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

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 settleable 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...
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 m3 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 m3 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 Algaltox-kit F™, MicroBio Tests Inc., was applied. This algal toxicity

<table>
<thead>
<tr>
<th>Odense</th>
<th>Stormwater runoff</th>
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<th>Stormwater runoff</th>
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<td>Heavy metals</td>
<td>PAHs</td>
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<tr>
<td>24</td>
<td>16</td>
<td>29</td>
<td>23</td>
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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 O₂ and CO₂. The cuvettes were used as incubation chambers. The cuvettes were made for each dilution, and 10 cm plastic cuvettes 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 O₂ and CO₂. 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 EC50-value [with the unit % pond water runoff]. EC50 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 EC50-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 EC50-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 EC50-value from that pond and if a weak toxic effect was observed an EC50-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

EC50-values for selected pure metal salts were determined for reference purposes. Solutions with Cd(NO₃)₂, Cu (NO₃)₂, Pb(NO₃)₂, Zn(NO₃)₂, Cr(NO₃)₂ and Ni(NO₃)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 Skul lerud, Norway (Vollersen et al. 2009b) particularly for
The initial tests with pure metals showed that the test organism *Selenastrum capricornutum* was highly sensitive towards copper, moderately sensitive towards zinc, and 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

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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 EC50-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 EC50 values and could potentially have caused high toxic effects. Medians of the metal concentrations in the Aarhus pond water were all below the corresponding EC50-values. However, the maximum concentrations of copper and zinc were 1.9 and 3.3 times higher than the EC50-values and could therefore potentially have caused toxic effects. Nickel had a maximum concentration which corresponded to half of the measured EC50-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.

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 EC50-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 EC50-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

**Table 5** | Determined EC50-values for pure metal salts and calculated standard deviations

<table>
<thead>
<tr>
<th></th>
<th>Cu (NO3)2</th>
<th>Pb (NO3)2</th>
<th>Zn (NO3)2</th>
<th>Cd (NO3)2</th>
<th>Ni (NO3)2</th>
<th>Cr (NO3)2</th>
</tr>
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<tbody>
<tr>
<td>EC50 [mg m⁻³]</td>
<td>39</td>
<td>3181</td>
<td>97</td>
<td>107</td>
<td>188</td>
<td>103</td>
</tr>
<tr>
<td>Std. Error</td>
<td>3.8</td>
<td>944</td>
<td>79</td>
<td>8.3</td>
<td>40</td>
<td>21</td>
</tr>
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</table>

**Figure 1** | Toxicity of the pond water towards the algae *Selenastrum capricornutum* and summarized concentration of PAHs in the pond water. Note that low EC50 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, 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...
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 EC50-value for nickel.
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.

REFERENCES


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