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Heavy metal composition in stormwater and retention in ponds dependent on pond age, design and catchment type

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Heavy metals have toxic effects on flora and fauna in the aquatic environments and are of great concern in stormwater. Heavy metal runoff was studied in 37 stormwater ponds in Denmark with varying heavy metal load, catchment type and pond design. The studied metals were Cu, Cr, Cd, Pb, Ni and Zn. The concentrations varied considerably depending on the catchment type, with the highest concentrations coming from industrial areas and the lowest from uncultivated and rural areas. Ponds can effectively remove heavy metals in particulate forms through sedimentation processes, but the dissolved forms are more difficult to retain. The removal efficiency in the ponds varied considerably, with the highest retention of Pb, Ni and Zn due to higher particulate fraction. The retention increased with increased pond volume-to-reduced catchment area ratio. In addition, the pond age affected the efficiency; whereas ponds less than 1–2 years efficiently removed all metals, 30–40-year-old ponds only removed Pb, Ni and Zn, but steeply decreasing over the years. Physical parameters such as pond size, age and sedimentation patterns were found to play a more significant role in the removal compared with chemical parameters such as pH, oxygen and organic matter. Input of metals to the ponds was reflected in the sediment content, but not significantly for all heavy metals probably due to low or varying retention caused by mineralization and re-suspension. The heavy metal concentration in the outlets was reduced to non-toxic levels, except for Cu and Cr at a few study sites.

Keywords: urban runoff; sedimentation; water quality; xenobiotics; ponds

Introduction

Worldwide climate changes are a major challenge. In the northern temperate zone, climate changes are currently causing more intense rain events due to a warmer atmosphere. The annual precipitation in Denmark is predicted to increase 30% in the period 2021–2050 compared with 1961–1990. This forces the society to initiate improvements of the urban stormwater management. The sewage systems built decades ago are often not designed to process the higher stormwater load as a consequence of both increased pavement and increasing cities caused by the growing human population. Increased pavement in urban areas are hindering natural infiltration processes that act as discharge buffers during rain events, as soil porosity and water permeability work as temporal and spatial buffers. Uncoupling these natural magazines increases the risks and impacts of urban floods.[1] Consequences increased hydraulic loading of the receiving water systems, and also the load of hazardous substances is rising.[1] Heavy metals are pollutants of great concern in stormwater runoff because they are potentially toxic for the downstream aquatic environments.

In general, heavy metals are known to be toxic and carcinogenic and due to their non-biodegradability they tend to accumulate in living organisms.[2] Runoff managers are concerned about the heavy metal content in urban runoff, because of the adverse effects on receiving waters, ecosystems and human health. Heavy metals are transported both in dissolved and particulate forms of which especially the dissolved forms are toxic in the aquatic environment, as they are readily bioavailable and highly mobile. The particulate forms do not cause instant risk, but can be transformed to dissolved forms under adverse environmental conditions,[3] for example (1) low oxygen concentrations where redox-dependent desorption processes are realized, (2) increasing mineralization processes exhausting the adsorption capacity or (3) through acid precipitation where pH-dependent desorption is activated.[4] Heavy metals such as Cu, Zn and sometimes Ni are important biological micro-nutrients. They are required in biological growth processes of many aquatic organisms, but at higher concentrations they become toxic, whereas metals such as Pb, Cr and Cd are not required for growth and are very toxic even in trace amounts.[5,6] Cu and Pb are often found to be the major toxic metals in stormwater with very low toxicity thresholds.[7]

The concentrations of heavy metals in stormwater vary considerably. Makepeace et al. [7] found Cu concentrations

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*Corresponding author: Email: saege@biology.sdu.dk ranging from 0.00006 to 1.4 mg L^{-1}, Cd concentrations from 0.00005 to 14 mg L^{-1}, Cr concentrations from 0.001 to 2.3 mg L^{-1}, Pb concentrations from 0.00057 to 26 mg L^{-1}, Ni concentrations from 0.001 to 49 mg L^{-1} and Zn concentrations from 0.0007 to 22 mg L^{-1}. Heavy metals are mostly transported in urban runoff associated with suspended solids, organic matter and particles, but they may also be in dissolved forms as seen for especially Cu and Cd.[7–10] Factors affecting the solubility could be pH, alkalinity, temperature, particles and organic matter as well as other substances in the water such as de-icing salts causing corrosion, see, for example.[11] Measurements indicated seasonal variations in the transport pattern with a dominating particle bound metal runoff during winter while the dissolved metal transport are realized during summer,[12] but also during dry period, with precipitation duration and intensity play important roles for the content.[13] In studies related to catchment types, Joshi et al. [3] found that Zn (436 µg L^{-1}) and Cr (186 µg L^{-1}) showed the highest concentrations in residential runoff, while Zn (1127 µg L^{-1}), Cr (214 µg L^{-1}) and Cu (241 µg L^{-1}) had the highest concentrations in industrial runoff. Pb had intermediate concentrations in both runoff types (51–90 µg L^{-1}), and finally Ni (9–15 µg L^{-1}) and Cd (2–5 µg L^{-1}) showed the lowest concentrations in both types of runoff. Overall, industrial runoff was much more polluted than residential runoff.

Both natural and anthropogenic pathways contribute to the origin of heavy metals in stormwater. Natural sources are volcanic, geothermal activity or geological weathering processes,[9,10,14] while anthropogenic important factors are corrosion of building materials and cars, transport, industrial sources and processes, mining activities, municipal wastes and use of fertilizers and pesticides. For many heavy metals, Ward [14] found a positive correlation with the intensity of traffic.

Increased runoff containing heavy metal can be addressed by introducing different kinds of stormwater ponds. Sizing and design of ponds has previously focused on reduction in the hydraulic loading to prevent flooding and downstream erosion, while no aims have been developed for retention of various substances. The particulate heavy metal fraction can be retained in the ponds by sedimentation processes, whereas the dissolved fraction requires additional mechanisms for its removal. Various studies examined the retention efficiency and authors found that stormwater ponds actually have the ability to retain especially particulate substances, but the retention efficiencies for different heavy metals vary considerably between studies and pond type.[12,15–18] Retention capacity depends on not only several pond-related factors, for example, type, age, volume/catchment ratio and hydraulic-based residence time, but also land use and runoff patterns are enforcing the amount and characteristics of the heavy metal input to the ponds as well as pH, alkalinity, organic matter and other substances. The retention capacity can be increased by combining the ponds with filter systems containing materials such as different sand types. Also other alternative materials are studied and tested, for example, peat, bark, fly ash or crushed concrete.[19–22] Many studies have investigated the efficiency of one or a few stormwater ponds, whereas studies looking into many ponds with varying design, size and catchments types are rare.

In this study, 37 stormwater ponds of different types with varying land use in the catchments were investigated regarding loading and retention of six different heavy metals: Cu, Cr, Cd, Pb, Ni and Zn. The aim was to study the concentration of heavy metals in the stormwater dependent on the catchment type and to evaluate the removal efficiency dependent on factors such as pond design, volume, age and distance between in- and outlet (water distance). Also the sediment in the ponds was studied to find a possible relation between the amount of heavy metals in the runoff and the amount of heavy metals found in the sediment of the ponds.

Materials and methods

All the 37 stormwater ponds in this study are situated in the Municipality of Aabenraa in the southern part of Denmark (characteristics are listed in Table 1). The ponds are a subset of 110 stormwater ponds in the area, all managed by the supply company Arwos. The selection of ponds was based on criteria such as catchment type, design, age, volume/catchment ratio and physical accessibility to take water samples in both in- and outlet. The land use in the studied catchment areas was divided into four types: uncultivated (5 ponds), rural (6 ponds, mostly villages in agricultural areas), urban (9 ponds) and industrial (17 ponds). The industrial areas can in a worldwide perspective be characterized as the light industry, since Denmark does not host any heavy industry. The ponds vary in type where the majority is wet ponds (26), wet ponds with filters (5), grooves (4), a dry pond and a ditch are represented in this study. The total catchment area varied from 1.0 to 95.6 ha, whereas the reduced catchment area is 0.6–47.8 ha. The volume of the ponds is 2–10,491 m^3 and they were constructed in the period 1975–2011 making retention as a function of age possible.

All ponds were sampled in the winter 2011/2012. Water samples were collected from inlets, in the middle of the ponds and outlets, whereas undisturbed sediment cores were taken by a Kajak gravity corer in the ponds close to the inlet in all ponds and close to the outlet in five ponds for verification of sediment homogeneity. Oxygen, pH and conductivity were measured by YSI electrodes. Additionally, water flow in inlets and outlets was measured on the sampling day by a Kleinflügel propeller instrument (triplicate measurements per site). If the water was flowing from a smaller pipe, then the ‘bucket method’ was used, where the time to fill a

Table 1. Main characteristics of the 37 investigated stormwater ponds.

Catchment type	No. of ponds	Pond type	Total catchment area (ha)	Reduced catchment (red ha)	Pond volume (m^3)	Construction year
Uncultivated	5	3 wet, 2 filter	3.4–23.2 **5.4**	1.0–7.0 **2.5**	203–3628 **634**	2002–2011 **2008**
Rural (villages in cultivated areas)	6	4 wet, 2 grooves	1.0–15.5 **6.3**	0.6–5.4 **2.0**	2–2219 **194**	1980–2011 **2001**
Urban areas (towns)	9	8 wet, 1 groove	5.0–20.1 **9.2**	1.5–25.6 **3.1**	188–1482 **396**	1986–2011 **2004**
Industry	17	11 wet, 3 filter, 1 groove, 1 ditch, 1 dry	6.1–95.6 **23.5**	2.8–47.8 **12.0**	3–10491 **2295**	1975–2011 **2000**

Note: Wet = wet retention pond, filter = wet retention pond followed by a vegetated filter zone with sand as filter material, groove = groove with overflow possibility to detention area, dry = dry detention pond, ditch = ditch as extra storage volume. Areas, volumes and ages are all given as range (first line) and median (second line, bold).

bucket with a defined volume was registered (triplicate measurements).

A known volume of all water samples was filtered through pre-washed, pre-ignited and pre-weighted GF/C-filters. The filters were dried for 24 h at 105°C, weighed and stored until later analysis. The particulate heavy metal fraction and loss of ignition (LOI) were measured on the filtered material. The filtrate was used for measurement of colour, dissolved organic carbon (DOC) and dissolved heavy metals. The latter was conserved with 4 M HNO_3 (750 µL per 100 mL sample). The sediment cores were sliced and the upper 5 cm was used for the measurements. The sediment samples were homogenized and about 20 g was transferred to pre-weighted crucibles and re-weighted after the samples were dried for 24 h at 105°C or until constant weight and afterwards stored for later analysis.

Filters with the particulate heavy metal fraction were solubilized by digestion in 6 mL 65% HNO_3 by a microwave digester for 30 min at 1600 W heating the solution to 180°C. Afterward the particulate heavy metal concentrations were measured in the liquid phase after dilution by ICP-OES (inductively coupled plasma with optical emission spectroscopy; Optima 2100 DV, Perkin Elmer). Heavy metal contents in the sediment were measured similarly with the exception that 0.5 g of dry sediment was digested in 10 mL 65% HNO_3. Dissolved heavy metal concentrations were measured directly by ICP-OES on the filtered water samples. LOI was analysed by igniting the filter material for two hours at 520°C. Colour was measured according to Wetzel [23] and Hongve et al. [24] on filtered water, whereas DOC was measured with an infra-red spectrophotometer on a TOC 5000 Total Organic Carbon analyser.

All statistical analyses were performed by SigmaPlot 12, Systat Software Inc. Possible differences between groups such as catchment types, pond size and age were tested by one-way ANOVA analysis. Possible relationships between measured parameters were tested by the linear regression analysis. For both tests, α was chosen to be 0.05.

Results

Heavy metals in stormwater

The concentration of heavy metals in inlets and outlets of the stormwater ponds varied depending on the metal and catchment type. Figure 1 presents the average concentrations of the total metal content in inlet and outlet water from the 37 studied ponds divided into four catchment types: uncultivated, rural, urban and industrial areas. The Zn concentrations in the inlets were significantly higher (124–280 µg Zn L^{-1}) than the five other metals (1–18 µg L^{-1}). The second most abundant metal in the inlet waters was Cu (8–18 µg Cu L^{-1}), whereas Cr, Pb and Ni were present approximately at the same level (1–11 µg L^{-1}) and Cd showed the lowest concentrations (0.7–1.4 µg Cd L^{-1}). Water from industrial catchments had in general the highest metal concentrations (significant for Pb and Ni). The only exception was Cd showing more or less equal low concentrations independent of catchment type. No significant differences were found between the inlet concentrations from uncultivated, rural and urban catchments.

The concentrations in the outlet water from the ponds showed more or less the same patterns described for the inlet samples. The concentrations were in general lower due to retention in the pond (discussed in detail later). The concentrations among the different catchment types were also more alike for the specific metals. There was significant difference only for Cd. The highest concentrations were measured in ponds with urban and industrial catchments.

The distribution between measured particulate and dissolved metal fractions in the water samples is very interesting, as the main functions in ponds are sedimentation processes. Figure 2 shows the proportion (%) of dissolved and particulate matter in the inlet samples separated after

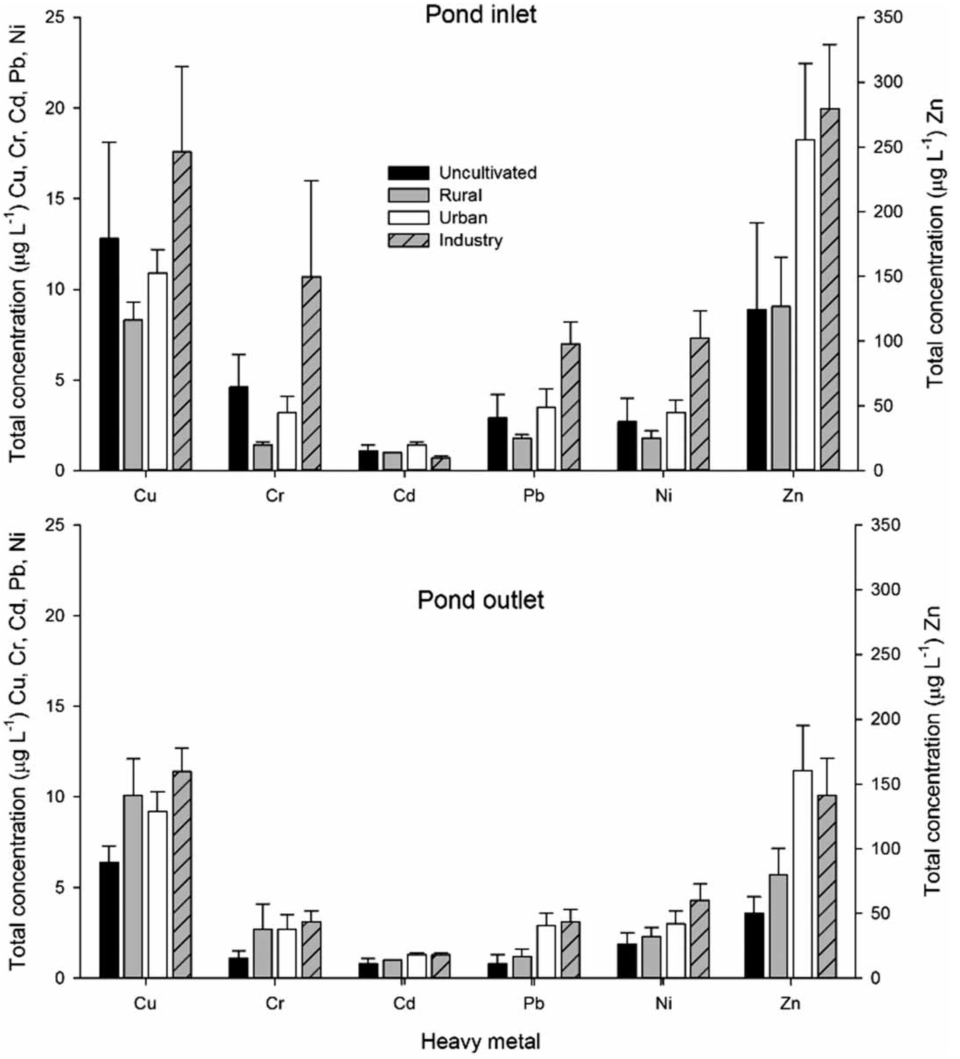

Figure 1. The total heavy metal concentrations (μg L^{-1}) and SEM of Cu, Cr, Cd, Pb, Ni and Zn in inlets and outlets from 37 ponds divided into catchment types.

catchment type and metal, whereas Table 2 presents the proportion (%) in inlets and outlets. The dissolved fraction of Cu was dominating in both inlet (63–89%) and outlet samples (75–93%) for all catchment types. It was similar for Ni with 57–73% dissolved in inlets and 63–95% in outlets. Dissolved fraction of Cr and Cd in inlet samples dominated in uncultivated, rural and urban catchments (56–75% for Cr and 71–98% for Cd), whereas the particulate fraction dominated in industrial catchments (Cr 93% and Cd 100%). In the outlet samples, dissolved Cr was still dominating (53–84%) in uncultivated, rural and industrial catchments, whereas only 46% dissolved Cr was found in urban areas. For Cd, the dissolved fraction was dominating in outlets of all catchments (78–100%). Pb and Zn had a higher proportion of particulate metals. For Pb, in inlet samples the dissolved fraction was dominating for uncultivated (57%) and rural catchments (67%), whereas the particulate fraction was dominating for urban (63%) and industrial catchments (68%). The same tendency was found for Pb in outlet samples where the particulate fraction dominated (52–65%) except for uncultivated catchments (4%). Finally, the particulate fraction of Zn in both inlet and outlet samples dominated for all catchments (50–81% and 58–72%, respectively). In summary, Cu and Ni were mainly dissolved, whereas Zn was mainly particulate fraction and Cr, Cd and Pb were a mixture of dissolved and particulate fractions dependent on the catchment type and whether the sample was taken at the inlet or outlet of the pond. In general, the proportion of dissolved metals was increasing from inlet to outlet except for the urban group where the proportion was more or less equal in inlets and outlets. Industrial catchments were characterized by mainly particulate heavy metals, whereas the opposite was the case for the other catchment types.

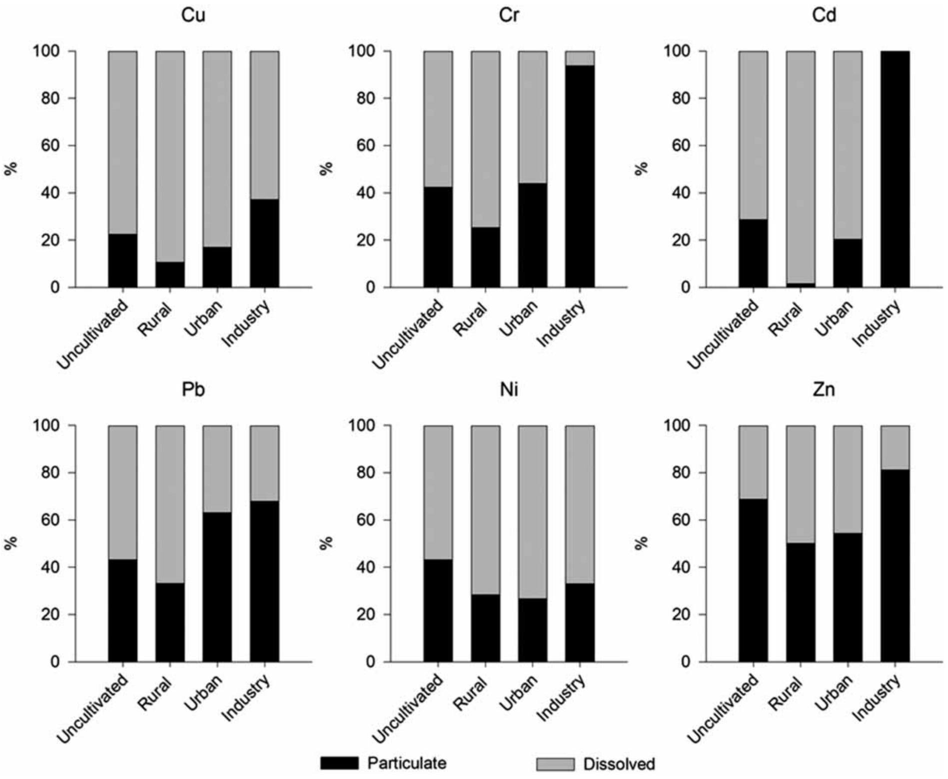

Figure 2. Proportion (%) of dissolved and particulate heavy metals in the inlets to the ponds divided into catchment types. Data are from 37 ponds in total.

Table 2. Distribution of particulate (Par) and dissolved (Dis) heavy metals in inlets and outlets from the 37 ponds. Data are given as average contents (%).

		Inlet (%)		Outlet (%)	
Catchment	Metal	Par	Dis	Par	Dis
Uncultivated	Cu	22	78	11	89
	Cr	42	58	42	58
	Cd	29	71	5	95
	Pb	43	57	4	96
	Ni	43	57	27	73
	Zn	69	31	69	31
Urban	Cu	17	83	18	82
	Cr	44	56	54	46
	Cd	20	80	21	78
	Pb	63	37	65	35
	Ni	27	73	37	63
	Zn	54	46	67	33
Rural	Cu	11	89	7	93
	Cr	25	75	16	84
	Cd	2	98	0	100
	Pb	33	67	52	48
	Ni	28	72	5	95
	Zn	50	50	58	42
Industry	Cu	37	63	25	75
	Cr	93	7	47	53
	Cd	100	0	20	80
	Pb	68	32	53	47
	Ni	33	67	30	70
	Zn	81	19	72	28

Retention in the ponds

The metal retention in the 37 studied ponds varied, but the retention was in general higher in the younger ponds (Figure 3(a)). Ponds with an age of 1–2 years showed positive retentions for all metals, whereas the retention was decreasing in older ponds depending on the metals. For Cu, Cr and Cd, the retention became negative after 1–2 years, whereas for Pb, Ni and Zn the retention also decreased but stayed positive even after 31–40 years, which was the age of the oldest studied ponds.

The pond-to-catchment ratio (pond volume/reduced catchment area) was also affecting the retention (Figure 3(b)). The tendency was a positive correlation between pond-to-catchment ratio and heavy metal retention. Cu, Cr and Cd had negative retentions at ratios up to 800 m^3 ha^{-1}, whereas Pb, Ni and Zn had positive retentions at all ratio intervals, with higher retention in ponds with increased ratio. The metals with the highest proportion of particulate-bound metal also showed the best retention in general.

No significant relations were found between retention and pond type, retention and water distance in the pond nor retention and pond volume (Figure 4(a–c)). There was a weak trend towards an increased or at least positive retention with larger volume or larger distance from inlet to outlet. Regarding pond type, dry ponds and ditches were only represented by one location and among wet ponds

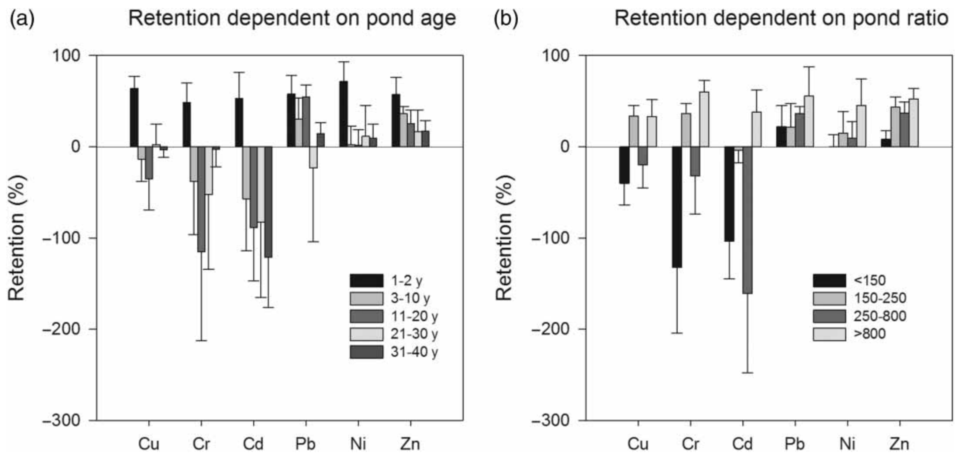

Figure 3. Retention (%) of heavy metals in the ponds divided into (a) pond age (years) and (b) pond-to-catchment ratio (pond volume (m^3)/reduced catchment area (ha)).

with and without filter as well as grooves there were no clear differences.

Table 3 gives the retention separated in catchment type, not because catchment type is expected directly to affect the heavy metal dynamics in the ponds but to present results for the same group of ponds throughout the paper. Zn had only positive retentions (12 ± 19% to 48 ± 13%) when averaged after catchment type, whereas the five remaining metals had both positive and negative average retentions. In uncultivated areas, the retention was positive for all metals, whereas industrial and rural catchments had high negative retentions. The metals with the highest proportion of particulate metals also show the highest retentions.

Heavy metals in the sediment

The measured sediment content of heavy metals in the ponds (mg kg^{-1} DW) is shown in Figure 5. Here the metal contents increased from uncultivated to rural, urban, and finally the highest content was found in ponds receiving runoff from industrial catchments. The Cd content in the sediments was very low (0.1–1.4 mg kg^{-1} DW), followed by Cu, Cr, Pb and Ni (18–62 mg kg^{-1} DW), whereas Zn had the highest content (166–451 mg kg^{-1} DW). The Pb sediment content was significantly higher ($p = 0.045$) in the oldest ponds (31–40 years) compared with younger ponds. The highest metal content was found in the ponds with the lowest pond volume-to-catchment ratio, whereas the metal content in the sediment decreased with a larger sediment area available in relation to the catchment size.

A high particulate metal content (mg kg^{-1} SS) in the inlet may also result in higher sediment content (mg kg^{-1} DW). For Cu and Cr (Table 4), there was a significant positive correlation between particulate inlet content and sediment content ($p < 0.001$ for both metals). The correlation was also close to significance for Ni ($p = 0.076$), whereas a significant correlation was not found for Cd, Pb and Zn ($p = 0.112$–0.605). The ratio between particulate water content and sediment content also differed among the metals (Table 4), with Ni having the lowest (3.9 ± 0.5), followed by Cu, Cr and Pb (ranging from 6.2 to 7.9), whereas the ratio for Cd was 25.6 ± 6.1, and finally Zn with 53.8 ± 11.3.

Discussion

Heavy metals in stormwater

The catchment type is influencing both the concentration and the composition of the six studied heavy metals in stormwater runoff (Figure 1). Runoff from industrial catchments generally had the highest concentration of heavy metals which is in accordance with the literature. The measured concentrations in the industrial runoff are though in the same range, but generally lower compared to previously reported values in the literature, for example.[3] The lower values may be explained by differences in intensities of industrial activities and the area-specific pavement in each of the catchments, varying regulations and different uses of industrial areas both within and between countries. The lack of local metal resources means that Denmark does not have any really heavy industry. An example of this is the study from Singapore reported by Joshi et al.,[3] where the industry is more intensive compared with this Danish study site. However, the water concentrations in the present study were only significantly higher for Pb and Ni from industrial catchments compared with the other catchment types, meaning that even though there is a tendency towards higher load from industrial areas, the industrial catchments are not causing severe loadings of Cu, Cr, Cd and Zn compared with the other catchment types. The most abundant heavy metals in agricultural soils are Zn and Cu, whereas Pb and Ni are available in low amounts in agricultural soils but in high amounts in industrial areas.[25] This may explain why the concentrations of Pb and Ni were

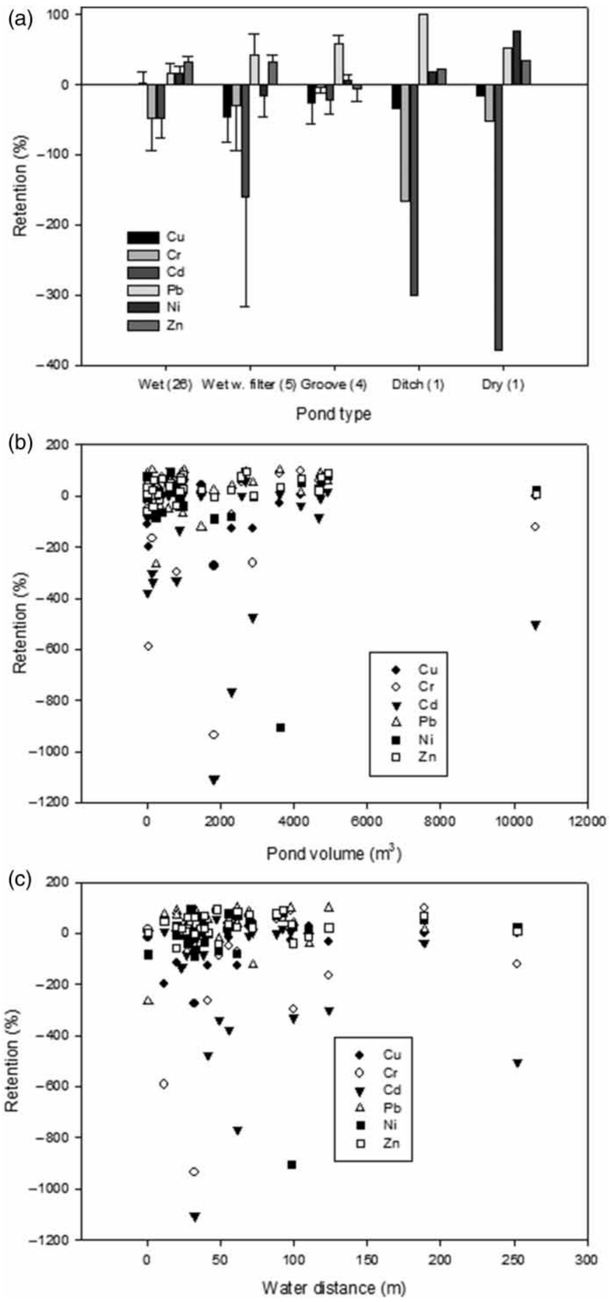

Figure 4. Retention (%) of heavy metals in the ponds divided by type (a) and related to pond volume (b) and water distance from inlet to outlet (c). For one pond the Ni retention was –4200% and this point is omitted as an outlier.

significantly higher in industrial runoff as all the investigated ponds are located in areas surrounded by agricultural land.

The lowest metal concentrations were found in stormwater from rural catchments draining mostly villages. Only minor areas with agricultural activity were connected, minimizing the possible influence of applied fertilizers, manure and slurry. Additionally, the samples were taken in December/January, which is a period without agricultural activity. We expected that water from uncultivated catchments would have the lowest metal concentrations, however it was not the case. The average concentrations were usually decreasing in the following order: industry > urban > uncultivated > rural. The uncultivated areas are all former agricultural land where leaching of heavy metals from earlier agricultural production is proceeding. Also digging activities due to construction work and runoff from roads may have affected the level of heavy metal concentrations.

As this study was performed during winter, spreading of de-icing salts on the roads was expected to potentially affect the results, as de-icing salts can cause corrosion phenomenon increasing the particulate heavy metal concentrations in the stormwater runoff.[11,12] Therefore, conductivity was measured on all inlet samples (data not shown), but there was no indication of de-icing salts on the days of sampling.

There were also big differences in the concentration of the six studied metals. The concentration of Zn was always a factor of 5–300 higher compared with the concentrations of the five other metals. Cd was always found in the lowest amount independent of the catchment type. Pb concentrations were generally the highest in the oldest ponds, which may be caused by the former use of Pb as an additive in gasoline. The distribution of dissolved and particulate heavy metals was in accordance with other results reported in the literature.[3,16,17] Except for Zn, which was mainly bound to particles, the majority of the heavy metal load was discharged in a dissolved form (Figure 2 and Table 2). That affected the removal efficiencies in the stormwater ponds, as these are mainly removing heavy metals bound to particulate matter and retaining them by sedimentation. An exception was runoff from industrial areas, where all metals were mainly found in particulate forms. The causality is not known, but it may be due to patterns of activities in the catchments. The air is usually more polluted in industrial areas and particle-bound heavy metals are reaching the ground through wet and dry deposition. The distribution varies depending on the catchment type and activities as well as physical conditions. The outlets from the ponds showed that heavy metals primarily were in dissolved forms except for ponds in urban catchments, where the majority were in particulate form. The very fine particulate matter found in runoff from urban areas was not supported by sufficient residence time to ensure settling of these fine substances.

Retention in the ponds

Catchment types cannot directly affect the retention of heavy metals in the ponds (Table 3), but there may be an indirect impact: the grain size composition may vary between different catchment types favouring a higher adsorption capacity in systems with small average particle sizes or there may be differences in the dissolved versus

Table 3. Retention of heavy metals in the 37 studied ponds given as averages in % ± SEM divided into catchment type.

Catchment type	Cu	Cr	Cd	Pb	Ni	Zn
Uncultivated	35 ± 24	59 ± 16	53 ± 27	48 ± 40	41 ± 40	48 ± 13
Rural	− 47 ± 47	− 107 ± 121	2 ± 2	35 ± 24	11 ± 5	12 ± 19
Urban	13 ± 7	16 ± 2	2 ± 3	− 14 ± 38	− 4 ± 15	29 ± 10
Industry	− 20 ± 22	− 88 ± 61	− 175 ± 50	46 ± 8	20 ± 14	31 ± 10

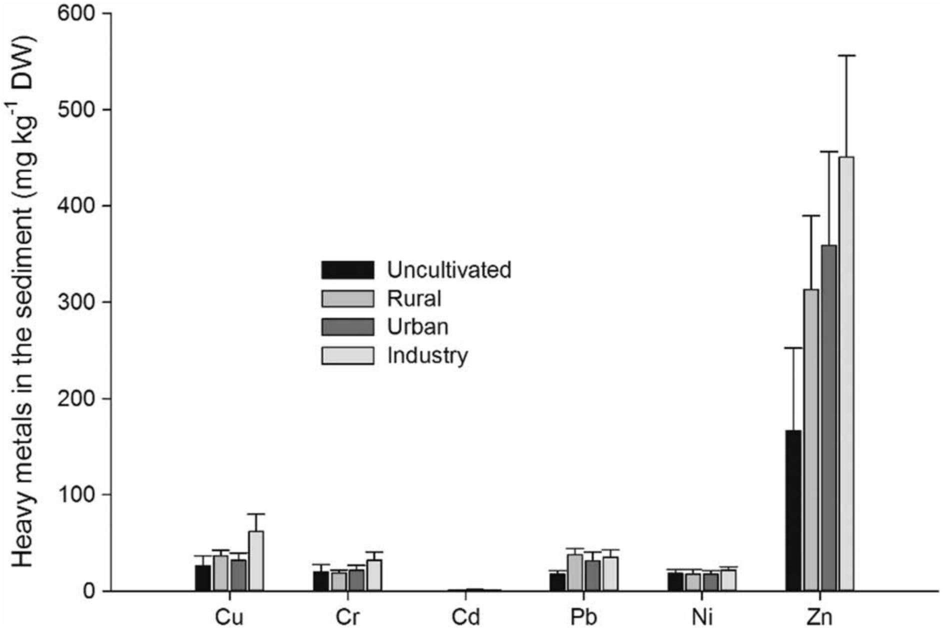

Figure 5. Total heavy metal content (mg kg^{-1} DW) in the pond sediments with SEM for the different catchment types.

particulate fraction. This might be the reason why ponds situated in uncultivated areas generally had higher heavy metals retention capacity, whereas the opposite was the case for ponds in industrial catchments.

In this study, we cannot conclude that the removal efficiency was dependent on the pond type. Some pond types where only represented at one location and the ponds within each category varied considerably with respect to size and design. Other factors were more important for the retention capacity, for example, the ratio between pond volume and reduced catchment area with increased removal at higher ratios (Figure 3(b)). The literature recommends a ratio from 150 to 250 m^3 red ha^{-1} to achieve satisfying removal efficiency facilitated by a sufficiently high residence time.[26] In the present study, we measured negative retentions of Cu, Cd and Cr up to a ratio of 150–800 m^3 red ha^{-1}, which can be explained by the high proportion of dissolved fractions, while we obtained positive retention for Pb, Ni and Zn, which mainly was particulate bound. The retention increased especially in the interval from 150–250 m^3 red ha^{-1}. The results are difficult to compare with the literature, for example,[17,18]

Table 4. Correlations between particulate heavy metal content (mg kg^{-1} DW) in the inlet water to the ponds and the sediment heavy metal content (mg kg^{-1} DW).

Metal	Equation	R^2	p-Value	Significant	Ratio water/sediment
Cu	$\mathrm{Cu_{sed}} = 0.254 \times \mathrm{Cu_{wat}} - 1.174$	0.601	< 0.001	Yes	6.8 ± 1.5
Cr	$\mathrm{Cr_{sed}} = 0.108 \times \mathrm{Cr_{wat}} + 11.653$	0.409	< 0.001	Yes	6.2 ± 0.7
Cd	$\mathrm{Cd_{sed}} = 0.007 \times \mathrm{Cd_{wat}} + 0.918$	0.026	0.334	No	25.6 ± 6.1
Pb	$\mathrm{Pb_{sed}} = 0.094 \times \mathrm{Pb_{wat}} + 19.298$	0.069	0.112	No	7.9 ± 1.6
Ni	$\mathrm{Ni_{sed}} = 0.156 \times \mathrm{Ni_{wat}} + 10.724$	0.085	0.076	No	3.9 ± 0.5
Zn	$\mathrm{Zn_{sed}} = 0.004 \times \mathrm{Zn_{wat}} + 297.689$	0.008	0.605	No	53.8 ± 11.3

Note: The table contains the equation for the linear correlation, the R^2 value for the regression line, the p-value for the linear regression, information about level of significance ($\alpha = 0.05$) and the ratio between water and sediment content, given as average ± SEM ($n = 37$).

where the authors' results usually are based on single ponds, while the present study is based on 5–15 ponds in each ratio interval. Heavy metals are often bound to the smaller particle fractions,[27] explaining why a higher residence time is needed to ensure settling of metals. This is also in accordance with Strigl,[28] who found that the concentration of Cu, Pb and Zn correlated to the accumulation of fine-grained sediment. To effectively remove heavy metals, the ponds must be well designed with a pond/catchment ratio of 250 m^3 red ha^{-1} as a minimum or even bigger if possible. We had also expected to see a relation between pond volumes or water distance versus retention, but it was not possible to make any clear conclusion in this study. For pond volumes, it can probably be explained by the very different catchments. For water distance (between inlet and outlet), the missing relation can be explained by macrophyte populations in some of the ponds which are increasing the effective water distance or variation in fetch and thereby wind-created turbulence in the water.

The age of the ponds was also affecting the removal efficiencies (Figure 3(a)). Already with a pond age > 1–2 years the retention became negative for Cu, Cd and Cr. Again this can be explained by a low particulate content. So, the net removal during the first couple of years is most probably caused by adsorption kinetics. For Pb, Ni and Zn, the retention continues even after several decades, but here sedimentation processes dominate the retention capacity even after many years. Less permanent water volume and water depth due to sediment accumulation during the years are negatively affecting the removal efficiency due to lowered residence times and decreasing depths increasing the risk of resuspension. This relation was clearly demonstrated in older ponds included in this study. The ponds varied in type, age, size and with respect to catchment size and type making the study as diverse as possible (Table 1). The only deviation was ponds draining industrial catchments. They are in general larger due to larger catchments, but it was not reflected in a better removal of the heavy metals.

Chemical parameters may also influence the retention of heavy metals in the ponds. Low pH may reduce the retention. Basak et al. [29] found that at pH < 5.5 the solubility of heavy metals was five times higher than that under neutral conditions. In the present study, average pH was 7.4 and the lowest pH value found was 6.5. The metal retention in the ponds with the lowest pH value was negative, except for Pb, but the same was also the case in ponds with higher pH, which showed no direct pH effect on the retention efficiency. Several studies reported that heavy metal dissolution is redox dependent in an environment with low oxygen concentrations.[15,30] We measured oxygen in the stormwater ponds but found no connection between either oxygen concentrations and heavy metal retention or oxygen content and dissolved heavy metal concentration in the pond outlet (except for Ni where there was a significant correlation ($p = 0.006$)), for example, one pond with a low oxygen level (35.2%) removed more than 90% of Pb. Including the measured nitrate concentration as an additional oxidation potential did not improve the statistical power. Also colour, DOC and organic matter (LOI) were measured in the ponds (data not shown) as representatives for humic substances, for example, Logan et al. [19] found that these substances could bind heavy metals, but no correlation was found in our set of stormwater ponds. In this study, the physical parameters were most important. It is difficult to interpret exactly which parameters were influencing the retention, as the removal rates in the ponds were not influenced by one parameter at a time, but by the full set of physical and chemical parameters spatially and temporally linked, for example, one of the ponds with industrial catchment had high retention values for all studied heavy metals, but it was also 1-year old with a recommend ratio between 150 and 250 m^3 red ha^{-1} (166), neutral pH (7.65) and a high oxygen level (95%).

Heavy metals in the sediment

Sediment analysis turned out to be a useful source of information about the heavy metal loading of the stormwater ponds. Here we found a direct positive relation between the concentrations of particulate heavy metal inputs to the ponds and the metal content in the sediments (Figure 5 and Table 4). Zn and Pb contents in the pond sediments were very close to the values found in another study.[31] The measured Cu, Cr, Cd and Ni contents were all in a comparable range to those found in the literature. The sediment content increased with age, but not always proportional, which could be caused by the dynamic loading of the ponds and different grain size distributions in the particulate matter entering the ponds, as reported by Kruopiene.[32] Given the mineralization processes, the metal content was expected to increase over time but this was only significantly for Pb. The study also revealed that part of the heavy metals was lost from the sediments, most probably through mineralization processes or resuspension events as less content was measured compared with the predicted content based on the retention rates. Degradation of organic matter by micro-organisms may release metals to the water as well as increasing the oxygen consumption at the sediment–water interface affecting the metal speciation in the pore water and increase the effluxes.[33,34] This may also explain why we observed a larger dissolved fraction of heavy metals in the pond outlets compared with the inlets. Another reason for the larger dissolved fraction in the outlets could be a time lack between inlet and outlet due to the residence time in the pond. As reported by Bhaduri et al.,[16] it may not always be the same water coming in as coming out during a storm event. It depends on pond volume, catchment area and size of the precipitation event. All the samples in this study were taken during a rain event after a dry period, which may have caused a build-up of dissolved heavy metals in the ponds recorded in the outlet samples.

Perspectives

Metal removal in stormwater ponds is not only an important management tool, but also for removal of certain kinds of heavy metals to protect the receiving water bodies and the downstream habitats. At the same time, it is a paradox that the number of natural ponds in Europe is decreasing while the number of manmade ponds is increasing,[35 in 31] and therefore these ponds are becoming increasingly important, also for biological conservation and biodiversity in the cities.[31,36,37] Besides these studies of pond retention capacities, it will in future be essential to investigate the effect of heavy metal accumulation in the ponds on the established biodiversity in these systems. Here studies of both benthic and pelagic flora and fauna should be performed.

Even after retention in the ponds, the outlet concentrations may still be above critical levels both with respect to toxicity and in order to fulfil national environmental quality standards for water. In Denmark, the standards are only provided for the dissolved fraction. For Pb, only 10 of the outlets were fulfilling the standard of 0.34 µg L^{-1}, but fortunately the highest dissolved Pb concentrations measured was 4 µg L^{-1}, which is well below the toxic levels reported in the literature, which is usually around 1000 µg L^{-1} as LC_{50}, EC_{50} and acute toxicity.[7,38–40] The standard for Cr was only exceeded in one outlet with a concentration of 8 µg Cr L^{-1} which has been reported toxic to Daphnids. The remaining outlets did not have toxic levels according to Makepeace et al.[7] Cu exceeded the standard (12 µg L^{-1}) in three outlets and several were close to the limit. Dissolved Cu is very toxic to aquatic organisms, especially in soft waters. Franklin et al. [41] reported $EC_{50} = 1.5$ µg L^{-1} at $pH < 6.5$ for *Chlorella* sp. This limit was exceeded in two outlets in the present study, with possible toxic effects in the receiving water body as a consequence. Ni exceeded the standard (3 µg L^{-1}) in four outlets and also for Ni several other outlets were close to the limit, but the measured Ni concentrations were though much lower than what is generally reported as toxic levels in the literature.[7,42] Also the Zn concentrations found were not in the toxic level.[40,43] The Danish standard for Zn is given as 7.8 µg L^{-1} above the background level and as the background level is not known in this study it is not possible to evaluate. Finally, Cd fulfilled the standard (5 µg L^{-1}) and was measured in non-toxic levels in all outlets.[7] In general, the concentration of dissolved heavy metals was not found in toxic levels, except for Cr and Cu, but several outlets exceeded the Danish quality standard, whereas others were close to the limits, indicating a need for treatment of the storm water to protect the receiving waters especially in industrial areas.

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