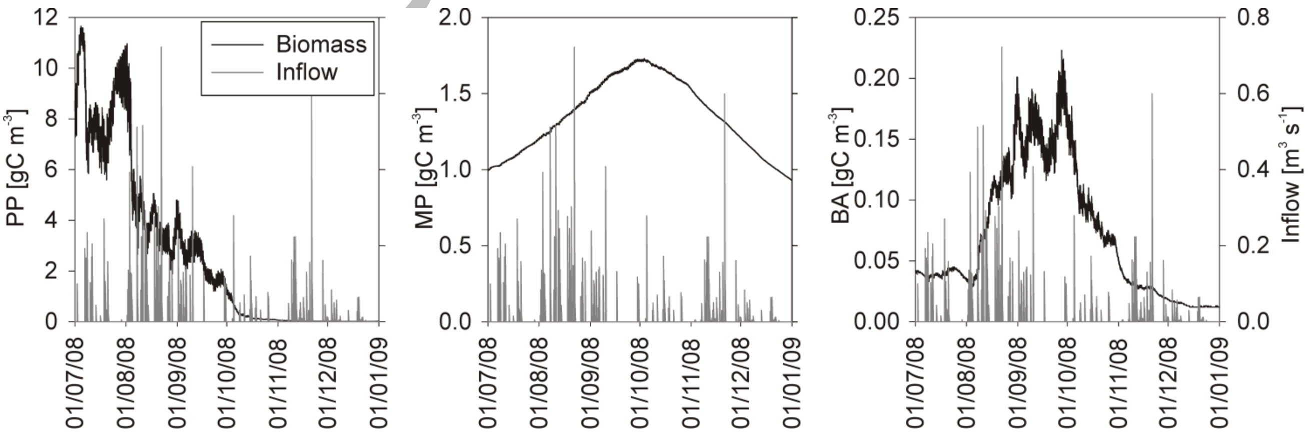

Figure 10: Simulated primary producer biomass and measured inflow to the Aarhus pond. *PP* to the left, *MP* in the middle and *BA* to the right, note the different axes for biomass.

Sorption Media for Stormwater Treatment—A Laboratory Evaluation of Five Low-Cost Media for Their Ability to Remove Metals and Phosphorus from Artificial Stormwater

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ABSTRACT: Five sorption materials were studied with a focus on polishing pretreated stormwater: crushed limestone, shell-sand, zeolite, and two granulates of olivine. These materials are commercially available at comparatively low cost and have been subjected to a minimum of modification from their natural states. The sorbents were tested for phosphorus, arsenic, cadmium, chromium, copper, nickel, lead, and zinc at concentration and conditions relevant for typical stormwater. The materials were tested for sorption capacity and kinetics. Desorption was tested under neutral and alkaline conditions and in the presence of chloride. For most sorbent/sorbate combinations, significant sorption occurred within the first minutes of contact between sorbent and sorbate. Treatment to the low microgram per liter range could be achieved by contact times of less than 1 hour. The study indicated that sorption filters can be designed for long life expectancy at comparatively low cost by applying the materials tested. *Water Environ. Res.*, **84,** 605 (2012).

KEYWORDS: sorption filter, stormwater treatment, sorption kinetics, sorption capacity, sorption isotherm, olivine, shell-sand, zeolite, limestone.

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Introduction

Stormwater from urban areas contains significant amounts of pollutants. Phosphorus causes, for example, algal bloom and subsequent oxygen depletion in receiving waters. Unlike many organic pollutants, heavy metals are not degraded and, therefore, accumulate, potentially causing acute or long-term toxic effects in the environment (Wium-Andersen et al., 2010; Marsalek et al., 1999). Consequently, treatment of stormwater to low concentration levels is often required to mitigate its potential negative ecological effects. Stormwater carries particle-bound as well as dissolved pollutants and, while technologies to remove the particle bound-fraction are well-established, technologies that remove the dissolved fraction are still largely at an experimental stage.

A stormwater treatment technology that has proven robust and efficient is the retention pond. A retention pond is an artificial lake for which a permanent water pool is combined with a detention volume that is active during runoff events. The retention pond allows flocculation, sedimentation, and degradation to occur, reducing the concentration of pollutants. The technology is especially efficient for pollutants in association with particles and suspended solids. However, the most bioavailable pollutants are those bound to colloids or truly dissolved. For this fraction, the retention pond only has limited effect and, in many cases, further treatment of the stormwater is necessary. One promising technology in this respect is filtration through sorption filters. A combination of a retention pond and a sand filter with a final step for polishing runoff water in a sorption filter is a promising technology. This combination has previously been described and tested in full scale (Vollertsen, Lange, Pedersen, Hallager, Bruus, et al., 2009).

Numerous studies have been carried out on the ability of sorption materials to remove heavy metals and phosphorus from stormwater runoff and wastewater effluents (e.g., Arias and Brix, 2005; Arias et al., 2001; Arias et al., 2003; Del Bubba et al., 2003; Jenssen et al., 2010). However, sorption capacities are often reported without specifying the sorption isotherms that relate water-phase concentrations to solid-phase concentrations at equilibrium. As the sorption capacity of a sorbent depends on the concentration in the water phase surrounding the material, this makes the results impossible to compare directly. In those cases where sorption isotherms are reported, they often were determined at rather high water phase concentrations compared with what is typical for urban and highway runoff. Subsequently, extrapolation down to concentrations relevant for stormwater runoff becomes associated with high uncertainty. However, some studies have been carried out at concentrations relevant for stormwater (e.g., Genç-Furhman et al., 2007). Furthermore, it is crucial to assess the efficiency of a sorbent when sorbates coexist (Pitcher et al., 2004; Wu and Zhou, 2009). It is also found important to take into account that sorption mechanisms are affected by temperature, pH, redox potential, contact time, and the presence of ions (Liu et al., 2004). The latter is a result of

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Table 1—Characteristics of the sorbents.

	Bulk density (g/cm^3)	Specific BET surface area (m^2/g)
Limestone	1.25*	0.59*
Zeolite	0.65–0.85**	60.30*
Shell-sand	0.8**	3.82*
Olivine I	2.81*	12.13*
Olivine II	2.31*	5.03*

* Measured.
**Given by the producer.

both changes of surface characteristic of the sorbent and changes of speciation of the sorbates present, altering competition among the ions and/or causing precipitation (Gadd, 2009). To obtain results by laboratory studies that are also valid under typical field conditions, it is important to control the environment of the tests so that conditions are realistic.

The present work aims to increase the understanding of low-cost sorption materials with potential for use in polishing pretreated stormwater runoff. It does so by studying sorption capacities and removal kinetics for substances relevant for stormwater in retention ponds. A wide range of sorption materials are commercially available. However, in the present study, focus was given on naturally occurring materials subjected to minor modification. Furthermore, low cost, high physical stability, and high sorption capacity were considered important.

Materials and Methods

Based on a literature survey, the following sorption materials were selected based on comparatively low costs, physical stability, and reported sorption potential: crushed limestone, shell-sand, zeolite, and two granulates of olivine. The following sorbents are named: limestone, shell-sand, zeolite, olivine I, and olivine II. As test sorbates, a mixture of phosphorus, arsenic, cadmium, chromium, copper, nickel, lead, and zinc was chosen, as these elements have been reported to potentially pose environmental concerns when present in stormwater (Rothwell et al., 2009; Marsalek et al., 1999; Sansalone and Buchberger, 1997). Three types of experiments were carried out with the five sorbents: study of the sorption isotherms, desorption characteristics of adsorbed sorbates, and the kinetics of sorption. All experiments were carried out with artificial stormwater containing eight sorbates (phosphorus, arsenic, cadmium, chromium, copper, nickel, lead, and zinc) in varying concentrations.

Sorption Media. To enhance the reproducibility of the experiments, all materials were sieved before use, washed with deionized water (Milli-Q from EMD Millipore, Billerica, Massachusetts), and dried at 105 °C for 5 hours. Only the 1- to 2-mm size fraction was used. The specific surface area of the media was measured by single-point BET N_2 adsorption (internal standard method) carried out by an authorized laboratory (FLSmidth, Mariager, Denmark). As similar size fractions were applied, the BET surface gives an indication of the porousness of the materials. The bulk density and specific BET surface of five types of sorbents is shown in Table 1.

Limestone. The limestone used is produced by FaxeKalk, Denmark. The material consists of a mixture of coral lime and bryozo lime. The limestone is a natural carbonatic mineral and is extracted from quarries. Subsequently, it is crushed, dried, and sieved. It has the product name ''Faxe Vandbehandlingskalk'' (Faxe Water Treatment Lime). The manufacturer states that it consists of 96.8% calcium carbonate ($CaCO_3$) and 1% magnesium carbonate ($MgCO_3$) with traces of aluminum oxide (Al_2O_3) (0.15%).

Zeolite. Zeolite is a highly porous aluminosilicate mineral originating from volcanic rocks and is extracted from quarries. Zeolite can be subdivided into different minerals. The one used in this study is Clinoptilolite ($[Ca, K_2, Na_2, Mg]_4Al_8Si_{40}O_{96} \cdot 24H_2O$) from Rota Mining, Turkey. According to the producer, the zeolite used consists of 88 to 95% clinoptilolite having a content of 65 to 72% silicone dioxide (SiO_2) and 10 to 12% Al_2O_3. The zeolite was reported without traces of the studied elements.

Shell-Sand. Shell-sand is a natural and porous carbonatic material derived from fossil deposits of mussels, crabs, and snails (Roseth, 2000). The shell-sand used is harvested from the Norwegian coastline followed by a drying, crushing, and sieving process (Einar Øgrey AS, Norway). The material consists of 33% calcium and 1% magnesium with traces of arsenic ($<$2 mg/kg), lead (5 mg/kg) and cadmium (0.05 to 0.1 mg/kg).

Olivine I and II. The mineral olivine is a magnesium iron silicate ($[Mg, Fe]_2SiO_4$) and is one of the most common minerals on earth. In the present study, two different olivine granulates have been used, produced by North Cape Minerals AS (now Sibelco Nordic), Norway. The olivine granulate is produced by crushing olivine to a powder and subsequently packing it into granulates applying a binder. According to the producer, this procedure optimizes the surface area and hydraulic conductivity. The binder contains Portland cement, which is used in different concentrations for the two types of granulate. The two granulates are referred to as olivine I and II. The cement in the binder contains chromium and has a high alkalinity. Both high pH and increased chromium concentration in full-scale filter effluent have been observed during previous applications of olivine granulates (Forsvarsbygg, 2009). As a result of these observations, the granulate production method was modified, resulting in the use of olivine II, which contains less cement than the original product, olivine I. In addition, the mineral phase composition of the two types of olivine granulate was determined by X-ray diffraction (XRD) (internal standard method) carried out by an authorized laboratory (FLSmidth, Mariager, Denmark). This XRD-analysis revealed that olivine I contained approximately 10% cement and olivine II contained approximately 3% cement. These values are subject to absolute uncertainties of 5 to 8%.

Sorption Capacity. Sorption capacities of the materials were found by batch experiments. Aquatic solutions with declining concentrations were made with deionized water and a mix of the tested sorbates. The highest initial sorbate concentration in the aquatic solution depended on the sorbent/sorbate combination and the concentration of the individual sorbates ranged from 200 to 40 000 μg/L. The concentrations were chosen based on initial tests and a desire to have maximum equilibrium concentrations in the synthetic stormwater, which were high but still relevant for natural stormwater. This resulted in the initial concentrations shown in Table 2. Four aquatic solutions with lower concentrations were made by reducing the highest initial sorbate concentrations by a factor of 2, 4, 8, and 100, respectively. For each sorbent, 10 g of material was placed

Table 2—Initial sorbate concentrations in the synthetic stormwater.

	Limestone (μg/L)	Shell-sand (μg/L)	Zeolite (μg/L)	Olivine I (μg/L)	Olivine II (μg/L)
As	200	200	200	200	200
Cd	40 000	40 000	4 000	40 000	40 000
Cr	40 000	40 000	8 000	40 000	8 000
Cu	40 000	40 000	2 000	40 000	8 000
Ni	200	2 000	4 000	8 000	4 000
P	8 000	8 000	200	40 000	4 000
Pb	40 000	40 000	40 000	40 000	40 000
Zn	40 000	8 000	2 000	40 000	4 000

in 1 L of aquatic solution. Equilibrium concentrations reached during agitation were determined by triple determination in parallel setups, resulting in 15 batches for each sorbent. In addition, blind tests with sorbent but without sorbate were conducted. The batch reactors were made of laboratory glassware and sorption at the reactor surfaces was assumed negligible.

Concentrations in the aquatic solutions were chosen by initial testing and a desire to identify equilibrium conditions for water-phase concentrations relevant for stormwater and effluent from retention ponds with sand filtration. The targeted concentration ranges are shown in Table 3.

Stock solutions of six of the eight sorbates (cadmium, chromium, copper, nickel, lead, and zinc) were made using reagent-grade nitrate salts of metals dissolved in deionized water. Commercial stock solutions were used for arsenic (1000 mg/L of As(III) in nitric acid [HNO_3]) and phosphorus (10 000 mg/L in HNO_3). The metals were added in a reduced or most stable stage. The arsenite would, to some degree, have been oxidized to arsenate in the stock solution and the exact speciation is not known. Furthermore, some oxidation of arsenite could have occurred in the aquatic solutions. Chromium was added as chromite and not chromate because chromite is typically the dominating chromium form in stormwaters and natural surface waters (Seigneur and Constantinou, 1995; Matos et al., 2009).

Relatively high concentrations of sorbates were used in some of the capacity tests, leading to low pH values because of the HNO_3 content in the arsenic and phosphorus stock solutions. Before addition of sorption material to the batches, pH was adjusted to between 3 and 4 with strong sodium hydroxide (NaOH) or sulfuric acid (H_2SO_4). The pH adjustment was carried out to ensure similar starting points for the 15 batches as well as minimize precipitation of the sorbates. Batches were gently agitated for 48 hours, after which they were left to settle, pH was determined, and a sample was extracted and filtered through a 0.45-μm GF filter. The filtered sample was acidified with pure H_2SO_4 before the concentrations of the eight sorbates were measured on inductively coupled plasma optical emission spectrometry (ICP-OES) (Thermo Scientific, iCAP 6000 series). The detection limit for phosphorus and zinc was greater than 5 μg/L; for arsenic, nickel, and copper, it was greater than 2 μg/L; and, for the rest of the elements, it was greater than 1 μg/L. The difference between the mass of a sorbate in the original aquatic solution and the mass of the sorbate in the filtrate after 48 hours of sorption was assumed to be equivalent to sorbate mass adsorbed to the sorbent.

Table 3—Reported concentrations in stormwater runoff and effluent from retention pond sand filters.

	Sand filter effluent (μg/L)	Stormwater (μg/L)
As	—	1–51[d]
Cd	0.05–0.48[a,b]	0.1–13[c]
Cr	0.5–1.1[a]	1–170[b]
Cu	2–25[a]	1–3416[c]
Ni	6–10[a]	3–190[b]
P	19–175[a]	10–674[b,c]
Pb	0.3–0.6[a]	1–33[b]
Zn	20–28[a]	5–4880[c]

[a] Vollertsen et al. (2009b).

[b] Hvitved-Jacobsen et al. (2010).

[c] Göbel et al. (2007).

[d] NURP (1983).

Data were evaluated by modeling with Linear, Freundlich, and Langmuir sorption isotherms; see eqs 1, 2, and 3, respectively. These isotherms are further described in Gadd (2009). The model parameters of eq 1 were determined by direct linear regression, the parameters of eq 2 were determined by linear regression after taking the logarithm of the equation, and the parameters of eq 3 were determined by linear regression after inverting the equation. Which model gave the best simulation of the data was determined by comparing the square of the difference between the logarithms of measured and simulated values.

$$C_S = aC_L + b \tag{1}$$

$$C_S = K_f C_L^{\frac{1}{n}} \tag{2}$$

$$C_S = \frac{K_L C_L}{1 + a_L C_L} \tag{3}$$

Where

C_S = sorbed solid-phase concentration at equilibrium (μg/g);

C_L = water-phase concentration at equilibrium (μg/L);

n = Freundlich isotherm constant related to the strength of the sorption (-);

K_f ($\mu g^{(n-1)/n}/L^{1/n} \cdot g$), K_L (L/g), a (L/g), and b (μg/g) = constants correlated with the quantity of sorbate associated with the sorbent; and

a_L = affinity parameter related to the bonding energy of the sorbate (L/μg).

Desorption. Desorption of adsorbed elements was analyzed by sequential extraction with extraction in three steps. The setup and extraction procedure followed the standard DS/EN 12457-1 (Dansk Standard Association, 2002), as did the first extraction step. Sequential extractions were made from sorbents in equilibrium with the highest initial sorbate concentration, that is, for sorbents that had absorbed the highest mass of elements. After sorption for 48 hours, sorbents were carefully washed for precipitates and dried. The removal of precipitates precludes calculations of absolute masses; however, the purpose of the test was to identify the relative desorption of elements for each extraction step and initial studies had shown the washing step to be beneficial with respect to obtaining reproducible results.

In the first step, the extraction liquid was pure deionized water, which was added to a ratio of 2 L/kg (60 mL of extraction solution and 30 g of solids). The batch was gently agitated to ensure mixing of solid and liquid for 20 hours. The batch was then left to settle, upon which 10 mL of sample was extracted, filtered (0.45 µm) and acidified (pure H_2SO_4) before storage and subsequently analyzed on ICP-OES. For the next extraction step, the liquid-to-solid ratio of 2 L/kg was maintained by adding 10 mL of deionized water. Sodium chloride was then added to a liquid concentration of 305 mg NaCl/L and the procedure described for the first extraction step was repeated. For the last extraction step, the liquid-to-solid ratio was again maintained by adding 10 mL of deionized water, upon which the pH of the batch was raised to 10.0 ± 0.2, with a 19 M NaOH solution. The addition between the extraction steps of 10 mL of deionized water for a total of 60 mL will only marginally have affected the sorbate solid–liquid equilibrium, as the mass of sorbate removed by the 10 mL of sample was low compared with the mass adsorbed to the sorbent.

The two final steps were added to simulate chemical changes that can occur in the water phase of stormwater retention ponds. The second extraction step simulates Danish winter conditions, for which NaCl is used as a deicing agent on roads, causing increased NaCl concentrations in stormwater runoff. As part of another study, Cl^- concentrations were measured in three Danish retention ponds during January 2009. In this month, road deicing was applied and the average chloride concentration in the three ponds was 185 mg Cl^-/L (Silkeborg Municipality, 2009; Vollertsen, Lange, Pedersen, Hallager, Brink-Kjær, et al., 2009), that is, corresponding to 305 mg NaCl/L. This concentration is similar to typical concentrations reported in stormwater by Göbel et al. (2007) and for two natural Swedish lakes reported by Thunqvist (2003). Significantly higher concentrations have been reported in snowmelt. However, the sorption filters are envisioned to be placed at the outlet of a wet detention pond, causing dilution of the runoff before sorption. The last extraction step was intended to simulate the high pH-levels that can occur in retention ponds during summertime (Vollertsen Lange, Pedersen, Hallager, Bruus, 2009).

Sorption Kinetics. Sorption kinetics were investigated by eight flow-through reactors operated in parallel (Figure 1). Residence times were varied to allow determination of sorption kinetics. The residence times were kept short to avoid equilibrium between sorbent and sorbate in the columns. A peristaltic pump with eight hoses pumped artificial stormwater from reservoirs to water-saturated columns containing filter media. The contact time between liquid and sorbent was varied by changing the flow through the columns by adjusting the pump rate. Contact times were 1, 5, 10, 30, 60, and—in some of the tests—720 minutes. Each column contained 5 mL of sorbent. The pH of the artificial stormwater was adjusted to 7.0 ± 0.1, with H_2SO_4 and NaOH; furthermore a concentration of 0.01 M NaCl was obtained to ensure equal chemical properties.

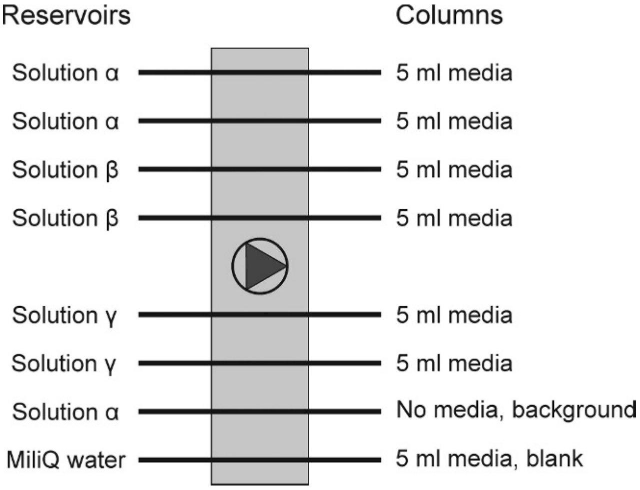

Figure 1—Schematic drawing of the setup for the column experiments. To the left are reservoirs with artificial stormwater, three different mixtures (α, β, and γ) of the pollutants in doublets (α, β, and γ), one with clean water used to reveal leakage from the sorbents, and one for determining the background sorption to the setup. To the right are seven columns with identical filter media. The background column did not contain any sorbents. The contact times were altered by changing the pump rate. This setup was repeated five times, one for each filter media.

When the contact time was altered, the effluent was not collected for analysis before three times the contact time had passed. This delay was introduced to ensure steady state in the columns and ensure that the collected effluent indeed had been in contact with the sorption medium for the chosen contact time. Hereafter, aliquots of effluent samples was collected, acidified (pure H_2SO_4), and analyzed on ICP-OES. The rest of the effluent samples were pooled and pH was measured. The order of the contact times was random to eliminate any effect on the removal rate by constant increasing or decreasing contact time.

The experiment, as illustrated in Figure 1, was repeated five times, one for each sorbent. In the reservoirs, three different solutions of artificial stormwater were held in doublets. The solutions were denominated α, β, and γ. A blank column (a column holding sorbent and receiving deionized water) was applied to reveal leakage of sorbates from the sorbent. A background column (a column receiving artificial stormwater but without sorbent) was applied to reveal sorption to the setup itself. No significant removal of sorbates was determined by the background columns; therefore, sorption to the setup was neglected in the calculations.

The artificial stormwater denominated ‘α’ held the lowest concentrations and ‘γ’ held the highest concentrations. The element concentrations covered a range of what is often found in stormwater (e.g., NURP, 1983; Hvitved-Jacobsen et al., 2010). For arsenic, cadmium, chromium, nickel, and lead, the range

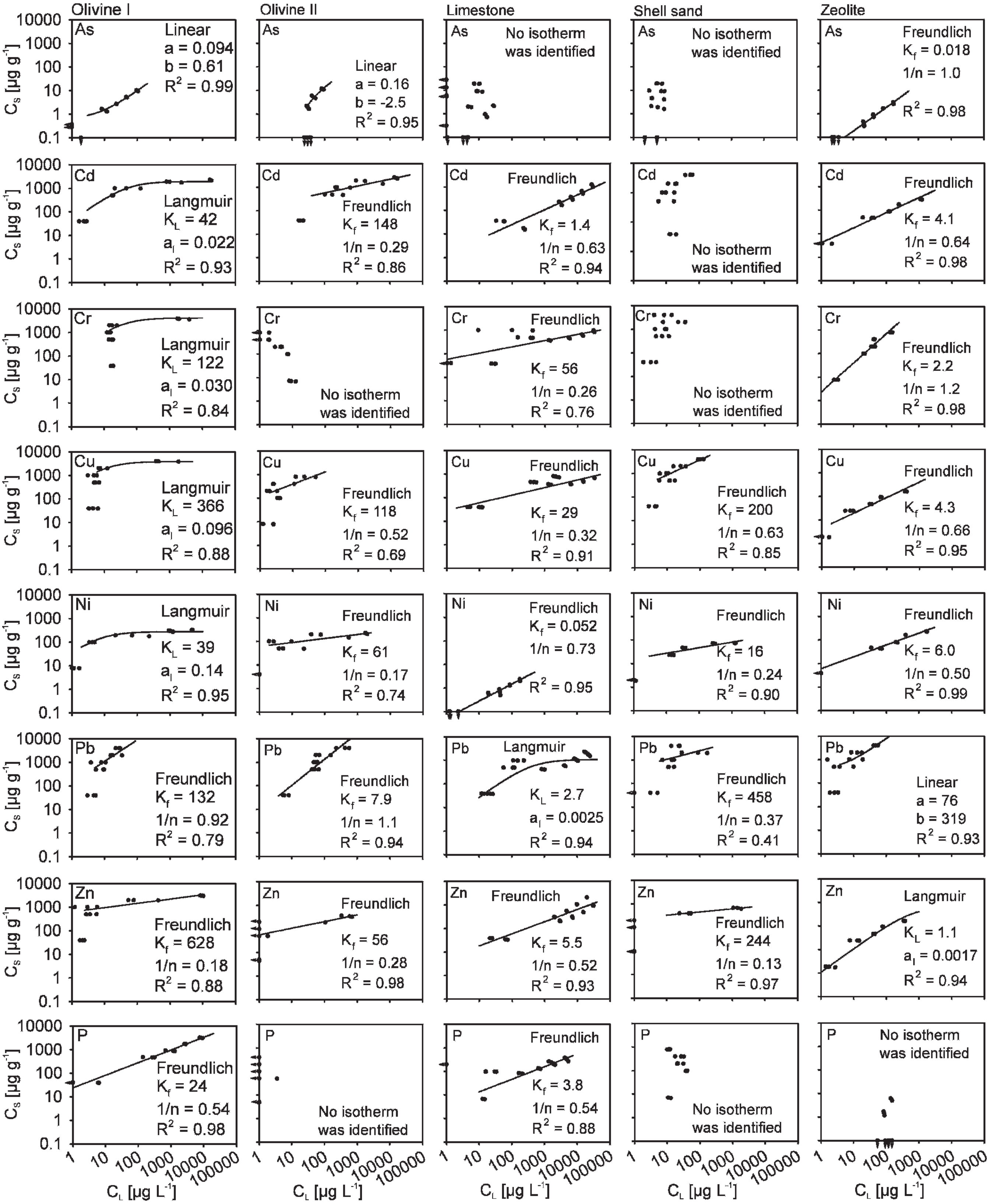

Figure 2—Measured data (circles) and modeled sorption isotherms (lines). Data points located on the axes indicate values at or below the respective values.

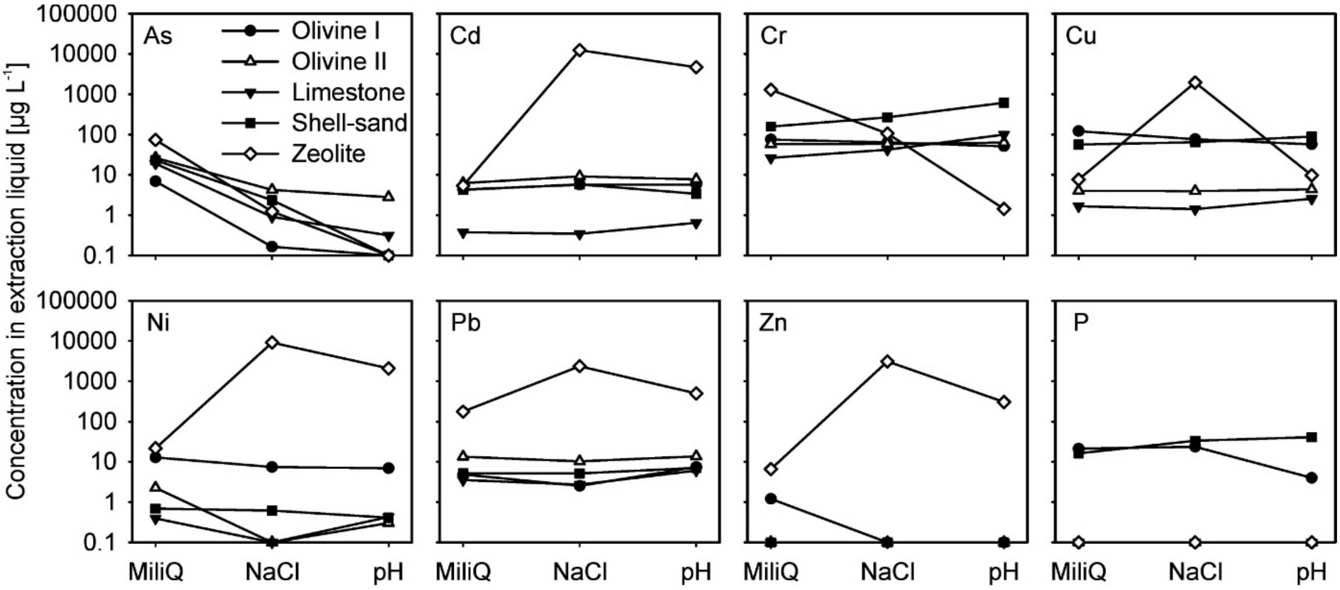

Figure 3—Concentrations of the eight elements at each of the three extraction steps. Data points located on the axes indicate values at or below the respective values.

also covered extreme concentration levels. The range of element concentrations for the sorption kinetics experiments differed from those for the sorption capacity experiments, as the initial pH differed, resulting in different solubility of compounds. Furthermore, not every experiment started with identical element concentrations, as initial precipitation in the reservoirs for artificial stormwater solution occurred to a varying degree, affecting the observed element concentrations at the inlet to the columns. The achieved range of initial concentrations were as follows: arsenic—9 to 900 µg/L, cadmium—5 to 300 µg/L, chromium—1.5 to 250 µg/L, copper—1.5 to 200 µg/L, nickel—30 to 2300 µg/L, phosphorus—90 to 9700 µg/L, lead—0.5 to 50 µg/L, and zinc—20 to 600 µg/L.

For each sorbent, aliquots of the effluent samples from the column experiment were pooled for each applied contact time and pH was measured (the blank and background were not included). This was done to reveal any changes of pH during contact with the various sorbents.

Results and Discussion

Sorption Capacity. All measured data and modeled isotherms for the five sorbents are presented in Figure 2. For some combination of sorbate and sorbent, there was a strong correlation between the water-phase concentration and the mass sorbed by the solid phase. For other combinations, this correlation was weaker or even absent at the water-phase concentrations investigated. This lack of correlation was most pronounced at low sorbate concentrations in the liquid. The goodness of correlation depended on the sorbate, and the same sorbent could express a good correlation for one sorbate while it expressed a poor correlation for another sorbate. Consequently, the occasional lack of correlation was not an artifact of the experimental conditions but a consequence of the involved sorbent/sorbate combinations and interactions. One cause of the variation is believed to be natural inhomogeneity of the tested sorbents.

For most elements, a threshold water concentration could be identified, down to which sorption occurred. Sorption to olivine I can illustrate it: chromium adsorbed to olivine I at water-phase concentrations of more than 16 µg/L, whereas no sorption occurred below this concentration. Similarly, there seemed to be a threshold for arsenic at approximately1 µg/L, for cadmium at approximately 3 µg/L, for copper at approximately 5 µg/L, for nickel at approximately 1.5 µg/L, for lead at approximately 4 µg/L, and for zinc at approximately 2 µg/L. A threshold value for phosphorus was not seen for olivine I but could exist somewhere at less than 1 µg/L. All threshold values were below the drinking water limits (tap water) in Denmark (Miljoestyrelsen, 2011), hence the limitation in performance of the materials was deemed unproblematic. For some combinations of sorbent and sorbate, a release of sorbate was observed at low initial bulk water concentrations, indicating that the sorbent contained a certain level of sorbate that was free to interchange with the liquid in which it was dissolved. An example thereof is the sorption of phosphorus to zeolite. At bulk water concentrations below approximately 100 µg/L, significant desorption of phosphorus occurred. Data points showing release of sorbate from the sorbents were excluded in the subsequent isotherm analysis.

Because of the natural inhomogeneity of the sorbent material, the means of the triplet determinations were used to determine the best isotherm for a sorbent/sorbate combination. Averages and standard deviations of the equilibrium concentrations for triplets were consequently not calculated. When determining the isotherms that best simulated the data, only data above the threshold values were included (Figure 2). In 23 out of the 40 cases, a Freundlich isotherm agreed best with the data; in three cases, a Linear isotherm was best; in six cases, a Langmuir isotherm yielded the best results; and, in eight cases, no isotherm could be fitted with reasonable accuracy.

Desorption. Desorption of the absorbed sorbates varied with sorbent, sorbate, and extraction method (Figure 3). A clear pattern for all sorbates and sorbents with respect to the

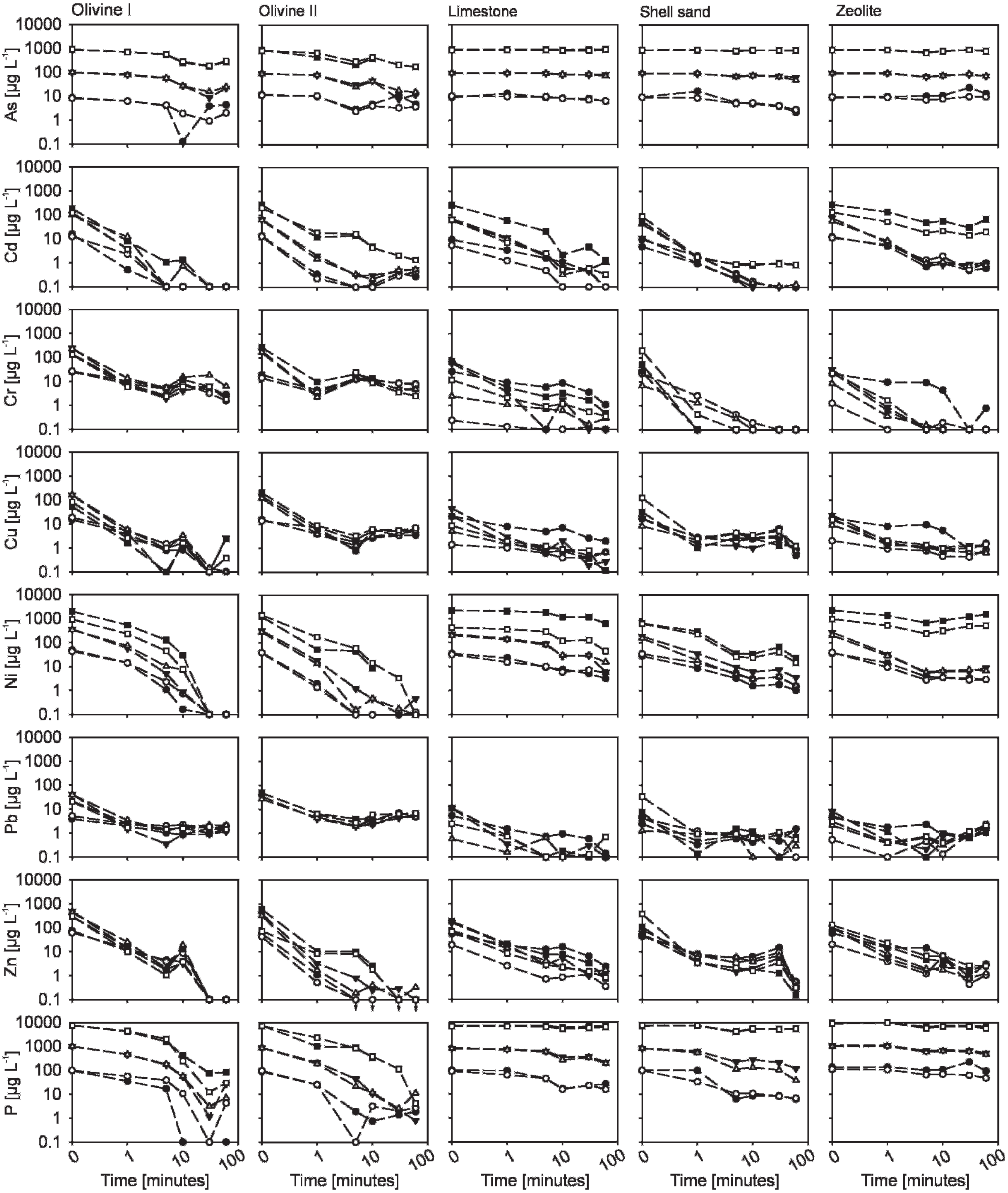

Figure 4—Measured sorption kinetics for contact times up to 60 minutes. Data points located on the axes indicate values at or below the respective values.

Table 4—Median initial removal efficiencies in percent of the original concentrations (25 and 75% percentiles are shown in brackets).

	Arsenic (% removal)	Cadmium (% removal)	Chromium (% removal)	Copper (% removal)	Nickel (% removal)	Lead (% removal)	Zinc (% removal)	Phosphorus (% removal)
Removal after 1 minute								
Olivine I	23.3 (19.9/24.2)	96.0 (89.7/96.7)	94.2 (74.0/95.2)	96.7 (80.6/97.0)	74.1 (71.5/78.0)	89.9 (61.7/91.9)	94.6 (87.6/96.3)	49.1 (43.8/54.2)
Olivine II	15.5 (13.5/18.5)	97.2 (95.9/97.6)	96.4 (77.1/98.6)	95.9 (74.8/96.3)	95.0 (94.4/95.6)	86.3 (84.8/87.4)	98.5 (98.1/99.1)	74.7 (72.0/77.8)
Limestone	0.1 (−0.5/0.5)	79.8 (77.1/83.0)	73.1 (58.2/89.2)	74.3 (64.9/88.7)	33.5 (18.8/35.6)	72.4 (72.3/93.0)	87.2 (82.9/88.4)	6.8 (2.4/11.0)
Shell-sand	0.5 (−1.7/2.8)	93.2 (83.2/96.6)	99.6 (91.1/99.7)	87.5 (83.3/95.5)	66.2 (59.7/78.0)	88.0 (74.3/95.3)	92.9 (87.3/95.8)	12.4 (2.0/31.1)
Zeolite	0.3 (−1.2/1.3)	59.6 (53.1/79.1)	94.1 (92.2/96.9)	84.3 (61.5/91.0)	68.5 (50.1/83.5)	81.9 (78.8/85.8)	83.1 (81.2/89.5)	−2.2 (−3.0/−0.2)
Removal after 10 minutes								
Olivine I	72.4 (71.4/75.9)	99.3 (99.3/99.8)	92.4 (77.6/94.8)	97.8 (95.3/98.1)	98.8 (98.3/99.5)	92.4 (81.5/94.7)	95.6 (95.0/98.0)	94.5 (94.3/96.2)
Olivine II	53.6 (49.8/59.1)	99.2 (98.4/99.5)	93.5 (43.9/94.8)	96.6 (83.2/97.4)	99.7 (99.4/99.8)	91.9 (89.2/92.5)	99.8 (99.6/99.9)	97.7 (95.8/98.8)
Limestone	9.6 (5.2/15.0)	99.1 (98.4/99.2)	82.4 (68.6/93.9)	86.0 (74.1/94.1)	79.8 (73.7/84.4)	95.8 (82.7/98.4)	96.4 (95.6/96.8)	62.5 (31.8/78.7)
Shell-sand	17.4 (5.3/35.8)	98.8 (98.6/99.1)	99.6 (99.2/99.8)	88.8 (81.5/93.8)	95.4 (94.5/96.6)	89.6 (85.6/91.5)	95.8 (91.8/97.8)	75.0 (37.7/87.8)
Zeolite	14.7 (10.2/19.1)	87.8 (83.4/96.5)	99.2 (88.2/99.6)	92.5 (80.8/95.1)	90.7 (73.8/95.3)	86.3 (82.0/87.3)	95.3 (90.2/97.3)	30.8 (25.4/36.1)

extraction method was seen for arsenic. For this element, the first extraction step (deionized water) caused the most desorption, whereas desorption decreased with the second extraction step (sodium chloride) and decreased further with the last extraction step (sodium hydroxide). For arsenic, it was zeolite that showed the highest desorption, whereas olivine I showed the lowest desorption. A similar trend was not seen for the other elements and, in general, there was no clear tendency that one extraction step caused more desorption than another.

With respect to the sorbents, there was a tendency that zeolite bound the sorbates the most poorly. At the same time, zeolite was in the lower range of the measured sorption capacities compared with the other sorbents (Figure 2) and, therefore, tended to have adsorbed lower amounts of the sorbates before the desorption experiments. The other sorbents bounded well with cadmium, nickel, phosphorus, lead, and zinc. Chromium desorbed more than the other elements, and copper desorbed significantly for olivine I and shell-sand.

For the majority of the combinations of sorbent, sorbate, and extraction step, no significant difference in the equilibrium concentrations at the three extraction steps was found. That is, the sorbent/sorbate equilibrium was not affected by the tested changes of chemical conditions in the extraction liquid. However, zeolite was highly affected by especially the sodium chloride of the liquid, an effect that was mitigated by raising the pH. Limestone generally bound the elements the strongest under the tested conditions.

Sorption Kinetics. In Figure 4, measured data on sorption kinetics are presented. In many of the sorbent/sorbate combinations, the adsorption of sorbates to sorbents occurred in what could be seen as two steps: a rapid initial adsorption followed by a somewhat slower adsorption. This finding is consistent with a two-step sorption mechanism (fast/slow) presented by Wilde and Benemann (1993) and Plazinski et al. (2009). They state that the first fast sorption step includes sorption to directly available surfaces of the sorbent and movement into large pores and that the following slower sorption is caused by diffusion into smaller pores and stronger chemical bonding to the sorbent and already adsorbed sorbates.

The amount of sorbate adsorbed within the initial minutes of contact time was considerable for most sorbent/sorbate combinations. No clear tendency towards higher inflow concentration giving higher initial removal efficiencies were observed, thus average initial removal efficiencies for each sorbent and each sorbate were calculated based on the complete set of tests (Table 4). Taking all sorbent/sorbate combinations into account, the median of the removal efficiency after 1 minute of contact time was 83% and 93% after 10 minutes of contact time. High initial removal has been reported in several other studies (e.g., Chen et al., 2010; Altun and Pehlivan, 2007).

Taking all sorbates into account, olivine II showed the highest initial removal efficiencies, closely followed by olivine I and shell-sand. Zeolite and limestone showed the lowest initial removal efficiencies. The sorbate with the poorest sorption kinetics was arsenic, for which especially the sorption to limestone, shell-sand, and zeolite was comparatively slow (Table 4). Arsenic had been added in its reduced form, for which it is known to bind less readily to sorbents (Mondal et al., 2006). Even though some of the arsenite might have been oxidized to arsenate, the choice of arsenite instead of arsenate as sorbate consequently yielded a conservative estimate of the sorbents' capabilities to bind arsenic.

The sorption following the first minute of initial contact time was simulated by first-order kinetics in the sorbate concentration and the correlation between sorbate influent concentrations and first-order removal rate constants was analyzed. In some columns, the removal rate constants increased with increasing influent concentration; in others, it decreased with increasing concentration and, in some, it was constant. In other words, there was no tendency towards correlation between the first-order rate constants obtained and the influent concentrations. However, the simulated rate constants were subject to rather high uncertainty and the results of the simulations are, therefore, not presented.

In most cases, the sorbate concentration decreased continuously during the first 60 minutes of contact time (Figure 4). However, for some combinations of sorbent/sorbate, there was an increase towards longer contact times, for example, for sorption of lead to olivine II. For those tests for which a contact time of 720 minutes was applied, this tendency became still more pronounced (data not shown). For all of the five sorbents, increasing concentrations of especially zinc, cadmium, and

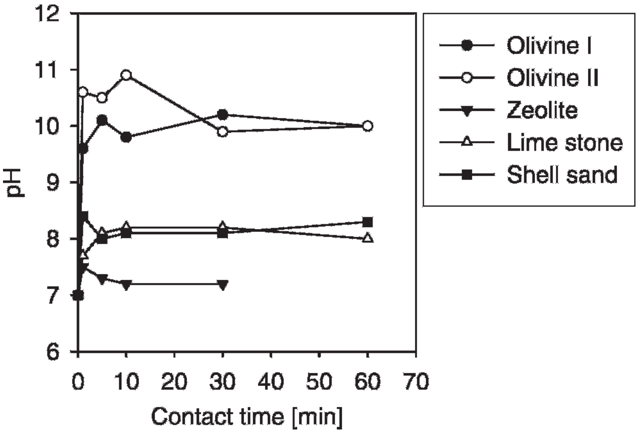

Figure 5—Variation of pH in the effluent of the column experiments (pool of six columns) at the contact times applied.

chromium were observed at 720 minutes, slightly reducing the sorption efficiency for these sorbent/sorbate combinations. Moreover, leakages of chromium from the blank columns were observed for the two olivine sorbents, an observation that is consistent with observations made by Forsvarsbygg (2009) on similar products. For olivine II, there was also a slight leakage of copper from the blank columns; limestone had a slight leakage of nickel; and zeolite had a slight leakage of arsenic and phosphorus.

Physical and Chemical Properties of the Sorbents. Sorbents may interact with acids and bases of the water phase, thereby causing changes in pH. Because pH is an important environmental parameter for aquatic ecosystems, the effect of the sorption process on the water-phase pH was investigated. pH was measured in the effluent from the column experiments (Figure 1), the results of which are presented in Figure 5. Because of the low flow, it was not possible to collect enough effluent samples at a contact time of 720 minutes to measure pH. Furthermore, pH had been measured in the sorption capacity batch experiments after 48 hours of contact time.

The pH of the effluent from the two olivine materials increased from 7 in the artificial stormwater to approximately 10. A similar increase in pH was also observed in the effluent from a pilot-scale filter setup applying a similar olivine granulate (Forsvarsbygg, 2009). The increase in pH is unwanted because a high pH can have negative effects on flora and fauna in receiving waters. A preliminary test showed that addition of shell-sand to the alkaline effluent neutralized pH. However, further experiments have to be carried out to reveal the optimal type of carbonatic material, quanta, and contact time to ensure pH neutralization. Limestone and shell-sand had an effluent pH of approximately eight. For zeolite, the pH increased somewhat at short contact times but stabilized slightly above 7 after 10 minutes. However, in the batch experiments for sorption capacity, the pH had dropped further to 5.1 ± 0.2 after 48 hours of contact time.

The sorption media were somewhat instable, which was observed in the desorption experiments, where significant quanta of suspended solids occurred in the batches after the first desorption step. In particular, zeolite turned the extraction solution into a viscous suspension in which the suspended solids did not settle. Significant amounts of fine particles were caused by physical breakdown of the material during agitation of the batches, indicating poor resistance to physical stress. If such breakdown occurs in a constructed filter, the suspended material will affect the hydraulic conductivity of the filter, thereby its hydraulic performance. Moreover, if dust and solids are washed out of the constructed filter, this may affect receiving waters.

Applicability for Stormwater Filters. Whether a sorbent is applicable as stormwater filter material depends first on its sorption capacity at relevant sorbate concentrations. For stormwater treatment, this corresponds to typical concentrations of soluble compounds in stormwater runoff from retention ponds, for example, as presented in Table 3 for sand filter effluents. In addition to the sorption capacity of the sorbent, desorption characteristics must be taken into account, as must physical stability and effluent pH.

Comparing the different materials, the tested limestone had a good physical stability, it was not prone to desorption, and the pH of the effluent was unproblematic. However, it had, for a number of elements, a comparatively low sorption capacity in the relevant concentration ranges, as exemplified in Table 3. For lead, there seemed to be a sorption threshold concentration of approximately 10 μg/L. As typical dissolved lead concentrations in stormwater are lower than this, the tested limestone will have little effect towards further reducing this compound. With respect to nickel, the tested limestone had a negligible sorption capacity at relevant concentrations ranges.

After a contact time of 10 minutes, removal efficiencies of the limestone for zinc and lead were higher than 95% and, for copper and chromium, were higher than 80%. For a sorption filter with horizontal flow, Jensen et al. (2011) report significantly lower removal efficiencies for these metals in a sorption filter with horizontal flow, although the contact time in this study was approximately 40 minutes. The poorer removal efficiencies despite the longer contact time can be explained by the difference in filter layout or by Jensen et al. (2011) applying natural stormwater and not artificial stormwater as in the present study. The removal efficiency for phosphorus reported by Jensen et al. (2011) was significantly higher than in the present study, perhaps because of the longer contact time.

The other carbonatic media, shell-sand, generally had a better sorption capacity than the limestone. It was more prone to desorption but was not additionally affected by sodium chloride or increase in pH. It had a moderate physical stability and contained a large fraction of fine particles. The pH of the effluent was unproblematic. Of the tested media, the shell-sand had some of the slowest sorption kinetics. However, for nickel, cadmium, and phosphorus, the kinetics was rather fast.

The sorption capacity of the tested zeolite was comparatively poor for most tested sorbates at relevant concentration ranges. An exception was lead, for which the capacity was good and the determined removal rate the highest measured for all combinations of sorbent and sorbate. Leppert (1990) and Bailey et al. (1999) also reported that zeolite had a strong affinity for lead in particular. Lead is, however, seldom a main target pollutant in stormwater because a main source—lead in gasoline—was phased out several decades ago. Genç-Fuhrmann et al. (2007) estimated sorption isotherms for arsenic, cadmium, chromium, copper, nickel, and zinc in combination with a zeolite in relevant ranges for stormwater and sand filter effluent. The reported capacities were generally smaller by a factor of 10 than the capacities determined in this study. However, at the stormwater concentrations exemplified in Table 3, the capacities for arsenic, copper, and nickel were comparable, whereas the reported capacities for chromium and cadmium were approximately smaller by a factor of 100. The zeolite tested in the present study had poor stability towards physical stress and desorbed several of the studied sorbates relatively easily.

The two olivine granulates had rather high sorption capacities at relevant sorbate concentrations and generally also the fastest sorption kinetics. The reason for the generally higher sorption capacity of olivine I compared with olivine II, despite the similarities between the two sorbents, is not known but could be attributed to the higher cement content of olivine I and/or its higher BET surface area. Both types of olivine granulates had a moderate physical stability. The binding of the elements studied was generally strong when subjected to sodium chloride and pH increase. However, leakage of chromium from unused sorbent (the blank column of the sorption kinetics tests) was observed for both types of granulates as well as reported in the literature (Forsvarsbygg, 2009). Most likely, the chromium leaked as a mix of chromate and chromite, as chromium is known to leak from cement in both oxidation stages (Yamaguchi et al., 2006). The pH of the effluent was high, potentially causing adverse effects on receiving waters. Over time, the effluent pH will likely decrease towards a more neutral level as the cement that binds the olivine granulate becomes carbonated.

Designing a Sorption Filter. Each of the tested low-cost sorbents had its strengths and weaknesses, and none of the tested sorbents met all requirements of the ideal sorption media for stormwater treatment. However, applying the sorbents in combination probably would make it possible to achieve low effluent concentrations for all tested elements. The issue of physical stability of some of the sorbents can be counteracted by mixing them into, for example, coarse sand and the issue of high or low effluent pH can be addressed by including a carbonatic material in the filter construction. Furthermore, some of the tested sorbents were more costly than others, which also should be taken into account when designing a full-scale sorption filter. At the time, the sorption tests were conducted and, for materials delivered in Northern Europe, the cost of shell-sand was significantly below 100 Euro per ton, while olivine granulates was in the range or 500 to 1000 Euro per ton. The limestone and zeolite could be purchased at prices in between.

Filter construction and layout has not been addressed in the present study, but the authors envision two different approaches when constructing a full-scale sorption filter: Either the filter is constructed as a vertical flow filter from layers of different sorbents or by mixing different sorbents, for example, as described by Fuerhacker et al. (2011). In both cases, it might be appropriate to mix the sorbent into coarse sand, for example, to enhance the physical strength of the filter. Alternatively, a sorption filter can be designed as a filter with horizontal flow (Jensen et al., 2011). If the filter is to be vegetated, a top layer containing organic material could be added. The organic matter in such a layer is also likely to retain a range of organic micropollutants that might not be retained by the inorganic sorption media (Janzen et al., 2009). Pond systems expanded with vegetated sand filters have been shown to consistently have concentrations of polycyclic aromatic hydrocarbons in effluents below detection limits (Istenič et al., 2011).

When dimensioning a sorption filter, a critical issue is the operation time before breakthrough of a given pollutant, a parameter that depends on pollutant load and sorption capacity. When the load on the filter and the sorption capacity of the material is known, the demand for sorption material can be estimated from sorption isotherms like the ones presented in Figure 2, selecting one or two target pollutants for the design. As an example, envision a filter designed to protect a sensitive lake towards phosphorus. The filter is constructed with a growth layer of sand containing some organic matter. Below the growth layer is a layer of shell-sand intended to remove the significant portion of pollutants, followed by a layer of olivine granulates intended to polish the water further. The bottommost layer consists of shell-sand or limestone intended to neutralize the pH of the effluent. The filter is slowly drained between runoff events. The filter is loaded with 35 $m^3/m^2 \cdot yr$ of stormwater corresponding to a filter the size of 200 m^2 per impervious hectare receiving an annual runoff of 700 mm. It is estimated that the dissolved phosphorus concentration in the water passing through the upper growth layer is 150 µg P/L, that is, in the range reported in Table 3. The filter is designed for a life expectancy of 25 years.

The uppermost layer of shell-sand is estimated to have a sorption capacity of approximately 500 µg P/g at the envisioned concentration of 150 µg P/L (Figure 2). It is expected to discharge at a concentration of 10 µg P/L (Figure 4). At the surface loading of 35 $m^3/m^2 \cdot yr$, the mass of phosphorus that must be adsorbed is consequently 4.9 g $P/m^2 \cdot yr$. To suffice for 25 years of life time, the required mass of shell-sand becomes 250 kg/m^2. The layer of olivine granulate is estimated to have a sorption capacity of approximately 100 µg P/g at the shell-sand layer effluent concentration of 10 µg P/L. It is expected to discharge phosphorus at a concentration of 1 µg P/L. The needed mass of olivine sorption material becomes approximately 80 kg/m^2. To counteract the increase in pH and the slight leakage of chromium from the olivine granulate, a layer of shell-sand could be placed beneath the olivine granulate layer. Mixing the sorbents with coarse sand to increase stability and taking the bulk densities of the sorption materials into account, the total filter depth can be held at less than 1 m. To ensure minimum desorption and avoid anaerobic conditions in the filter, the filter could be drained between runoff events.

Assuming that other elements are in the range of sand filter effluent concentrations shown in Table 3, the filter will further reduce the concentrations of copper, zinc, and nickel, whereas the elements arsenic, cadmium, chromium, and lead probably are present in concentrations too low to be further reduced by the sorption filter. At the assumed concentration levels, the filter life-time with respect to copper, zinc, and nickel is larger than for phosphorus. A sorption filter like the one outlined above will ensure protection against accidental or illicit discharges of the tested elements.

Conclusion

Five commercially available sorbents were studied with respect to stormwater treatment, namely a crushed limestone, a shell-sand, a zeolite, and two granulates of olivine. The sorbents were tested for sorption of phosphorus, arsenic, cadmium, chromium, copper, nickel, lead, and zinc at concentration levels and conditions relevant for typical stormwater.

The olivine granulates had the highest unit cost but, in general, also the highest sorption capacity and the fastest sorption kinetics. However, they caused pH to rise to approximately 10, which in many applications for stormwater treatment cannot be accepted. Furthermore, they leaked chromium, which is also undesirable. The olivine granulates had moderate physical stability. The shell-sand had the lowest unit cost but still had rather high sorption capacity and reasonably fast sorption kinetics. It was of moderate physical stability and caused pH to stabilize to approximately 8. The zeolite generally showed poor sorption capacities and slow sorption kinetics, with lead as the exception. The zeolite had the poorest physical strength, showed the most desorption of adsorbed elements, and resulted in a comparatively low pH. The limestone had good physical stability but comparatively low sorption capacity and comparatively slow sorption kinetics. It resulted in a pH of approximately 8.

For a number of sorbent/sorbate combinations, there seemed to be a sorption threshold below which no further sorption occurred. For example, the shell-sand did not sorb phosphorus below approximately 10 μg P/L, whereas olivine granulates bound phosphorus to levels lower than 1 μg P/L. It should be kept in mind that applied media are natural products, hence sorption behavior will vary within the same media quarried at different locations and times.

None of the tested sorption materials was found to be the ideal sorbent for all tested sorbates. However, when combining sorption materials, the strength of the materials can be combined and their weaknesses can be overcome. Combining the filter materials with sorption capacity, sorption rate, and cost/effectiveness in mind promises the design and construction of a versatile filter at a reasonable cost.

Credits

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Improved urban stormwater treatment and pollutant removal pathways in amended wet detention ponds

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Dissolved and colloidal bound pollutants are generally poorly removed from stormwater in wet detention ponds. These fractions are, however, the most bio-available, and therefore three wet detention ponds were amended with planted sand filters, sorption filters and addition of precipitation chemicals to enhance the removal of dissolved pollutants and pollutants associated with fine particles and colloids. The three systems treated runoff from industrial, residential and combined (residential and highway) catchments and had permanent volumes of 1,990, 6,900 and 2,680 m^3, respectively. The treatment performance of the ponds for elimination of total suspended solids (TSS), total nitrogen (Tot-N), total phosphorous (Tot-P), PO_4-P, Pb, Zn, Cd, Ni, Cr, Cu, Hg were within the range typically reported for wet detention ponds, but the concentrations of most of the pollutants were efficiently reduced by the planted sand filters at the outlets. The sorption filters contributed to further decrease the concentration of PO_4-P from 0.04 ± 0.05 to 0.01 ± 0.01 mg L^{-1} and were also efficient in removing heavy metals. Dosing of iron sulphate to enrich the bottom sediment with iron and dosing of aluminium salts to the inlet water resulted in less growth of phytoplankton, but treatment performance was not significantly affected. Heavy metals (Pb, Zn, Cd, Ni, Cr and Cu) accumulated in the sediment of the ponds. The concentrations of Zn, Ni, Cu and Pb in the roots of the wetland plants were generally correlated to the concentrations in the sediments. Among 13 plant species investigated, *Rumex hydrolapathum* accumulated the highest concentrations of heavy metals in the roots (Concentration Factor (CF) of 4.5 and 5.9 for Zn and Ni, respectively) and *Iris pseudacorus* the lowest ($CF < 1$). The translocation of heavy metals from roots to the aboveground tissues of plants was low. Therefore the potential transfer of heavy metals from the metal-enriched sediment to the surrounding ecosystem via plant uptake and translocation is negligible.

Keywords: Heavy metal, wetland plant, sediment accumulation, sorption filter, aluminium dosing, iron dosing.

Introduction

Stormwater runoff originating from roads, highways, urban and industrial areas often contains high contents of suspended solids, biodegradable organic matter, nutrients, heavy metals and organic micropollutants that may have adverse effects in the receiving water bodies.[1, 2] Additionally, stormwater flow and its concentration of pollutants fluctuate dramatically over time depending on the physical characteristics of the catchment area and the frequency and intensity of the rain events. Pollutants from urban surfaces are often mixed into large water volumes during rain events with resulting low concentrations, except for the first flush, which can contain high pollutant concentrations. Because of these stochastic irregularities of rain events and pollutant loads, the design and operation of stormwater treatment facilities are confronted with the challenge of reducing both high pollutant concentrations during the first flush and low pollutant concentrations thereafter.[3]

Several alternative stormwater treatment systems are in use, including infiltration systems, grass swales, filter strips, wet detention ponds and constructed wetlands. Wet detention ponds and constructed wetlands are among the most used and reliable technologies, achieving relatively good and consistent pollutant removal.[4–6] The detention of runoff water in a pond buffers the hydraulic and pollutant peaks and enables the removal of suspended solids and some of the associated pollutants. Dissolved pollutants are eliminated primarily by chemical and biological processes,[7] but the capacity of wet detention ponds to remove colloidal and dissolved pollutants is rather low.[8] Soluble pollutants such as orthophosphate and heavy metals can, however, be removed with the use of different types of

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sorption filters[9–11] or by the addition of precipitation chemicals such as alumina or iron salts.[12, 13]

Stormwater systems are often placed in areas with recreational value and therefore must be designed with urban landscape architecture in mind. A mixture of wetland plant species contributes to a pleasant appearance of a pond and can also attract a diverse fauna. Wetland plants also play an active role in the removal of pollutants mainly by modifying the hydraulics and thereby increasing the potential for sedimentation in the pond and by maintaining or improving the hydraulic characteristics of the filter units.[14] Sand filters planted with the common reed (*Phragmites australis*) have been shown to be particularly efficient for the removal of suspended solids and heavy metals from stormwater.[1]

Here we present results from three wet detention ponds that were designed and constructed in the scope of an European LIFE-Environment project (LIFE-TREASURE) for testing and demonstrating technologies for efficient stormwater treatment. The three systems were amended with additional technologies for enhancing the elimination of dissolved and colloidal pollutants originating from stormwater runoff. The additional technologies included planted sand filters at the outlets, fixed-media sorption filters, enrichment of pond bottom sediments with iron salts, and addition of aluminium salts to the incoming stormwater.

These technologies are used in wastewater treatment, drinking water preparation and restoration of eutrophic water bodies; however, integration of these technologies in wet ponds and their efficiency in stormwater treatment has not been studied so far. The systems were intended to be capable of enhancing the removal of colloidal particles, dissolved organics, including polycyclic aromatic hydrocarbons, and heavy metals compared to traditional wet detention ponds.

This article describes the treatment performance of the systems during the initial two years of operation for suspended solids, nitrogen, phosphorus and heavy metals. Furthermore, the accumulation of heavy metals in the wetland plants, which might potentially constitute a pathway for entrance of heavy metals into the food chain, is reported and related to the concentrations in the pond sediments. Plant species that are suitable for phytoremediation of stormwater runoff are outlined. The results show that the amendment of traditional wet detention ponds with planted sand filters, fixed-media sorption filters and the addition of precipitation chemicals to the soil or water can improve the removal of dissolved and colloidal pollutants from the stormwater.

Materials and methods

Site description

In 2007 three full-scale stormwater treatment systems were established in the cities of Aarhus, Silkeborg and Odense, in Denmark. The characteristics of the three catchments differ in terms of land use and hence expected stormwater quality and treatment needs (Table 1). The stormwater treatment systems were designed as 1.0 to 1.5 m deep traditional wet detention ponds with 1 m surge volume and with bar screens and sand traps at the inlets.[4] The ponds were amended with sand filters planted with *P. australis* at the outlets. In addition, the three systems were each amended with an additional technology targeted at improving the removal of dissolved and colloidal phosphorous, organic micro-contaminants and heavy metals. The ponds were planted with a mixture of plant species to establish a "natural" appearance and integration into the landscape.

Table 1. General characteristics of the three stormwater wet detention ponds.

Characteristics	*Odense*	*Aarhus*	*Silkeborg*
Type of catchment	Light industry	Residential (blocks)	Residential (detached houses) and highway
Advanced treatment technology	Fixed-media sorption	Iron enrichment	Aluminium addition
Annual precipitation	657 mm y^{-1}	661 mm y^{-1}	719 mm y^{-1}
Total catchment area	27.4 ha	57.4 ha	21.5 ha
Impervious catchment area	11.4 ha	25.8 ha	8.8 ha
Permanent wet volume	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
Pond volume per catchment area	175 m^3 ha	267 m^3 ha	305 m^3 ha
Length to width ratio	4.5	2.5	5
Permanent water depth, max	1.45	1.25	1.0
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

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

**The height of the sand filter was to the maximum water level of the detention volume.

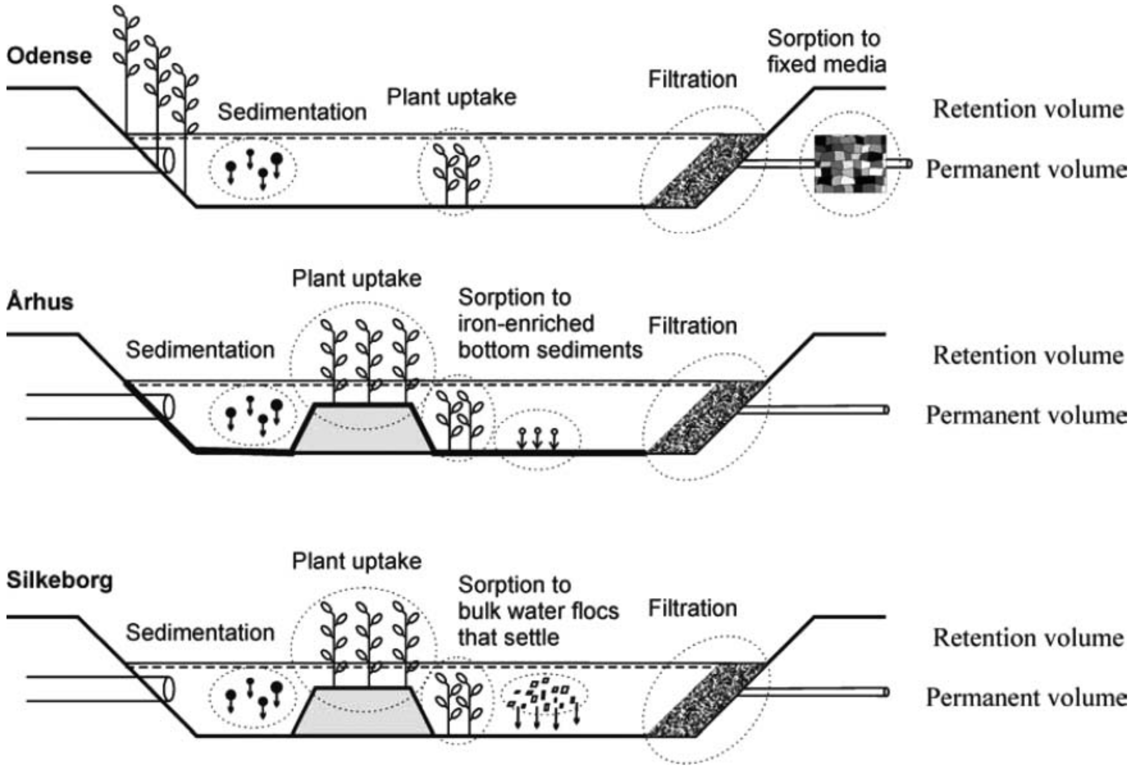

Fig. 1. Schemes of the wet detention pond in Odense, Aarhus and Silkeborg.

The Odense system serves an industrial area and is designed as a single 1.5 m deep wet detention pond with a permanent volume of 1,990 m^3 and detention volume of 1,300 m^3. The additional technology tested in this system was fixed-media sorption filters containing Oyta Shells, type OYTA 0 (Oytaco Ltd., Denmark), a natural product obtained from deposits of fossil oyster shells in the shallow waters of the North Sea. The filter has a rectangular shape with an area of 24 m^2 and a volume of 55 m^3.

The system also contained smaller test filters with granulated olivine (Filtersil 2749 from North Cape Minerals, Norway) and Oyta Shells combined with olivine. The test filters were of circular shape with surface area of 1.23 m^2 and a volume of 2.5 m^3. The pond was planted with relatively tall and robust wetland species (*Typha* sp. and *Rumex* sp.) along the side facing an industrial area and around outlet structures. Smaller species that can stabilize banks and are also ornamental giving the system a pleasant appearance (e.g., *Sagittaria sagittifolia, Alisma lanceolatum, Iris pseudacorus, Caltha palustris, Nymphaea/Nuphar* sp.) were planted next to a public walk path passing the system (Fig. 1).

The Aarhus facility receives runoff from an urban residential catchment and has a permanent volume of 6,900 m^3 and a detention volume of 1,400 m^3. The system is located on a wet meadow close to the receiving Lake Brabrand in an important recreational area with bird observation towers and public walk paths. The banks of the ponds were left unplanted, but the sand filter was planted with *P. australis* to counteract clogging. Three high ground zones (polders) planted with *Schoenoplectus lacustris* were established within the pond to make the visual appearance resemble the neighbouring Lake Brabrand. The bottom sediment of the pond was iron-enriched by dosing with iron sulphate in the water phase in order to enhance the phosphorus removal capacity of the system (Fig. 1). A total of 3,000 kg of iron chloride/sulphate solution (PIX 118, Kemira Water Denmark A/S) was added in one campaign. The acid solution contained 116 g Fe^{3+} kg^{-1}.

The wet detention pond at Silkeborg has a permanent volume of 2,680 m^3 and a detention volume of 3,230 m^3 and receives runoff water from a residential area and a section of a highway passing through the district. The pond is divided into three sections by two transversal sand dikes through which the stormwater is filtered. At high water flow, when the water level rises, the water passes over the dikes. The system is located in a recreational area, and the planting scheme reflected integration into the natural environment. The transversal sand dikes and outlet filters were planted with *P. australis* because of its deep and dense root system that counteract erosion and helps to maintain a high hydraulic permeability of the filters. The system in Silkeborg is equipped with a flow proportional injection system to dose aluminium salts which form aluminium hydroxide flocks that co-precipitate with phosphate and heavy metals in the pond (Fig. 1). The alkaline solution contained 155 g Al^{3+} kg^{-1} (alumin_10, Remondis

Production GmbH) and was added in concentration of 5.2 g Al per m^3 of inflow water.

Monitoring and sampling

The three systems were fully equipped with flow meters to monitor inlet and outlet flow as well as *in-situ* sensors to monitor water level, pH, temperature, dissolved oxygen, and water turbidity. Flow or time proportional water samples of inlets and outlets were collected by automated water samplers. Parameters analysed in the water samples included total suspended solids (TSS), total nitrogen (Tot-N), total phosphorous (Tot-P), orthophosphate (PO_4-P) and heavy metals (Pb, Zn, Cd, Ni, Cr, Cu and Hg). Water quality parameters were measured according to Standard methods.[15] Heavy metals were analysed using ICP-OES (Plasma 2000, Perkin Elmer Instruments, USA).

Sediment samples were taken in transects along the water flowpath in each pond in autumn 2008 and summer 2009. Samples were collected and stored in plastic containers and analysed for loss on ignition (550°C to constant weight). In summer 2009, the wetland plant species planted at the edge of the ponds and in the sand filters were sampled. After careful cleaning in tap and demineralised water the plants were fractionated into roots, rhizomes, stems and leaves and then dried at 80°C for at least 48 hours. Dried subsamples of the homogenised sediment and ground plant samples were analysed for concentration of nutrient elements and heavy metals. 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 1 h. After digestion, samples were diluted and analysed for P, K, Ca, Fe, Mn, Na, Al, Pb, Zn, Cd, Ni, Cr, and Cu by ICP-OES (Plasma 2000, Perkin Elmer Instruments, USA).

Statistical analysis of the results was performed using Statgraphics Centurion XV centurion version 15.1.02 (StatPoint, Inc., USA). Data were tested for variance homogeneity (Levene's test) and logarithmic or square root transformed when necessary. The post hoc Bonferroni test was used to identify significant differences between means at the 5% probability level. Nutrient and metal concentrations in the plant shoots and roots were compared to the concentrations in the sediment for each pond. The Concentration Factor (CF), i.e., ratio between the metal concentration in plant roots and the corresponding concentration in the sediment, and the Accumulation Coefficient (AC), i.e., the ratio between the metal concentration in the aboveground plant tissues and the corresponding concentration in the sediment, were calculated.

Results

Water

The composition of the influent water to the three ponds was characteristic for urban stormwater, and the concentration of total suspended solids (TSS) and other pollutants fluctuated with flow as indicated by the high standard deviations for inlet concentrations (Table 2). In general, TSS, total nitrogen (Tot-N) and total phosphorous (Tot-P) were removed efficiently in the ponds and the sand filters at the effluent. A detailed description of the monitored physical and chemical conditions in the ponds as well as overall treatment performance for TSS and nutrients have been presented by Vollertsen et al.[16, 17]

Concerning heavy metals, the Odense pond received significantly higher concentrations of Pb, Zn, Ni and Cu compared to the other two ponds (Table 3). In all ponds, the concentrations of Pb, Zn, Cd, Cr and Cu decreased significantly by passing through the systems, and the concentrations in the pond water were considerably lower than in the inlets indicating significant removal by sedimentation. At the Aarhus and Silkeborg systems no reduction of Pb, Cd, Cr and Cu concentrations by passing through the sand filters could be detected possibly due to already low heavy metal concentrations in the pond water. However, sand filters in all three systems showed significant reduction of Zn, which generally occurred in higher concentrations in the pond water compared to the other metals. The Ni concentrations decreased along the Odense pond. However, in Aarhus and Silkeborg, the Ni concentration increased in the basin and outflow, respectively, indicating a release of Ni from the pond sediment in Aarhus and from the sand filters in Silkeborg.

Sediment

The accumulated sediment at the bottom of the ponds had the highest organic content at the inlets (7.9–18.3% dry weight (DW)) and decreasing contents towards the effluent end of the ponds (Table 4). The concentrations of the major cations (Ca, Fe, Al), which occurred in high concentrations, did not mirror the organic content as they probably were mainly associated with the minerogen particles in the sediments. The concentrations of P also did not correlate with the organic content in the three systems. In Odense, the sediment P concentrations were significantly lower than in the two other ponds, but the loss on ignition did not differ significantly between the three systems.

The heavy metal concentrations in the sediment decreased in the following order: $Zn > Cu \geq Cr > Ni > Pb$ in Aarhus and Silkeborg. In Odense the heavy metal concentrations were generally higher, particularly for Cu, Pb and Zn, and the sediment concentrations decreased in the following order: $Cu > Zn > Pb > Cr > Ni$. The concentrations of Pb, Zn, Ni, Cr and Cu in the sediment of the pond at Odense were up to two orders of magnitude higher than in the other two systems. The concentrations of heavy metals were generally higher in the sediments sampled at the inlets compared to the sediments at the outlets.

This probably reflects prevailing sedimentation in the front end of the ponds. The transversal sand dikes and the

Table 2. Average water quality parameters (± 1 standard deviation) in samples from the stormwater treatment systems in Odense (n = 22 to 29), Aarhus (n = 21 or 22) and Silkeborg (n = 13 or 14).

	Odense				*Aarhus*			*Silkeborg*		
	Inlet	*Basin*	*Outlet sand filter*	*Outlet sorption filter*	*Inlet*	*Basin*	*Outlet*	*Inlet*	*Basin*	*Outlet*
TSS (mg L^{-1})	48 ± 43^c	17 ± 10^b	15 ± 17^b	4 ± 4^a	53 ± 37^b	8 ± 7^a	5 ± 3^a	37 ± 33	5 ± 5	2 ± 2
Tot-N (mg L^{-1})	3.2 ± 1.7	2.2 ± 0.7	1.3 ± 0.8	1.1 ± 1.6	2.3 ± 1.1^b	0.8 ± 0.4^a	0.7 ± 0.3^a	2.4 ± 3.0^b	1.6 ± 1.6^b	0.5 ± 0.2^a
PO_4-P (mg L^{-1})	0.13 ± 0.16^c	0.04 ± 0.06^b	0.04 ± 0.05^b	0.01 ± 0.01^a	0.13 ± 0.12^b	0.01 ± 0.02^a	0.02 ± 0.02^a	0.10 ± 0.27	0.00 ± 0.00	0.01 ± 0.01
Tot-P (mg L^{-1})	0.31 ± 0.22	0.15 ± 0.08	0.18 ± 0.17	0.03 ± 0.02	0.28 ± 0.16^b	0.07 ± 0.07^a	0.14 ± 0.10^a	0.22 ± 0.36	0.03 ± 0.01	0.02 ± 0.01

Different superscript letters within rows for a system indicate significant differences at the 5% probability level.

Table 3. Average heavy metals concentrations (± 1 standard deviation) in water samples from the stormwater treatment systems in Odense (n = 22 to 29), Aarhus (n = 25) and Silkeborg (n = 13 or 14).

	Odense				*Aarhus*			*Silkeborg*		
	Inlet	*Basin*	*Outlets and filter*	*Outlet sorption filter*	*Inlet*	*Basin*	*Outlet*	*Inlet*	*Basin*	*Outlet*
Pb (μg L^{-1})	24 ± 28	6.7 ± 4.6	0.4 ± 0.3	0.6 ± 1.2	4.7 ± 2.9	0.9 ± 0.8	0.4 ± 0.4	5.4 ± 4.0^{c}	2.4 ± 1.4^{b}	0.8 ± 0.8^{a}
Zn (μg L^{-1})	433 ± 488^{c}	268 ± 317^{c}	28 ± 36^{b}	5 ± 4.2^{a}	181 ± 77	71 ± 50	16 ± 15	114 ± 27	79 ± 48	21 ± 14
Cd (μg L^{-1})	0.11 ± 0.07^{b}	0.06 ± 0.04^{a}	0.05 ± 0.03^{a}	0.04 ± 0.03^{a}	0.07 ± 0.05	0.03 ± 0.02	0.04 ± 0.03	0.07 ± 0.06	0.03 ± 0.00	0.03 ± 0.01
Ni (μg L^{-1})	28 ± 39	12 ± 12	6 ± 4	5 ± 8	7 ± 5^{a}	31 ± 21^{b}	9 ± 10^{a}	10 ± 5	2 ± 2	60 ± 86
Cr (μg L^{-1})	5.5 ± 3.7^{c}	1.2 ± 0.9^{b}	0.5 ± 0.3^{a}	0.5 ± 0.5^{a}	4.3 ± 2.6^{b}	0.7 ± 0.6^{a}	0.7 ± 2.1^{a}	2.6 ± 2.1^{b}	0.7 ± 0.6^{a}	1.0 ± 0.8^{a}
Cu (μg L^{-1})	451 ± 757	197 ± 213	25 ± 20	4 ± 7	19 ± 11^{c}	6 ± 6^{b}	2 ± 3^{a}	15 ± 6^{b}	8 ± 8^{a}	4 ± 5^{a}
Hg (μg L^{-1})	0.09 ± 0.19	0.05 ± 0.08	0.06 ± 0.11	0.05 ± 0.06	0.21 ± 0.81	0.04 ± 0.03	0.09 ± 0.15	1.3 ± 4.4	0.07 ± 0.07	0.03 ± 0.01

Different superscript letters within rows for a system indicate significant differences at the 5% probability level.

Table 4. Average nutrients and metal concentrations and loss on ignition (LOI) (± 1 standard deviation) in sediment samples from the stormwater treatment systems in Odense (n = 5, 6 or 9), Aarhus (n = 8 or 9) and Silkeborg (n = 6 or 9).

	Odense			*Aarhus*			*Silkeborg*		
	Inlet	*Middle*	*Outlet*	*Inlet*	*Middle*	*Outlet*	*Inlet*	*Middle*	*Outlet*
P (mg g^{-1} DW)	0.09 ± 0.10	0.32 ± 0.80	0.60 ± 0.53	1.52 ± 0.56	1.81 ± 0.32	1.75 ± 0.38	1.65 ± 0.65^{c}	0.67 ± 0.15^{b}	0.36 ± 0.11^{a}
K (mg g^{-1} DW)	3.4 ± 0.5	3.8 ± 0.3	3.3 ± 0.4	4.1 ± 1.7	5.1 ± 1.9	4.5 ± 1.5	4.5 ± 1.5^{b}	3.2 ± 0.6^{ab}	2.2 ± 0.92^{a}
Ca (mg g^{-1} DW)	32 ± 9	28 ± 5	26 ± 2	38 ± 17	44 ± 20	35 ± 12	8 ± 4	4 ± 2	5 ± 4
Fe (mg g^{-1} DW)	22 ± 2^{a}	28 ± 4^{b}	23 ± 4^{ab}	18 ± 5^{a}	24 ± 3^{b}	22 ± 5^{ab}	23 ± 7^{b}	16 ± 2^{b}	10 ± 4^{a}
Mn (mg g^{-1} DW)	0.41 ± 0.07	0.40 ± 0.05	0.45 ± 0.16	0.41 ± 0.10	0.42 ± 0.14	0.37 ± 0.06	0.78 ± 0.39^{c}	0.44 ± 0.11^{b}	0.21 ± 0.06^{a}
Na (mg g^{-1} DW)	0.47 ± 0.18	0.40 ± 0.11	0.30 ± 0.06	0.39 ± 0.24	0.32 ± 0.09	0.36 ± 0.16	0.52 ± 0.19^{b}	0.19 ± 0.05^{a}	0.13 ± 0.06^{a}
Al (mg g^{-1} DW)	23 ± 8	30 ± 9	24 ± 10	21 ± 9	36 ± 17	25 ± 11	32 ± 10^{b}	23 ± 6^{ab}	14 ± 6^{a}
Pb (μg g^{-1} DW)	220 ± 88^{b}	198 ± 92^{b}	83 ± 38^{a}	10 ± 11	10 ± 13	6 ± 9	22 ± 12	<2	<2
Zn (μg g^{-1} DW)	1361 ± 538^{b}	1051 ± 372^{ab}	760 ± 22^{a}	234 ± 96	240 ± 78	190 ± 68	378 ± 172^{c}	82 ± 31^{b}	26 ± 9.5^{a}
Cd (μg g^{-1} DW)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Ni (μg g^{-1} DW)	42 ± 12^{b}	31 ± 7^{a}	22 ± 5^{a}	19 ± 7	23 ± 4	19 ± 5	29 ± 10^{b}	16 ± 3^{a}	10 ± 4^{a}
Cr (μg g^{-1} DW)	80 ± 34^{b}	62 ± 20^{ab}	39 ± 7^{a}	38 ± 17	43 ± 14	35 ± 11	44 ± 16	26 ± 4	17 ± 7
Cu (μg g^{-1} DW)	3293 ± 1018^{b}	3137 ± 1185^{b}	1625 ± 642^{a}	133 ± 202	171 ± 263	129 ± 171	45 ± 34^{b}	6 ± 6^{a}	4 ± 2^{a}
LOI (% of DW)	18.3 ± 10.2	11.8 ± 2.5	8.9 ± 2.8	7.9 ± 3.9	8.5 ± 2.8	6.9 ± 2.1	9.1 ± 4.2^{c}	2.1 ± 0.7^{b}	0.9 ± 0.3^{a}

Different superscript letters within rows for a system indicate significant differences at the 5% probability level.

favourable length to width ratio in the pond at Silkeborg affected the sediment composition. The concentrations of both phosphorus and heavy metals in the sediments decreased by a 2 to 10 factor from the first section of the pond to the last section. A decrease in sediment heavy metal concentration from inlet to outlet was also significant in Odense, but not in Aarhus, where heavy metals were more evenly distributed throughout the pond. Although Cd was frequently detected in the water samples, the concentrations of Cd in the sediments were consistently below the detection limit of 0.5 μg g^{-1} DW in all samples.

Plants

Phragmites australis in the sand filters. In all three systems, a sand filter planted with *P. australis* was established at the effluent. The plants in these filters were expected to receive higher loads than the plants growing on the banks of the ponds, as all the water passed through these filters. Hence, we compared the nutrient and metal accumulation in the plants in the filters to evaluate plant accumulation and potential transfer to the food chain in the three ponds, and we correlated plant accumulation to sediment concentrations.

Concentrations of most nutrient and mineral elements in the *P. australis* plant tissues were within 'normal' background levels and no difference was observed between plants from the three ponds (data not shown). Only tissue P and K concentrations in *P. australis* from Aarhus were slightly higher compared to the plants from Odense and Silkeborg, which correlates to the higher P and K concentrations in the sediment at the Aarhus pond. The concentrations of most heavy metals in the plant tissues, particularly the roots, were elevated and correlated with the concentrations in the pond sediments.

Figure 2 shows the concentrations of Zn, Ni, Cr and Cu in roots, rhizomes, stems and leaves of *P. australis* plotted against the sediment concentrations in the three ponds. Two patterns are obvious from the graphs. First, the tissue concentrations are generally higher in the belowground tissues (roots and rhizomes) than in the aboveground tissues (stems and leaves). Second, the tissue concentrations in the roots, but not stems and leaves, correlate with the concentrations in the sediments.

The pattern of tissue Cr (Fig. 2c) deviates somewhat from the pattern for Zn, Ni and Cu as concentrations in

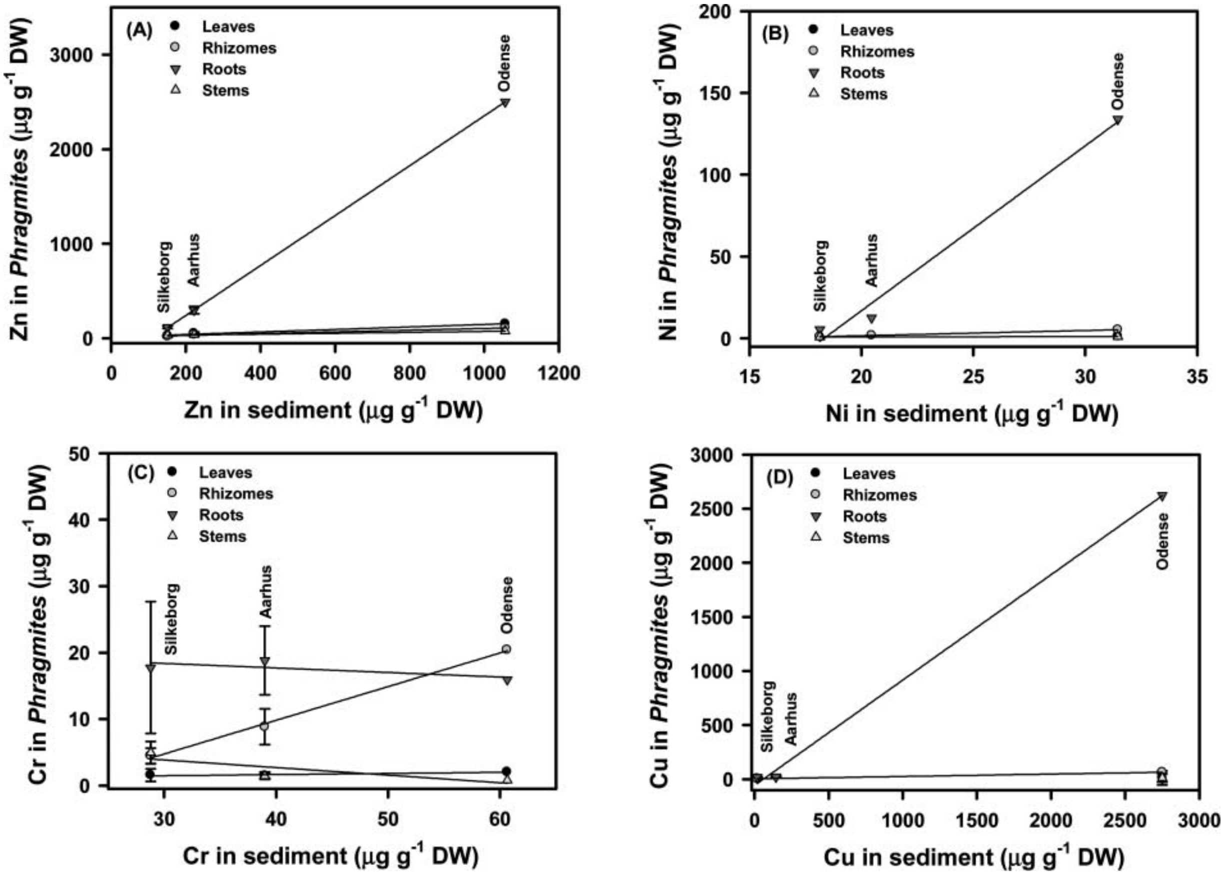

Fig. 2. Heavy metal concentrations in *Phragmites australis* tissues in the effluent sand filters compared to the concentrations in the sediment from stormwater treatment systems in Odense, Aarhus and Silkeborg.

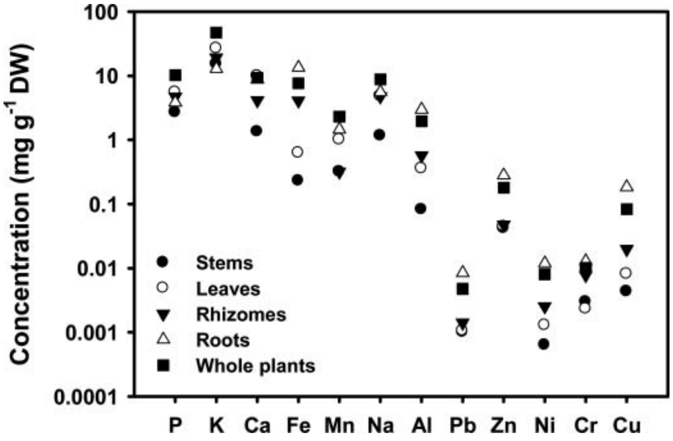

Fig. 3. Concentrations of nutrients and metals in different plant tissues of the investigated plant species from stormwater treatment ponds at Aarhus, Odense and Silkeborg.

rhizomes, but not roots, correlated with the concentrations in the sediment. Also the concentrations of Pb in roots were positively correlated to the sediment concentrations with more than 20-times higher concentration in Odense (100 μg g^{-1} DW) than at Aarhus (data not shown). Pb was below the detection limit in roots at Silkeborg and in rhizomes and aboveground tissues in all systems.

Other wetland species. Most wetland species, except *P. australis* as reported above, occurred only in one or two of the pond systems. Hence, species comparisons across ponds could not be made. As for *P. australis* the tissue concentrations of most nutrient and mineral elements were within the normal background levels. Figure 3 shows the tissue nutrient and metal concentrations in aboveground plant tissues, whole plants (for partially submerged aquatic species) and roots and rhizomes. The graph shows that the heavy metals mainly accumulated in the roots of the investigated plant species, whereas P, K and Ca concentrations were highest in the leaves. In the plant species with partially submerged leaves the concentrations of both nutrient, mineral and heavy metal elements were generally high.

Plant uptake and translocation. The uptake of heavy metals by the plants and the translocation to aboveground tissues can be evaluated by the so called Concentration Factor (CF), i.e. the ratio between the metal concentration in plant roots and the corresponding concentration in the sediment, and the Accumulation Coefficient (AC), i.e., the ratio between the metal concentration in the aboveground plant tissues and the corresponding concentration in the sediment. The average CFs for all investigated heavy metals were mostly <1 showing that the heavy metal accumulation in the roots in general was low (Fig. 4). However, there was a marked difference between the wetland species. The highest CFs were found for Zn and Ni at the Odense pond in the roots of *Rumex hydrolapathum* (4.5 and 5.9 for Zn and Ni, respectively), followed by *P. australis* (1.8 and 3.2 for Zn and Ni, respectively). Also *Typha* sp., *C. palustris*, *Ranunculus lingua*, and *Scirpus maritimus* concentrated Zn and Cu in the roots. *Iris pseudacorus* was generally the species with the lowest CFs for all heavy metals.

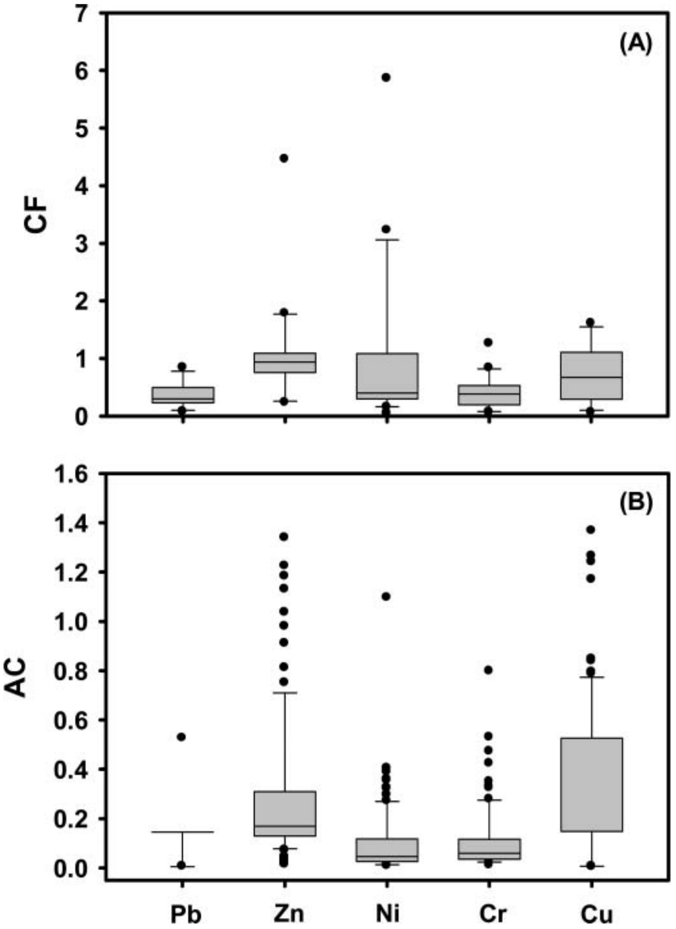

Fig. 4. Concentration Factors (CF) (A) and Accumulation Coefficients (AC) (B) for heavy metals in the investigated plant species from stormwater treatment ponds at Aarhus, Odense and Silkeborg.

The plants mostly did not transport the heavy metals in significant quantities to the aerial tissues as the concentrations in the aerial tissues were generally significantly lower than in the roots. Also the ACs were generally much lower than one for all heavy metals (Fig. 4). However, ACs were higher than one for Zn in *Stratiotes aloides*, *S. sagittifolia* and *P. australis*, for Cu in *A. lanceolatum* and *S. sagittifolia* and for Ni in *R. lingua*. Lead was detected only in the belowground tissues. Cadmium was detected in the water, but despite this the Cd concentrations were below the detection limit in all plant species in the investigated ponds which is consistent with the low Cd levels in the sediments.

Discussion

Water quality improvement

The wet detention ponds were efficient in removal of TSS, Tot-N, Tot-P and PO_4-P from stormwater which is consistent with data reported in other studies.[1, 17, 18] The main removal of these pollutants occurred in the open water part of the systems indicating that they were predominantly removed by sedimentation in the ponds. Pollutants that are inherently associated with the particulates sink to the bottom in the slowly flowing water of the pond and accumulate in the sediment. Several heavy metals are associated with the particulate matter and are thus removed in concert with the suspended solids.[7, 19, 20] However, some heavy metals such as Zn, Cu and Ni appear in stormwater mainly in the dissolved fraction[21, 22], and are expected to be barely removed by sedimentation. Nevertheless, there was moderate removal of those metals already in the open water part of all three systems.

The sand filters at the effluent end, which was included as an additional technology in all three systems in the present study, enhanced the removal of Zn in all systems, and also Cu in the system at Aarhus. The removal of Ni and other dissolved pollutants by the sand filters was not consistent, probably because of the release of Ni from the media and generally low concentrations entering the sand filters. The sand filters were planted with *P. australis,* which is a wetland species with a deep-growing root system known to counteract clogging of the filter media.[14]

The tissues of *P. australis* (especially roots) in the sand filter contained higher concentrations of heavy metals than tissues of *P. australis* growing at the bank of the ponds, which indicate that plant uptake contributed to the elimination of heavy metals from the stormwater, as has also been shown in other studies.[5, 23,24] Furthermore, some soluble and colloidal pollutants may also co-precipitate with the particles or with added aluminium salts like in the system at Silkeborg.[5,25] Our study shows that the sand filters at the outlet can contribute significantly to enhance the removal of dissolved heavy metals and probably also other soluble and colloidal pollutants from stormwater.

The sorption filters that were established as an additional polishing technology at the pond at Odense showed good performance in removal of P and further removal of Zn and Cu, which were still in relatively high concentrations while entering the sorption filter. The long-term capacity of the filter is however not known. The enrichment of the bottom sediment at the pond at Aarhus and the dosing of aluminium salts at Silkeborg did not influence the treatment efficiency of the pond consistently. However, in both ponds, the dosing resulted in less growth of phytoplankton in the ponds. The quantity of algae in the water, measured as chlorophyll concentration (data not shown), was significantly higher in Odense compared to Aarhus and Silkeborg. Because there was no difference in PO_4-P and Tot-P concentrations between the ponds, and as the ponds did not differ much in macrophyte cover, the reduced algae growth in Aarhus and Silkeborg were most probably caused by the addition of Al/Fe salts, which reduced the amount of bio-available P and thus algal growth.[26–28]

Accumulation in the sediment and plants

The concentrations of nutrients and heavy metals in the sediments of the wet detention ponds were greatly elevated compared to sediments in natural reference lakes as reported by Samecka-Cymerman and Kempers [29] reflecting the pollutant load of the stormwater. The concentrations of P were from 36–150 times higher, Pb 5–80 times higher, Ni 400–700 times higher, Cu 76–10,000 times higher, and Zn 27–170 times higher than in the reference lake sediments. The difference between the heavy metal levels in the sediment of the three systems is most likely caused by the different catchment and runoff characteristics and the ratio between pond volume and impervious catchment area. Both ponds at Aarhus and Silkeborg treated stormwater runoff from residential area, had similar ratio between pond volume and catchment area and did not differ significantly in inflow pollutant concentrations.

The pond at Silkeborg also received runoff from a short section of highway but this did not result in higher concentrations of heavy metals in water and sediment. The concentrations of heavy metals in the sediment at the Aarhus and Silkeborg ponds are comparable to concentrations reported from other stormwater wet detention ponds.[1, 5, 19, 23] The sediment heavy metal concentrations in the Odense pond are much higher and caused by high inflow heavy metal concentrations and the lowest pond volume per catchment area compared to the other two ponds. High inflow and sediment heavy metal concentrations in Odense are suspect and probably reflect an illegal discharge from a polluting industry.

The concentrations of Pb, Zn, Ni and Cu in the sediment correlated with the concentrations in the *P. australis* roots. Others have reported opposing results concerning the relationship between sediment and root heavy metal concentration. Cardwell et al. [30] reported increasing concentrations in the plant tissues with increasing sediment concentrations for Zn, but not for Cu. Samecka-Cymerman and Kempers [29] found a positive correlation between Zn in the sediment and plants in open cut mining lakes. In the present study, roots of *P. australis* in the sand filters accumulated all heavy metals, except Cr and Cd. No accumulation of Cr in roots is reported also by Scholes et al.[5] In the roots of the other investigated wetland species, the heavy metal concentrations in their roots were usually lower than in the adjacent sediment. In comparison, Sasmaz et al.[31] found higher concentrations of Zn, Pb, Cd and occasionally Ni and Cu in *Typha latifolia* roots compared to the sediment in a wastewater polluted stream.

The CF for Zn in their study ranged between 2.5 and 11.2 compared to 1.0 in *T. latifolia* and 4.5 in *R. hydrolapathum* in the present study. For Ni the CF in *T. latifolia* was similar in both studies, but in *R. hydrolapathum* the CF in our study was higher. The concentrations of heavy metals in the different plant species differed between species, with highest concentrations in *R. hydrolapathum* and lowest in *I. pseudacorus*. This is consistent with other studies. [32, 33] The concentrations in the shoots of all species investigated were, however, low compared to the root and sediment concentrations. Hence, potential transfer of heavy metals from the metal enriched sediment to the food chain via plant uptake and translocation to the aboveground tissues is negligible.

Conclusions

This study has reported the performance of three stormwater detention ponds amended with additional technologies for enhancing the elimination of dissolved and colloidal pollutants. Additionally, the study has presented the accumulation of heavy metals in wetland plants and their relation to the accumulation in the sediment. According to the results, the following conclusions can be made:

I. The amendment of traditional wet detention ponds with additional technologies can improve the removal of dissolved and colloidal pollutants from stormwater and thus contributes to the reduction of pollution of receiving water bodies.
II. Nutrients and heavy metals removed from stormwater accumulate in the sediment of wet detention ponds suggesting that the stormwater treatment can be improved by enhancing the sedimentation process. The resulting high pollutant concentrations in the pond sediments suggest that further research on sediment accretion rates and sediment remediation technologies are needed.
III. Integration of wetland plants into wet detention ponds is essential for enhanced elimination of pollutants as well as for improved aesthetical appearance of the systems.
IV. Plants growing in stormwater wet detention ponds do not present a risk for potential transfer of heavy metals from the metal-enriched sediment to the surrounding ecosystem via plant uptake, because the translocation of heavy metals to the aboveground tissues of plants is negligible.

Acknowledgments

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Monitoring the startup of a wet detention pond equipped with sand filters and sorption filters

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ABSTRACT

The startup of a wet retention pond designed for extended stormwater treatment was monitored by more than one year of continual measurement of hydraulic parameters, nutrients and quality parameters in the pond itself (pH, temperature, dissolved oxygen, turbidity). The data revealed that photosynthesis played an important role for dissolved oxygen and pH for most of the year. Another important observation was that the pond behaved more like a completely mixed reactor than like a plug flow reactor—even though the length to width ratio was as high as 4.5:1. The pond was equipped with sand filters and sorption filters whereby very good nutrient removal efficiencies were achieved.

Key words | colloidal pollutants, continuous monitoring, retention pond, stormwater

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INTRODUCTION

Stormwater runoff from urban surfaces, highways and roads contain numerous pollutants that cause harm in the aquatic environment. Many of the discharged organic and inorganic micropollutants have the potential to accumulate in the ecosystem, causing long term effects on the aquatic fauna. Other pollutants, e.g. phosphorus, cause more direct harm in terms of eutrophication of lakes and coastal waters and must therefore be removed to prevent deterioration of the receiving water bodies. The type and amount of pollutants entrapped in stormwater runoff depends on

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land use, such as traffic intensities, industries, building materials, etc.

In contrast to discharges of urban wastewater, urban stormwater runoff is discharged through a large number of separate outlets. Many small facilities are therefore needed when treating stormwater runoff. For this reason as well as the intermittent nature of the runoff process, technologies for treatment of stormwater runoff must be simple, robust, dependable and easy to operate. In addition hereto, the technologies must be appropriate to treat rather dilute pollutants as they occur in stormwater runoff. For facilities treating such runoff, today's technologies successfully manage pollutants associated with particulate matter, whereas soluble and colloidal pollutants typically are managed with less success. Among the commonly applied technologies, wet basins and constructed wetlands are cost-effective with respect to removal of particles. Wet basins have a lower requirement for land compared to constructed wetlands, and are therefore in most cases the technology chosen for stormwater treatment.

Wet ponds for stormwater treatment perform excellently with respect to particulate matter removal. However, removal of dissolved and colloidal pollutants is comparatively low (Marsalek *et al.* 1999; Semadeni-Davies 2006; Tuccillo 2006; Vollertsen *et al.* 2007). Unfortunately, pollutants on dissolved form or associated with colloids are more mobile in the aquatic ecosystem and more available for biological uptake. They consequently have a higher potential for causing ecotoxic impacts on the receiving water bodies.

It is therefore an environmental issue to remove dissolved and colloidal pollutants in stormwater. The technologies are in principle available, and numerous laboratory studies and field studies have proven the effect of a large array of methods for removal of such pollutants. Furthermore, extensive knowledge on lake restoration can be transferred for application on stormwater treatment ponds. An EU LIFE Environment demonstration project–TREASURE–implements such technologies in full-scale stormwater treatment ponds. In the context of that project, 3 full-scale wet retention ponds are constructed. Each pond consists of a silt trap, a vegetated pond, sand filters and a technology for sorption of dissolved and colloidal pollutants. The sorption technologies differ between the facilities, namely:

- Fixed media sorption in a separate filter unit
- Precipitation and sorption in the bulk water by continuous addition of aluminium salts
- Sorption to iron oxide enriched pond sediments

The facilities are constructed with monitoring in mind, and contain equipment for continuous measuring of flow and water quality parameters as well as flow proportional water sampling. It is the objective of this paper to present the treatment facility that applies fixed media sorption in a separate filter unit. The layout of and concept behind the facility is presented together with on-line monitoring results as well as results on the removal of nitrogen and phosphorus.

MATERIALS AND METHODS

The catchment

The facility is located in a recreational area in the southern part of Odense, Denmark. The catchment contains light industry and covers 27.4 ha of which 11.4 ha are impervious. The annual precipitation in the area has over the last 26 years been determined to 657 mm year^{-1}, and the annual average runoff from the catchment is estimated to 55.500 m^3. A permanent rain gauge from the Danish SVK system is located a few kilometres from facility.

The layout of the facility

The stormwater is piped to the facility by two 800 mm concrete pipes. The facility contains a grit chamber, a wet retention pond, sand filters and fixed media sorption filters (Figure 1). The sand filter unit is constructed as 3 separate filters and the sorption filter unit consists of 1 large filter and 3 smaller test filters. Green plants are furthermore integrated to enhance treatment as well as for aesthetic purposes. Flow is measured at the inlet and after the sand filters. Stormwater samples are collected at the inlet, in the pond, after the sand filters and after the sorption filters. DO, pH, temperature, and turbidity are measured continuously in the pond water. Measurement was initiated primo 2008.

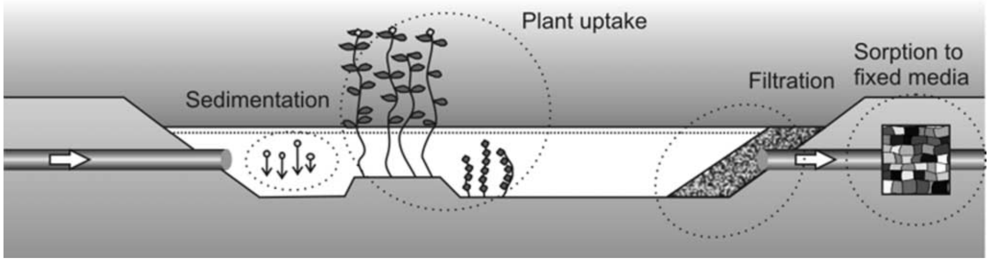

Figure 1 | Schematics of the facility with sorption in fixed media filters.

Wet pond

The retention volume of the wet pond is 1,992 m^3 with a surface area of 2,064 m^2 and a maximum depth of 1.45 m. The detention volume is 1,310 m^3 with a maximum surface area of 1,689 m^2. The maximum outflow from the facility is 25 $L\,s^{-1}$. The permanent pond volume per impermeable catchment area is 186 $m^3\,m^{-2}$ and the total pond volume per impermeable catchment area is 296 $m^3\,m^{-2}$–i.e. in the range of values recommended by e.g. Hvitved-Jacobsen *et al.* (1994), Pettersson *et al.* (1999) and Vollertsen *et al.* (2007).

Sand filters

Sand filters are prone to clogging from particles depositing on the filter surface, creating a colmation layer. This layer will typically have a much lower hydraulic conductivity than the filter medium, controlling the overall filter capacity. The limiting parameter for the filter capacity consequently becomes the depth and hydraulic conductivity of the colmation layer, which again is governed by parameters like filter loading, growth on the filters and drying out between storm events. Different filter layouts are consequently expected to behave differently with respect to long-term capacity.

In the scope of the LIFE Treasure project, three different sand filter layouts are tested (Figure 2):

- A horizontal filter placed in level with the permanent water level.
- A sloping filter placed in the embankment. The filter area starts in level with the permanent water level and goes up to the maximum level of the storage volume.
- A vertical filter placed in the pond. The filter area starts in level with the permanent water level and goes up to the maximum level of the storage volume.

The sand filters were designed based on a leakage factor approach as e.g. applied by Vollertsen & Hvitved-Jacobsen (2003) for exfiltration of wastewater from sewers. Assuming the colmation layer to be homogenous with a well defined depth and the conductivity of the layer much lower than the conductivity of the underlying filter material, the flow through the colmation layer occurs as saturated flow and can as a first estimation be described by Darcy's law, ignoring the underlying soil (e.g. Rauch & Stegner 1994). i.e. the flow through the colmation layer can be described by Equation (1).

$$Q_{\text{out}} = A_{\text{out}} \Delta h \, L_{\text{out}} \tag{1}$$

where Q_{out} is the filter capacity [$m^3\,s^{-1}$], A_{out} is the area through which water is filtered [m^2], Δh is the water pressure on the filter [m] and L_{out} is the leakage factor [s^{-1}]–i.e. the hydraulic conductivity of the colmation layer [$m\,s^{-1}$] divided by the colmation layer depth [m].

The reported hydraulic conductivities of colmation layers from wastewater infiltration and river beds lead to

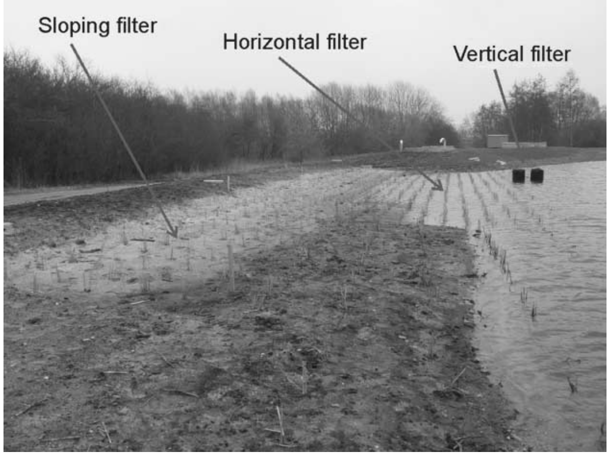

Figure 2 | Sand filters.

the conclusion that the hydraulic conductivity of a colmation layer formed under a permanent water level is likely to be at least $10^{-7}\,\mathrm{m\,s^{-1}}$, with a likely value 1–2 decades higher (Houston *et al.* 1999; Calver 2001; Vollertsen & Hvitved-Jacobsen 2003; Reed *et al.* 2006). Dechesne *et al.* (2005) report stormwater infiltration field measurements for 4 infiltration basins that had been in operation between 10 and 21 years. For the basin with the lowest infiltration capacity, they report an infiltration rate of around $1.1 \times 10^{-4}\,\mathrm{m^3\,m^{-2}\,s^{-1}}$ at 0.5 m of water depth, i.e. a leakage factor of $2.2 \times 10^{-4}\,\mathrm{s^{-1}}$. For stormwater infiltration through a filter with intermittent loading, a design leakage factor of around $10^{-4}\,\mathrm{s^{-1}}$ therefore seemed a conservative choice. The horizontal sand filter was assumed to develop the deepest colmation layer, followed by the sloping filter and the vertical filter. The filter sizes were chosen based here on: 1 filter of 20 m length and 5 m width; 1 filter of 30 m length, 3 m width and slope 1:5; 4 filters of 0.5 m diameter and 0.55 m height (Figure 2).

Sorption filters

Materials containing calcite ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$) like limestone, marble, dolomite rock and different types of fossil shells are efficient in retaining phosphorus (Brix *et al.* 2001; Vohla *et al.* 2005; Westholm 2006). When it comes to the control of heavy metals, materials containing alumina and iron have proven efficient (Genc-Fuhrman *et al.* 2007). Designing sorption filters, it is essential that the selected filter media has a high sorption capacity at the rather low pollutant concentration levels characteristic of stormwater runoff, allowing for efficient long-term use of the filter media. In order to reduce the required contact time, the kinetics of the sorption process must be rapid. Furthermore must the sorption material be commercially available at an affordable price/effect ratio. The sorption materials applied in the present project have been chosen taking the mentioned aspects into account. The filter medium must furthermore have a good hydraulic conductivity and clogging of the material must be avoided. Prior to treatment by the sorption filter, the stormwater is therefore pre-treated by the sand filters.

The sorption filters are divided into 1 large filter and 3 smaller test filters. The larger filter is rectangular with a footprint of $24\,\mathrm{m^2}$ and holds $55\,\mathrm{m^3}$ of Oyta Shells, type OYTA 0 (Oytaco Ltd, Denmark), a natural product obtained from deposits of fossil oyster shells in the shallow waters of the North Sea. The size of the material is 0.5–2 mm and consists to 96% of $CaCO_3$ and $MgCO_3$ with a Calcium content of 38%. The water runs through the filter by gravitation.

The smaller test filters are circular with a surface area of $1.23\,\mathrm{m^2}$. One filter holds $2.5\,\mathrm{m^3}$ of Oyta Shells, another holds $2.5\,\mathrm{m^3}$ of granulated olivine (Filtersil 2749 from North Cape Minerals, Norway). The last filter is built as a sandwich filter with $0.5\,\mathrm{m^3}$ of Oyta Shells as the bottom layer, followed by $0.5\,\mathrm{m^3}$ of iron oxide coated olivine (Filtersil TOC from North Cape Minerals, Norway) and $1.5\,\mathrm{m^3}$ of Oyta Shells as the top layer. The 3 test filters are fed by intermittent pumping in order to precisely control the flow rate and pattern through the filters.

Monitoring and sampling

Inlet flow measurement consists of 2 full flowing magnetic flow meters coupled in series together with a rectangular weir coupled in parallel with the two magnetic flow meters. The flow meters are protected against silting by a grit chamber of $26\,\mathrm{m^3}$. The magnetic flow meters are of type Krone Optiflux, DN 150 mm and DN 500 mm, respectively. The resulting measurement accuracy is better than 1% for flow rates between $5\,\mathrm{L\,s^{-1}}$ and approximately $1\,\mathrm{m^3\,s^{-1}}$, at which flow rate the rectangular weir starts to convey part of the flow. The flow over the weir is metered by a pressure gauge located in the middle of the silt trap and a preliminary flow rate is calculated from a weir equation.

The flow from each of the 3 sand filters is measured by a full flowing magnetic flow meter of type Krone Optiflux, DN 80 mm with accuracy better than 1% for flow rates above $1.5\,\mathrm{L\,s^{-1}}$.

Flow proportional water samples are collected by automated water samplers of type Maxx TP IV, holding 24 one-litre bottles. Water is sampled from the inlet, the downstream part of the pond, after the sand filters and after the sorption filters. The sampler at the inlet is controlled by the combined measurement of the inlet flow whereas the other samplers are controlled by the combined measurement of the flow out of the sand filters.

DO, turbidity, pH, temperature and water level are continuously measured and registered. DO is measured by an optical device of type FDO 700 from WTW with a nominal accuracy of 0.1 mg L^{-1}. Turbidity is measured by a VisoTurb 700 meter from WTW with a nominal accuracy of 0.05 FNU. Both the FDO 700 probe and the VisoTurb 700 probe are supplied with compressed air cleaning heads. The pH is measured by a SensoLyt SEA probe from WTW and temperature is registered through the NTC temperature probe build into the pH-meter. The water level is metered by a Hydrobar I pressure transducer from Klay-Instruments with an accuracy of 1 cm.

The instruments are placed on a movable frame to facilitate maintenance of the probes. The frame is placed in the pond at approximately 1 m of water, ensuring 0.5–0.7 m of water coverage over the sensors. The pressure transducer is fixed at the bottom of the pond by means of a concrete slab.

RESULTS AND DISCUSSION

Figure 3 shows the result of continued water quality measurement in the pond for the period February 12, 2008 till April 5, 2009. The total inflow to the pond in this period was 79,900 m^3, corresponding to an average residence time of the stormwater of approximately 10 days.

The variability in pH and DO during spring, summer and autumn were large compared to the variability during winter. During much of the summer the DO was above 20 g m^{-3}–i.e. more than 200% of oxygen saturation–whereas it at other times fell to zero, albeit only for short durations. The DO supersaturation was most likely caused by suspended algae as the rooted plants were newly planted and only covered the brinks of the pond. Low oxygen levels occurred mainly during night and early morning and could have been caused by algae as well as bacteria in the pond sediments. The periodic oxygen supersaturation began middle of April and lasted till middle of November. In other words, photosynthesis played a significant role from early spring till late autumn.

Stormwater inflow events caused rapid changes in oxygen, pH and turbidity. As an example hereof, Figure 4 shows data from April 14 to May 14, 2008. The first and the second inflow event caused pH to drop approximately one pH unit–the larger inflow event causing the larger pH-drop. At the first event, the DO concentration dropped by approximately 7 g m^{-3}, the cause being that the pond water was supersaturated with oxygen prior to this event whereas the stormwater probably was saturated. At the second inflow event, the DO was only slightly affected, as DO in the pond was close to saturation.

The turbidity of the pond water increased upon these events, and slowly decreased during the following dry weather periods with a rate that was approximately exponential (Figure 4). Whether the increase in turbidity during storm events was caused by the incoming stormwater, by resuspension of bottom sediments or by a combination is not clear.

From the beginning of May, the pond water turbidity showed diurnal variations during dry weather (Figure 4). Turbidity increased during the day and decreased during the night. Similarly, DO exhibited clear diurnal variation with variations as high as 5–8 g m^{-3}. Some days of July, DO fell overnight from supersaturation to nearly zero (Figure 3). Bulk water pH varied over the day with as much 1 pH unit. All three parameters peaked in the late part of the day. Such variability is typical for photosynthesis, but also bacterial activity could have played a role.

The pond water temperature varied with daily amplitudes up to 3°C. The lowest temperature occurred in the morning and the highest temperature in late afternoon. The temperature variations in the pond were only insignificantly affected by even the largest of the storm events, indicating that the incoming stormwater was of a temperature similar to the pond water.

Scrutinizing the turbidity of the pond water in comparison with the inflow to the pond, increases in turbidity were often seen to occur within 1–2 hours of the onset of inflow. The response time of the turbidity on the incoming stormwater tended to decrease with increasing inflow rates. Similarly, changes in pH and DO due to inflowing stormwater occurred within hours of the onset of a storm event. The average retention time of stormwater from individual events was significantly larger than the time until the turbidity, DO and pH in the middle of the pond was affected, meaning that the flow through the pond did not

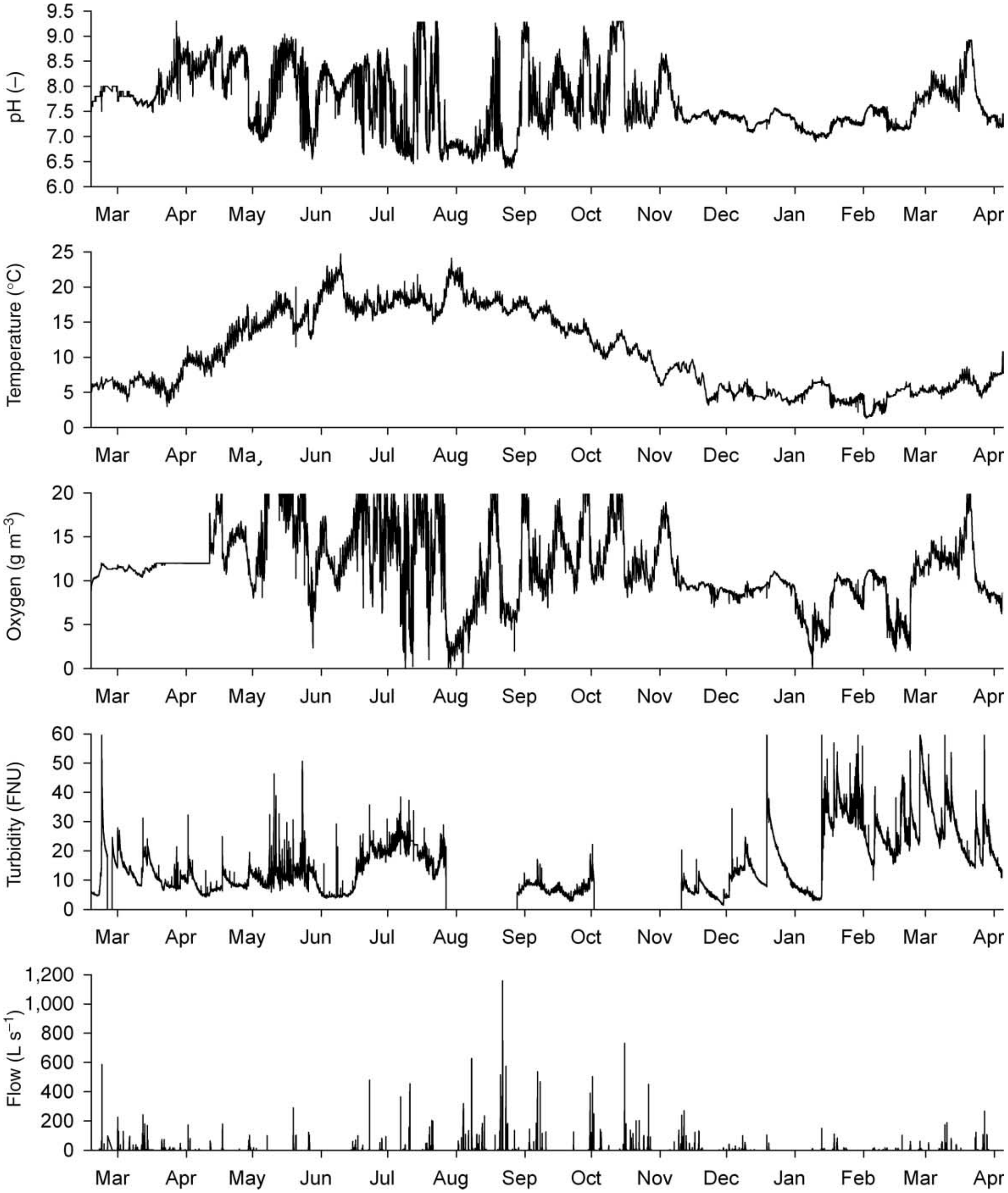

Figure 3 | pH, Temperature DO and turbidity in the middle of the pond as well as pond inflow for the period February 12, 2008 till April 5, 2009.

occur as plug-flow and that the incoming stormwater was rapidly mixed with the water initially in the pond. Vollertsen *et al.* (2007) reports a similar observation analyzing the treatment efficiency of a Norwegian stormwater pond of comparable geometry.

Length to width ratios of retention ponds have typically been recommended to above 3:1 to ensure that the incoming stormwater does not shortcut its way to the outlet (Mays 2001). However, as even the length to width ratio of 4.5:1 applied in the studied pond resulted in a flow pattern closer

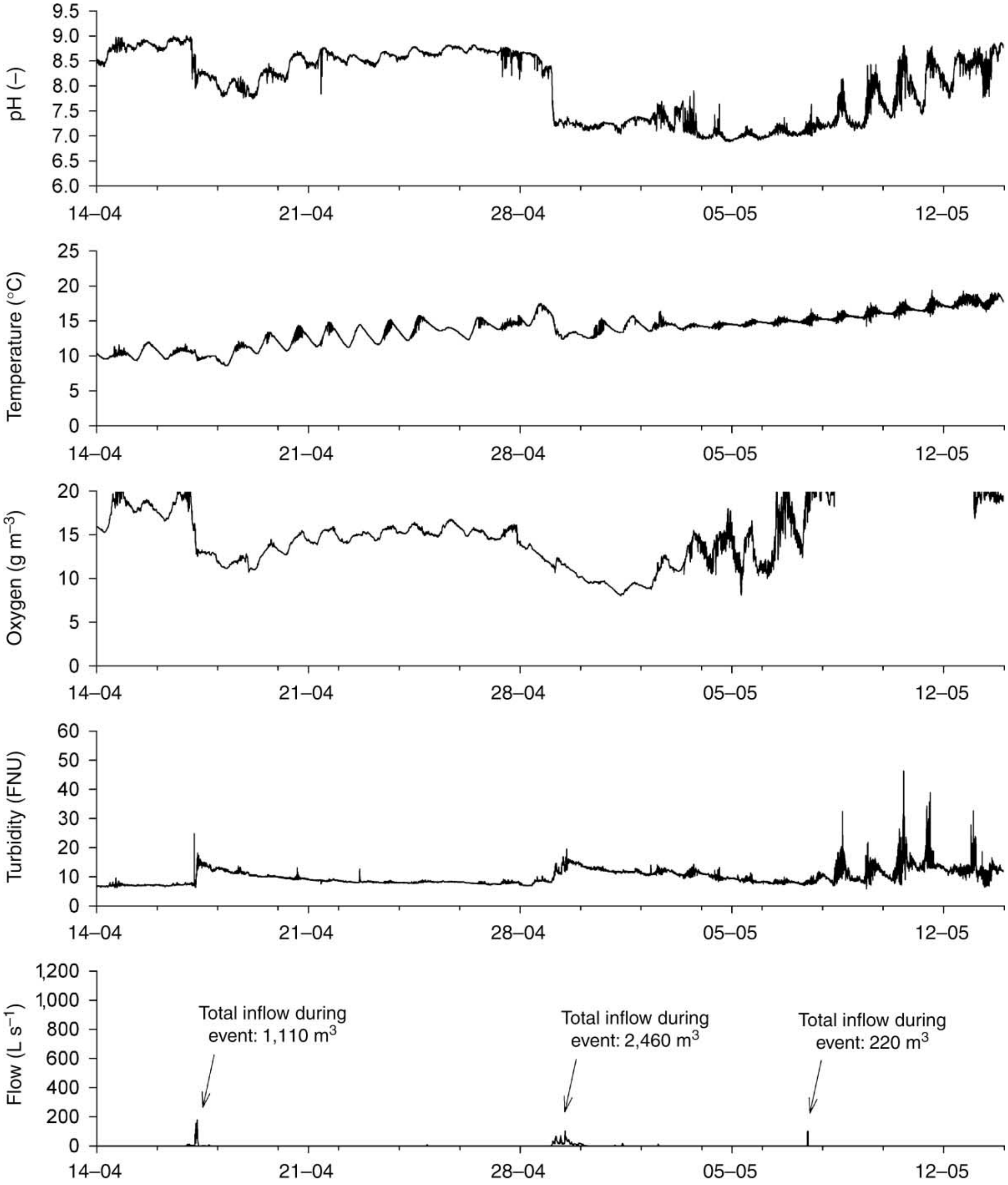

Figure 4 | One month of the continual measurements shown in Figure 3.

to a completely mixed reactor than to a plug flow reactor, the important design parameter is not so much the length to width ratio but the avoidance of shortcuts between inlet and outlet. The later can be achieved with any pond configuration when designing the inlet and outlet appropriately.

With respect to removal of nitrogen and phosphorus the treatment train consisting of wet pond, sand filter and sorption filter was very efficient (Figure 5). It removed orthophosphate to below the detection limit (0.005 g P m^{-3}) for 75% of the time, total phosphorus to an average of

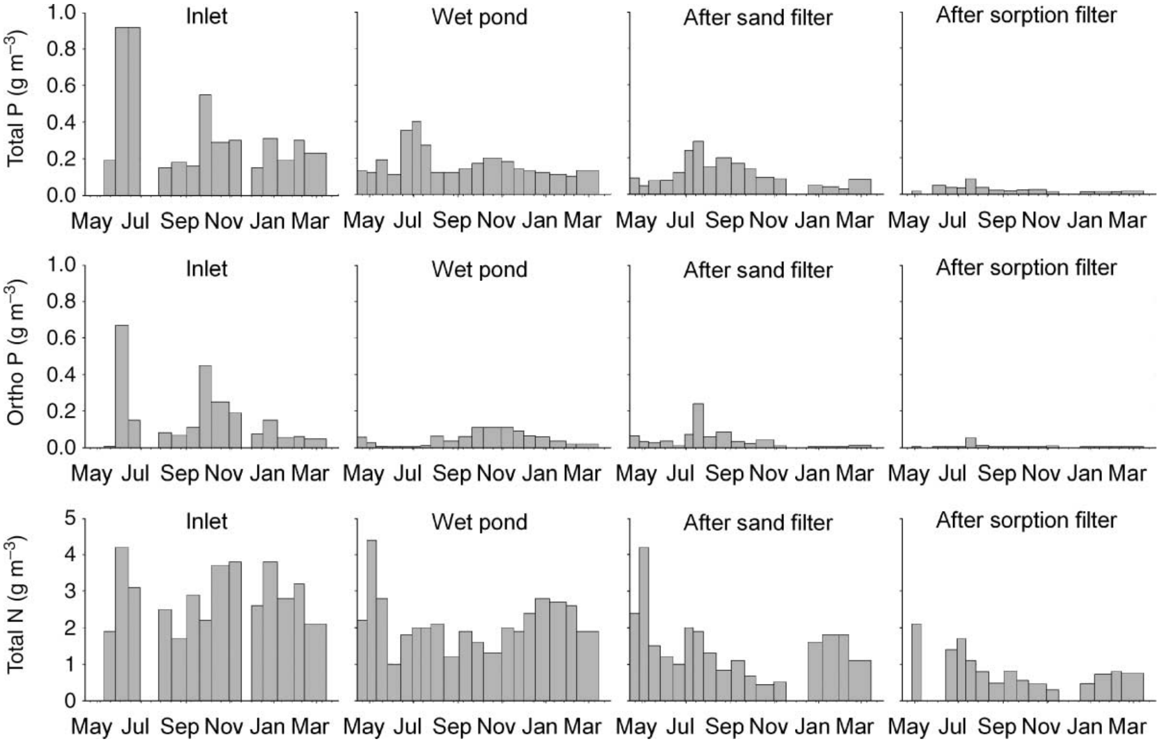

Figure 5 | Total phosphorus, orthophosphate and total nitrogen from April, 2008 till March, 2009.

$0.028\,\mathrm{g\,P\,m^{-3}}$ and total nitrogen to an average of $1.3\,\mathrm{g\,N\,m^{-3}}$.

The removal processes in such a treatment train is a combination of sedimentation, biological uptake, filtration and sorption. Taking for example phosphorus in the pond, an increase in total phosphorus in June and July was accompanied by low concentrations of orthophosphate because the algae bloom during this period caused a depletion of bioavailable phosphorus. The sand filters removed some total phosphorus but little orthophosphate, while the sorption filters were much more effective in this respect. With respect to nitrogen, the sedimentation in the wet pond and the sand filtration was the most effective unit operations.

CONCLUSION

Continuous measurements of pH, turbidity, temperature and DO have been applied to monitor the startup of a newly established stormwater retention pond. The data showed for example that algal photosynthesis was important from early spring till late autumn. During this part of the year, diurnal variations in DO and pH were quite significant and DO could over night go from supersaturation to nearly zero. Another important observation was that the flow through the pond did not occur as plug flow but that the water rapidly became completely mixed–even though the length to width ratio was as high as 4.5:1. The removal of phosphorus and nitrogen in the facility was very good, and the effect of the different unit operations in the treatment train was documented. For total phosphorus and orthophosphate the sorption filters were crucial to ensure low outlet concentrations, whereas they played a minor role for total nitrogen.

The monitoring of the pond continues till autumn 2009, and includes measurement of heavy metals and PAH. Together with the online measurements, the chemical water quality parameters are expected to yield knowledge on the detailed behavior of the pond which will allow an improved understanding of the pollutant removal mechanisms in wet retention ponds.

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