Dissolved metal adsorption capacities and fractionation in filter materials for use in stormwater bioretention facilities

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A B S T R A C T

The dissolved metal adsorption and association was determined for ten different filter materials recommended and/or implemented in bioretention facilities. Batch adsorption and batch kinetic experiments were performed at lab-scale using both single and multi-metal solutions. Metal strengths and association were determined by sequential extraction analysis. All materials adsorbed metals and 90% of adsorption occurred within 1 h. However, as metal solutions became more complex, adsorption behavior changed. Generally, filter materials classified as sand with a naturally high pH, relatively low organic matter (OM) content and large specific surface area seem to be good choices for removing dissolved metals. Additionally, a chalk additive might improve metal adsorption whereas biochar did not significantly improve metal retention and may be an unwanted (due to degradation over time) extra source of OM. Regardless of filter material, metals primarily adsorbed to the exchangeable form which indicates that metal adsorption might not be permanent, but rather substantially reversible in some cases. More research is needed to assess whether dissolved metals adsorbed in filter materials of bioretention systems pose a delayed threat instead of an immediate threat. Finally, the authors strongly recommend filter materials intended for stormwater bioretention facilities to be tested prior to implementation. © 2019 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Given the increased awareness about stormwater pollution and treatment needs, the use of stormwater bioretention as an on-site stormwater control measure is increasing in many countries around the world. Stormwater can contain a variety of pollutants, e.g. metals, sediment, pathogens, nutrients and organic pollutants. Although target pollutants for bioretention systems vary depending on regulations, region, and receiving water body, metals are often a main concern (Hunt et al., 2012) as urban stormwater runoff is considered a major source of metal contamination in receiving water bodies (e.g. Becouze-Lareure et al., 2019). Depending on their prevalence, toxicity and resistance to degradation and/or chemical transformation metals might negatively affect the ecological status of surface waters (Søberg et al., 2017). A large number of field and laboratory studies have shown efficient total metal removal for bioretention systems, often exceeding 80–90% (e.g. Hatt et al., 2008; Søberg et al., 2017). However, reported removals of dissolved metals are fewer and contradictory including both efficient removal and significant leaching (e.g. Muthanna et al., 2007; Søberg et al., 2017).

The vegetation has been shown to contribute to the total metal removal in stormwater bioretention systems (Muthanna et al., 2007; Sun and Davis, 2007; Read et al., 2008). However, the filter material accounts for the majority of metal removal (Muthanna et al., 2007; Blecken et al. 2009, 2011) and hence, filter material composition is crucial for achieving effective dissolved metal treatment. The filter material serves two functions; I) to retain and delay flow by temporary storage and infiltration and II) to treat stormwater runoff by a combination of physical, chemical and biological processes. The material should have a hydraulic conductivity ensuring both adequate retention for adsorption to occur and adequate infiltration capacity to avoid overflow (Fassman et al., 2013). It should have physical and chemical properties to support plant life, enhance treatment and avoid clogging (Fassman et al., 2013). At present, many filter materials are marketed and used in actual bioretention facilities without any previous testing. Hence, research is needed to understand how their composition affects...
pollutant retention performance.

In some regions or countries, rigorous recommendations for filter material compositions are specified in design manuals (e.g. Payne et al. (2015); DWA, 2005; Payne et al. (2015); NCDEQ, 2018). However, depending on the target pollutants, different recommendations for filter material composition exist (Hunt et al., 2012). In other countries, e.g. Sweden, there are no such national specifications, so consultants and/or local stormwater managers define filter materials on a case-by-case basis. Choices of filter materials are often based on hunches or preferences of a few individuals and are not tested prior to or after implementation. Further, some filter materials may not efficiently remove or may even leach targeted pollutants because other objectives (e.g. support of plant growth) are prioritized during their development.

A considerable ratio of metals can be present in the dissolved phase in urban stormwater runoff (Lindfors et al., 2017). Although dissolved metals are more difficult to remove and usually more bioavailable compared to particulate metals, thereby posing a greater risk (Fassman et al., 2013; Flanagan et al., 2019), bioretention studies have generally focused on total metal removal (Hunt et al., 2012). Moreover, recent work showed that a substantial amount of the dissolved metals (usually defined as <0.45 µm) may be present in mobile species (free ions) which further emphasizes the importance of investigating adsorption processes in stormwater treatment facilities (Lindfors et al., 2017).

At present, no studies have systematically evaluated and compared the dissolved metal adsorption capacities of different filter materials recommended/implemented in stormwater bioretention worldwide. Most studies concerning filter material in stormwater bioretention are I) done on entire bioretention systems at either lab-, pilot- or full-scale (e.g. Li and Davis, 2008; Wang et al., 2017) and not only on the filter material itself; II) Examine the function of the entire system when enriching the filter material with some type of additive (aluminum coating, iron coating, biochar, fly ash etc.) (e.g. Li et al., 2016; Afroz and Boehm, 2017) or II) Test alternative low-cost materials or adsorbents (e.g. red soil, perlite, vermiculite, coco-peat, construction waste etc.) (e.g. Vijayaraghavan et al., 2010; Wang et al., 2017).

When choosing a filter material, long-term retention rather than short-term adsorption is most relevant. To address the manage-ment and/or lifetime of bioretention systems, together with poten-tial risks for leaching of adsorbed metals (Hatt et al., 2008; Söberg et al., 2017), it is essential to understand processes by which the metals are bound to the filter material. For instance, it is well known that OM (e.g. peat, compost) favors metal adsorption. However, such OM degrades under oxidizing conditions, leading to release of soluble trace metals into stormwater as it passes through the filter (Tessier et al., 1979). Hence, the partitioning of adsorbed metals into different chemical forms and their risks of desorption under various environmental conditions warrant attention. Relatively large amounts of metals may be present in potentially available fractions in analogous materials from other stormwater treatment facilities, e.g. pond sediments (Karlsson et al., 2016). Only one study has addressed such fractionation in bioretention systems. The results indicated that metals were mainly trapped (>50%) in the residual fraction, but the tests were restricted to filter materials with lignin in lab-scale bioretention columns (Wang et al., 2017).

Hence, the objective of this study was to evaluate and compare dissolved metal adsorption capacities of 10 filter materials recommended and/or implemented in bioretention facilities worldwide. The chosen materials are manufactured according to current guidelines (DWA, 2005; NCDEQ, 2018), have been tested in scientific studies (Blecken et al., 2009; Grotehusmann et al., 2016; Söberg et al., 2017), or are national market leaders. The materials’ dissolved metal adsorption capacities were evaluated in laboratory batch and kinetic adsorption experiments, using both single- and multi-metal solutions to obtain indications of the effects (if any) of competition between metals on their adsorption capacities. Furthermore, the metals’ ‘fractionation was examined by sequential extraction analysis to gain knowledge about possible changes in their adsorption capacity over time, e.g. if desorption is likely to occur.

2. Material and methods

2.1. Adsorbents

Ten commonly implemented and/or recommended filter materials (listed in Table 1 and briefly described here) for bioretention facilities were examined. LTU top-layer is a sand-based material developed by the urban water research group at Luleå University of Technology based on recommendations by the Facility for Advancing Water Biofiltration (FAWB, 2008). However, it has a lower percentage of fines than recommended by the FAWB to enhance infiltration during freeze-thaw cycles (Blecken et al., 2011). Several pilot-scale studies (Blecken et al., 2011; Söberg et al., 2017) have shown this material to be an efficient metal adsorbent. Heklä®Regnbådd® and Heklä®Regnbådd®-biokol (Heklä®Regnbådd with supplemental biochar) were developed by the Swedish supplier Bara Minerals. Hasselfors was developed by another Swedish supplier called Hasselfors Garden, and also contains biochar. Originally, these materials were intended to support plant growth (having high OM contents and water-holding capacities; Table 2). They are now commonly used in Swedish bioretention facilities intended to improve water quality, although they have not been subjected to laboratory or field tests. The DWA and DWA-chalk materials are fabricated according to the German water manual DWA M-187. Their original purpose was implementation in bioretention systems for highway runoff and CSO treatment (so called retention soil filters). The addition of chalk is recommended to enhance metal adsorption and compensate for low OM content (Grotehusmann et al., 2016; DWA, 2005). Orbicon Standard Field Topsoil #1 was developed by the Danish consultancy Orbicon and is intended for road beds. Three bioretention soils from the United States were also evaluated: one from Wade Moore Equipment Co. (North Carolina) and two from companies in Ohio. Each mix met the respective states’ current guidelines for bioretention soil (generally a sandy blend with varying amounts of OM). The mixes were developed to target pollutants of particular local concern: nutrients and sediment in North Carolina and Ohio, respectively. Therefore, none of these bioretention soils had specific amendments designed to target metal retention. Origins or suppliers and abbreviations of the materials that will be used hereafter are presented in Table 1, and the filter materials are illustrated in Fig. S1.

2.2. Filter material characterization

To obtain indications of potentially relevant factors for metal adsorption, the OM content, specific surface area (SSA), pH and particle size distributions of each material were determined. The OM content was measured from ignition residues according to Swedish standard SS 028113. The SSA was determined by an accredited, external laboratory (Escubed limited, Wetherby, UK) using the Brunauer-Emmett-Teller (BET) method. pH was determined according to the international standard ISO 10390, using a WTW pH 310F field pH-meter, and particle size distributions (PSDs) were determined by dry sieving according to Swedish standard SS-ISO 11277:2009, and expressed in terms of D50 (diameter at which smaller particles comprise 50% of a sample’s mass, or median
2.3. Initial leaching

To examine if the materials can act as a source of metals, the initial leaching capacity was examined by shaking 10 g of dry material diluted in 100 mL (VWR ISO/4788 measuring cylinders with an accuracy of ±0.5 mL at 20 °C) milli-Q water for 24 h. Aqueous phase metal contents were then determined using methodology described in section 2.8.

2.4. Batch adsorption experiments

The metal adsorption capacity of each material was examined using batch adsorption experiments with single-metal solutions (containing either Cu or Zn at 1, 10, 50, 100 and 1000 mg/L) and multi-metal solutions. The latter contained Cu, Zn, and Ni at 1, 10, 50, 100 and 1000 mg/L, 10-fold lower concentrations of Cr and Pb; and 100-fold lower concentrations of Cd. As in the leaching experiments, 10 g samples of dry material were shaken in 100 mL milli-Q water for 24 h. Metal concentrations in solution, determined by methodology described in section 2.8, were then used to calculate adsorption percentage and the adsorption capacity (Q) of each material by equations (1) and (2), respectively.

\[
\text{Adsorption} (\%) = \frac{C_i - C_f}{C_i} \times 100
\]

\[
Q = \frac{(m_{\text{metal}})}{m_{\text{sample}}} = \frac{(C_i - C_f)}{m_{\text{sample}}} \times V
\]

Here, \(C_i\) (mg/L) is initial concentration and \(C_f\) (mg/L) is final concentration of the metal in solution, \(m_{\text{sample}}\) (g) is the weight of the sample (10 g) and \(V\) (mL) is volume of adsorbate (100 mL).

The adsorption data were fitted to linear, Freundlich, Langmuir, Temkin and Dubinin-Radushkevich sorption isotherms. Generally, the Langmuir, Temkin and Dubinin-Radushkevich sorption isotherms provided the best fits (i.e., highest \(R^2\) values), so the Linear and Freundlich isotherms will not be discussed further. However, it is important to emphasize that these equations are merely numerical relationships used to fit data, and the isotherm equation parameters are only valid for the chemical conditions under which the experiment was conducted. Thus, they cannot be used to predict metal adsorption behavior in environments with differences in ionic strength, pH, metal concentrations, presence of other substances, longer or shorter contact times, etc.

Underlying assumptions of the Langmuir isotherm (used in the linear form here: equation (3)) are that the adsorbent has a homogenous surface with monolayer adsorption at a finite number of identical and equivalent sorption sites with equal affinity for the adsorbate. Moreover, it is assumed that there is no lateral interaction or steric hindrance between adsorbed molecules, even at adjacent sorption sites (Foo and Hameed, 2010). Note, steric hindrance would limit \(q_{\text{max}}\), but lateral interaction could potentially either restrict or increase it.

\[
\frac{Q_f}{Q_e} = (q_{\text{max}} K_L)^{-1} + \frac{C_f}{q_{\text{max}}}
\]

Here, \(Q_f\) is the final concentration of a metal, \(Q_e\) (mg/g) is the equilibrium adsorption capacity, \(q_{\text{max}}\) (mg/g) is the maximum adsorption capacity, and \(K_L\) (L/mg) is the affinity constant. The characteristics of the Langmuir adsorption process can be expressed in terms of a dimensionless constant known as the separation factor (\(R_L\)).
The value of $R_t$ indicates whether adsorption is unfavorable ($R_t > 1$), linear ($R_t = 1$), favorable (0 < $R_t < 1$) or irreversible ($R_t = 0$). By plotting $C_f/Q_e$ vs. $C_e$, the Langmuir constants can be calculated from the slope and intercept, respectively (Foo and Hameed, 2010).

Assumptions underlying the Temkin isotherm (using the linear form in equation (5)) are that bonding energy is uniformly distributed, with the heat of adsorption decreasing linearly with coverage, ignoring extremely low and very high concentrations.

Linearized Temkin: $Q_e = B \ln K_T + B \ln C_f$

where $B = \frac{R T}{b_T}$ is a constant related to the heat of adsorption:

$R = \frac{K_T}{b_T}$ (4)

In its linearized form, used here:

$\frac{t}{q_t} = \left( \frac{1}{K_2 q_e^2} \right) + \left( \frac{t}{q_e} \right)$

where $t$ (min) is time, $q_t$ (mg/g) is metal uptake at time $t$, $q_e$ (mg/g) is equilibrium adsorbate concentration and $K_2$ (g/mg min) is the pseudo-second-order rate constant. $K_2$ and $q_e$ were found by linear regression of the relationship between $t/q_t$ and $t$. Furthermore, the initial sorption rate $h$ (mg/g min) was determined by equation (12) and the half-life of the reactant $t_{1/2}$ (min) was determined by equation (13) (Kango & Kumar 2016):

$h = K_2 q_e^2$

$t_{1/2} = \frac{1}{K_2 C_i}$

2.6. Sequential extraction

To examine the fractions of the materials where metals are adsorbed, 100 mL of a multi-metal solution with 100 mg/L of Cu, Zn and Ni, 10 mg/L of Pb and Cr, and 1 mg/L of Cd were added to 10 g of each filter material and shaken for 24 h. The adsorbed metals were then subjected to sequential extraction analysis by an accredited laboratory as follows. A sample of each material was ground in a steel dish and treated according to the Swedish standard SS 02817-1. It was then acidified by adding 1% HNO₃ (v/v) and analyzed by ICP-SFMS (Cd and Pb) according to standards SS EN ISO 17294-1, 2 (modified) and EPA-method 200.8 (modified) or ICP-AES (Cr, Cu, Ni, Zn) according to standards SS EN ISO 11805 (modified) and EPA-method 200.7 (modified). To determine residual amounts of metals in the samples, they were dried at 50 °C and treated according to standards ASTM D3682 (2013), ASTM D4503 (2008) and SS EN 13656 (2003), then analyzed by ICP-SFMS according to standards SS EN ISO 17294-2: 2016 and EPA-method 200.8 (1994).

Six fractions were extracted: (I) adsorbed and exchangeable metals and carbonates; (II) labile organic forms; (III) amorphous Fe- and Mn-oxides; (IV) crystalline Fe-oxides; (V) stable organic forms and sulfides and (VI) residuals. Fractions I–V are potentially mobile. Fraction I contains easily leached metals likely to be mobilized by changes in ambient water's ionic composition. Fraction II includes metals bound to OM, which will degrade and release captured metals under oxidizing conditions. Fraction III includes metals bound to amorphous Fe- and Mn-oxides, which behave as metal sinks under oxidizing conditions but are unstable under anoxic conditions. Fraction IV includes metals bound to more stable crystalline Fe-oxides that only become unstable under persistently anoxic conditions which in most cases are unlikely to occur in bioretention. Fraction V includes metals bound to stable organic forms and sulfides, which mobilize under oxidizing conditions. Fraction VI contains metals that are not likely to be released in solution under conditions normally present in nature (Tessier et al., 1979).

$E = \frac{1}{\sqrt{-2K_{DR}}}$

where $E$ indicates whether the adsorption is largely physical ($E < 16$ KJ/mol), due to ion exchange ($8 < E < 16$ KJ/mol) or chemical ($E > 16$ KJ/mol). By plotting $\ln Q_e$ vs. $\epsilon^2$, the Dubinin-Radushkevich constants can be calculated from the slope and intercept, respectively (Foo and Hameed, 2010).

2.5. Batch adsorption kinetics

Metal uptake rates and contact times needed for completion of adsorption reactions were assessed by batch kinetic experiments with two single-metal solutions (Cu and Zn, concentration 10 mg/L) and one multi-metal solution (with: 10 mg/L of Cu, Zn and Ni, 1 mg/L of Pb and Cr, and 0.1 mg/L of Cd). The time steps were 1 h, 3 h, 6 h, 10 h and 24 h and the protocol was the same as that applied in the batch adsorption experiments, except that samples were collected for analysis at each time step.

Data were fitted against pseudo-first-order and pseudo-second-order kinetic models, with the pseudo-second-order kinetic model (equation (10)) providing the best fit (highest $R^2$ values). Hence, the pseudo-first-order kinetic equation will not be discussed further.

$K_T = \frac{1}{1 + K_0 C_f}$
2.7. Reagents

Solutions were made using the following laboratory grade chemicals: (Zn(NO₃)₂·6H₂O (ACROS Organics, Cas-No. 10196-18-6), Cd(NO₃)₂·4H₂O (Alfa Aesar, Cas-No. 10022-68-1), Cu(NO₃)₂·3H₂O (MERCK, Cas-No. 10031-43-3), Ni(NO₃)₂·6H₂O (MERCK, Cas-No. 13478-00-7), Pb(NO₃)₂ (MERCK, Cas-No. 10099-74-8), and Cr(NO₃)₃·9H₂O (MERCK, Cas-No. 7789-02-8) diluted in milli-Q water. To avoid precipitation of undesired metal-salts, metal-nitrates were used, since nitrates have no any affinity for metals. To avoid precipitation of metal oxides, the pH of the solutions was not adjusted. Hence, they had partly lower pH (4–6.5 depending on metal and solution) than what is common for stormwater runoff. The actual concentrations of all solutions were determined by an accredited, external laboratory (ALS Scandinavia, Luleå, Sweden) by ICP-SFMS.

2.8. General procedures/analytical methodology

All experiments were conducted at room temperature (18.6 °C ± 0.6; according to two Ebro EBI310 temperature loggers). Before weighing samples for the experiments, all filter materials were dried in incubators for at least 24 h at 35 °C (above which OM may oxidize, thus changing material properties). Then, the materials were mixed with a plastic spoon and 10 g of material was randomly collected. The solid to liquid ratio in all experiments was 1:10 (10 g of dry material to 100 mL of solution). All experiments (except the sequential leaching) were run in duplicate, however, if results differed markedly, an extra replicate was run (which was only the case in a very few instances). Controls (solution without filter material) were included in all runs. Samples were shaken on two orbital shaking tables set to 200 RPM in all cases. The pH of the metal solutions was measured using a field pH-meter (pH330, WTW GmbH, Weilheim, Germany).

After shaking, all samples were filtered through 0.45 μm filters (Filtropur S) and sent for analysis of the dissolved metals at an accredited laboratory (ALS Scandinavia, Luleå, Sweden). At the laboratory, each liquid sample was acidified by addition of 1 mL HNO₃ per 100 mL then analyzed by ICP-SFMS according to standards SS EN ISO 17294-1, 2 (modified) and EPA-method 200.8 (modified).

3. Results and discussion

3.1. Filter material characteristics

As shown in Table 2, the pH of LTU-Top and NC-USA were 6.1 and 6.3, respectively, the pH of DWA-chalk was 9.2, and the pH of all the other materials ranged from 7.7 to 8.8. Materials with biochar additive (Hekla-B and Hasselfors) had the highest SSA and OM contents. In contrast, the sand-based materials LTU-Top, DWA and DWA-chalk without biochar additives have low OM contents and small SSA.

Hasselfors had by far the largest D₅₀ and second lowest Cₜ (Table 2), so it is much coarser (mainly gravel) and more heterogeneous material than the others (Fig. 1). Despite variations in D₅₀ and Cₜ, the PSD analysis confirmed that all the other materials are primarily sandy materials (Fig. 1).

3.2. Initial leaching

After 24 h of shaking in 100 mL milli-Q water Cd and Cr concentrations in the water were most often below the detection limit (Table 3). All materials except DWA and DWA-chalk including the control leached Cu (Table 3). Ni, Pb and Zn leaching from some of the other materials cannot be regarded

### Table 3

Aqueous concentrations of metals (µg/l) after initial leaching tests.

| Material   | Cd   | Cr   | Cu   | Ni   | Pb   | Zn   |
|------------|------|------|------|------|------|------|
| LTU-TOP    | <0.05| 1.63 | 4.64 | 1.07 | 1.34 | 3.76 |
| Hekla      | <0.05| <0.5 | 10.01*| 2.44 | 1.93 | 15.6*|
| Hekla-B    | <0.05| <0.5 | 7.68*| 1.985| 1.34 | 13.1*|
| DWA        | <0.05| <0.5 | <1   | <0.5 | <0.2 | <2   |
| DWA-chalk  | <0.05| <0.5 | <1   | <0.5 | <0.2 | <2   |
| Hasselfors | <0.05| <0.5 | 4.4  | <0.5 | 0.45 | 3.19 |
| NC-USA     | <0.05| <0.5 | 1.72 | <0.5 | 0.88 | <2   |
| KB-OHIO    | <0.05| <0.5 | 3.27 | 2.17 | <0.1 | <2   |
| BN-OHIO    | <0.05| <0.5 | 6.16 | 4    | <0.2 | <2   |
| Orbicon    | <0.05| <0.5 | 3.37 | 0.56 | 0.24 | <2   |
| Control    | <0.05| 1.82 | <0.5 | <0.2 | 2.31 |

Values with * below detection limit. “significantly higher than control (one-way ANOVA with Tukey’s comparison).
as actual leaching. Furthermore, Hekla and Hekla-B had the highest leachates of Pb and Ni as well. Unfortunately it was not possible to clarify the reason(s) for the leaching of Cu and Zn in the controls, but the concentrations detected in the initial leaching tests (Table 3) are much lower than concentrations used in the batch adsorption, batch kinetic and sequential extraction experiments, so leaching from the materials did not substantially influence the results.

3.3. Batch adsorption experiments

Large variations in metal adsorption between the materials were detected (Fig. 2), especially at the highest metal concentrations. While some materials adsorbed most of the metals, even at the highest initial concentrations, DWA, NC-USA and LTU-TOP adsorbed Zn, Ni and Cd less efficiently, especially from the multi-metal solutions.

As shown in Fig. 2, amounts of the metals adsorbed generally increased with increases in initial concentration. While the materials had sufficient adsorption sites to adsorb all/most metals at the lower initial concentrations, the potential adsorption capacity became increasingly saturated as initial concentration increased until the amount of metals exceeded the number of adsorption sites (Meena et al., 2008). Thus, all materials adsorbed essentially all

**Fig. 2.** Sorption (mg/g) of metals by the 10 filter materials from single- and multi-metal solutions. Note, the legend is at the top of the figure, the scale of the y-axes varies, and some values of sorption (y-axis) from multi-metal solutions were negative for Znmulti, Nimulti, and Cdmulti. CV: coefficient of variance.
available metals at the two lowest initial concentrations, whereas differences in adsorption capacity between materials appeared at the higher initial concentrations. Furthermore, adsorption of Zn, Ni and Cd from the multi-metal solution were lower at the highest initial concentration than at the second highest concentration. More Cu and (especially) Zn were generally adsorbed from the single-metal solutions than from the multi-metal solutions at the three highest initial concentrations (Fig. 2). This was probably, due to a lack of adsorption sites as well as competition between metals for available adsorption sites. KB-OHIO and BN-OHIO were consistently amongst the three materials with the highest adsorption capacities, while LTU-TOP, DWA and NC-USA were amongst the three with the lowest adsorption capacities.

Furthermore, for the materials LTU-TOP, NC-USA, DWA and Hekla-B in some cases higher final metal concentrations were recorded at the highest initial concentrations (Fig. 2). This observation was not due to leaching, since these concentrations (Table 3) were far lower than the increase in metal concentrations observed at these high initial concentrations (1000 mg/L for Cu, Zn and Ni; 100 mg/L for Cr and Pb; 10 mg/L for Cd). These concentrations exceeded the metal sorption capacity by far. Thus, the percentage of the metals which was adsorbed by these materials was rather negligible and consequently initial and final concentrations were approximately the same. The uncertainty of the analytical method (approximately 20% at the highest initial concentrations) involved that in some samples the reported final concentration was slightly higher than the initial one. Hence, the observed higher final concentrations is most likely explained by that analytical uncertainty. This is further supported by the fact that the duplicates did not deviate considerably from each other. Several of the materials included in this study have been previously tested in pilot and field scale. Although it showed very low adsorption capacities in the present study (Fig. 2), LTU-TOP efficiently removed metals in pilot-scale bioretention facilities under various ambient conditions (e.g. Blecken et al., 2009; Blecken et al., 2011; Søberg et al., 2017). DWA-chalk consistently adsorbed more metals than DWA (Fig. 2), in accordance with a previous survey of full-scale bioretention facilities with these filter materials (Grotheusmann et al., 2016). This also confirmed the importance of adding chalk for metal adsorption, as recommended in the German guidelines for bioretention (DWA, 2005). In an evaluation of two full-scale bioretention cells at North Carolina State University, Luell (2011) observed relatively low removal of total Cu (23–43%), dissolved Cu (17–49%), and total Zn (79%). This is consistent with NC-USA being amongst the three materials with the lowest adsorption capacities in the present study (Fig. 2). The KB-OHIO material removed 68 and 83% of total Zn and Pb, respectively, in previous field-scale bioretention tests, but leached Ca, Cu, Fe, Mg and Mn (Winston et al. 2015). In the present study, KB-OHIO showed excellent adsorption of all tested metals and was consistently amongst the top three materials (Fig. 2). However, it should be noted that Winston et al. (2015) and Luell (2011) focused on full-scale systems exposed to numerous, uncontrolled factors in contrast to the lab-scale systems maintained under controlled conditions in the present study. Additionally, field-scale tests also account for particulate bond metals, unlike the current study. No previous tests of metal adsorption by Hekla, Hekla-B, Hasselfors or Orbicon have been published, despite their widespread use in bioretention in Sweden and Denmark.

The isotherm that provided the best fit to the data depended on the metal, type of solution and filter material. For the two single-metal solutions, the Langmuir isotherms generally provided the best fit. However, for the single-metal solutions, all isotherms had high (>0.8) R² values (Table S1).

The isotherm of best fit for adsorption from the multi-metal solutions depended on the metal. In these cases: the Langmuir isotherm provided the best fit for Cu, Ni and Pb adsorption; the Dubinin-Radushkevich isotherm the best fit for Zn and Cd adsorption; and the Temkin isotherm the best fit for Cr adsorption (Table S1). However, the other isotherms could also be applied for most of the metals, apart from Cr from multi-metal solutions, albeit while generating somewhat lower R² values (Table S1).

These findings illustrate that the complexity of metal adsorption increases with increases in the number of metals present due to competition between metals for binding sites, so different metals do not necessarily exhibit the same behavior under identical conditions (Bradl, 2004). This phenomenon is evidenced by the observed lower adsorption of Cu and Zn from multi-metal solutions than from single-metal solutions (Fig. 2).

The calculated isotherm parameters (Table S1) confirm that LTU-TOP, DWA and NC-USA consistently adsorbed the lowest quantity of metals. For example, the Langmuir maximum adsorption capacity constant, the Dubinin-Radushkevich adsorption capacity constant and the Temkin heat of adsorption constant for adsorption of Cu from single and multi-metal solutions, Zn from single-metal solutions and Pb from multi-metal solutions were consistently lowest for these three filter materials. Accordingly, the Temkin model constant and Dubinin–Radushkevich mean sorption energy were consistently higher in these cases. The relatively poor performance of LTU-TOP, DWA and NC-USA was also supported by the Temkin isotherm model constants for adsorption of Cr from the multi-metal solutions (Table S1). However, the trends were less clear for adsorption of Zn, Ni and Cd from multi-metal solutions, and were only supported by the Dubinin-Radushkevich model constants, despite the Langmuir isotherm providing a better fit for adsorption of Ni, and relatively high R² values for adsorption of Zn and Cd from the multi-metal solutions.

For some of the filter materials, final concentrations of Zn, Ni and Cd in experiments with the most concentrated multi-metal solution were higher than the initial concentrations. This resulted in negative adsorption capacity values, which reduced the Langmuir maximum adsorption capacities and probably explains the relatively indistinct patterns in adsorption of Zn, Ni and Cd from multi-metal solutions (Table S1).

With a few exceptions, the calculated isotherm parameters (Table S1) also confirm that KB-OHIO and BN-OHIO generally provided the best dissolved metal adsorption. For example, the Langmuir maximum adsorption capacity constant, Dubinin-Radushkevich adsorption capacity constant and Temkin heat of adsorption constant were highest for these materials, while the Temkin model constant and Dubinin–Radushkevich mean sorption energy were lowest (Table S1).

3.4. Batch adsorption kinetics

The batch adsorption kinetic data fitted the Lagergren Pseudo-second-order kinetic equation well, with R² values close to 1 (Table S2). Despite differences between materials, the adsorption process was relatively fast. Within an hour, most of the materials had adsorbed >90% of the metals (Fig. 3) and half-life times of less than a minute were observed (Table S2).

Adsorption by LTU-TOP, NC-USA and DWA was generally lower and slower than the other materials (Fig. 3). DWA-chalk had a lower initial adsorption rate and longer half-life time than the remaining six materials (Table S2), but equally high equilibrium adsorbate concentrations (Fig. 3; Table S2). Hekla and Hekla-B had slower and lower adsorption of Cr from multi-metal solutions (Fig. 3), and thus the longest half-life times and lowest equilibrium adsorbate concentrations for Cr (Table S2).

With typical infiltration rates of <300 mm/h (FAWB, 2008; Hunt et al., 2012) contact times for a 600 mm deep filter are generally at
least 2 h, although, in practice, the infiltration rate of course varies depending on the type of material, filter depth, root macro pores, bioturbation, and level of clogging. As >90% of the metals were adsorbed within an hour, actual retention times in full-scale bio-retention should be adequate for high metal removal. It has been commonly observed that a majority of metal adsorption happens in the upper layers of bio-retention (e.g. Søberg et al., 2017) which would support the assumption of rather quick adsorption processes. Further, stormwater sediment and thus particulate metals are trapped on top of the filter which also contributes to the high metal concentrations in this layer.

3.5. Sequential extractions

The sequential extractions revealed that in most cases the largest fraction of the metals adsorbed by all of the materials was fraction I (the exchangeable fraction), followed by the labile organic forms (II) and amorphous Fe- and Mn-oxides (III) fractions (Fig. 4). The high percentages of potentially leachable fractions imply an obvious risk of adsorbed metals being desorbed by changes in the ionic composition of ambient water or development of oxidizing conditions (Tessier et al., 1979), for instance during extended dry periods (which have been shown to affect metal removal in bio-retention; Blecken et al., 2009) and/or after maintenance (Karlsson...
et al., 2016). The latter becomes evident considering that metals primarily accumulate in the top 5 cm of bioretention filter materials (e.g. Søberg et al., 2017).

Generally, the filter materials having high OM contents (Hekla, Hekla-B, Hasselfors and BN-OHIO, Table 2) had higher percentages of adsorbed metals in Fraction II (labile organic forms, Fig. 4). Particularly, percentages of adsorbed Cu and Pb in fraction II were relatively high in the Hekla (B) and BN-OHIO materials. Hence, the addition of OM in forms of e.g. a top mulch layer as previously recommended in the USA (Li and Davis, 2008) or compost for the enhancement of metal removal (Fassman et al., 2013) may not be sustainable for efficient metal removal on a long-term basis, since these metals are likely to be released to solution as the OM degrades.

The partitioning of Cr was distinctive, as the percentage adsorbed in the exchangeable fraction was low in several materials (Fig. 4). Moreover, substantial percentages of Cr (but no other metals) adsorbed by several materials were detected in fractions IV and V. For example, 18% of Cr adsorbed to fraction V (stable organic forms and sulfides) in Hasselfors and 15% adsorbed to fraction IV.

![Figure 4](image-url) Metal fractionation as percentages of total extractable metal contents (mg/kg) in indicated fractions of each material found in the sequential extraction (with total amounts of adsorbed metals in mg/kg).
There were no obvious similarities between the six filter materials that adsorbed higher proportions of Cr in fractions II–V than in fraction I (Table 2). However, Cr(III) is rapidly adsorbed by soil, specifically by Fe and Mn oxides, having particularly high affinities for Fe oxides (Bradl, 2004). Furthermore, Cr adsorption increases with increases in pH and OM content, but decreases in the presence of competing cations, including ions of the other five metals considered here (Bradl, 2004). This might at least partly explain why fractionation patterns of Cr strongly differed from those of the other metals.

3.6. Discussion

Conflicting results have been observed in previous studies regarding removal of dissolved metals in stormwater bioretention systems. Some have found that dissolved metals are efficiently retained (e.g. Blecken et al., 2011; Wang et al., 2017), while others have found substantial leaching (e.g. Muthanna et al., 2007; Hatt et al., 2008; Seberg et al., 2017). Efficient removal indicates that metals are bound to the filter material in more stable forms than found in this study or that oxidation of OM did not occur. However, metals in the exchangeable fraction are likely to be desorbed and potentially re-adsorbed further down in the filter material. Moreover, the bioretention systems examined in the cited studies (Muthanna et al., 2007; Hatt et al., 2008; Blecken et al., 2011; Wang et al., 2017; Seberg et al., 2017) were relatively young (<2 years) and found metals to be adsorbed in the top 5 cm of the filter material. Hence, these systems were far from saturated with metals. Thus, the zone with higher metal concentrations might gradually extend downwards in the filter material.

The metal fractionation results from this study indicate that substantial amounts of metals in filter materials may be in potentially leachable forms. This has clear implications for the materials’ long-term performance, during and after long dry periods and their disposal after maintenance (when risks of metal desorption during excavation and movement of excavated filter material must be considered). Sequential extractions of filter materials from two approximately four-year-old full-scale bioretention facilities in Washington D.C. and Maryland (USA) indicated that adsorbed metals were strongly bound to the bioretention filter material and largely immobile (not in the exchangeable fraction) (Li and Davis, 2008; Jones and Davis, 2013). However, after extended dry periods (promoting aeration and oxidation of the filter material) high metal concentrations in bioretention effluent have been detected by Blecken et al. (2009). This may have been due to metal adsorption in potentially leachable forms, although the filter material (similar to LTU-TOP) was not subjected to confirmatory sequential extraction. In contrast, in a laboratory-scale study of Cd removal by four bioretention filter materials (fine sand, zeolite, sand and quartz sand) accumulated Cd was detected mainly in the residual form (Wang et al., 2017). Moreover, another study of metal fractionation in soil underlying infiltration facilities (i.e. not in engineered bioretention filter material) found that metal fractionation changed over time; proportions of Cu and Pb in the exchangeable fraction decreased, while proportions of Zn and Cd increased (Kumar, 2016). These partly conflicting results, in combination with findings of this study and previously reported effects of drying, clearly show that further analyses of metal fractionation in bioretention filter material are required. Inter alia, there are needs to evaluate risks posed by remobilization of adsorbed metals in bioretention filter materials under various ambient conditions, and with different filter material compositions (e.g. contents of compost, biochar and similar organic substances which may degrade over time, Fassman et al., 2013).

Both chemisorption and physisorption of metals release heat, but the amounts of heat released differ substantially, in ranges of ca. 80–400 KJ/mol and 5–45 KJ/mol, respectively (Bolis, 2013). The Temkin isotherm heat of adsorption constants and Dubinin-Radushkevich mean sorption energies obtained in this study were <1.2 and <5.1 KJ/mol, respectively (Table S1), indicative of physical sorption processes. The Langmuir separation factors (Table S1) also indicate that the adsorption processes were favorable, but not irreversible (0<R<1), and thus largely physical. In physical adsorption, the bonds are relatively weak and easily break (Bolis, 2013). Further, the metals may be adsorbed in several layers of molecules, and easily desorbed by changes in temperature or other ambient water variables (Bolis, 2013). These observations are consistent with findings in the present study that most of the adsorbed metals were in the exchangeable (I), labile organic (II), and amorphous Fe- and Mn-oxides (III) fractions (Fig. 4), where metals are easily desorbed by changes in ambient water ionic composition and under oxidizing conditions (Tessier et al., 1979).

Chalk (calcium carbonate) contents of soils have been associated with metal fixation, and are considered important for metal adsorption and hence their soluble concentrations (Alloway et al., 1988). Its addition seemed to enhance metal adsorption since DWA-chalk consistently adsorbed higher amounts of metals than DWA (Fig. 1). The relatively low SSA, low OM content, high D50 and high coefficient of uniformity (Table 2) of DWA-chalk are not favorable characteristics for metal adsorption. Hence, its high pH (due to the chalk additive) is presumably the main characteristic that favors metal adsorption.

In recent years biochar has received considerable attention as a soil additive for heavy metal adsorption in stormwater treatment systems because it has various metal ion-binding functional groups and increases SSA due to its high porosity (Mohanty et al., 2018). However, no significant difference (p = 0.872 for a two-sample T-test at 95% CI) in metal adsorption were observed between Hekla and Hekla-B, which are identical except for the presence and absence of biochar (Figs. 2 and 3). Further, adsorption parameters of both Hasselfors and Hekla-B (the materials containing biochar) were moderate and did not substantially differ from those of the other materials (Figs. 2 and 3). Accordingly, a recent review of the utility of biochar as an additive in stormwater treatment systems concluded that it has varying capacity to remove metals (Mohanty et al., 2018). Results herein would not support its use for metal removal.

The materials with the highest metal adsorption (KB—OHIO, BN-OHIO and Orbicon) all have relatively high pH and SSA, low to medium OM contents, and are classified as sand with relatively uniform grain size (Table 2). Conversely, DWA, LTU-TOP and NCUSA, the materials with the lowest metal adsorption, have markedly lower pH than the other materials, small SSA and low OM contents (Table 2). Hence, filter materials with a naturally high pH, low to medium OM contents, large SSA and uniform particles in the sand range seem optimal for retaining dissolved metals in stormwater bioretention systems.

The Hasselfors material is coarser than the other materials (based on gravel rather than sand; Fig. 1, Table 2). Thus, it is likely to provide shorter retention times than the other materials, and its metal adsorption rates may be lower than those observed in this study in practice. In contrast, the Orbicon material has much smaller particles than the other materials (Fig. 1, Table 2), which might pose risks for clogging and thus overflow or bypass. A major challenge when selecting bioretention filter materials is balancing high infiltration rates (but lower adsorption and contact time) offered by coarse materials, and potentially higher adsorption and longer contact time (but higher overflow) offered by finer materials.
Previous studies have found that percentages of most metals in exchangeable fractions of stormwater sediments (pond sediments, gully pot sediments, road dust etc.) are low or non-detectable (Marsalek and Marsalek, 1997; Karlsson et al., 2016; Jayarathne et al., 2017). However, Jayarathne et al. (2017) found approximately 50% of adsorbed Zn and Cd in the exchangeable fraction. Furthermore, Li and Davis (2008) found a close relationship between capture of metals and runoff particles. Hence, the sediment trapped by stormwater bioretention systems will affect the metal fractionation as well as the filter material.

Results of this study show that filter materials for stormwater bioretention have numerous differences and complex, sometimes conflicting characteristics, all of which may affect metal treatment. Hence, identifying the optimal mixture is challenging, especially as other objectives (e.g. supporting plants, treatment of other pollutants, and low cost) must also be met.

4. Conclusion

All the tested materials adsorbed metals, although as metal concentrations increased and metal solutions became more complex the adsorption of some metals decreased. Furthermore, adsorption was generally fast and within an hour more than 90% of most metals was adsorbed. The material that performed best depended on both the metal and solution (single- or multi-metal). However, filter materials with a naturally high pH, relatively low to moderate OM content, large SSA and uniform sand-sized particles (e.g. KB-OHIO, BN-OHIO and Orbicon) generally seems to be good choices for removing dissolved metals. Addition of chalk may also help to improve metal adsorption by increasing the filter material’s pH, while biochar addition seems to have no direct impact, despite increasing materials’ SSA and OM contents. Moreover, adding it may be undesirable due to its degradation over time. High percentages of the adsorbed metals were found in the potentially leachable fractions, with obvious implications for long-term performance of the materials, their functionality under varying conditions and the maintenance of bioretention facilities. However, given the inconsistency of research findings, further research is needed, including evaluations of existing full-scale systems.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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