Stormwater bioretention: Pollutant occurrence and accumulation in filter materials and forebays

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Preface

This licentiate thesis presents a summary of research work from the Urban Water Engineering Research Group at the Department of Civil, Environmental and Natural Resources Engineering at the Luleå University of Technology. This work is a part of the DRIZZLE – Centre for Stormwater Management and financially supported by NCC R&I, SBUF (Grant no. 13623) and VINNOVA (Grant no. 2016-05176).

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Robert Furén

Abstract

Urban areas are affected by anthropogenic activities and produce pollutants that are transported to recipients and receiving waters during precipitation. Untreated stormwater runoff is a main driver of environmental degradation, and the interest in stormwater quality treatment has increased with the awareness of stormwater pollution. Several pollutants, including metals PAHs, PCBs, phthalates, and phenols, pose a hazard to aquatic life and are listed among the 45 priority substances in The European Water Framework Directive list (Directive 2013/39/EU).

Stormwater bioretention technology is employed to efficiently remove pollutants during stormwater treatment in urban areas. However, the resulting accumulation of pollutants in bioretention facilities could ultimately create a pollutant depot. Hence, it is important to understand the occurrence, availability, and mobility of pollutants in bioretention facilities, as well as the processes that control their accumulation and mobility over time. The aim of the work in this licentiate thesis was to investigate the occurrence, accumulation, distribution, and concentration of organic micropollutants and metals in bioretention facilities after long-term stormwater treatment in urban areas of Ohio, Michigan, and Kentucky in November 2019.

Samples were collected from 29 bioretention facilities, 20 of which were equipped with forebays. A total of 269 samples were analysed for metals commonly found in stormwater (Cr, Cu, Ni, Pb, and Zn), and a five-step sequential extraction method was used to assess the metal mobility in the filter material. Additionally, 116 samples from 12 sites were analysed for 38 organic micropollutants (OMPs), including 16 PAHs, 7 PCBs, 13 phthalates, and 2 alkylphenols.

All studied metals were found in all samples, except for Cd, which was detected in 245 samples (91%). For the OMPs, 32 of 38 analytes were detected in at least one sample. PAHs and PCBs were the most frequently detected pollutants, and were found in 12 and 10 sites, respectively. The bioretention sites showed large variations in the concentrations of pollutants. The concentration of OMPs was highest in the upper 10 cm of the filter material and decreased with increasing depth, while a similar, but less obvious trend was observed for Cr, Cu, Pb, and Zn. A trend of decreasing concentration with increasing distance from the inlet was observed for OMPs but was less clear for the metals. The forebays, which contain sediment but no filter material, had the highest concentrations of OMPs. A strong correlation was observed between the pollutant concentrations and the ratio between the filter area and catchment area in a Principle Component Analysis. The accumulation and pathways of particle-bound OMPs and particle-bound metals showed similarities.

These results will assist with improving the methods used for stormwater management. Importantly, regular replacement of the top filter layer and regular forebay maintenance may prevent pollutant accumulation and clogging, thereby extending the filters' treatment function.

Sammanfattning

Våra städer påverkas av mänskliga aktiviteter och verksamheter vilka producerar föroreningar som vid nederbörd leds till och blir en belastning för sjöar och vattendrag. Förståelsen för dagvatten och föroreningar har ökat intresset för att rena och behandla dagvatten. European Water Framework Directive (Directive 2013/39/EU) har bland annat listat metaller, PAH, PCB, ftalater och fenoler att kunna utgöra en fara för vattenlevande organismer.

Biofilter anses vara effektiva för att rena dagvatten och är populära för hantering av dagvatten. Många föroreningar ackumuleras i filtermaterialet. Forskning har identifierat föroreningar ackumulerade i biofilter som en föroreningsdepå och potentiell föroreningskälla. Därav är det av stor vikt att förstå och känna till föroreningars förekomst, mobilitet och de processer som styr ackumulering till biofilter och filtermaterialet.

Syftet i denna uppsats har varit att studera förekomst, ackumulering och koncentration av föroreningar i biofilteranläggningar vilka syftat till att rena dagvatten i urbana miljöer under längre tid. För att bättre förstå dessa processer utfördes en fältstudie med provtagning av 29 biofilter varav 20 försedda med en försedimentering.

Förekomst av metaller (Cr, Cu, Ni, Pb och Zn) analyserades i 269 prover och en femstegs sekventiell lakning användes för studier av metallers mobilitet i filtermaterial. Från 12 filter analyserades 116 prover för innehåll av 38 organiska föroreningar (16 PAH, 7 PCB, 13 ftalater och 2 alkylfenoler).

Samtliga undersökta metaller hittades i alla prover förutom Cd vilket påvisades i 91% av undersökta prover. Organiska föroreningarna detekterades för 32 av 38 undersökta ämnen. Bland organiska föroreningarna var PAH:er och PCB:er mest frekventa, där PAH påvisades i 12 undersökta filter och PCB i 10 filteranläggningar. Sex organiska föroreningar (fem ftalater och en PAH) påvisades aldrig. Stora variationer i koncentration av föroreningar påvisades mellan olika biofilter, särskilt för organiska ämnen. Koncentrationer var högst i de översta 10 cm av filtermaterialet och minskade med ökat djup. Denna trend var tydligast för de organiska ämnena men observerads även för Cr, Cu, Pb och Zn. En trend av minskande koncentrationer med ökat avstånd från inlopp kunde observeras för organiska ämnena men var mindre tydlig för metaller. Högst koncentrationer av föroreningar detekterades i försedimenteringar, vilka dock endast innehåller sediment och inget filtermaterial.

En Principle Component Analysis visade ett starkt samband mellan koncentration och förhållandet mellan biofiltrens area och avrinningsområdets area. Resultaten i denna studie visade även på likheter i ackumulering till filtermaterialet mellan partikelbundna organiska ämnen och partikelbundna metaller.

Slutsatserna i denna avhandling bidrar med kunskap till att utveckla bättre metoder för dagvattenhantering och därigenom en hållbar utveckling av framtida städer. Av praktisk betydelse är att regelbundet underhåll och periodvis byte av översta filterlagret kan säkerställa en bibehållen reningsfunktion över längre tid.

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List of papers

Paper I Furén, R., Flanagan, K., Winston, R. J., Tirpak, R.A., Dorsey, J. D., Viklander, Blecken, G.-T. Occurrence, concentration, and distribution of 38 organic micropollutants in the filter material of 12 stormwater bioretention facilities. Science of the Total Environment. Volume 846, Article number 157372.

Paper II Furén, R., Österlund, H., Winston, R. J., Tirpak, R.A., Dorsey, J. D., Viklander, Blecken, G.-T. Fractionation of metals by sequential extraction in bioretention filters for stormwater treatment: Field study. (Submitted to Environmental Science: Water Research & Technology, 2022-10-17)

Paper III Furén, R., Flanagan, K., Winston, R. J., Tirpak, R.A., Dorsey, J. D., Viklander, Blecken, G.-T. Occurrence and concentrations of organic micropollutants in bioretention filter media. Presented at NORDIWA 2021

Table 1. Contribution to above papers.

						Publication process	
Paper No.	Development of idea	Research study design	Data collection	Data processing and analysis	Data interpretation	Manuscript preparation for submission	Responding to reviewers
I	Contributed	Shared responsibility	Responsible	Shared responsibility	Shared responsibility	Responsible	Responsible
II	Contributed	Shared responsibility	Responsible	Shared responsibility	Shared responsibility	Responsible	Responsible
III	Contributed	Shared responsibility	Responsible	Contributed	Shared responsibility	Responsible	NA

Responsible – developed, consulted (where needed) and implemented a plan for completion of the task.

Shared responsibility – made essential contributions towards the task completion in collaboration with other members of the research team.

Contributed – worked on some aspects of the task completion.

No contribution – for a valid reason, did not contribute to completing the task (e.g., joined the research project after the task completion).

NA – not applicable.

1 Introduction

Urban areas are affected by anthropogenic activities and produce a pollutant load, generated and stored on surfaces, which by surface runoff from participation and/or snowmelt is subsequently conveyed to receiving water bodies (Müller et al., 2020). Untreated stormwater runoff is recognized as a main driver of environmental degradation in urban watersheds (Walsh et al., 2005). As awareness of stormwater pollution and its impacts has increased (Makepeace et al., 1995; Müller et al., 2020), interest in stormwater quality treatment has grown (Fletcher et al., 2015).

Stormwater bioretention facilities are an increasingly popular treatment technology (Davis et al., 2009) commonly applied for stormwater treatment in urban areas as a low impact development practice (Kratky et al., 2017). They are considered an efficient method for the removal of various pollutants, e.g. total suspended solids (Hsieh and Davis, 2005), metals (Blecken et al., 2009a) and a wide range of organic micropollutants (Zhang et al., 2014). Bioretention facilities treat water from surrounding surfaces, mainly by vertical filtration through a filter medium. The filter medium typically comprises an engineered (often) sand or sandy soil (0.7 – 1.0 m) drained by a perforated underdrain pipe installed in a drainage gravel layer. The filter is sometimes topped with a surface mulch layer and/or topsoil planted with a variety of plant species (Lange et al., 2020b). In some cases, bioretention facilities are equipped with a forebay at the inlet. Although a study has shown notable accumulation of pollutants (P and Zn) in forebays, few studies have examined sediment-borne pollutants in bioretention forebays (Johnson and Hunt, 2016).

Metals (e.g. Cd, Cu, Pb and Zn) are commonly regarded as pollutants of concern in stormwater that contribute to water degradation (Göbel et al., 2007). Such metals are transported by stormwater to receiving water bodies, where they can adversely affect the environment. Therefore, there is a need to treat stormwater before being discharged (Barbosa et al., 2012). Particulate metals are mainly removed from storwater through filtration (Tedoldi et al., 2016) and primarily retained in the 5-10 cm top layer of the filter (Blecken et al., 2011; Li and Davis, 2008). Similar trends have been observed for dissolved metals (Al-Ameri et al., 2018). Since most metals in bioretention are removed by filtration or adsorption to soil particles (Blecken et al., 2009a), the filter medium is important for both dissolved and particulate metal removal. Whereas several studies have investigated metal behaviour in bioretention, few have assessed accumulation, characteristics, and behaviour of accumulated metals in the filter material. Thus, to better understand the accumulation and distribution processes of metals in bioretention systems, further studies are needed. Fractionation of metals by sequential extraction can provide information on the mobility and leachability of metals (Gleyzes et al., 2002; Pueyo et al., 2008) in a filter material, which could help to evaluate risks of metal release during operation, maintenance or disposal at the end of a filter's functional lifespan. So far, few studies have used sequential extraction to assess the availability of metals.

Recent studies have also shown that organic micropollutants (OMPs) are a pollutant group of concern because of their environmental persistence and tendency for bioaccumulation, which may have long-term and harmful effects on receiving water bodies, aquatic life and also humans (Barbosa et al., 2012; Markiewicz et al., 2017). To date, compared to metals, few studies have assessed treatment of OMPs in stormwater by bioretention. Zhang et al. (2014) have shown that bioretention can efficiently remove a wide range of OMPs. Field studies have also demonstrated high removal (>90%) of PCBs and PAHs (David et al., 2015; Flanagan et al., 2018; Gilbreath et al., 2019) but also high mass load reductions of 87% for PAHs (DiBlasi et al., 2009). However, less is known about other OMPs, e.g., phthalates and alkylphenols. Limited research has also been conducted on the pathways and accumulation of OMPs in filter materials. Therefore, there is a need for further studies to better understand the accumulation processes and distribution of OMPs in bioretention facilities.

Together, the pollutants captured in a bioretention facility create a pollutant depot (Davis et al., 2003). Characterization of different pollutants' accumulation, occurrence, availability, and mobility in bioretention filter materials and forebays is important to identify successful design and maintenance needs for sustainable long-term performance in treating polluted storm water in urban areas.

1.1 Aim and research objectives

The overall aim of the work described in this licentiate thesis was to study pollutant occurrence, accumulation, and concentration in bioretention filter materials and forebays after long-term stormwater treatment in urban areas. The findings contribute towards knowledge and understanding of the requirements for design, long-term operation, maintenance, and waste management for improving pollutant treatment and reducing the environmental impact and risks that may occur with bioretention or similar technologies for treating stormwater in urban areas.

The main objectives of the study were as follows:

1) What are the occurrence, concentration and distribution of organic micropollutants in bioretention filters after long-term stormwater treatment in urban areas?
2) How available are metals accumulated in bioretention filter media after long-term treatment of urban stormwater?
3) What are the pollutant occurrence, concentration and distribution in bioretention forebays and filter media after long-term stormwater treatment in urban areas?

1.2 Thesis structure

This licentiate thesis is based on research carried out during a three-year period including a major field sampling campaign. The research resulted in the three appended papers, referred to as Paper I, Paper II and Paper III.

Paper I describes a field study of accumulation, occurrence and concentration for assessment of pathways of various organic pollutants (PAHs, PCBs, phthalates and alkylphenols) in a bioretention filter medium after long-term operation.

Paper II presents a study of six metals (Cd, Cr, Cu, Ni, Pb and Zn) and how these metals bind to a filter medium after long-term operation based on a five-step sequential extraction method for assessing metal availability. The study also evaluated the distribution of metals in the filter medium.

Paper III reports a broader study of the bioretention facility by measuring the occurrence, distribution, and concentrations of OMPs in the forebay and filter material.

This thesis expands upon the work described in Paper III by including metal data from forebays, which have not yet been included in any paper.

The papers complement each other, as illustrated in Figure 1. In combination, they give a broad perspective of pollutant accumulation, distribution, and availability in bioretention filter material for stormwater treatment after long-term operation. Such information is needed to understand long-term bioretention performance.

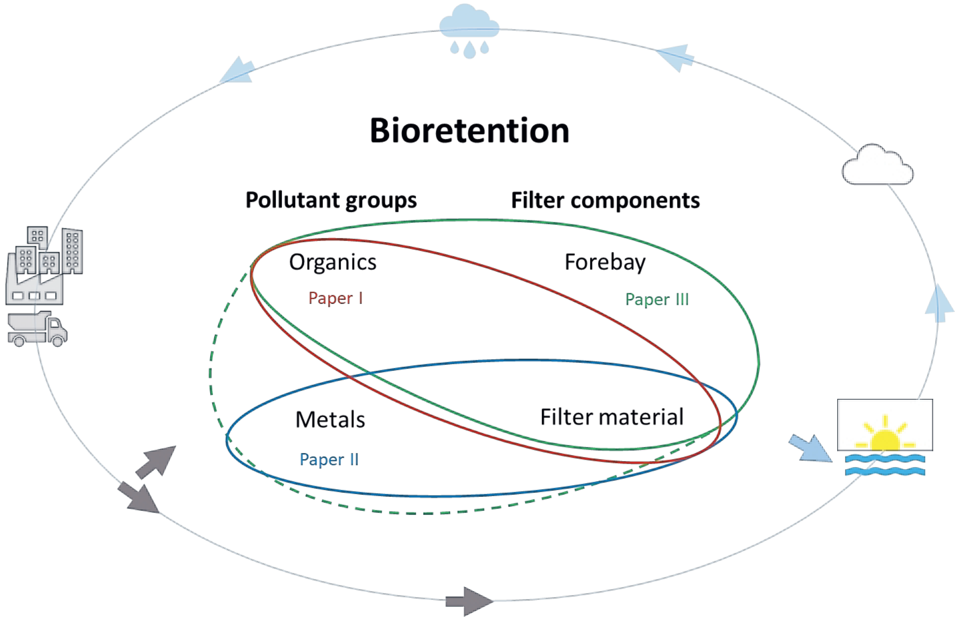

Figure 1. Synthesis of papers included in this thesis. The dotted green line indicates work not published in papers but included in this thesis.

2 Background

This review of sustainable urban stormwater treatment focus on improved best management practice and design of bioretention or similar technologies to demonstrates the need for increased knowledge and further research on long-term performance, pollutant pathways and accumulation in filter materials, as well as design features for facilitated maintenance and risk management. The increased implementation of stormwater quality treatment technologies, e.g. bioretention, makes it important to understand their long-term function (Blecken et al., 2017).

2.1 Urban stormwater

Stormwater is an important part of the urban water cycle. As urban areas continue to expand through urbanization and a growing global population, it has become apparent that the modern urban landscape affects the natural hydrological cycle. Impervious surfaces reduce infiltration and evapotranspiration but also increase runoff velocities, and therefore result in more rapid runoff with higher flow peaks. Due to the impact of various sources and anthropogenic activities (e.g. atmospheric deposition, vehicular transportation roads and building materials), urban stormwater contains a variety of contaminants e.g. sediments, metals, organic pollutants, nutrients, bacteria, chlorides (Makepeace et al., 1995). During runoff events, these pollutants are transported to receiving water bodies where they can affect the local environment and ecosystems (Müller et al., 2020). Untreated stormwater runoff is recognized as a main driver of environmental degradation (Walsh et al., 2005), which can affect public health. Thus, stormwater should be treated or managed before being discharged (Barbosa et al., 2012; Göbel et al., 2007; Markiewicz et al., 2017; McGrane, 2016). Ecological degradation including changed flow patterns and pollutant loadings with their associated impact on streams draining urban land is also referred to as "the urban stream syndrome" (MacKenzie et al., 2022; Walsh et al., 2005) and summarize an important part of the challenges in urban water management.

2.2 Pollutants

Previous research on stormwater has identified a number of pollutants that could pose a potential hazard to humans and aquatic life (Makepeace et al., 1995). It is well known that stormwater can transport large quantities of contaminants (Barbosa et al., 2012). The European Water Framework Directive (WFD, 2014) lists in Directive 2013/39/EU (2013/39/EU, 2013) 45 priority substances in the field of water policy for which environmental quality standards have been set. These substances include metals, PAHs, PCBs, phthalates, and phenols. Research has shown the significance of these priority substances as well as their environmental effects (Zgheib et al., 2011). Using a theoretical approach, Eriksson et al. (2007) examined 25 selected stormwater priority pollutants, including PAHs, phenols, di(2-ethylhexyl) phthalate, PCB28 and the metals Cd, Cr, Cu, Ni, Pb, Pt and Zn together with water quality parameters (Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Suspended Solids (SS), N, P and pH).

Practical studies have also been conducted on the occurrence and concentrations of the priority substances (Zgheib et al., 2011). Several other studies have also focused on the occurrence and concentrations of conventional stormwater contaminants, such as Total Suspended Solids (TSS), PAHs and metals (Cd, Cu, Pb and Zn) (Gasperi et al., 2014; Göbel et al., 2007; Zgheib et al., 2012, 2011) but also less documented pollutants, such as nonylphenols (Björklund et al., 2009; Gasperi et al., 2014), octylphenols (Gasperi et al., 2014; Zgheib et al., 2011), (Bergé et al., 2013; Björklund et al., 2009; Järlskog et al., 2021; Markiewicz et al., 2017; Müller et al., 2021) and PCBs (Cao et al., 2019; Gilbreath et al., 2019).

2.2.1 Organic micropollutants

OMPs have been highlighted as a pollutant group of concern owing to their environmental persistence and tendency to bioaccumulate, which may have long-term effects on receiving water bodies (Barbosa et al., 2012; Markiewicz et al., 2017). A variety of OMPs have been frequently detected in stormwater (Masoner et al., 2019), such as hydrocarbons, including PAHs (Brown and Peake, 2006; Minervini, 2010), PCBs (Andersson et al., 2015; Cao et al., 2019), alkylphenols and phthalates (Björklund et al., 2009; Clara et al., 2010; Flanagan et al., 2019b). Many of these pollutants are related to vehicle- and traffic-related organic pollutants, e.g. phthalates, alkylphenols and polycyclic organic hydrocarbons (Markiewicz et al., 2020). Field studies have detected OMPs such as polycyclic aromatic hydrocarbons (PAHs) (Smith et al., 2000), polychlorinated biphenyls (PCBs) (Hwang and Foster, 2008), phthalates (Björklund et al., 2009) and alkylphenols (Lamprea et al., 2018) in urban runoff. Numerous sources contribute to OMP contaminants, e.g. coal tar sealants, traffic, leaching from construction materials and industrial use (Bergé et al., 2013; Brown and Peake, 2006; Crane, 2014; Lamprea et al., 2018; LeFevre et al., 2012; Markiewicz et al., 2017). Since high stability PCBs are persistent, and therefore classified as persistent organic pollutants (POPs). They are considered as one of the important classes of POP chemicals alongside alkylphenols (Jones and de Voogt, 1999; Stockholm Convention, 2008). PCBs have been detected in road runoff sediments from areas with various land uses (Cao et al., 2019). Samples of stormwater have been shown to contain up to 80 times higher levels of PCBs than base flow (Hwang and Foster, 2008). The main sources of PCBs include transformer oils, small capacitors, heat transfer fluids, hydraulic fluids, liquid filled cables, paints, pesticides, and insecticides. Studies of sediments have revealed that there are still active sources contributing PCBs and that stormwater is the main pollutant pathway (Andersson et al., 2015). Nonylphenols and phthalates are considered to be endocrine disrupting (Björklund et al., 2009), and petroleum hydrocarbons are suspected human carcinogens (Fent, 2003; LeFevre et al., 2012; Mastrangelo et al., 1996). In a study of 1100 compounds to identify priority pollutants, PAHs, alkylphenols and phthalates were listed among the four highest ranked priority pollutants (Markiewicz et al., 2017). All together this highlights the need of further studies of long-term accumulation and distribution of OMPs in bioretention facilities.

2.2.1 Metals

Metals are naturally occurring in the environment (Alloway, 2013a). However, in urban areas, due to anthropogenic activities, they are also a major source of contamination of stormwater and runoff (Müller et al., 2020). Various metals (e.g. Cd, Cu, Pb, Zn) contribute to the degradation of water (Göbel et al., 2007) and are considered contaminants of concern for human and aquatic life (Pitt et al., 1994). In road runoff, the Nationwide Urban Runoff Program (NURP) has classified several metals (especially Cu, Pb and Zn) as toxic (US EPA, 1983), and the European Water Framework Directive (WFD, 2014) lists metals such as Cd, Pb and Ni as priority substances. In a list of 25 selected stormwater priority pollutants, Eriksson et al. (2007) also included the metals Cd, Cr, Cu, Ni, Pb, Pt and Zn. Metals either occur in particulate forms or as dissolved fractions in stormwater (Lange et al., 2020a). Huber et al. (2016) discussed the importance of stormwater treatment strategies from the perspective that Zn, Cu, Ni and Cd are the largest fractions in the dissolved phase, whereas Pb and Cr are mainly particle bound. Even though there are many studies of bioretention technology and metals, there are few larger field studies assessing metal accumulation and fractionation in stormwater treatment facilities and long-term performance.

2.3 Bioretention

As awareness of stormwater pollution has increased, interest in stormwater quality treatment has grown and several studies have studied stormwater treatment in urban areas. Bioretention is one of the most commonly used techniques and has been suggested to be a best management practice or low impact development for stormwater control measures (Johnson and Hunt, 2016; McGrane, 2016). In bioretention facilities, also referred to as biofilters, biofiltration systems or raingardens, stormwater is received from surrounding (impervious) areas and treated by percolating vertically through a filter, before being released to a downstream system (receiving water, stream, or stormwater drainage system). Bioretention facilities typically consist of a filter medium drained by an underdrain pipe embedded in gravel (Figure 3). The filter medium is often topped with mulch and/or topsoil, and planted with a variety of plant species (Lange et al., 2020b; LeFevre et al., 2015). An overflow device enables bypassing of high flows during rain events that exceed designed flows, and some facilities are also equipped with a forebay or a pre sedimentation.

2.3.1 Long-term function

Even if bioretention technology is a popular treatment technology and often studied, to date only limited research has been conducted to evaluate pollutant accumulation and associated risks, e.g. were high concentration of pollutants in parts of the facilities could pose risks to the local environment, wildlife and humans (Blecken et al., 2017). Therefore, increased knowledge of pollutant (both metals and OMPs) accumulation and fates in the filter is needed to enable improved design and assessment of bioretention technology and long-term performance (Davis et al., 2009). Regular maintenance is needed to keep the long-term performance of a bioretention facility, (Johnson and Hunt, 2016). To gain a perspective of long-term functioning, further research is required with a specific focus on older facilities to identify maintenance needs and measures (Blecken et al., 2017; Lucke et al., 2017).

The concept of "long-term" is vague and requires definition in the context of this thesis. Whereas a short-term perspective assesses a facility's ability to remove pollutants during several rain events (e.g., during one or few years or a season), a long-term perspective assesses the results of aged (in this thesis, at 7-16 years old) facilities. The latter includes many series of rain events, as well as processes occurring between them, such as evapotranspiration, plant uptake, dry periods and biodegradation, but also external actions, such as maintenance and reconstruction (Gavric, 2020). A long-term perspective of pollutant accumulation, pathways, and their availability in bioretention filter material can help to identify improvements in design and maintenance to increase performance during long-time operation in treating stormwater runoff in urban areas.

2.3.2 Filter material

The main function of the filter is to retain or delay flow and to treat stormwater quality by various processes (Fassman-Beck et al., 2015; Søberg et al., 2019). There are a number of filter material configurations, typically engineered sand with low organic matter, loamy sand or a mixture of sand with additives e.g. organic matter, biochar, chalk to support e.g. plant growth or metal treatment (Hatt et al., 2011; Søberg et al., 2019). Somteimes, filters are topped with a mulch layer (Davis et al., 2009; Hunt et al., 2012).

The filter material should ensure sufficient retention of the water to ensure sufficient contact time for adsorption processes, but also relatively high infiltration to avoid overflow. Further, it has also to support plant life and avoid clogging (Fassman-Beck et al., 2015). These filter material requirements are partly conflicting.

The filter material removes pollutants from the infiltrating water using different processes including adsorption, precipitation, and filtration (Hsieh and Davis, 2005). Plants in the filter foster infiltration and reduce the outflow load due to root zone development (Muthanna et al., 2007). However, most studies show that the filter media play the main role, at least for metal treatment (Blecken et al., 2011; Muthanna et al., 2007). Generally, filter materials classified as sand with naturally high pH, low organic matter and large specific surface area is recommended for dissolved metals and chalk additive to improve metal adsorption (Søberg et al., 2019).

Most previous studies of bioretention have focused on metals (Tedoldi et al., 2016) and investigated mainly particle-bound metals (Lange, 2021). Most particulate metals are removed by filtration or adsorption to soil particles (Blecken et al., 2009a; Tedoldi et al., 2016) and are primarily trapped in the top layer (0-10 cm) of the filter medium (Lange et al., 2020a; Li and Davis, 2008). Studies have shown high reductions of suspended solids and metals, with pollutant removal that often exceeds 70-90% (Blecken et al., 2009b; Flanagan et al., 2018; Hsieh and Davis, 2005; LeFevre et al., 2015). Similar trends have been observed for dissolved metals: Al-Ameri et al. (2018) reported that 70% of dissolved metals were trapped in the top layers (0-7 cm) of the filter medium. However, other studies also reported poor treatment and leaching from the filter material (Lange et al., 2020b; Søberg et al., 2017).

Previous studies have also estimated the time for metal accumulation to reach regulatory limit concentrations of environmental and health reasons in the filter material e.g. to e.g. 20, 77, 16 and 16 years for Cd, Cu, Pb and Zn (Davis et al., 2003) and 12-15 years of operation to exceed ecological guideline values requiring special disposal for Cd, Cu and Zn (Hatt et al., 2011). Leaching and desorption potential also affect the long-term function (Okaikue-Woodi et al., 2020) since there is a potential risk of leaching from polluted filter material and during disposal of filter material removed from polluted facilities. Because of this leaching potential, regular replacement of sediment and pollutant accumulated filter material has been recommended after, e.g., 20-25 years (Kluge et al., 2018). Al-Ameri et al. (2018) have suggested from a study of metals that for less contaminated catchment areas (where clogging rather than high concentrations may limit bioretention function), regular maintenance could involve replacing the top 10 cm of filter material.

Further studies of metal fractionation can provide information about potential metal behaviour, e.g., to reduce such leaching risks. Although several studies have investigated metal behaviour in bioretention few studies have assessed the availability of metals using sequential extraction methods. Previous laboratory studies using sequential extraction have studied Cd in a bioretention column lab-scale experiment (Wang et al., 2016) and evaluated adsorbed dissolved metals in bioretention filter materials (Søberg et al., 2019). In a lab study, Søberg et al., (2019) also found metals as primarily adsorbed to exchangeable forms. Another lab study found that 88–97% of Zn, Cu, Pb were captured in the filter material while only 0.5–3.3% in the plants why the filter media play an important role in metal treatment (Sun and Davis, 2007). Two field studies have used five-step sequential extraction methods to study metal capture (Cu, Pb and Zn) and environmental availability (Jones and Davis, 2013; Li and Davis, 2008). Jones and Davis, (2013) found metals to be strongly bound to the filter media and largely immobile. Li and Davis, (2008) found that most captured metals were of anthropogenic origin but also correlations between soluble-exchangeable forms with dissolved metals while more stable forms were associated to modeled runoff and media particulate metals. A recent field study also used sequential extraction to assess metal (Cr, Cu, Ni and Zn) mobility of road runoff in bioretention (Rommel et al., 2021). However, there are few larger studies assessing older field sites using sequential extraction methods.

Compared to metals, only limited data is available on OMP removal and, specifically, accumulation to filter material. Most studies on OMP fate in bioretention facilities have focussed on hydrocarbons, particularly PAHs. However, some studies have indicated efficient removal of a wide range of OMPs (Zhang et al., 2014), with high concentration reductions (>90%) for PCBs and PAHs (David et al., 2015; Flanagan et al., 2018; Gilbreath et al., 2019) but more variable performance for treatment of alkylphenols and phthalates (49 – 76% and 8-74%, respectively) (Flanagan et al., 2018). There are today few studies concerning the filter material itself (Søberg et al., 2019) and for metals there are knowledge gaps in long-term retention, risks for leaching of adsorbed metals and accumulation processes to the filter material (Hatt et al., 2008; Søberg et al., 2017). For OMPs, only limited research has been conducted to evaluate the pollutant accumulation in the filter material and long-term function. High OMP concentrations in the filters could pose risks to local environment. Therefore, increased knowledge of pollutant pathways and filter accumulation of both metals and OMPs is needed to enable improved design and assessment of bioretention long-term performance. Kratky et al., (2017) also recommended further research on long-term performance studies and disposal studies of disposal requirements of polluted filter media.

2.3.3 Forebay

A forebay could be implemented to provide pre-sedimentation at the inlet to minimise sediment transport to the filter surface, and thus prevent clogging. Bioretention forebays may comprise a small steel or concrete settling basin placed at the inlet as a velocity dissipator and/or for erosion protection but may also be a rock structure with a pooling function. In studies of ponds and wetland high levels of toxicity were commonly found in forebay sediments (McNett & Hunt, 2011). However, these forebays are commonly larger sedimentation facilities compared to bioretention.

To date, only few studies have examined forebays in bioretention (McNett and Hunt, 2011). In a study of biofilter wetlands, Kallin et al. (2004) suggested that a good design should incorporate a forebay for settling of large suspended sediments and periodically removing pollutants. (McNett and Hunt, 2011) assessed the toxicity of various metals (Cd, Cr, Cu, Fe, Pb, Ni and Zn) in forebay sediments from stormwater wetlands and wet ponds and concluded that according to US Environmental Protection Agency standards for the land application of biosolids (U.S. EPA, 1993), the sediments posed no threat to the environment. However, it was suggested that the presence of PCBs and PAHs (not assessed in the study) may restrict the possibilities for land application. (Johnson and Hunt, 2016) studied the accumulation and distribution of Zn, Cu and P in filter media from an 11-year-old bioretention cell. Their results showed significant variations in pollutant distribution with depth and distance from the inlet and correlation with humic matter in the filter material but also

3 Methods

3.1 Field study

In November 2019, a field study of stormwater bioretention systems was performed in Ohio, Michigan, and Kentucky (USA). Filter material was sampled from 29 bioretention sites (including 20 with a forebay) used for treating stormwater in urban areas for 7–16 years.

3.1.1 Field sites and site characteristics

The contributing catchment areas were a mixture of urban and high urban, residential and industrial/commercial areas mainly treating road runoff and urban stormwater, as summarised in Table 2. Sampled filter materials were analysed in the laboratory and data were obtained on the occurrence, concentration, and accumulation of OMPs (16 PAHs, 7 PCBs, 14 phthalates and 2 alkylphenols) and metals (Cd, Cr, Cu, Ni, Pb and Zn) in the filter material and forebays. Metal fractionation was also assessed using a five-step sequential extraction method.

Figure 2. Selected bioretention sites from field sampling in Ohio, Michigan, and Kentucky in November 2019. The upper left picture site #18, upper right site #27, lower left site #22 and lower right site #26.

Table 2. Field sites and site characteristics.

Site	Analyse	Forebay	Age [yr]	Location	Catchment area characteristics	Catchment Area [m²]	Filter Area [m²]	FA/CA [%]
1	omp/metal	Yes	9	Upper Arlington, OH	Residential	318488	950	0.3
2	metal	Yes	9	Upper Arlington, OH	Residential	1253311	1200	0.1
3	metal	Yes	9	Upper Arlington, OH	Residential	223791	900	0.4
4	metal	Yes	9	Upper Arlington, OH	Residential	145687	1900	1.3
5	omp/metal	No	8	Upper Arlington, OH	Commercial	750	40	5.3
6	omp/metal	No	10	Columbus, OH	Industrial	6000	300	5.0
7	metal	Yes	8	Westerville, OH	Parking/Roads	12000	600	5.0
8	metal	Yes	8	Westerville, OH	Parking/Roads	2000	50	2.5
9	omp/metal	Yes	7	Westerville, OH	Commercial	4000	170	4.3
10	metal	Yes	9	Columbus, OH	Parking/Roads	4500	580	12.9
11	omp/metal	Yes	9	Columbus, OH	Downtown Urban	300	40	13.3
12	omp/metal	Yes	8	Columbus, OH	Downtown Urban	50	10	20.0
13	metal	Yes	12	Hamilton, OH	Industrial	4500	200	4.4
14	omp/metal	Yes	12	Hamilton, OH	Industrial	4500	300	6.7
15	metal	Yes	12	Hamilton, OH	Industrial	4500	200	4.4
16	metal	No	16	Cincinatti, KY	Commercial	3000	190	6.3
17	metal	No	9	Toledo, OH	Residential	250	50	20.0
18	omp/metal	No	12	Lansing, MI	Downtown Urban	600	50	8.3
19	omp/metal	Yes	11	Lansing, MI	Downtown Urban	500	50	10.0
20	metal	Yes	14	Ann Arbor, MI	Parking/Roads	2250	156	6.9
21	metal	No	11	Seven Hills, OH	Commercial	1200	200	16.7
22	omp/metal	Yes	8	Parma, OH	Fueling station	2500	200	8.0
23	omp/metal	No	13	Twinsburg, OH	Fueling station	2000	70	3.5
24	metal	No	10	Orange Village, OH	Residential	250	20	8.0
25	metal	No	10	Orange Village, OH	Residential	250	20	8.0
26	metal	Yes	11	Kent, OH	Fueling station	800	70	8.8
27	metal	Yes	13	Akron, OH	Parking/Roads	6500	180	2.8
28	omp/metal	Yes	12	North Canton, OH	Fueling station	1250	180	14.4
29	metal	Yes	12	North Canton, OH	Fueling station	1000	100	10.0

3.1.2 Field sampling

The methodology used was hypothesis guided sampling of filter material from 29 bioretention sites, similar to a method previously used by (Tedoldi et al., 2017) and illustrated in Figure 3. The main aim of this approach was to determine length/depth profiles of the accumulated pollutants. At each bioretention site, filter material was also collected from the forebay if present (see Table 2).

Filter material samples were collected at three locations along each filter (i.e., three different distances from the inlet) located approximately 1 m, 3 m and 6 m from the inlet. Since some sites were shorter (sites #5, #8, #12), the distances were scaled to fit three sampling locations within the site, and for site #24 and #25, only one sample point each was included. Further, some filters either had multiple inlets (site #5, #16, #23 and #26) or stretched out inlets along one of the sides (site #13, #14, #15, #24 and #25). For these sites, sampling locations were selected by judgement of the likely main flow path based on topography and sediments. Therefore, before sampling, mapping and examination of the local site hydrology and topography were performed, with catchment areas, inlets, sediments, and erosion studied to define the main inlet from which the sampling points then measured.

At each sampling location, filter material was collected at three depths (0-5 cm, 10-15 cm, and 30-50 cm). While the samples from the two shallower depths were always taken at 0–5 and 10–15 cm, the depth of filter material in some facilities (i.e., at sites #6, #7, #8, #23 and #27) was less than 50 cm. In these cases, the deepest sample was collected from the filter layer between 35 cm and the bottom of the filter material. In general, nine samples were collected from each filter (except at site #24 and 25, where only 3 samples were taken) and one sample was collected from each of the 20 forebays, resulting in a total of 269 samples. For each sample, a replicate was also taken.

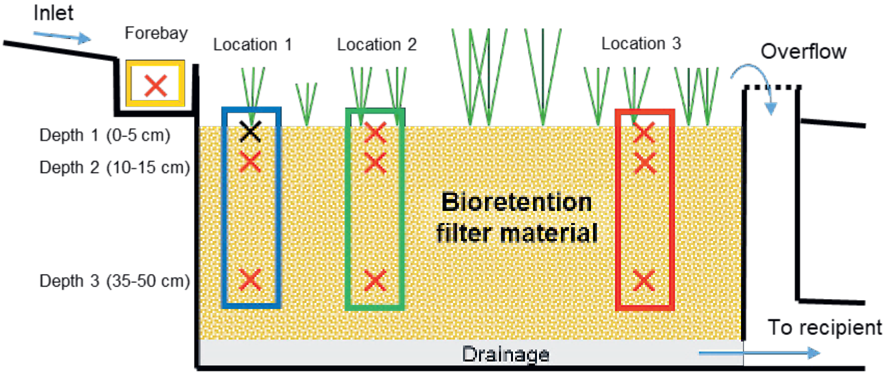

Figure 3. Cross-section of a bioretention facility illustrating the 10 sampling points (forebay, three locations in the filter and at three depths) all illustrated with a black “X” except “Depth 1” and “Location 1” marked with a black “X” indicating that a sequential extraction also was performed on the sample. The coloured rectangles indicate different locations in the filter.

Samples were collected in the field by cutting/digging out a core of filter material (5cm x 15cm x 15cm for layer 1 and 10 cm x 10 cm x 10 cm for layers 2 and 3). The filter material (about 1 kg) was placed into diffusion-tight plastic bags (18 cm x 35 cm) that were sealed shut with cable ties. At the time of sampling, the outdoor temperature was between -12 and +6 °C. After sampling, the samples were refrigerated prior to analysis. The forebay samples consisted of sediments collected from sites with a forebay or structure of similar function, i.e., a pre-treatment facility of steel, concrete or large stones or rock structures with a pooling function or where sediment deposited.

Figure 4. Left picture sampling of filter material consisting of sand with a covering mulch layer at site #22. Right picture a forebay with sediments.

3.2 Sample analysis

All samples were analysed for the concentration of six metals (Cd, Cr, Cu, Ni, Pb and Zn). The metal analysis was conducted using a five-step sequential extraction method for all 29 sites at location 1 and depth 1 (Figure 3). For these samples, the total organic carbon (TOC) content and pH were also analysed. Further, for all samples, the concentrations of 38 organic pollutants from four pollutant groups (16 PAHs, 7 PCBs, 13 phthalates and 2 alkylphenols) were analysed for 12 sites (including eight sites with a forebay). For these 12 sites, TOC, and loss on ignition (LOI) were also analysed, and in two of the samples from each site (location 1, depth 1 and depth 2), the specific surface area (SSA) was analysed. All samples were sent to an external accredited laboratory ALS Scandinavia AB (ALS Global, 2022) for pretreatment and analysis.

OMP concentrations were analysed using gas chromatography – mass spectrometry (GC – MS.

Concentrations of 16 PAHs (i.e. naphthalene (Nap), acenaphthylene (Acyl), acenaphthene (Acen), fluorene (F), phenanthrene (Phen), anthracene (A), fluoranthene (Fluo), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chry), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DahA), benzo(g,h,i)perylene (Bper) and indeno(1,2,3-cd) pyrene (IP)) were analysed according to US EPA 8270 (Pitt et al., 1994) and ISO 18287 (ISO, 2006). Σ_{16}PAH was calculated as the sum of the concentrations of all 16 PAHs. The sum of PAHs with low molecular weights (PAH-L) was calculated as the sum of naphthalene, acenaphthylene and acenaphthene concentrations, PAHs with medium molecular weights (PAH-M) as the sum of fluorene, phenanthrene, anthracene, fluoranthene and pyrene concentrations, and PAHs with high molecular weights (PAH-H) as the sum of benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene concentrations. Concentrations of seven PCB indicator congeners (i.e. PCB 28, PCB 52, PCB 101, PCB118, PCB 153, PCB 138, PCB 180) were analysed following DIN ISO 10382 (DIN ISO, 2002), and Σ_7PCB was calculated as the sum of their concentrations. The concentrations of 13 phthalates (i.e. dimethylphthalate (DMP), diethylphthalate (DEP), di-*n*-propylphthalate (DPP), diisobutylphthalate (DIBP), di-*n*-butylphthalate (DBP), di-*n*-pentylphthalate (DNPP), di-*n*-octylphthalate (DNOP), di-(2-ethylhexyl)phthalate (DEHP), butylbenzylphthalate (BBP), dicyclohexylphthalate (DCP), diisodecyl phthalate (DIDP), diisononyl phthalate (DINP) and di-*n*-hexylphthalate (DNHP)) were analysed following E DIN19742 (E DIN, 2014). Finally, the concentrations of two alkylphenols (4-tert-octylphenol (OP) and 4-nonylphenol (NP)) were analysed. All OMP detection limits are presented in Appendix I (paper II, Table 2, page 4).

Besides the OMP concentrations, total organic carbon (TOC was measured using CSN EN 13137 (CSN EN, 2018) and CSN ISO 10694 (CSN ISO, 1995). Loss on ignition (LOI was measured using gravimetric analysis based on CSN EN 12879 (CSN EN, 2014), CSN 72 0103 (CSN, 2009) and CSN 46 5735 (CSN, 1991), dry matter (DM) was measured using appropriate methods for each pollutant group and Specific surface area (SSA was measured according to BS ISO 9277:2010 (BS ISO, 2010) (gas adsorption - Brunauer, Emmett and Teller (BET) method).

For determination of total metal concentration, the samples were dried (at 50°C) and sieved (2 mm) according to Swedish standards (SS, 2004a; (SS, 2004b). Drying at 105°C was carried out in parallel to the analysed samples to calculate the DM concentration. Microwave assisted digestion was performed on the dried samples in 5 ml concentrated HNO_3 and 0.5 ml H_2O_2.

Sequential extraction is a fractionation method developed for laboratory simulations of leaching. It can be used to analyse the availability of metals (such as Cd, Cr, Cu, Ni, Pb and Zn) in soils and sediments to determine whether they are leachable to the environment, and hence a potential pollutant. The method used for analysis in the present work was based on one used previously by Hall et al. (1996a, 1996b) and consisted of five different fractionation steps of extraction to provide information about the availability and leachability of different metals. Samples of metal leachate water were acidified with 1 ml nitric acid (HNO_3; suprapur for trace analysis) per 100 ml and analysed using Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) according to Swedish standards (SS-EN ISO, 2016, 2006) (mod) and U.S. EPA method (U.S. EPA, 1994a) (mod). Inductively Coupled Plasma Optica Emission Spectrometry (ICP-OES or ICP-AES) was also performed according to Swedish standard (SS-EN ISO, 2009) (mod) and U.S. EPA method (U.S. EPA, 1994b) (mod). Detection limits (DLs) were affected in one sample (site 16, step 2 for Cd, Cr and Ni). Thus, in this case, there was a need for extra dilution to reduce matrix effects.

Table 3. Metal fractionation steps in the five-step sequential extraction (ALS, 2018).

#	Form	Leaching solution	Description
1	Adsorbed and exchangeable metals and carbonates	1.0 M sodium acetate buffer, pH 5	Mimics the effects of acidified conditions. Easily soluble substances or adsorbents loosely adhered to material surfaces are released, including those bound to carbonate phases. The exchangeable fractions are released by ion exchange. Easily leached forms mobilized during precipitation are a direct threat to the environment.
2	Labile organic forms	0.1 M sodium pyrophosphate, pH 9	Releases metal impurities bound in labile organic forms, such as humus and fulvic acids. This leaching step reveals what could be potentially bioavailable.
3	Amorphous Fe- and Mn-oxides	0.25 M NH2OH·HCl in 0.1 M HCl 60°C, pH 1	Indicates the proportion that can be released if the redox potential in the soil is significantly reduced and anoxic conditions prevail in the material, e.g., at elevated groundwater levels, when covering results in reduced oxygen uptake or at high oxygen consumption due to high levels of organic material. To some extent, the release of metals in hydroxide form may be due to an acidic environment rather than altered redox potential
4	Crystalline Fe oxides	1.0 M NH2OH·HCl in 25% acetic acid 90°C, pH approx. 1	The material is leached under greatly reduced conditions, which reduce crystalline iron oxides, (e.g., ingot, hematite and magnetite), releasing metals bound to these phases. These forms are more stable than amorphous Fe/Mn oxides and only problematic if anoxic conditions prevail for a long time
5	Stable organic forms and sulphides	K-chlorate 12 M HCl, 4 M HNO3 90°C	Stable organic forms and sulphides. Upon exposure to air and water, sulphides dissolve to form sulphuric acid, which can then release metals

3.2 Data analysis

The data and statistical analysis are described in detail in the appended papers. In addition, a complementary principal component analysis (PCA) model was performed for analysis of forebay impact, as described below.

The software SIMCA 17 was used to summarize the data and for easy visualization of the main characteristics and examine correlations between parameters. In total, four PCA models were considered: one model of OMPs from 12 different sites (Paper I), one model of metals from 29 sites (Paper II) and two additional models in this thesis (metals and OMPs from 12 different sites; metals, OMPs and forebays from 8 different sites). The PCA models also included observations of concentrations from the laboratory analysis and the variables depth, location (Figure 3), SSA, LOI, TOC, age, ratio between filter area and catchment area, land use (commercial, industrial, downtown urban, roads and parking and fuel stations). The models were UV scaled, and log transformed (auto transformed) on skewed variables.

Since most of the datasets were non-normally distributed, a nonparametric method (Kruskal-Wallis test) was used after censoring data at the highest reporting limit (Helsel, 2012) to test the statistical significance of differences between the examined parameters (i.e. concentration, depth and location).

4 Results

4.1 Organic micropollutants

34 of the 38 studied organic analytes were detected in at least one of 116 samples of filter material. Four substances, one PAH (acenaphthalene) and three phthalates (diethylphthalate (DEP), di-*n*-octylphthalate (DNOP) and dicyclohexylphthalate (DCP)).

PAHs were found above the detection limit in 79% of all 116 samples and detected at all twelve examined sites. Of the 16 analysed PAHs, only acenaphthylene was not detected at all. PCBs were detected in 77% of all samples and therefore, together with the PAHs, the most frequently observed group of organic micropollutants. In total, all PCBs aside from PCB28 were detected at all but two (#3 and #7) of the 12 sites. The most frequently occurring PCB were PCB 153, which was detected in 76% of all samples. The least frequently detected PCB (PCB 28) was detected at four sites (#5, 19, 22 and 23) and in 17% of all samples. Phthalates were detected at eleven sites and in 59 of 108 samples (51 %). 10 of the13 studied phthalates were detected in at least one sample. The most frequently detected phthalate was di-2-ethylhexylphthalate (DEHP), which was detected in 49% of the samples, whereas all other phthalates were only detected occasionally in ≤7% of all samples. Alkylphenols had the lowest occurrence rate of the studied OMPs. The most frequently detected alkylphenol was NP, which was detected at 10 of 12 sites and in 26 out of a total of 107 samples (23%). OP was only found above the detection limit in one sample out of 107 (<1% detection frequency).

Of the twelve examined sites, eight had a forebay (site # 1, 9, 11, 12, 14, 19, 22 and 28), and for those, NP was detected in seven forebays (site # 9, 11, 12, 14, 19, 22 and 28) but only in four of the corresponding filters materials (site # 11, 12, 19 and 28). For the PAHs, phthalates and NP, the concentrations were statistically higher (Kruskal-Wallis, $p<0.05$) in the forebay than in the other sampled surface locations (location 1, 2 and 3), and for PCBs, a similar trend of higher concentrations in the forebay were observed (Figure 3). Two phthalates (di-*n*-pentylphthalate (DNPP) (site #11) and diisodecyl phthalate (DIDP) (site #22)) were detected in only one sample each and only in the forebay. At three sites, NP (tech. mixture) was only detected in the forebay (site #9, 14 and 22) and OP was detected in two samples, one in the forebay (site #22) and one in the top layer (Site #5).

For the PAHs and PCBs, molecules with higher molecular weights were more abundant than those with lower molecular weights. Among the PAHs, PAH-H and PAH-M had higher concentrations than PAH-L.

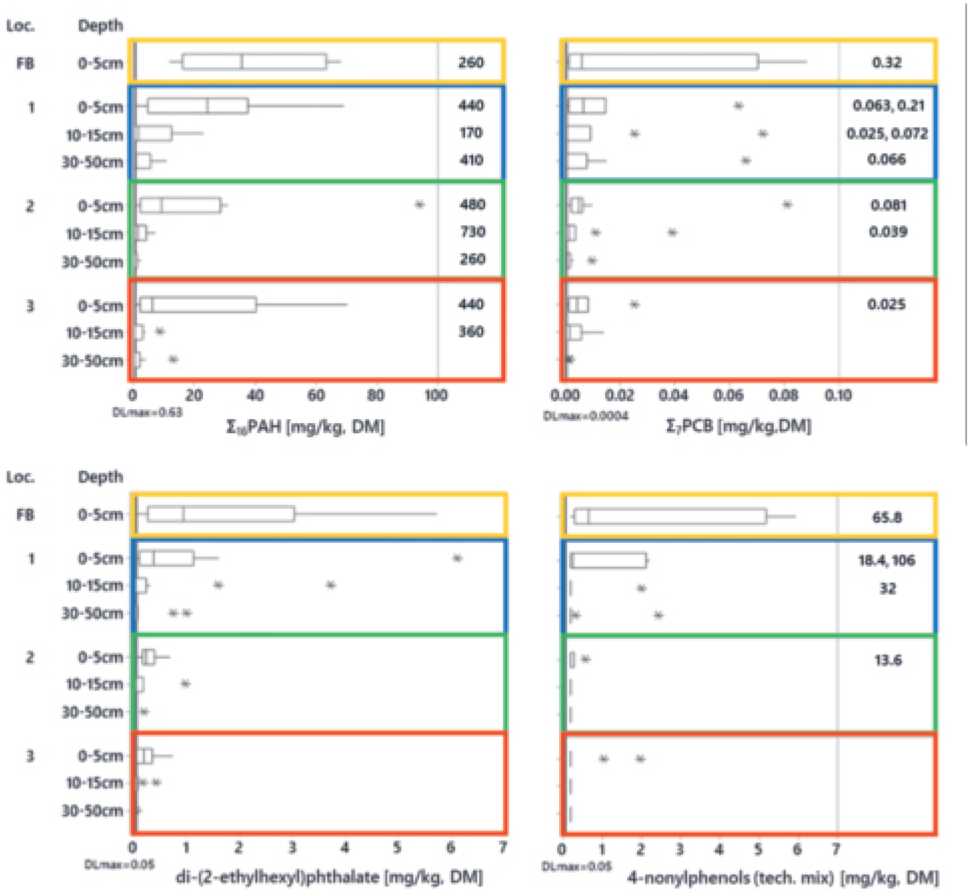

Figure 5. Boxplots of concentrations Σ_{16}PAH, Σ_7PCB, di-2-ethylhexyl phthalate and 4-nonylphenols (tech. mix) in the forebay (FB) and at three filter locations (Loc. 1, 2 and 3) and three depths (0-5 cm, 10-15 cm and 30-50 cm). Each location is marked with coloured rectangles according to depth corresponding to those in Figure 3.

From the boxplots in Figure 5, it can be seen that the pollutant concentrations of PAHs, PCBs and phthalates was highest in the surface layers but also detected in the deeper layers, albeit less frequently and at lower concentrations. For alkylphenols, detected concentrations were mainly found in the top layer close to the inlet and forebay. Concentrations also decreased significantly with depth between depth 1 (0–5 cm) and the deeper depths (depth 2 (10–15 cm) and depth 3 (35–50 cm)) for the three studied groups of OMPs (PAHs, PCBs, phthalates) and the more frequently detected NP (tech. mix). A trend of decreasing concentrations with increasing distance from the inlet was observed for all four groups of pollutants. However, no significant difference was detected. Another trend observed for all four organic micropollutants was the large variation in concentrations within and between different sites, particularly in the forebay but also for PAHs in all surface layers.

4.2 Metals

All metals except for Cd (i.e. Cr, Cu, Ni, Pb and Zn) were found in all 269 analysed samples (Table 4). Cd was detected in 245 of 269 analysed samples. 21 of the 24 non-detectable samples were from the four sites with the lowest concentrations (site # 13, 14, 15 and 27). s

The concentration ranges observed in this study were generally lower for Cr, Cu, Ni, Pb and Zn compared to other similar studies, whereas comparable or slightly higher concentrations were observed for Cd (Al-Ameri et al., 2018; Rommel et al., 2021). However, the concentrations in the present study varied greatly between different facilities. Deeper layers of the filter material had similar levels to soil background concentrations (England, USA and median global average) (Alloway, 2013b). A trend of decreasing concentration with increasing depth was observed for Cd, Cr, Cu, Pb and Zn but not Ni. This trend was statistically significant (Kruskall-Wallis, $p<0.05$; Figure 6) for Cr, Cu, Pb and Zn, whereas the trend for Cd was only observed in boxplots. However, looking at each site separately revealed that all metals, including Cd and Ni, at most sites showed a similar trend of concentrations decreasing with depth. Also, a trend of decreasing concentration with increasing distance from the inlet was observed for Cr and Zn, mainly in the top layer of the filters. A similar tendency was observed for Cu and Pb, but the difference was not statistically significant (Kruskal-Wallis, $p=0.05$).

Cr, Cu and Zn showed slightly higher concentrations in the forebays (at 20 of the 29 sites, Table 2) than the filter material (Figure 6). In contrast, Ni did not show any difference in concentration and Cd and Pb showed lower concentrations in the forebay than in the rest of the filter. However, these trends were not statistically significant (Kruskall-Wallis, $p<0.05$).

Table 4. Metal total concentrations, concentrations measured after five steps of fractionation (mg/kg, DM) and occurrence rates (%). * Indicates that for Cd, Cr and Ni, one sample had a higher detection limit from the analysis (double value) than the other detection limits. Values of total concentration are from the external accredited laboratory analysis of total concentration.

Metal	Fraction	Median	Min	Max	Max DL	Occurance >DL
			[mg/kg,DM]			
Cd	total	0.35	0.10	1.58	0.10	91%
	1	0.20	0.06	0.42	-	100%
	2	-	-	-	0.3*	0%
	3	0.05	0.01	0.10	-	100%
	4	0.05	0.02	0.10	-	100%
	5	0.02	0.01	0.06	-	100%
Cr	total	8.75	2.66	60.9	-	100%
	1	1.02	0.47	3.63	-	100%
	2	<3	<3	3.19	3*	3%
	3	0.41	0.16	4.53	-	100%
	4	5.27	1.84	27.1	-	100%
	5	6.40	1.44	26.8	-	100%
Cu	total	20.7	4.89	93.6	-	100%
	1	1.26	0.19	5.81	-	100%
	2	<8.65	<6	32.8	6	66%
	3	0.42	0.03	9.33	-	100%
	4	13.3	5.22	87.6	-	100%
	5	4.95	2.21	100	-	100%
Ni	total	14.8	3.67	64.0	-	100%
	1	1.37	0.33	3.90	-	100%
	2	<3	<3	4.99	3*	7%
	3	1.25	0.08	6.78	-	100%
	4	6.97	3.35	25.8	-	100%
	5	4.28	1.27	31.4	-	100%
Pb	total	16.00	2.89	122	-	100%
	1	3.51	0.59	22.5	-	100%
	2	<2.50	<1	29.0	1	76%
	3	4.57	0.32	33.8	-	100%
	4	9.24	2.06	36.4	-	100%
	5	1.16	0.32	3.40	-	100%
Zn	total	84.6	16.9	813	-	100%
	1	53.9	4.48	304	-	100%
	2	<13.8	<11	78.6	11	66%
	3	33.6	2.63	330	-	100%
	4	55.9	13.0	214	-	100%
	5	14.5	3.69	26.1	-	100%

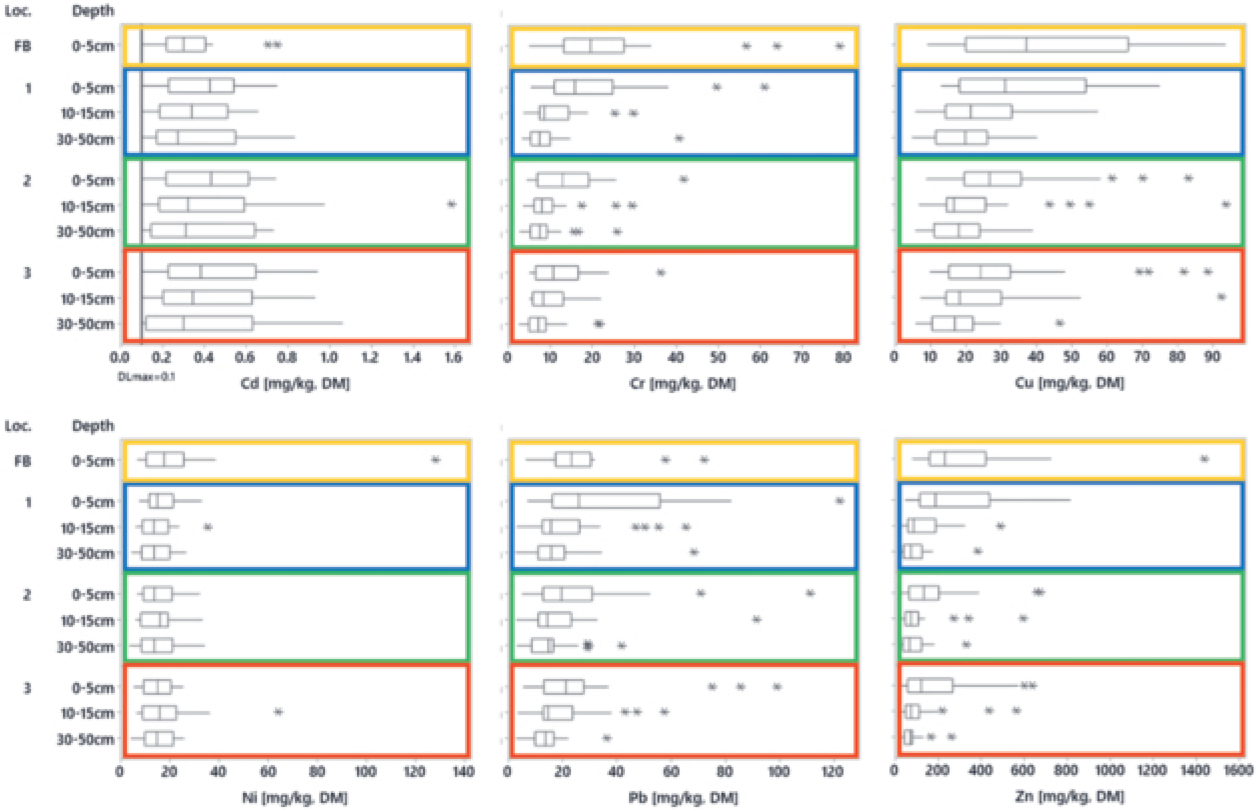

Figure 6. Boxplots of total concentration of Cd, Cr, Cu, Ni, Pb and Zn at three different depths and three locations. Sequential extraction analysis was performed on samples at location 1 (close to the inlet) at the first depth (0-5 cm) marked in grey in the boxplot. Data for Cd with an occurrence of 90% are censored to DLmax=0.1 mg/kg, DM. Each location is marked with a coloured rectangle corresponding to those in Figure 3.

4.2.1 Fractionation

To study the selected metals (Cd, Cr, Cu, Ni, Pb, Zn) potential ability to leach a fractionation of the metals was performed. The method used for the fractionation was a five-step sequential extraction on samples collected closest to the inlets in the top layer (Figure 3, location 1, depth 1), i.e., samples with (in most cases) the highest metal concentrations. The results showed that all studied metals were present in all five fractions and that all analysed metals (Cd, Cr, Cu, Ni, Pb, Zn) were available in potentially mobile forms in the filter material to varying degrees, with Cd being the most mobile metal and Cr the least. The content of all the metals was highest in fraction 4 and lowest in fraction 2. In fraction 2, for all the metals, several of the total 29 analysed samples were below the detection limit ($Cd_{<DL}$ = 29, $Cr_{<DL}$ = 28, $Cu_{<DL}$ = 10, $Ni_{<DL}$ = 27, $Pb_{<DL}$ = 7 and $Zn_{<DL}$ = 10, Table 5 and Figure 7). The reason for non-detects in fraction 2 could either be low concentrations in the samples and/or combination of the level of detection limits in the method. For all metals, most of the detected mass was in the first four fractions (Table 4 and Figure 7). Cr was the only metal in the study that had the highest content in fraction 5. For Cu, Ni and Pb, the highest content was found in fraction 4 (Table 4 and Figure 7). When comparing the fractionation results between the 29 sampling sites, large variations were observed between the various sites. However, the distribution between the fractions was rather uniform for each metal (Cd, Cr, Cu, Ni, Pb and Zn). Thus, the main trend was the variation in mobility between the different metals, e.g., Cd high in fraction 1 and Cr mainly in fraction 4 and 5.

Table 5. Distribution between fractions as a percentage of detected metal content calculated from median concentrations with detection limits reported by the external accredited laboratory.

	Cd	Cr	Cu	Ni	Pb	Zn
Fraction 1	63%	7%	4%	9%	20%	36%
Fraction 2	0%	1%	22%	2%	14%	10%
Fraction 3	14%	5%	4%	10%	23%	22%
Fraction 4	16%	38%	48%	47%	39%	26%
Fraction 5	7%	48%	22%	32%	4%	6%

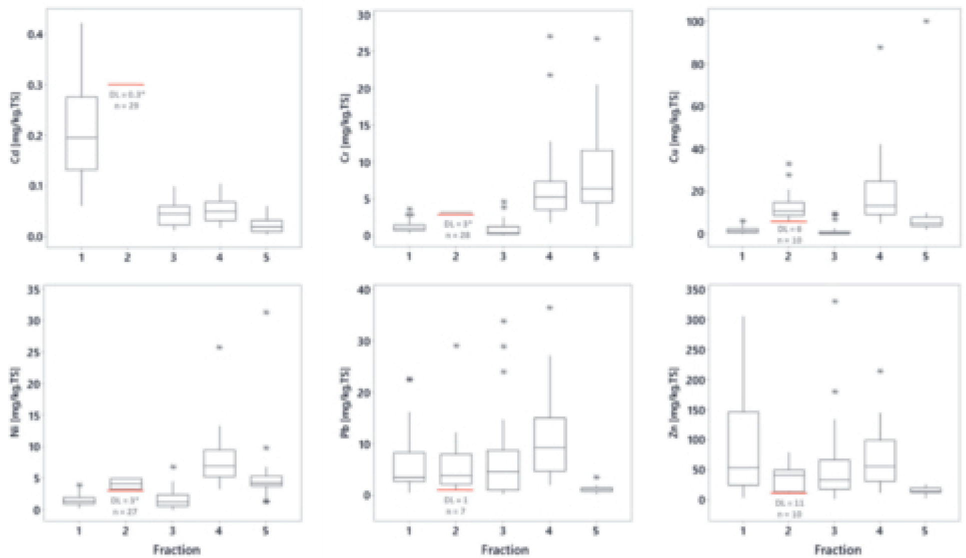

Figure 7. Boxplots of median concentration for metals in five different fractions. For all metals, the detection limit (DL) is indicated in fraction 2 and marked with a horizontal line. "n" indicates the number of values below DL out of a total of 29 samples. * Indicates that for Cd, Cr and Ni, one sample in the analysis had a higher DL (double value) than the other DLs (i.e., Cd_{DL}=0.3 for 28 samples and Cd_{DL}=0.6 for one sample, Cr_{DL}=3 for 27 samples and Cr_{DL}=6 for 1 sample, Ni_{DL}=3 for 26 samples and Ni_{DL}=6 for 1 sample).

Cd was mainly present in fraction 1 but also in fraction 3, 4 and 5 (Table 4). Of all the analysed metals, Cd had the highest proportion in fraction 1 and a high sum of content from fraction 1 to fraction 4 ($Cu_{\Sigma F1\text{-}F4}$=93 %) but a rather low proportion in fraction 5 (Table 4). For Cd, all 29 samples in fraction 2 were below DL.

Cr was found mainly in fraction 5 (48%) and fraction 4 (38%). Cr was to a less extent present in fraction 1 and 3 and rarely detected in fraction 2 (Cr_{F1} = 7%, Cr_{F2} = 1%, Cr_{F3} = 5%, Cr_{F4} = 38%, Cr_{F5} = 48%). In fraction 2, Cr was detected in only one sample out of 29 (DL_{Cd}=3 mg/kg and 6 mg/kg in one sample). Cr had the highest percentage metal content in fraction 5 of all the metals analysed and the lowest sum of content in fraction 1 to 4 ($Cr_{\Sigma F1\text{-}F4}$ = 52%).

Cu had the highest detected metal content in fraction 4 and fraction 2 but also some content in fraction 5 ($Cu_{\Sigma(2+4+5)}$ = 92%), while concentrations in fraction 1 and fraction 3 were rather low. The distribution of Cu between the different fractions was as follows: Cu_{F1} = 4%, Cu_{F2} = 22%, Cu_{F3} = 4%, Cu_{F4} = 48%, Cu_{F5} = 22%. In fraction 2, Cu was detected in 19 of the 29 analysed samples above DL (DL=6 mg/kg, 5 mg/kg for two samples). The total sum of Cu content in fraction 1 to fraction 4 ($Cu_{\Sigma 1\text{-}4}$) was 78%, and the sum of fraction 2 and fraction 4 was 70 % ($Cu_{\Sigma F2+F4}$=70%).

Ni was found with the highest concentration in fraction 4 and a high concentration in fraction 5. Less was detected in fraction 1, 2 and 3. In fraction 2, Ni was only detected in 2 of the 29 samples (3.28 and 4.99 mg/kg with DL_{Ni} = 3 mg/kg for all samples but one with DL_{Ni}=6 mg/kg). The distribution in Ni content between the different fractions was as follows: Ni_{F1} = 9%, Ni_{F2} = 2%, Ni_{F3} = 10%, Ni_{F4} = 47%, Ni_{F5} = 32%. After Cr, Ni had the highest content in fraction 5 and the least sum of fraction 1 to fraction 4 ($Ni_{\Sigma(F1-F4)}$ = 68%).

Pb had a high content in fraction 1, 3 and 4, a lower content in fraction 2 and only a small content in fraction 5. Among all the metals, Pb had the highest sum of content from fraction 1 to fraction 4 ($Pb_{\Sigma(1-4)}$ = 96%) and the least content in fraction 5.

Zn had a relatively even spread in metal content, mainly between fraction 1 and 4, with the highest content in fraction 4 and the least content if fraction 5. The Zn distribution between the different fractions was as follows: Zn_{F1} = 31%, Zn_{F2} = 8%, Zn_{F3} = 20%, Zn_{F4} = 33%, Zn_{F5} = 8%. Zn had the second highest (after Pb) sum of content in fraction 1 to fraction 4 ($Zn_{\Sigma(1-4)}$ = 94%) and the second highest (after Cd) content in fraction 1 (36%).

4.3 pH, TOC

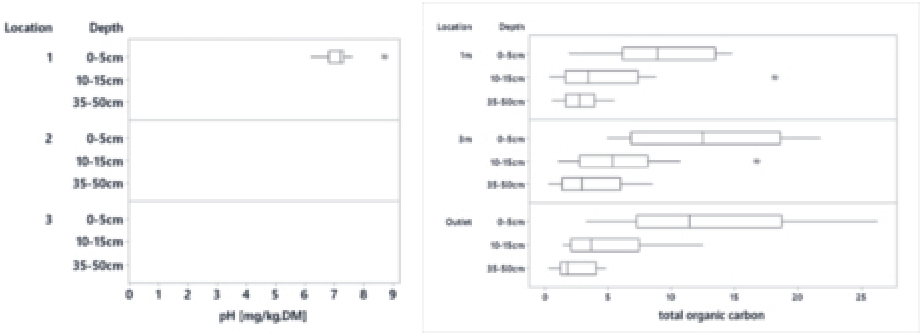

Figure 8. Left: boxplot of pH and depth. Samples were analysed from the top layer close to the inlet. Right: boxplot of total organic carbon (TOC) from 12 of the total 29 sites (site 1, 5, 6, 9, 11, 12, 14, 18, 19, 22, 23 and 28) according to depth and location.

The mean values of TOC obtained in this study corresponded to typical USA geometric mean values for texture classes sandy (6.0 mg/kg), coarse loamy (10.3-10.8 mg/kg) and coarse silty (18.1 mg/kg) (Alloway, 2013a, Table 13.2). The top layer had a significantly higher (Kruskall-Wallis, $p<0.01$) TOC than the deeper layers. pH was measured at location 1 and depth 1 and had a median value of pH 7.2 and range 6.2 to 8.7.

4.4 Principal component analysis

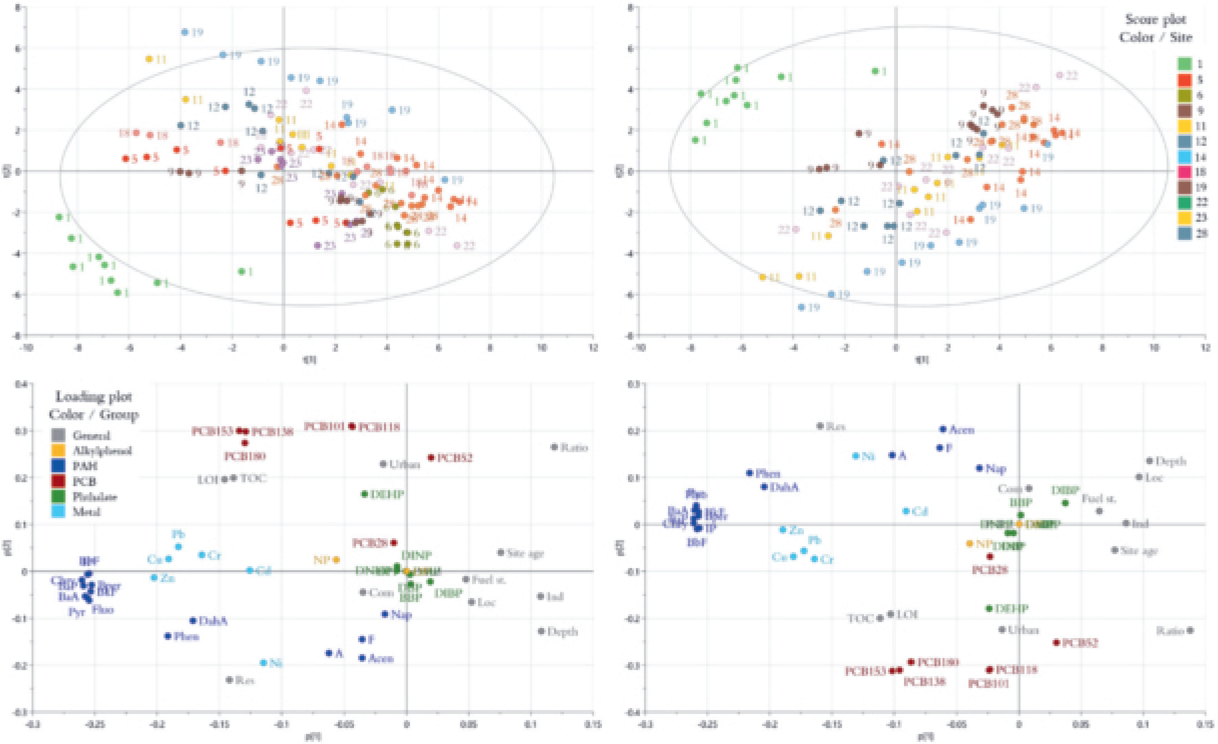

Figure 9. PCA of OMPs and metals at 12 sites without a forebay (left plots) and 8 sites with a forebay (right plots). Score plots (upper) and loading plots (lower) for principal components 1 and 2. The score plot is coloured according to the site number and the loading plot according to pollutant group (alkylphenols, PAHs, PCBs, phthalates and metals), general parameters (depth, location (Loc), loss on ignition (LOI), total organic carbon (TOC)), age, ratio (filter area/catchment area) and land use parameters (commercial (Com), industrial (Ind), downtown urban (Urban) and fuel stations (FS)). The ellipse in the score plots denotes Hotelling's T2 for 95%.

To obtain an overview of potential relations between metals, OMPs and other analysed parameters, a PCA model (principal component analysis) was constructed with data from the 12 sites (#1, 5, 6, 9, 11, 12, 14, 18, 19, 22, 23, and 28) with analyses of both metals and organic pollutants. The PCA model was a three-component model with R^2Xcum = 0.664 (cumulative X-variation modelled after all three components) and Q2(cum) = 0.569 (cumulative overall cross-validated R^2X). The variation for each component was $R^2X(p1) = 0.382$, $R^2X(p2) = 0.173$ and $R^2X(p3) = 0.11$. The model was UV scaled and log transformed (auto transformed on all skewed variables). The PCA showed similar correlations for the 8 sites with a forebay as for the 12 sites without a forebay.

The main trends identified in the score plot are as follows. The observations were clustered in groups site by site, and most sites were stretched out with a slight angle along the t[2] axis from lower left to upper right. Site 1 was mainly grouped outside Hotelling's T2 (95%) as outliers with high significance and just slightly stretched out. Sites #5, 9, 11, 12, 14, 18, 19 and 22 were clearly stretched out, while sites 1 and 23 were slightly stretched out and sites 6 and 28 more clustered. This trend of stretched out observations in the score plot corresponded to trends between the area ratio (between catchment area size and filter area) and land use but also between depth and concentration in the loading plot. The latter trend indicated a large variation in concentration between sites as well as within the sites. In the loading plot, the main trend was that concentrations of PAHs, metals, PCBs, NP, DEHP and the general parameters TOC and LOI were located towards the left. A negative correlation was observed between them and the general land use parameters depth, ratio, industrial, location and site age as the latter were located on the opposite side of the plot. The catchment characteristic variables (commercial, fuel station, industrial, residential, and urban land use) were spread around the origin in the loading plot. Data for residential, urban, and industrial land use were located far from each other and the origin, indicating a high impact in the model, whereas those for fuel station and commercial land use were located closer to the origin.

The PAHs with the highest molecular weights were located further to the left, and therefore had a stronger negative correlation to the parameters to the right (depth, ratio, industrial, location, site age and fuel stations), whereas PAHs with lower molecular weights were located closer to the origin in the first component (p[1]). A similar trend was also observed for PCBs, with PCB 153, PCB180 and PCB138 located far to the left, PCB101 and PCB118 also to the left and PCB28 and PCB52 located closer to the origin in p[1]. TOC and LOI seemed to correlate to PCBs, phthalates and DEHP but also showed some correlation to the metals Cd, Cr, Cu Pb and Ni rather than the other pollutants in the loading plot.

Comparing the loading plot with the score plot, one can see that some sites were more correlated to certain pollutant groups, e.g., site #1 to PAHs, #11 and #19 to PCBs, and site #5 to metals. Another observation was that patterns where sites were stretched out in the score plot from lower left to upper right seemed to correspond to a diagonal from left to right in the loading plot with a relation between depth and concentrations, especially for the OMPs. The other diagonal from upper left to lower right, where sites #1, 5, 18, 11 and 19 grouped, seemed to correspond with the negative correlation between area ratio and residential land use, especially for the PAH group and site #1. For example, a low ratio between filter area and catchment area, i.e., large catchment area compared to filter area at sites #1, 2 and 3 (Table 2) correlated to higher concentrations of PAHs. Urban/downtown areas seemed to correlate to PCBs. Otherwise, there was no clear correlation between usage and concentration. All pollutants with high occurrence rates showed a strong negative correlation between ratio and depth but also location and age.

5 Discussion

Occurrence, concentration, and accumulation of OMPs and metals in bioretention filter materials are the result of numerous processes, material properties, filter characteristics and local conditions. Some of these processes are dependent on the pollutant substance properties, such as hydrophobicity, solubility, biodegradation, and volatilization, which can affect the accumulation over time. Geographical and seasonal conditions, such as temperature, precipitation patterns (wet and dry periods), pollutant load and emissions from catchment areas, global and local sources, may also have an impact, as can filter design, filter material, maintenance, road maintenance with de-icing salts and local hydrology.

5.1 Occurrence and concentration

OMPs were frequently detected in the analysis. PAHs and PCBs showed a higher occurrence than alkylphenols and phthalates, while metals showed an overall high occurrence. The different occurrence of metals and OMPs may partly be explained by the fact that the metals are naturally occurring, and therefore more widely spread, whereas OMPs originate mainly from anthropogenic sources, and may therefore be more localised. The concentrations observed in the filter materials were slightly lower for Cr, Cu, Ni, Pb and Zn than in some other similar studies (Al-Ameri et al., 2018; Rommel et al., 2021) but comparable or higher for Cd. Comparing the metal concentrations to soil background concentrations, e.g. in England and USA, the levels in the deeper layers of the filter materials were within normal background concentrations (Alloway, 2013c). OMP concentrations had similar ranges as in previous studies. However, extremely high PAH concentrations (DiBlasi et al., 2009; Tedoldi et al., 2017) were detected at one particular site (site #1).

Large differences were observed in the concentrations and occurrence between various sites for both metals and OMPs. However, this trend was not as clear for metals as for OMPs. This large variation in concentrations may be explained by variation in the catchment characteristics, such as the ratio between catchment area to filter area and different land use, which may contribute different pollutant types and loads (Cao et al., 2019; Crane, 2019) and local hydrology. The PCA demonstrated that the observations from different sites were grouped together and often correlated to a certain group of pollutants (Figure 9). For example, according to the PCA, the highest concentrations of PCBs were in urban areas with downtown/city centre areas characterised by high population density and traffic, whereas lower concentrations were found in less densely populated suburban residential areas with more green space. Therefore, differences in sources may play an important role, especially for the OMPs, since these pollutants are mainly anthropogenic. This was supported by the fact that nonylphenol was more frequently detected and at higher concentrations than octylphenol, which may be because nonylphenol ethoxylates have a greater industrial use than octylphenol ethoxylates (Bergé et al., 2012). Regarding the correlation between phthalates (OP and NP) in stormwater sediments and industrial use, previous studies have shown that concentrations may be lower in USA than in Europe (Crane, 2019; Flanagan et al., 2021), which could reflect different legislation concerning the use of phthalates in industry.

5.1.1 Spatial distribution of pollutants in the filter material

One important observation, especially for OMPs (i.e., PAHs, PCBs and, when detected, phthalates and alkylphenols, e.g., DEHP and NP) was that occurrence frequencies and concentrations were higher in the top layers of the filters and decreased with increasing depth from the surface. A possible explanation for this is that, e.g. PAHs and PCBs, are often associated with suspended solids in stormwater, (LeFevre et al., 2015; Marsalek et al., 1997; Hwang and Foster, 2008) and have similar properties to other particle-bound pollutants. Therefore, they may be primarily removed in the surface layers through sedimentation and filtration of particles (Blecken et al., 2009a). Alkylphenols and phthalates exhibit more variable speciation in stormwater and are more mobile (Flanagan et al., 2018), and therefore occur in lower concentrations near the surface.

Metal concentrations also generally decreased with increasing depth in the bioretention material. This variation was significant (Kruskall-Wallis, $p<0.05$) for Cr, Cu, Pb and Zn, but was also observed for Cd and Ni at some sites. Similar results have been shown by previous studies (Blecken et al., 2009a; Li and Davis, 2008; Muthanna et al., 2007). An explanation for this could be that like OMPs, accumulated metals may be associated with particles, and therefore removed from stormwater by filtration through sediments, reducing the concentration with depth from the surface (Al-Ameri et al., 2018; Tedoldi et al., 2016).

Concentrations and occurrence frequencies also decreased with increasing distance from the inlet for OMPs, whereas for metals (PCA paper I and II), this trend was only seen for Cr and Zn, partly for Cu and to some extent for Pb but only in the top layer (see boxplots in Figure 6). Among the OMPs, this trend was most clear for PAHs and PCBs, and to a lesser extent for alkylphenols and phthalates. However, for the more occurring alkylphenols (NP) and phthalates (DEHP), this trend was highly correlated. Variation of occurrence and concentration with increasing distance from the inlet may be explained by the pollutants being mainly particle-bound coupled with long-term effects of filter hydrology. For example, the more frequently occurring smaller rainfall events could cause a higher pollutant load close to inlets, resulting in higher pollutant accumulation (Al-Ameri et al., 2018; Jones and Davis, 2013).

An explanation for the observed decrease of pollutant concentrations with depth could be that both OMPs and metals (as discussed in (Al-Ameri et al., 2018; Blecken et al., 2009a; Li and Davis, 2008; Muthanna et al., 2007; Tedoldi et al., 2016)) accumulate in the filter as particle-bound pollutants due to their ability to attach to other particles (e.g. suspended solids). However, in this study, this trend was more pronounced for OMPs than metals. This difference could be due to a lower pollutant load of metals, and thus lower concentrations levels closer to background concentrations. However, metals may occur either as dissolved or particle bound depending on environmental conditions, e.g., pH, concentration, organic matter, and the presence of other metals (Fe, Mn) and deicing salts and therefore less accumulated over time in the filter medium.

In the case of OMPs, pollutants with higher molecular weight (i.e., PAH-H and heavier PCBs) were better retained in the filter medium, and therefore occurred in higher concentration and were more frequently detected than substances with lower molecular weights (e.g., PAH-L and lower weight PCBs). This may be because heavy molecules are generally more hydrophobic than lighter molecules (PAHs), and therefor to a higher degree retained in the filter media but also less soluble, more strongly particle bound, less biodegradable and less volatile (Crane, 2014; David et al., 2015; Flanagan et al., 2018; MacKay, 2006). This explanation is supported by the findings of in Paper I, which showed the highest PAH concentrations for Fluo, Pyr, Phen (PAH-M), Chry and BbF (PAH-H), similar as in a previous study of soil accumulated PAHs in stormwater infiltration facilities (Tedoldi et al., 2017). Also, PCB concentrations in the bioretention filter medium showed a trend of decreased with decreased molecular weight with the order PCB 153 > PCB 138 > PCB 180 > PCB 118 ≈ PCB 101 > PCB 52 > PCB 28. For PCBs, however this may also be related to the degree of chlorination since the hydrophobicity of PCBs also increases with increasing chlorination. Thus, more chlorinated PCBs tend to be more effectively retained in bioretention facilities than less chlorinated PCBs (David et al., 2015). More highly chlorinated PCBs are also less biodegradable and less volatile (MacKay, 2006).

Phthalates and alkylphenols were less commonly found in the filter material, which may reflect their lower industrial use (Bergé et al., 2013). Another explanation could be that they are less effectively treated in bioretention facilities than, e.g. PAHs (Flanagan et al., 2018), but are more biodegradable compared to heavy PAHs and PCBs (Mackay, 2006), which may reduce filter accumulation over time. Biodegradation is considered to be one of the most important treatment processes for OMPs (Zhang et al., 2014). Since it predominantly occurs during long dry periods, it is likely to be a major fate process in long-term contaminant patterns.

PCA (Figure 9) confirmed the major trends observed for metals (Figure 5) and OMPs (Figure 6) but also indicated that the ratio between the catchment and filter areas had a strong correlation with concentration, especially for metals. These correlations are particularly clear in the PCA results presented in Paper I and II but are also evident in the PCA with both OMPs and metals in Figure 9. PCA also indicated correlations between PCBs and urban catchment areas, metals and commercial areas and a negative correlation between metals and industrial areas, but rather weak effect from other catchment areas. However, the impact of land use should not be over interpreted from the PCA, especially not for the OMPs, owing to the low number of examined sites (12 sites) compared to the number of land use categories (6, all treating mainly road runoff). Given the few sites for each land use type, variations within each land use group may have contributed to these trends as a result of other specific catchment area characteristics, e.g., the industrial areas that showed high impact on metal concentrations also had the highest catchment area ratios, which according to the PCA of metals has a higher impact than area use. The Kendall's-tau (τ) correlation test was used to study the variation in concentrations between detected OMPs. Stronger correlations were observed within each pollutant group (i.e., for PAH with PAH and PCB with PCB) than between groups. This finding corresponds well with the general observations from the PCA, where the OMP families were grouped together (Figure 9). When adding the metals as a group in the PCA, the metals also seemed to group together. However, this mainly applied to Cr, Cu, Pb and Zn, whereas the data for Cd and Ni were sometimes spread out, largely because they did not show any differences in concentration with depth and distance.

The concentrations in general seem to depend on a combination of pollutant sources, local pollutant load, hydrology accumulation processes and pollutant properties. The main similarities between OMP and metal concentrations was the variation with depth and distance, correlation with filter ratio and site-specific variations. The main difference between the OMP and metal concentrations was that the OMPs showed larger variations between sites, with depth and along the surface and in the forebay, whereas the metals were more evenly spread in the filter material and forebay. It seems like he higher the concentration, the more significant were the similarities or differences and the stronger the correlation.

5.1.2 Forebay

The distribution of OMPs in this study showed overall higher occurrence and concentrations in the forebay. In contrast, for metals, the concentrations were more similar in the forebay to those in the rest of the filter. However, variations in concentrations were detected between the various metals, e.g., were Cr, Cu and Zn had slightly higher concentrations in the forebay, Ni do not show any difference in concentration in the forebay compared to the rest of the filter, and Cd and Pb exhibited lower concentrations in the forebay.

Since the forebay samples were collected from the surface and close to the inlet, one would expect similar trends in forebay concentration and occurrence as in the top layer of the filter, such as generally higher than in deeper filter layers. However, when comparing concentrations in the forebay to those in the filter material, it is important to consider that the forebay samples mainly consisted of stormwater sediments, whereas the filter samples consisted of both of sediments and filter material. This could be one explanation for the higher concentrations of OMPs in the forebays. For metals this may also impact since metal are naturally occurring and widely spread why filter media also could be a source for metals while the anthropogenic OMPs rather are expected in the sediments. The similarities and variations in concentrations in the forebay samples between OMPs, metals as a group but also within each metal may also be due to different substance properties, such as the ability to attach to particles, hydrophobicity, and mobility, which for metals also could be related to their ability to dissolve.

5.2 Fractionation

When assessing risks of metal leaching (Cd, Cr, Cu, Ni, Pb and Zn) from bioretention technologies, it is important to consider not only the total concentration but also the metal mobility and bioavailability (Bacon and Davidson, 2008; Karlsson et al., 2016). Fractionation by sequential extraction is one way of assessing the metal leaching potential (Gleyzes et al., 2002; Stone and Marsalek, 1996; Tessier et al., 1979). One major observation from the sequential extraction was that the metal content was spread over all five fractions. This indicates that all examined metals (Cd, Cr, Cu, Ni, Pb and Zn) to some extent were mobile in the filter material, and therefore could pose a potential risk of leaching from the filter over time or from disposed filter material, which could have a negative environmental impact (Barbosa et al., 2012; Göbel et al., 2007). The fractionation results also indicated that the properties of the different metals affected the potential risk of leaching.

A high content in fraction 1 indicated that the metal was easily soluble and could potentially be leached or mobilized from the filter material during normal precipitation. Cd had the highest content in fraction 1, and hence was the most mobile and available metal in the study. Therefore, Cd in used filter material could pose a threat to sensitive recipients or environments.

A high concentration in fraction 5 indicated that the substance may be associated with stable organic forms, and therefore only potentially mobile and bioavailable under extreme conditions, e.g., when sulphides in contact with air, oxygen and or water dissolve to form sulphuric acid, which could result in the release of metals. Fraction 4 simulated the conditions where a substance is potentially mobile under anoxic conditions after a long time, conditions which reduce crystalline iron oxides, releasing metals bound to these phases. Cr had the highest content in both fraction 4 and 5 ($Cr_{\Sigma F4+F5}$ = 89 %), suggesting it was the most stable metal in the study, and therefore the least mobile and bioavailable. The conditions in fraction 5 are also unlikely to occur in bioretention (Søberg et al., 2019), meaning that Cr is likely to be stable rather than mobile in bioretention filter media.

Fraction 2 was associated with soil organic matter and resulted from extraction of metals bound in labile organic forms, such as humus and fulvic acids, which can potentially leach over time if organic matter in the filter breaks down. Such conditions are possible in bioretention, involving the breakdown of organic matter in the filter medium and top mulch layers or degradation of vegetation over time. This is reflected in the results from the sequential extraction of Cu, showing high content in fraction 2 (highest in the study, Cu_{F2} = 22%) and 4. Cu in soil has a high affinity for organic matter and often exists in complexed forms with soluble organics, such as humic materials, whose stability is pH dependent. Thus, Fe displaces Cu below pH=5.7 (Bradl, 2004) and Fe oxides have a strong influence on Cu mobility. In the present study, Cu was extracted from fraction 2 but also fraction 4. This could indicate that Cu may become mobile under anoxic conditions after a longer time, and therefore should be regarded as a potentially mobile metal in bioretention filter media and sediments but also potentially bioavailable. Both Cu and Cr had significantly higher concentrations in the top layer, which could be related to the higher content of organic matter in the top layers (Figure 6 and figure 8).

Ni was distributed within all 5 fractions, indicating potential for mobility and bioavailability in the studied filter medium. However, Ni seemed most stable after Cr since it had a low proportion in fractions 1, 3 and 5 and the highest proportion in fraction 4. Therefore, Ni may be potentially mobile under certain conditions. Ni, similarly to Cu, has a high affinity for organic matter in soil (Alloway, 2013d), and hence correlated with TOC (Figure 8).

Pb was primarily distributed between fractions 1 to 4, with the highest proportion in fraction 4 and the lowest proportion in fraction 5. Therefore, it may be mobile to some extent in most bioretention environments. The distribution of Pb may result from complex processes, e.g., specific adsorption to solid phases, precipitation to stable compounds and formation of complexes. Factors such as pH and the presence of carbonates (fraction 1) and organic matter (fraction 2) play a role in adsorption by affecting the ionic strength (Bradl, 2004). The Pb content in fractions 3 and 4 was most likely an effect of Pb adsorption to Fe- and Mn-oxides (Bradl, 2004).

Zn was present in fractions 1 to 4, with high content in fraction 1, which can partly be explained by Zn being adsorbed to carbonates in calcareous and alkaline soils. Zn surface charge increases with increasing pH. Therefore, Zn seems to have a high potential for mobility in filter media.

To sum up the discussion about fractionation and mobility of the studied metals, the order of the total content in fraction 1 from high to low was Cd>Zn>Pb>Ni>Cr>Cu and the total content in F1-F4 Pb>Zn>Cd>Cu>Ni>Cr. Thus, it was concluded that Cd, Pb and Zn were very mobile in the filter medium, and Cr, Cu and Ni were to some degree mobile. Cd was probably the most mobile metal analysed in the study, whereas Cr was the least.

5.3 Comparison of concentrations to soil quality guidelines

To further assess the risks of polluted filter material or sediments, we compared the results from the analysis of concentrations and fractionation to quality guidelines for contaminated soil. The concentrations of metals (Figure 10) and OMPs (Figure 11) were compared to the Swedish national guidance limits for classification of soil, "soil for sensitive land use" (abbreviated KM) and "soil for less sensitive land use" (abbreviated MKM), published by the Swedish Environmental Protection Agency (Swedish EPA, 2009). Among the metals, Zn seemed to be the most limiting metals in the sampled filter material. Zn occurred frequently above KM but also occasionally above MKM. Pb occurred frequently above KM but not above MKM. Previous studies have suggested Pb as one of the limiting metals for bioretention accumulation (Li and Davis, 2008). Cd and Cu also occurred above KM but less frequently than Zn and Pb. Ni only occurred with two outliers above KM, with one also above MKM. The least mobile metal according to the fractionation study was Cr, which was also the only metal not detected above the KM limit for total Cr (Cr_{III} and Cr_{VI}). However, compared to Cr_{VI} limits for KM and MKM, Cr would be considered one of the most limiting metals. The fractionation results indicated that the total concentration of Cr in the study mainly comprised the more stable Cr_{III} form rather than the more mobile Cr_{VI} since it predominantly occurred in fractions 4 and 5. This implies that before removing filter material from a site, depending on the local circumstances and legislation, further investigations may be needed of the soil and sediment quality.

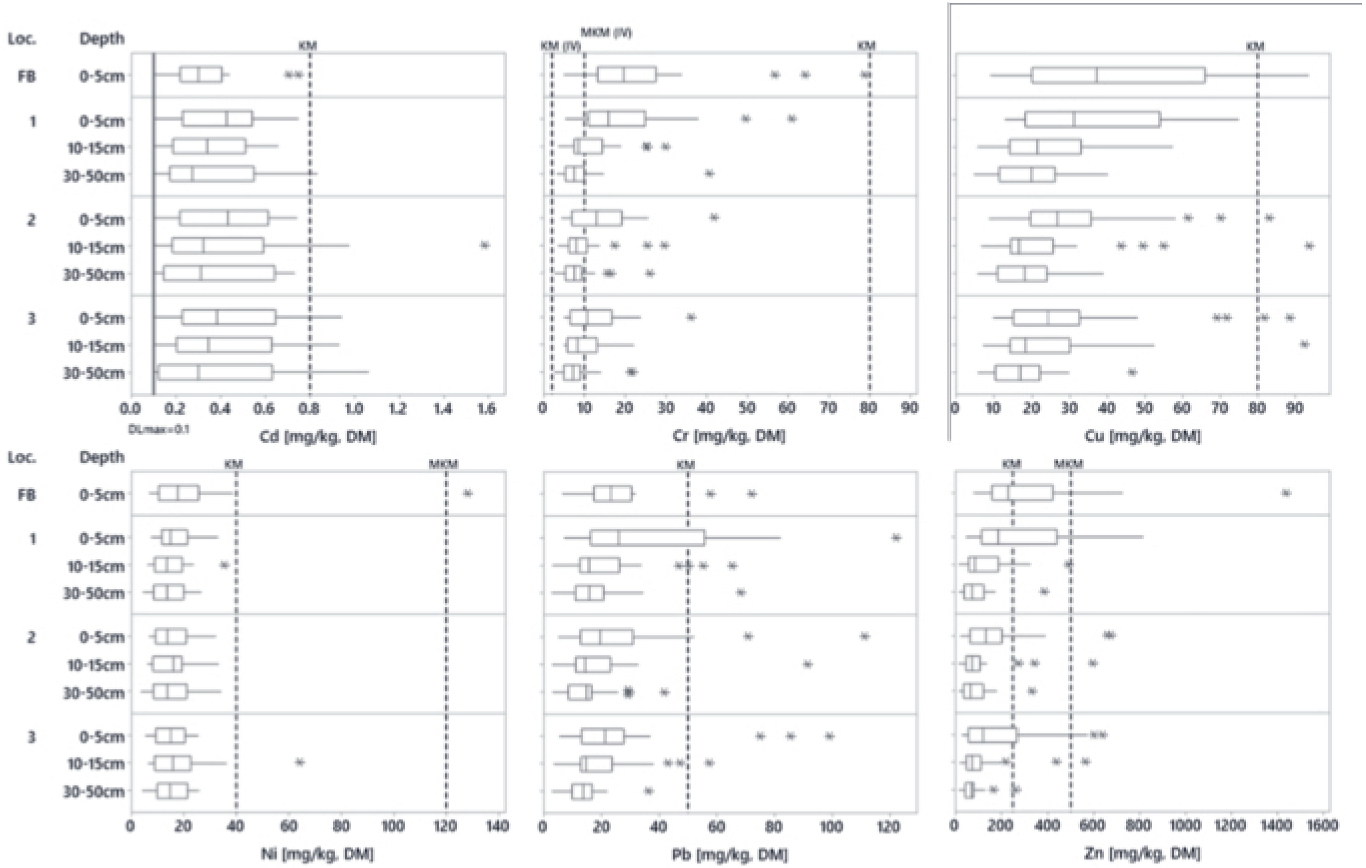

Figure 10. Boxplots of concentrations of Cd, Cr, Cu, Ni, Pb and Zn (mg/kg, DM) at different distances from the inlet (locations, Figure 3) and surface (depth, Figure 3) The concentrations are compared to Swedish guidelines for pollutant concentrations relating to soil classifications KM (soil for sensitive land use) and MKM (soil for less sensitive land use).

Among the OMPs PAH-H showed the greatest exceedance of the guidelines, frequently above both KM and MKM, followed by PAH-M and the sum of seven PCBs.

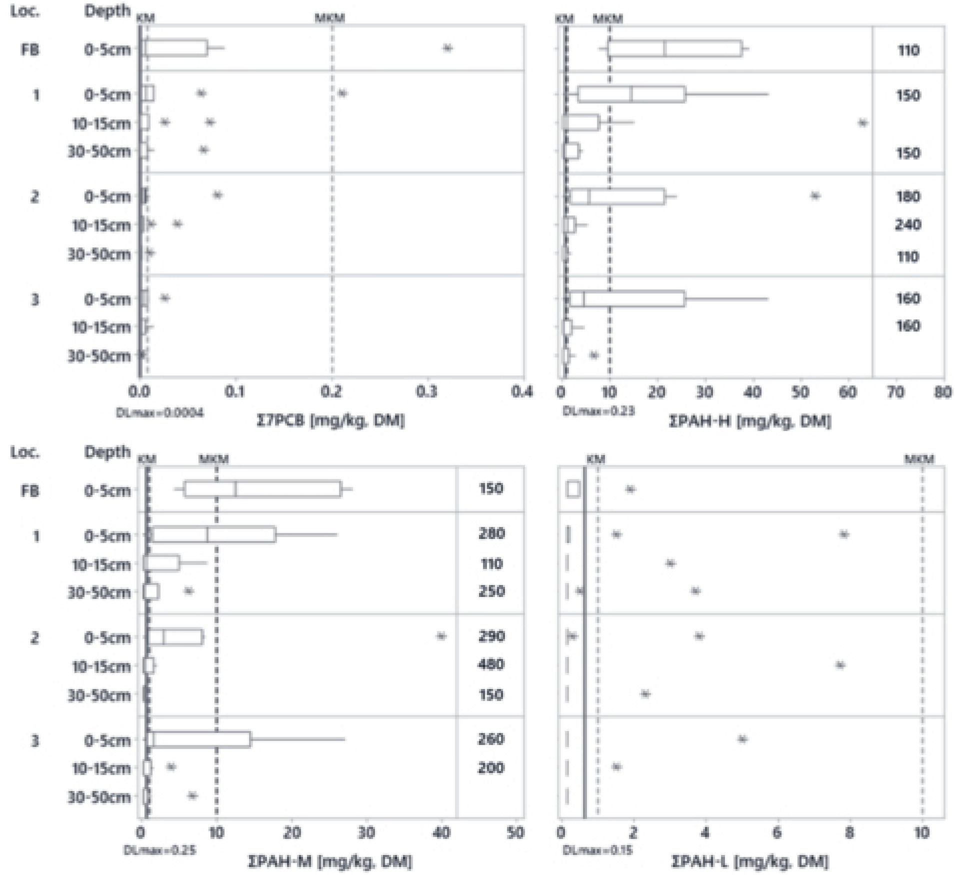

Figure 11. Boxplots of concentrations of Σ_7PCB, PAH-H, PAH-M and PAH-L (mg/kg, DM) for different distances from the inlet (locations, Figure 3) and surface (depth, Figure 3). In addition to those plotted as asterisks (*), outliers above 100 mg/kg, DM are indicated as text on the right for plotting purposes. The concentrations of PAH-H, PAH-M and PAH-L are compared to Swedish guidelines for pollutant concentrations relating to soil classifications KM (soil for sensitive land use) and MKM (soil for less sensitive land use).

Concentrations above the MKM level are classified as hazardous waste (FA) and require certified transportation and disposal at licensed landfill sites. For the OMPs, and in some cases metals, most concentrations above MKM were detected in the upper layer and close to the inlet.

5.4 Practical implications

These results could contribute towards improving the design and maintenance of bioretention facilities. Knowledge of pollutant accumulation in filter material and forebays is important for proper design that facilitates maintenance to preserve filter function during long-term treatment of stormwater but also to understand risks associated with used filter material and sediments. The highest concentrations of pollutants were generally found in the top 10 cm of the filters, especially for the anthropogenic OMPs. Compared to local guidelines (Swedish EPA, 2009), the most critical concentrations were found in the top layer of the filter material for both metals and OMPs and for OMPs in the forebay. The fractionation results showed that there was a risk of metal leaching over time from the filter material and sediments. Taken together, this knowledge is of great importance for bioretention operators because it implies that removing only the top layer of the filter medium periodically may be all that is needed to ensure that the entire filter medium does not saturate, with the risk of pollutant discharge.

This conclusion is in line with previous guidance for maintaining bioretention facilities considering metals and OMPs (e.g. Al-Ameri et al., 2018; Blecken et al., 2011; Tedoldi et al., 2017). Also, when removing filter material, e.g. during maintenance work, when filter media may need to be replaced due to clogging (Al-Ameri et al., 2018), or when retrofitting an area, it may be sensible to consider the filter material and sediments as possibly dangerous waste, especially material from close to the surface and inlets. However, to further optimize operation and maintenance, one should also consider the impact of a forebay. A forebay could, if regularly maintained, reduce the risk of clogging of the filter's surface and the pollutant load to the filter, which over time would keep concentrations at a lower level, especially the OMPs.

5.5 Further studies

Further work on the short- and long-term functioning and maintenance is required to better understand the accumulation and distribution of metals, OMPs (and other particle-bound and dissolved pollutants) in bioretention systems. The present study did not include biodegradation due to the lack of information on pollutant loads and uncertainties associated with calculations of pollutant mass (Flanagan et al., 2019a). Measurement of stormwater quality and quantity in and out at sampled bioretention cells together with mass balance calculations in forebays and filter material could provide information on the amount of pollutants in forebays but also leaching and biodegradation processes. Previous studies have shown variations in emissions over time (Markiewicz et al., 2017). Therefore, continued sampling of filter material from previous sampled sites and targeted sampling campaigns over yearly cycles and longer period of time could enable a broader understanding of time perspectives. Studies including a broader age variation of new filters and those in operation for a longer period of time than in the present study could complement by providing information on pollutant accumulation trends expected over a bioretention system's lifetime. Owing to different national/regional regulations, use of building materials, etc., further studies should also include samples from other countries to evaluate the geographic variability of these pollutants as well as geographical ambient variations, e.g., in temperature, humidity and precipitation hydrographs. Results from field studies are always to some extent site-specific but also restricted by the specific analysis and methods used. Therefore, studies from other geographic locations as well as other pollutants would contribute to a wider understanding of filter function. Since the nature of the filter medium affects the amount of dissolved species as well as particulate pollutant removal, further studies of different filter materials (e.g., by varying particle size distribution, composition, use of amendments) are also needed.

6 Conclusions

All metals (Cd, Cr, Cu, Ni, Pb, and Zn) and OMPs (16 PAHs, 7 PCBs, 13 phthalates, and 2 alkylphenols) analysed in this study were commonly detected in the filter materials of bioretention facilities in Michigan, Ohio, and Kentucky (USA) aged 7–16 years. All analysed metals were detected in all samples, except for Cd, which was detected in 91% of the 269 samples. For OMPs, 32 of 38 substances were detected in at least one filter material sample, while six substances (five phthalates and one PAH) were never detected. PAHs and PCBs were the most frequently detected OMPs, whereas phthalates and alkylphenols were detected the least. The bioretention sites showed large variations in the concentrations of OMPs, and metals to a lesser extent, most likely due to differences in pollutant sources. OMPs were found at the highest concentration in the upper 10 cm of the filter material and then decreased with increasing depth in the filter. For metals, a similar, but less clear trend was observed for Cr, Cu, Pb, and Zn. A trend of decreasing concentration with increasing distance from the inlet was observed for all four groups of OMPs (PAHs, PCBs, phthalates, and alkylphenols), but was less clear for the metals. Besides depth and distance from the inlet, the ratio of the catchment area to filter area also showed a strong correlation with concentration. Given the similarities in the pathways and accumulation between particle-bound OMPs and metals, the long-term performance and maintenance requirements may also be similar.

A metal fractionation in the top layer of bioretention filter material show that all studied metals (Cd, Cr, Cu, Ni, Pb, Zn) have a potential risk of leaching over time. The highest risk of leaching according to metal mobility was Cd, Zn, and Pb, potentially mobile already during precipitation, while Cr, Cu and Ni was more stable. Metals are also at a potential risk of leaching from filter material or sediments if removed from the bioretention sites why conditions at deposit are important.

Regular forebay maintenance and replacement of the top layer of the filter may be sufficient to ensure prolonged filter function and prevent pollutant accumulation and clogging. Safe disposal of contaminated filter material is important when removing material from a bioretention facility. Therefore, filter material should be regularly sampled and analysed for concentrations of OMPs and metals to enable better environmental assessment of the material.

7 References

2013/39/EU, 2013. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy Text with EEA relevance [WWW Document]. Document 32013L0039. URL http://data.europa.eu/eli/dir/2013/39/oj

Al-Ameri, M., Hatt, B., Le Coustumer, S., Fletcher, T., Payne, E., Deletic, A., 2018. Accumulation of heavy metals in stormwater bioretention media: A field study of temporal and spatial variation. Journal of Hydrology 567, 721–731. https://doi.org/10.1016/j.jhydrol.2018.03.027

Alloway, B.J. (Ed.), 2013a. Heavy Metals in Soils Trace Metals and Metalloids in Soils and their Bioavailability, Table 13.2 p. 371., 3rd ed, Environmental Pollution. Springer, Dordrecht, Department of Soil ScienceUniversity of ReadingReadingUnited Kingdom.

Alloway, B.J. (Ed.), 2013b. Heavy Metals in Soils Trace Metals and Metalloids in Soils and their Bioavailability, 3rd ed, Environmental Pollution. Springer, Dordrecht, Department of Soil ScienceUniversity of ReadingReadingUnited Kingdom.

Alloway, B.J. (Ed.), 2013c. Heavy Metals in Soils Trace Metals and Metalloids in Soils and their Bioavailability, Table 2.8 p. 38., 3rd ed, Environmental Pollution. Springer, Dordrecht, Department of Soil ScienceUniversity of ReadingReadingUnited Kingdom.

Alloway, B.J. (Ed.), 2013d. Heavy Metals in Soils Trace Metals and Metalloids in Soils and their Bioavailability, p. 319., 3rd ed, Environmental Pollution. Springer, Dordrecht, Department of Soil ScienceUniversity of ReadingReadingUnited Kingdom.

ALS, 2018. Sequential extraction information sheet [WWW Document]. ALS Global. URL https://www.alsglobal.se/miljoanalys/laktester/sekventiella-lakningar (accessed 11.8.21).

ALS global, 2022. ALS Scandinavia [WWW Document]. ALS Global. URL https://www.alsglobal.se/ (accessed 11.8.21).

Andersson, M., Bogen, J., Ottesen, R.T., Bønsnes, T.E., 2015. Polychlorinated Biphenyls in Urban Lake Sediments and Migration Potential from Urban Stormwater in Bergen, Norway. J. Environ. Eng. 141, 04015028. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000957

Bacon, J.R., Davidson, C.M., 2008. Is there a future for sequential chemical extraction? Analyst 133, 25–46. https://doi.org/10.1039/B711896A

Barbosa, A.E., Fernandes, J.N., David, L.M., 2012. Key issues for sustainable urban stormwater management. Water Research 46, 6787–6798. https://doi.org/10.1016/j.watres.2012.05.029

Bergé, A., Cladière, M., Gasperi, J., Coursimault, A., Tassin, B., Moilleron, R., 2013. Meta-analysis of environmental contamination by phthalates. Environ Sci Pollut Res 20, 8057–8076. https://doi.org/10.1007/s11356-013-1982-5

Bergé, A., Cladière, M., Gasperi, J., Coursimault, A., Tassin, B., Moilleron, R., 2012. Meta-analysis of environmental contamination by alkylphenols. Environmental Science and Pollution Research 19, 3798–3819. https://doi.org/10.1007/s11356-012-1094-7

Björklund, K., Cousins, A.P., Strömvall, A.-M., Malmqvist, P.-A., 2009. Phthalates and nonylphenols in urban runoff: Occurrence, distribution and area emission factors. Science of The Total Environment 407, 4665–4672. https://doi.org/10.1016/j.scitotenv.2009.04.040

Blecken, G.-T., Hunt, W.F., Al-Rubaei, A.M., Viklander, M., Lord, W.G., 2017. Stormwater control measure (SCM) maintenance considerations to ensure designed functionality. Urban Water Journal 14, 278–290. https://doi.org/10.1080/1573062X.2015.1111913

Blecken, G.-T., Marsalek, J., Viklander, M., 2011. Laboratory Study of Stormwater Biofiltration in Low Temperatures: Total and Dissolved Metal Removals and Fates. Water Air Soil Pollut 219, 303–317. https://doi.org/10.1007/s11270-010-0708-2

Blecken, G.-T., Zinger, Y., Deletić, A., Fletcher, T.D., Viklander, M., 2009a. Influence of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters. Water Research 43, 4590–4598. https://doi.org/10.1016/j.watres.2009.07.008

Blecken, G.-T., Zinger, Y., Deletić, A., Fletcher, T.D., Viklander, M., 2009b. Impact of a submerged zone and a carbon source on heavy metal removal in stormwater biofilters. Ecological Engineering 35, 769–778. https://doi.org/10.1016/j.ecoleng.2008.12.009

Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soils constituents. Journal of Colloid and Interface Science 277, 1–18. https://doi.org/10.1016/j.jcis.2004.04.005

Brown, J.N., Peake, B.M., 2006. Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. Science of The Total Environment 359, 145–155. https://doi.org/10.1016/j.scitotenv.2005.05.016

BS ISO, 2010. BS ISO 9277:2010 Determination of the specific surface area of solids by gas adsorption. BET method [WWW Document]. URL https://www.en-standard.eu/bs-iso-9277-2010-determination-of-the-specific-surface-area-of-solids-by-gas-adsorption-bet-method/

Cao, S., Capozzi, S.L., Kjellerup, B.V., Davis, A.P., 2019. Polychlorinated biphenyls in stormwater sediments: Relationships with land use and particle characteristics. Water Research 163, 114865. https://doi.org/10.1016/j.watres.2019.114865

Clara, M., Windhofer, G., Hartl, W., Braun, K., Simon, M., Gans, O., Scheffknecht, C., Chovanec, A., 2010. Occurrence of phthalates in surface runoff, untreated and treated wastewater and fate during wastewater treatment. Chemosphere 78, 1078–1084. https://doi.org/10.1016/j.chemosphere.2009.12.052

Crane, J.L., 2019. Distribution, Toxic Potential, and Influence of Land Use on Conventional and Emerging Contaminants in Urban Stormwater Pond Sediments. Arch Environ Contam Toxicol 76, 265–294. https://doi.org/10.1007/s00244-019-00598-w

Crane, J.L., 2014. Source Apportionment and Distribution of Polycyclic Aromatic Hydrocarbons, Risk Considerations, and Management Implications for Urban Stormwater Pond Sediments in Minnesota, USA. Arch Environ Contam Toxicol 66, 176–200. https://doi.org/10.1007/s00244-013-9963-8

CSN, 2009. ČSN 72 0103 (720103) Základní postup rozboru silikátů - Stanovení ztráty žíháním (Basic procedure for the analysis of silicates - Determination of loss by annealing) [WWW Document]. URL https://www.technicke-normy-csn.cz/csn-72-0103-720103-218183.html

CSN, 1991. ČSN 46 5735 (465735) Průmyslové komposty (CSN 46 5735 (465735) Industrial composts) [WWW Document]. URL https://www.technicke-normy-csn.cz/csn-46-5735-465735-206692.html

CSN EN, 2018. ČSN EN 13137 (838021) Charakterizace odpadů - Stanovení celkového organického uhlíku (TOC) v odpadech, kalech a sedimentech (Waste characterisation - Determination of total organic carbon (TOC) in waste, sludge and sediment) [WWW Document]. URL https://www.technicke-normy-csn.cz/csn-en-13137-838021-231701.html

CSN EN, 2014. ČSN EN 12879 (758005) Sludge characterization - Determination of loss by annealing (Sludge characterization - Determination of loss by annealing) [WWW Document]. URL https://www.technicke-normy-csn.cz/csn-en-12879-758005-226751.html

CSN ISO, 1995. ISO 10694:1995 Soil quality — Determination of organic and total carbon after dry combustion (elementary analysis) [WWW Document]. URL https://www.iso.org/standard/18782.html

David, N., Leatherbarrow, J.E., Yee, D., McKee, L.J., 2015. Removal Efficiencies of a Bioretention System for Trace Metals, PCBs, PAHs, and Dioxins in a Semiarid Environment. J. Environ. Eng. 141, 04014092. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000921

Davis, A.P., Hunt, W.F., Traver, R.G., Clar, M., 2009. Bioretention Technology: Overview of Current Practice and Future Needs. J. Environ. Eng. 135, 109–117. https://doi.org/10.1061/(ASCE)0733-9372(2009)135:3(109)

Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., Winogradoff, D., 2003. Water Quality Improvement through Bioretention: Lead, Copper, and Zinc Removal. Water Environment Research 75, 73–82. https://doi.org/10.2175/106143003X140854

DiBlasi, C.J., Li, H., Davis, A.P., Ghosh, U., 2009. Removal and Fate of Polycyclic Aromatic Hydrocarbon Pollutants in an Urban Stormwater Bioretention Facility. Environ. Sci. Technol. 43, 494–502. https://doi.org/10.1021/es802090g

DIN ISO, 2002. Soil quality - Determination of organochlorine pesticides and polychlorinated biphenyls - Gas-chromatographic method with electron capture detection (ISO 10382:2002) [WWW Document]. URL https://www.iso.org/standard/32422.html

E DIN, 2014. DIN 19742:2014-08 Soil quality - Determination of selected phthalates in sludge, sediment, solid waste and soil after extraction and determination by mass spectrometric gas chromatography (GC-MS) [WWW Document]. URL https://www.beuth.de/de/norm/din-19742/207273179

Eriksson, E., Baun, A., Scholes, L., Ledin, A., Ahlman, S., Revitt, M., Noutsopoulos, C., Mikkelsen, P.S., 2007. Selected stormwater priority pollutants — a European perspective. Science of The Total Environment 383, 41–51. https://doi.org/10.1016/j.scitotenv.2007.05.028

Fassman-Beck, E., Wang, S., Simcock, R., Liu, R., 2015. Assessing the Effects of Bioretention's Engineered Media Composition and Compaction on Hydraulic Conductivity and Water Holding Capacity. J. Sustainable Water Built Environ. 1, 04015003. https://doi.org/10.1061/JSWBAY.0000799

Fent, K., 2003. Ecotoxicological problems associated with contaminated sites. Toxicology Letters 140–141, 353–365. https://doi.org/10.1016/S0378-4274(03)00032-8

Flanagan, K., Blecken, G.-T., Österlund, H., Nordqvist, K., Viklander, M., 2021. Contamination of Urban Stormwater Pond Sediments: A Study of 259 Legacy and Contemporary Organic Substances. Environ. Sci. Technol. 55, 3009–3020. https://doi.org/10.1021/acs.est.0c07782

Flanagan, K., Branchu, P., Boudahmane, L., Caupos, E., Demare, D., Deshayes, S., Dubois, P., Kajeiou, M., Meffray, L., Partibane, C., Saad, M., Vitart de Abreu Lima, M., Gromaire, M.-C., 2019a. Stochastic Method for Evaluating Removal, Fate and Associated Uncertainties of Micropollutants in a Stormwater Biofilter at an Annual Scale. Water 11, 487. https://doi.org/10.3390/w11030487

Flanagan, K., Branchu, P., Boudahmane, L., Caupos, E., Demare, D., Deshayes, S., Dubois, P., Meffray, L., Partibane, C., Saad, M., Gromaire, M.-C., 2019b. Retention and transport processes of particulate and dissolved micropollutants in stormwater biofilters treating road runoff. Science of The Total Environment 656, 1178–1190. https://doi.org/10.1016/j.scitotenv.2018.11.304

Flanagan, K., Branchu, P., Boudahmane, L., Caupos, E., Demare, D., Deshayes, S., Dubois, P., Meffray, L., Partibane, C., Saad, M., Gromaire, M.-C., 2018. Field performance of two biofiltration systems treating micropollutants from road runoff. Water Research 145, 562–578. https://doi.org/10.1016/j.watres.2018.08.064

Fletcher, T.D., Shuster, W., Hunt, W.F., Ashley, R., Butler, D., Arthur, S., Trowsdale, S., Barraud, S., Semadeni-Davies, A., Bertrand-Krajewski, J.-L., Mikkelsen, P.S., Rivard, G., Uhl, M., Dagenais, D., Viklander, M., 2015. SUDS, LID, BMPs, WSUD and more – The evolution and application of terminology surrounding urban drainage. Urban Water Journal 12, 525–542. https://doi.org/10.1080/1573062X.2014.916314

Gasperi, J., Sebastian, C., Ruban, V., Delamain, M., Percot, S., Wiest, L., Mirande, C., Caupos, E., Demare, D., Kessoo, M.D.K., Saad, M., Schwartz, J.J., Dubois, P., Fratta, C., Wolff, H., Moilleron, R., Chebbo, G., Cren, C., Millet, M., Barraud, S., Gromaire, M.C., 2014. Micropollutants in urban stormwater: occurrence, concentrations, and atmospheric contributions for a wide range of contaminants in three French catchments. Environ Sci Pollut Res 21, 5267–5281. https://doi.org/10.1007/s11356-013-2396-0

Gavric, S., 2020. Enhancement of stormwater quality in grass swales: removal and immobilisation of metals.

Gilbreath, A., McKee, L., Shimabuku, I., Lin, D., Werbowski, L.M., Zhu, X., Grbic, J., Rochman, C., 2019. Multiyear Water Quality Performance and Mass Accumulation of PCBs, Mercury, Methylmercury, Copper, and Microplastics in a Bioretention Rain Garden. J. Sustainable Water Built Environ. 5, 04019004. https://doi.org/10.1061/JSWBAY.0000883

Gleyzes, C., Tellier, S., Astruc, M., 2002. Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. TrAC Trends in Analytical Chemistry 21, 451–467. https://doi.org/10.1016/S0165-9936(02)00603-9

Göbel, P., Dierkes, C., Coldewey, W.G., 2007. Storm water runoff concentration matrix for urban areas. Journal of Contaminant Hydrology 91, 26–42. https://doi.org/10.1016/j.jconhyd.2006.08.008

Hall, G.E.M., Vaive, J.E., Beer, R., Hoashi, M., 1996a. Selective leaches revisited, with emphasis on the amorphous Fe oxyhydroxide phase extraction. Journal of Geochemical Exploration 56, 59–78. https://doi.org/10.1016/0375-6742(95)00050-X

Hall, G.E.M., Vaive, J.E., MacLaurin, A.I., 1996b. Analytical aspects of the application of sodium pyrophosphate reagent in the specific extraction of the labile organic component of humus and soils. Journal of Geochemical Exploration 56, 23–36. https://doi.org/10.1016/0375-6742(95)00046-1

Hatt, B.E., Fletcher, T.D., Deletic, A., 2008. Hydraulic and Pollutant Removal Performance of Fine Media Stormwater Filtration Systems. Environ. Sci. Technol. 42, 2535–2541. https://doi.org/10.1021/es071264p

Hatt, B.E., Steinel, A., Deletic, A., Fletcher, T.D., 2011. Retention of heavy metals by stormwater filtration systems: breakthrough analysis. Water Science and Technology 64, 1913–1919. https://doi.org/10.2166/wst.2011.188

Helsel, D.R., 2012. Statistics for censored environmental data using Minitab and R, 2nd ed. ed, Wiley series in statistics in practice. Wiley, Hoboken, N.J.

Hsieh, C.-H., Davis, A.P., 2005. Multiple-event study of bioretention for treatment of urban storm water runoff. Water Science and Technology 51, 177–181. https://doi.org/10.2166/wst.2005.0589

Huber, M., Welker, A., Helmreich, B., 2016. Critical review of heavy metal pollution of traffic area runoff: Occurrence, influencing factors, and partitioning. Science of The Total Environment 541, 895–919. https://doi.org/10.1016/j.scitotenv.2015.09.033

Hunt, W.F., Davis, A.P., Traver, R.G., 2012. Meeting Hydrologic and Water Quality Goals through Targeted Bioretention Design. J. Environ. Eng. 138, 698–707. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000504

Hwang, H.-M., Foster, G.D., 2008. Polychlorinated biphenyls in stormwater runoff entering the tidal Anacostia River, Washington, DC, through small urban catchments and combined sewer outfalls. Journal of Environmental Science and Health, Part A 43, 567–575. https://doi.org/10.1080/10934520801893527

ISO, 2006. Soil quality — Determination of polycyclic aromatic hydrocarbons (PAH) — Gas chromatographic method with mass spectrometric detection (GC-MS) [WWW Document]. URL https://www.iso.org/standard/33387.html

Järlskog, I., Strömvall, A.-M., Magnusson, K., Galfi, H., Björklund, K., Polukarova, M., Garção, R., Markiewicz, A., Aronsson, M., Gustafsson, M., Norin, M., Blom, L., Andersson-Sköld, Y., 2021. Traffic-related microplastic particles, metals, and organic pollutants in an urban area under reconstruction. Science of The Total Environment 774, 145503. https://doi.org/10.1016/j.scitotenv.2021.145503

Johnson, J.P., Hunt, W.F., 2016. Evaluating the spatial distribution of pollutants and associated maintenance requirements in an 11 year-old bioretention cell in urban Charlotte, NC. Journal of Environmental Management 184, 363–370. https://doi.org/10.1016/j.jenvman.2016.10.009

Jones, K.C., de Voogt, P., 1999. Persistent organic pollutants (POPs): state of the science. Environmental Pollution 100, 209–221. https://doi.org/10.1016/S0269-7491(99)00098-6

Jones, P.S., Davis, A.P., 2013. Spatial Accumulation and Strength of Affiliation of Heavy Metals in Bioretention Media. J. Environ. Eng. 139, 479–487. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000624

Kallin, P.L., Lucas, W.C., Bergstrom, J.D., 2004. The Biofilter Wetland in Urban Situations: Design and Construction Considerations-Case Studies and Lessons Learned. American Society of Civil Engineers, Reston, Va.

Karlsson, K., Blecken, G.-T., Öhlander, B., Viklander, M., 2016. Environmental Risk Assessment of Sediments Deposited in Stormwater Treatment Facilities: Trace Metal Fractionation and Its Implication for Sediment Management. J. Environ. Eng. 142, 04016057. https://doi.org/10.1061/(ASCE)EE.1943-7870.0001122

Kluge, B., Markert, A., Facklam, M., Sommer, H., Kaiser, M., Pallasch, M., Wessolek, G., 2018. Metal accumulation and hydraulic performance of bioretention systems after long-term operation. J Soils Sediments 18, 431–441. https://doi.org/10.1007/s11368-016-1533-z

Kratky, H., Li, Z., Chen, Y., Wang, C., Li, X., Yu, T., 2017. A critical literature review of bioretention research for stormwater management in cold climate and future research recommendations. Front. Environ. Sci. Eng. 11, 16. https://doi.org/10.1007/s11783-017-0982-y

Lamprea, K., Bressy, A., Mirande-Bret, C., Caupos, E., Gromaire, M.-C., 2018. Alkylphenol and bisphenol A contamination of urban runoff: an evaluation of the emission potentials of various construction materials and automotive supplies. Environ Sci Pollut Res 25, 21887–21900. https://doi.org/10.1007/s11356-018-2272-z

Lange, K., 2021. Metal and microplastic treatment in stormwater bioretention. Luleå University of Technology.

Lange, K., Österlund, H., Viklander, M., Blecken, G.-T., 2020a. Metal speciation in stormwater bioretention: Removal of particulate, colloidal and truly dissolved metals. Science of The Total Environment 724, 138121. https://doi.org/10.1016/j.scitotenv.2020.138121

Lange, K., Viklander, M., Blecken, G.-T., 2020b. Effects of plant species and traits on metal treatment and phytoextraction in stormwater bioretention. Journal of Environmental Management 276, 111282. https://doi.org/10.1016/j.jenvman.2020.111282

LeFevre, G.H., Hozalski, R.M., Novak, P.J., 2012. The role of biodegradation in limiting the accumulation of petroleum hydrocarbons in raingarden soils. Water Research 46, 6753–6762. https://doi.org/10.1016/j.watres.2011.12.040

LeFevre, G.H., Paus, K.H., Natarajan, P., Gulliver, J.S., Novak, P.J., Hozalski, R.M., 2015. Review of Dissolved Pollutants in Urban Storm Water and Their Removal and Fate in Bioretention Cells. J. Environ. Eng. 141, 04014050. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000876

Li, H., Davis, A.P., 2008. Heavy Metal Capture and Accumulation in Bioretention Media. Environ. Sci. Technol. 42, 6776–6776. https://doi.org/10.1021/es8019808

Lucke, T., Dierkes, C., Boogaard, F., 2017. Investigation into the long-term stormwater pollution removal efficiency of bioretention systems. Water Science and Technology 76, 2133–2139. https://doi.org/10.2166/wst.2017.382

MacKay, D., 2006. Handbook of physical-chemical properties and environmental fate for organic chemicals, 2. ed., rev. ed. ed. CRC/Taylor & Francis, Boca Raton, Fla.

Mackay, D. (Ed.), 2006. Handbook of physical-chemical properties and environmental fate for organic chemicals, 2. ed., rev. ed. ed. CRC/Taylor & Francis, Boca Raton, Fla.

MacKenzie, K.M., Gharabaghi, B., Binns, A.D., Whiteley, H.R., 2022. Early detection model for the urban stream syndrome using specific stream power and regime theory. Journal of Hydrology 604, 127167. https://doi.org/10.1016/j.jhydrol.2021.127167

Makepeace, D.K., Smith, D.W., Stanley, S.J., 1995. Urban stormwater quality: Summary of contaminant data. Critical Reviews in Environmental Science and Technology 25, 93–139. https://doi.org/10.1080/10643389509388476

Markiewicz, A., Björklund, K., Eriksson, E., Kalmykova, Y., Strömvall, A.-M., Siopi, A., 2017. Emissions of organic pollutants from traffic and roads: Priority pollutants selection and substance flow analysis. Science of The Total Environment 580, 1162–1174. https://doi.org/10.1016/j.scitotenv.2016.12.074

Markiewicz, A., Strömvall, A.-M., Björklund, K., 2020. Alternative sorption filter materials effectively remove non-particulate organic pollutants from stormwater. Science of The Total Environment 730, 139059. https://doi.org/10.1016/j.scitotenv.2020.139059

Marsalek, J., Brownlee, B., Mayer, T., Lawal, S., Larkin, G.A., 1997. Heavy Metals and PAHs in Stormwater Runoff from the Skyway Bridge, Burlington, Ontario. Water Quality Research Journal 32, 815–828. https://doi.org/10.2166/wqrj.1997.044

Masoner, J.R., Kolpin, D.W., Cozzarelli, I.M., Barber, L.B., Burden, D.S., Foreman, W.T., Forshay, K.J., Furlong, E.T., Groves, J.F., Hladik, M.L., Hopton, M.E., Jaeschke, J.B., Keefe, S.H., Krabbenhoft, D.P., Lowrance, R., Romanok, K.M., Rus, D.L., Selbig, W.R., Williams, B.H., Bradley, P.M., 2019. Urban Stormwater: An Overlooked Pathway of Extensive Mixed Contaminants to Surface and Groundwaters in the United States. Environ. Sci. Technol. 53, 10070–10081. https://doi.org/10.1021/acs.est.9b02867

Mastrangelo, G., Fadda, E., Marzia, V., 1996. Polycyclic aromatic hydrocarbons and cancer in man. Environmental Health Perspectives 104, 1166–1170. https://doi.org/10.1289/ehp.961041166

McGrane, S.J., 2016. Impacts of urbanisation on hydrological and water quality dynamics, and urban water management: a review. Hydrological Sciences Journal 61, 2295–2311. https://doi.org/10.1080/02626667.2015.1128084

McNett, J.K., Hunt, W.F., 2011. An Evaluation of the Toxicity of Accumulated Sediments in Forebays of Stormwater Wetlands and Wetponds. Water Air Soil Pollut 218, 529–538. https://doi.org/10.1007/s11270-010-0665-9

Minervini, W.P., 2010. Of: Characteristics of Highway Stormwater Runoff in Los Angeles: Metals and Polycyclic Aromatic Hydrocarbons , S. Lau, Y. Han, J. Kang, M. Kayhanian, M. K. Stenstrom, 81, 308-318 (2009). Water Environment Research 82, 861–862. https://doi.org/10.2175/106143009X12465435982818

Müller, A., Österlund, H., Marsalek, J., Viklander, M., 2021. Comparison of three explorative methods for identifying building surface materials contributing pollutants to stormwater. Journal of Environmental Management 299, 113574. https://doi.org/10.1016/j.jenvman.2021.113574

Müller, A., Österlund, H., Marsalek, J., Viklander, M., 2020. The pollution conveyed by urban runoff: A review of sources. Science of The Total Environment 709, 136125. https://doi.org/10.1016/j.scitotenv.2019.136125

Muthanna, T.M., Viklander, M., Blecken, G., Thorolfsson, S.T., 2007. Snowmelt pollutant removal in bioretention areas. Water Research 41, 4061–4072. https://doi.org/10.1016/j.watres.2007.05.040

Okaikue-Woodi, F.E.K., Cherukumilli, K., Ray, J.R., 2020. A critical review of contaminant removal by conventional and emerging media for urban stormwater treatment in the United States. Water Research 187, 116434. https://doi.org/10.1016/j.watres.2020.116434

Pitt, R., Clark, S., Parmer, K., 1994. Potential groundwater contamination from intentional and nonintentional stormwater infiltration. Universuty of Alabama at Birmingham.

Pueyo, M., Mateu, J., Rigol, A., Vidal, M., López-Sánchez, J.F., Rauret, G., 2008. Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. Environmental Pollution 152, 330–341. https://doi.org/10.1016/j.envpol.2007.06.020

Rommel, S.H., Stinshoff, P., Helmreich, B., 2021. Sequential extraction of heavy metals from sorptive filter media and sediments trapped in stormwater quality improvement devices for road runoff. Science of The Total Environment 782, 146875. https://doi.org/10.1016/j.scitotenv.2021.146875

Smith, J.A., Sievers, M., Huang, S., Yu, S.L., 2000. Occurrence and phase distribution of polycyclic aromatic hydrocarbons in urban storm-water runoff. Water Science and Technology 42, 383–388. https://doi.org/10.2166/wst.2000.0407

Søberg, L.C., Viklander, M., Blecken, G.-T., 2017. Do salt and low temperature impair metal treatment in stormwater bioretention cells with or without a submerged zone? Science of The Total Environment 579, 1588–1599. https://doi.org/10.1016/j.scitotenv.2016.11.179

Søberg, L.C., Winston, R., Viklander, M., Blecken, G.-T., 2019. Dissolved metal adsorption capacities and fractionation in filter materials for use in stormwater bioretention facilities. Water Research X 4, 100032. https://doi.org/10.1016/j.wroa.2019.100032

SS, 2004a. Determination of dry matter and ignition residue in water, sludge and sediment SWEDISH STANDARD · SS 28113 [WWW Document]. URL https://www.sis.se/produkter/miljo-och-halsoskydd-sakerhet/vattenkvalitet/avloppsvatten/ss28113/

SS, 2004b. Determination of dry matter and ignition residue in water, sludge and sediment SWEDISH STANDARD · SS 28113-1 [WWW Document]. URL https://www.sis.se/produkter/miljo-och-halsoskydd-sakerhet/vattenkvalitet/avloppsvatten/ss28113/

SS-EN ISO, 2016. Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of selected elements including uranium isotopes (ISO 17294-2:2016) [WWW Document]. URL https://www.sis.se/produkter/miljo-och-halsoskydd-sakerhet/vattenkvalitet/undersokning-av-vatten-efter-kemiska-substanser/sseniso1729422016/

SS-EN ISO, 2009. Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 11885:2007) [WWW Document]. URL https://www.sis.se/en/produkter/environment-health-protection-safety/water-quality/general/sseniso118852009/

SS-EN ISO, 2006. Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 1: General guidelines (ISO 17294-1:2004) SS-EN ISO 17294-1:2006 [WWW Document]. SIS swedish institute for standards. URL https://www.sis.se/en/produkter/environment-health-protection-safety/water-quality/examination-of-water-for-chemical-substances/sseniso1729412006/

Stockholm convention, 2008. Stockholm Convention [WWW Document]. URL http://chm.pops.int/TheConvention/ThePOPs/The12InitialPOPs/tabid/296/Default.aspx (accessed 12.21.21).

Stone, M., Marsalek, J., 1996. Trace metal composition and speciation in street sediment: Sault Ste. Marie, Canada. Water Air Soil Pollut 87, 149–169. https://doi.org/10.1007/BF00696834

Swedish EPA, 2009. Riktvärden för förorenad mark Modellbeskrivning och vägledning (Naturvårdsverket publikation No. 5976). Sweden.

Tedoldi, D., Chebbo, G., Pierlot, D., Kovacs, Y., Gromaire, M.-C., 2017. Assessment of metal and PAH profiles in SUDS soil based on an improved experimental procedure. Journal of Environmental Management 202, 151–166. https://doi.org/10.1016/j.jenvman.2017.06.063

Tedoldi, D., Chebbo, G., Pierlot, D., Kovacs, Y., Gromaire, M.-C., 2016. Impact of runoff infiltration on contaminant accumulation and transport in the soil/filter media of Sustainable Urban Drainage Systems: A literature review. Science of The Total Environment 569–570, 904–926. https://doi.org/10.1016/j.scitotenv.2016.04.215

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51, 844–851. https://doi.org/10.1021/ac50043a017

U.S. EPA, 1994a. Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry Revision 5.4. Cincinnati, OH [WWW Document]. URL https://www.epa.gov/esam/epa-method-2008-determination-trace-elements-waters-and-wastes-inductively-coupled-plasma-mass

U.S. EPA, 1994b. Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry Revision 4.4. Cincinnati, OH [WWW Document]. URL https://www.epa.gov/esam/method-2007-determination-metals-and-trace-elements-water-and-wastes-inductively-coupled-plasma

U.S. EPA, 1993. Standards for the Use or Disposal of Sewage Sludge (40 CFR Part 503). Fed. Regist., Vol 58, No. 32 [WWW Document]. URL https://www.epa.gov/biosolids/biosolids-laws-and-regulations#standards

US EPA, 1983. US-EPA, 1983. Final Report of the Nationwide Urban Runoff Program. U.S. Environmental Protection Agency, Water Planning Division; Washington DC, USA. [WWW Document]. URL https://nepis.epa.gov/Exe/ZyNET.exe/9100JH5T.txt?ZyActionD=ZyDocument&Client=EPA&Index=1981%20Thru%201985&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&UseQField=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5CZYFILES%5CINDEX%20DATA%5C81THRU85%5CTXT%5C00000018%5C9100JH5T.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=1#

Walsh, C.J., Roy, A.H., Feminella, J.W., Cottingham, P.D., Groffman, P.M., Morgan, R.P., 2005. The urban stream syndrome: current knowledge and the search for a cure. Journal of the North American Benthological Society 24, 706–723. https://doi.org/10.1899/04-028.1

Wang, J., Zhang, P., Yang, L., Huang, T., 2016. Cadmium removal from urban stormwater runoff via bioretention technology and effluent risk assessment for discharge to surface water. Journal of Contaminant Hydrology 185–186, 42–50. https://doi.org/10.1016/j.jconhyd.2016.01.002

WFD, 2014. European Commission, Directorate-General for Environment, The EU Water Framework Directive, Publications Office, 2014, [WWW Document]. The EU Water Framework Directive. URL https://data.europa.eu/doi/10.2779/75229

Zgheib, S., Moilleron, R., Chebbo, G., 2012. Priority pollutants in urban stormwater: Part 1 – Case of separate storm sewers. Water Research 46, 6683–6692. https://doi.org/10.1016/j.watres.2011.12.012

Zgheib, S., Moilleron, R., Saad, M., Chebbo, G., 2011. Partition of pollution between dissolved and particulate phases: What about emerging substances in urban stormwater catchments? Water Research 45, 913–925. https://doi.org/10.1016/j.watres.2010.09.032

Zhang, K., Randelovic, A., Page, D., McCarthy, D.T., Deletic, A., 2014. The validation of stormwater biofilters for micropollutant removal using in situ challenge tests. Ecological Engineering 67, 1–10. https://doi.org/10.1016/j.ecoleng.2014.03.004

Paper I

Robert Furén, Kelsey Flanagan, Ryan J. Winston, R. Andrew Tirpak, Jay D. Dorsey,
Maria Viklander, Godecke-Tobias Blecken

Occurrence, concentration, and distribution of 38 organic micropollutants in the filter material of 12 stormwater bioretention facilities

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Occurrence, concentration, and distribution of 38 organic micropollutants in the filter material of 12 stormwater bioretention facilities

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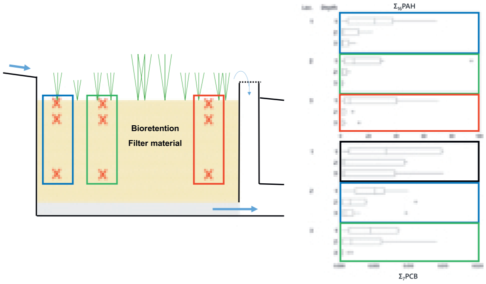
HIGHLIGHTS

- Large scale field study of accumulation of organic micro pollutants in bioretentions
- Most PAHs and PCBs were frequently detected.
- Of 13 phthalates and two alkylphenols, DEHP and nonylphenol were quantified regularly.
- Large inter and intra-site variations with highest levels in filter top layers
- Pollution was detected in all filters regardless age, size and catchment land use.

GRAPHICAL ABSTRACT



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ABSTRACT

The increased use of bioretention facilities as a low impact development measure for treating stormwater runoff underscores the need to further understand their long-term function. Eventually, bioretention filter media must be (partly) replaced and disposed of at the end of its functional lifespan. While there are several studies of metal accumulation and distributions in bioretention media, less is known about organic pollutant pathways and accumulation in these filters. The present study considers the occurrence and accumulation of 16 polycyclic aromatic hydrocarbons, 7 polychlorinated biphenyls, 13 phthalates, and two alkylphenols throughout 12 older bioretention facilities (7–13 years old) used for stormwater treatment in Michigan and Ohio, USA. These pollutant groups appear to behave similarly, with greater instances of detection and higher concentrations in the upper media layers which decrease with increased depth from the surface. The patterns of detection and concentration in the filter material may be explained by characteristics of the pollutants, such as molecular structures and solubility that affect the removal of the organic pollutants by the filter material. There is also a large variation in concentration magnitudes between the bioretention sites, most likely due to differences in pollutant sources, contributing catchment size and/or land uses.

1. Introduction

Significant pollutant loads are generated and stored on urban surfaces which are subsequently conveyed to receiving water bodies by surface runoff from rain events and/or snowmelt (Müller et al., 2020) The impacts of untreated stormwater runoff are recognized as a main driver of

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environmental degradation in urban watersheds (Davis et al., 2009; Walsh et al., 2005).

While contaminants such as metals, nutrients, and sediments are ubiquitous in stormwater, recent studies have pointed to organic micropollutants (OMPs) as a pollutant group of emerging concern that may detrimentally affect receiving water bodies, aquatic life and humans (Barbosa et al., 2012; Markiewicz et al., 2017), e.g. some phthalates, alkylphenols and polycyclic organic hydrocarbons are considered as genotoxic substances (Markiewicz et al., 2020), nonylphenols and phthalates as endocrine disrupting (Björklund et al., 2009) and petroleum hydrocarbons as suspected human carcinogens (Fent, 2003; LeFevre et al., 2012; Mastrangelo et al., 1996). Polychlorinated biphenyls are classified as persistent organic pollutant (Stockholm Convention, 2008) that may increase risk for certain cancers and cause negative reproductive effects also on humans (Helmfrid et al., 2012).

Field studies have detected OMPs such as polycyclic aromatic hydrocarbons (PAHs) (Smith et al., 2000), polychlorinated biphenyls (PCBs) (Hwang and Foster, 2008), phthalates (Björklund et al., 2009) and alkylphenols (Lamprea et al., 2018) in urban runoff. Numerous diffuse sources contribute these contaminants to runoff, such as coal tar sealant, traffic, and leaching from construction materials including polyvinyl chloride (PVC) (Bergé et al., 2013; Brown and Peake, 2006; Crane, 2014; Lamprea et al., 2018; LeFevre et al., 2012). Besides these, a wide variety of organic contaminants has been frequently detected in stormwater, many of which are hydrophilic compounds with a wide application spectrum (e.g. herbicides, biocides, flame retardants, anti-icing) (Masoner et al., 2019). A study with the aim to identify organic priority pollutants, PAHs alkylphenols and phthalates were listed out of 1100 compounds in priority order among the 4 highest ranked (Markiewicz et al., 2017).

As the awareness of stormwater pollution and its impacts has increased over the past decades (Makepeace et al., 1995), the interest in stormwater quality treatment has concurrently grown (Fletcher et al., 2015). Stormwater bioretention facilities, also known as stormwater biofilters are an increasingly popular treatment technology (Davis et al., 2009). Bioretention facilities typically consist of an engineered (often sandy soil) filter media drained by a perforated underdrain enveloped in gravel. They are often topped with mulch and/or top soil planted with a variety of plant species. Studies show that bioretention facilities provide efficient removal of numerous pollutants, such as total suspended solids (TSS) (Hsieh and Davis, 2005) and metals (Blecken et al., 2009a). Their removal often exceeds 70–80 %. Particulate metals, which have been evaluated comprehensively in bioretention studies, are mainly removed through filtration (Tedoldi et al., 2016) and primarily retained in the 5–10 cm top layer of the filter (Li and Davis, 2008; Blecken et al., 2011). Similar trends have been observed for dissolved metals: Al-Ameri et al. (2018) reported 70 % of dissolved metals were trapped in the top 7 cm of filter media. This is likely due to rapid adsorption of dissolved metals to the filter material (Søberg et al., 2019). Previous studies of bioretention facilities indicated good removal of phosphorus (70 to 85 % provided that a suitable filter material is implemented) (Søberg et al., 2020), while nitrogen behavior is complex due to the biogeochemical complexity of the nitrogen species and insufficient removal or even leaching of nitrogen has been reported for facilities without a submerged zone (Biswal et al., 2022).

Compared to other pollutants, limited research has evaluated the removal of OMPs by bioretention. Although less data is available with respect to OMPs than metals or nutrients, bioretention efficiently removed a wide range of OMPs (Zhang et al., 2014). Field studies of OMP removal from stormwater in bioretention facilities show high concentration reductions (>90 %) for PCBs and PAHs (David et al., 2015; Flanagan et al., 2018; Gilbreath et al., 2019) and mass load reductions of 87 % for PAHs (DiBlasi et al., 2009). Flanagan et al. (2018) found more variable performance with respect to alkylphenols and phthalates (−49–76 % and 8–74 %, respectively). While there are several studies of metal distribution in bioretention filter media (Al-Ameri et al., 2018; Jones and Davis, 2013), less is known about OMP pathways and accumulation in the filter material. Most studies on OMP fate in bioretention facilities focus on hydrocarbons, particularly PAHs. LeFevre et al. (2012) showed that raingarden soils contained bacteria capable of mineralizing petroleum hydrocarbons (TPH), limiting the accumulation of TPH to concentrations below regulatory limits. On the other hand, PAHs, particularly those with high molecular weights, tend to accumulate in the top layer of soil, sometimes reaching concentrations well above regulatory limits (DiBlasi et al., 2009; Flanagan et al., 2018; Tedoldi et al., 2017).

In summary, these studies highlight that further studies are needed to understand the accumulation and distribution of a wider range of OMPs in the soil of bioretention facilities, with a specific focus on older facilities, both to gain perspective on the long-term function of these facilities and to characterize maintenance needs and measures. Indeed, bioretention filter media must be replaced and disposed of when they reach the end of their functional lifespan. Characterizing the accumulation of pollutants in the filters is essential to evaluating the risks associated with managing bioretention media throughout its lifecycle. High OMP concentrations in (parts of) the filter material could further pose a risk for humans or wildlife due to acute or chronic toxicity.

To address these research needs, the present study characterizes the occurrence and accumulation of 16 PAHs, 7 PCBs, 13 phthalates, and two alkylphenols in 12 field-scale bioretention systems used for stormwater treatment. These bioretention systems had been filtering stormwater for 7–13 years at the time of sampling. To the best of our knowledge, this is one of the most comprehensive studies investigating the occurrence, accumulation, and distribution of OMPs in bioretention filter media to date.

2. Methods

A field study of organic pollutants in the filter media of bioretention systems used for stormwater treatment was carried out in Ohio and Michigan (US) in November 2019. Filter material samples were collected from 12 bioretention systems and analysed for 38 different organic pollutants.

2.1. Field sites

This study focused on twelve 7–13 years old vegetated bioretention facilities treating runoff from dense urban catchments with different land uses characteristics in Michigan (MI) and Ohio (OH), USA. These included roads, highly urban and industrial/commercial areas, as well as residential areas. At the time of sampling, the facilities varied in age from 7 to 13 years and filter areas ranged from 10 m^2 to approximately 2000 m^2. The contributing catchment areas varied from approximately 50 m^2 to 318,000 m^2 (Table 1).

2.2. Sample collection

Following a methodology similar to that used by Tedoldi et al. (2017), nine filter material samples were collected from three different locations in each bioretention facility (i.e. different distances from the inlet) and at three depths (0–5 cm, 10–15 cm and 35–50 cm), as illustrated in Fig. 1. While the samples from the two shallower depths were always taken at 0–5 and 10–15 cm, the filter material in some facilities (i.e., sites #3 and #11) was shallower than 50 cm. In these cases, the deepest sample was collected in the filter layer between 35 cm and the depth of the bottom of the filter material. This resulted in a total of 108 samples. For each sample a replicate were also taken.

The three locations along each bioretention facility were situated approximately 1 m, 3 m and 6 m from the inlet. However, for sites #2 and #6, which were smaller, the distances were scaled down (approximately 0.5 m, 1.5 m and 3 m) to permit three separate sampling locations within the facilities. Further, some filters had multiple inlets; for these sites, the sampling locations were positioned based on the inlet most likely to contribute the majority of the inflow. Therefore, the field work for each site started with a visual examination and mapping of the site. Catchment areas, inlets, and patterns of sediment deposition and erosion were studied to define a “main inlet” from which the sampling points were then measured out.

Table 1
Site characteristics of sampled bioretention facilities. Ratio is the percentage of the filter area in comparison to the contributing catchment area.

Site nr	Age [yr]	Location	Catchment area characteristics	Catchment area [m^2]	Filter area [m^2]	Ratio [%]	Mulch layer/top soil
1	9	Upper Arlington, OH	Residential/commercial	318000	950	0.3	Yes
2	8	Upper Arlington, OH	Commercial	750	40	5.3	Yes
3	10	Columbus, OH	Industrial	6000	300	5.0	No
4	7	Westerville, OH	Commercial	4000	170	4.3	Yes
5	9	Columbus, OH	Downtown urban	300	40	13.3	Yes
6	8	Columbus, OH	Downtown urban	50	10	20.0	Yes
7	12	Hamilton, OH	Industrial	4500	300	6.7	Yes
8	12	Lansing, MI	Downtown urban	600	50	8.3	Yes
9	11	Lansing, MI	Downtown urban	500	50	10.0	Yes
10	8	Parma, OH	Fueling station	2500	200	8.0	Yes*
11	13	Twinsburg, OH	Fueling station	2000	70	3.5	Yes
12	12	North Canton, OH	Fueling station	1250	180	14.4	Yes

* Indicate mulch layer of wood chips.

Samples were collected using a steel spade to cut out a core of filter material which was poured into diffusion-tight plastic bags (18 cm × 35 cm) for organic samples. The bags were sealed shut with cable ties. Approximately 1 kg of material was collected at each sampling point. The outdoor temperature during sampling was between −12 to +6 °C and the samples were refrigerated prior to laboratory analysis.

2.3. Chemical analysis

The samples were analysed for their concentrations of organic compounds that included four groups of pollutants: 16 PAHs, seven PCBs, 13 phthalates and two alkylphenols. The OMP concentrations were analysed using gas chromatography–mass spectrometry. Concentrations of 16 PAHs (i.e., naphthalene (Nap), acenaphthylene (Acyl), acenaphthene (Acen), fluorene (F), phenanthrene (Phen), anthracene (A), fluoranthene (Fluo), pyrene (Pyr), benzo(*a*)anthracene (BaA), chrysene (Chry), benzo(*b*)fluoranthene (BbF), benzo(*k*)fluoranthene (BkF), benzo(*a*)pyrene (BaP), dibenzo(*a*,*h*)anthracene (DahA), benzo(*g*,*h*,*i*)perylene (Bper), and indeno(1,2,3-cd) pyrene (IP)) were analysed according to US EPA 8270 (Pitt et al., 1994) and ISO 18287 (ISO, 2006). The Σ_{16}PAH was calculated as the sum of the concentrations of all 16 PAHs. The sum of PAHs with low molecular weights (PAH-L) was calculated as the sum of naphthalene, acenaphthylene and acenaphthene, PAHs with medium molecular weights (PAH-M) as the sum of fluorene, phenanthrene, anthracene, fluoranthene, and pyrene, PAHs with high molecular weights (PAH-H) as the sum of benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(*a*,*h*)anthracene, and benzo(*g*,*h*,*i*)perylene. Concentrations of seven PCBs indicator congeners (i.e., PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180) were analysed following DIN ISO 10382 (DIN ISO, 2002). The grouping Σ_7PCB was calculated as the sum of these seven PCBs. Concentrations of 13 phthalates (i.e., dimethylphthalate (DMP), diethylphthalate (DEP), di-n-propylphthalate (DPP), diisobutylphthalate (DIBP), di-n-butylphthalate (DBP), di-n-pentylphthalate (DNPP), di-n-octylphthalate (DNOP), di-(2-ethylhexyl)phthalate (DEHP), butylbenzylphthalate (BBP), dicyclohexylphthalate (DCP), diisodecyl phthalate (DIDP), diisononyl phthalate (DINP) and di-n-hexylphthalate (DNHP)) were analysed following E DIN19742 (E DIN, 2014). The concentrations of two alkylphenols (i.e., 4-tert-octylphenol (OP) and 4-nonylphenols (NP) were analysed. All OMP detection limits (DL) are presented in Table 2.

Besides the OMPs, total organic carbon (TOC) was measured using CSN EN 13137 (CSN EN, 2018) and CSN ISO 10694 (CSN ISO, 1995). Loss on ignition (LOI) was measured using gravimetric analysis based on CSN EN 12879 (CSN EN, 2014), CSN 720103 (CSN, 2009), and CSN 465735 (CSN, 1991). Dry matter (DM) were measured using appropriate methods for each pollutant group. Specific surface area (SSA) was measured following BS ISO 9277:2010 (BS ISO, 2010) (gas adsorption — BET method).

One sample (Site #6, location 2, depth 35–50 cm) of the total 108 collected samples could not be analysed for PAHs or alkylphenols due to insufficient sample volume.

2.4. Statistical analysis

Boxplots were used to illustrate pollutant distribution and their concentration in the bioretention filter material. Since parts of the data were non-normally distributed and others censored, the nonparametric Kruskal-Wallis test was used, after censoring data at the highest reporting limit (Helsel, 2012), to test statistical significance of differences between the examined parameters (i.e., depth and location). To test the cross-correlations between pollutant concentrations, the non-parametric Kendall's-tau (τ) correlation test, applicable for the analysis of censored data, was performed using the NADA package in R for

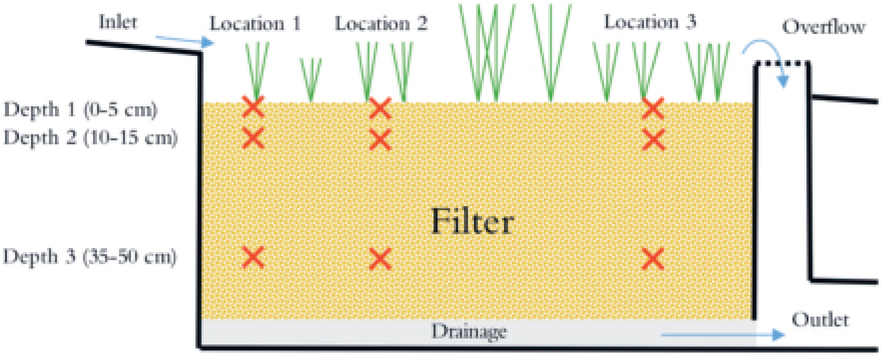

Fig. 1. Cross-section of a bioretention facility illustrating the nine sampling points (at three locations and at three depths) used in this study.

Table 2
Summary of the occurrence and concentrations of analysed OMPs above detection limits (DL).

Group/units	Substance name	Nr of samples	Occurrence		DL	Concentrations			
						Top layer/layer 1 median	All data		
			Nr > DL	% > DL			Median	Max	Min
PAH [mg/kg, DM]	Naphthalene (Nap)	107	13	12 %	0.10	<0.10	<0.10	1.49	<0.10
	Acenaphthylene (Acyl)	107	0	0 %	0.10	–	–	–	–
	Acenaphthene (Acen)	107	15	14 %	0.10	<0.10	<0.10	6.98	<0.10
	Fluorene (F)	107	14	13 %	0.10	<0.10	<0.10	8.98	<0.10
	Phenanthrene (Phen)	107	51	48 %	0.10	0.29	<0.10	127	<0.10
	Anthracene (A)	107	24	22 %	0.10	<0.10	<0.10	19.4	<0.10
	Fluoranthene (Fluo)	107	76	71 %	0.10	1.02	0.32	186	<0.10
	Pyrene (Pyr)	107	74	69 %	0.10	0.83	0.25	138	<0.10
	Benzo(*a*)anthracene (BaA)	107	73	68 %	0.05	0.52	0.11	45.9	<0.05
	Chrysene (Chry)	107	81	76 %	0.05	0.92	0.18	58.7	<0.05
	Benzo(*b*)fluoranthene (BbF)	107	83	78 %	0.05	1.56	0.33	52.7	<0.05
	Benzo(*k*)fluoranthene (BkF)	107	68	64 %	0.05	0.41	0.08	18.5	<0.05
	Benzo(*a*)pyrene (BaP)	107	76	71 %	0.05	0.67	0.16	32.9	<0.05
	Dibenzo(*a*,*h*)anthracene (DahA)	107	44	41 %	0.05	0.14	<0.05	3.98	<0.05
	Benzo(*g*,*h*,*i*)perylene (Bper)	107	67	63 %	0.10	0.78	0.20	24.5	<0.10
	Indeno(1,2,3-*cd*)pyrene (IP)	107	76	71 %	0.05	0.63	0.16	15.0	<0.05
	PAH sum Low weight (PAH-L)	107	16	15 %	0.15	<0.15	<0.15	7.80	0.11
	PAH sum medium-weight (PAH-M)	107	76	71 %	0.25	2.10	0.57	480	0.12
	PAH sum high-weight (PAH-H)	107	83	78 %	0.23	5.90	1.30	240	0.07
	PAH 16 sum (Σ16PAH)	107	83	78 %	0.63	8.00	1.90	730	0.07
PCB [μg/kg, DM]	PCB 28	108	18	17 %	(0.20–0.40)	<0.10	<0.10	18.00	<0.06
	PCB 52	108	55	51 %	0.10	0.33	<0.10	19.00	<0.10
	PCB 101	108	66	61 %	0.10	0.71	0.19	39.00	<0.10
	PCB 118	108	65	60 %	0.10	0.65	0.22	46.00	<0.10
	PCB 138	108	78	72 %	0.10	1.05	0.37	36.00	<0.10
	PCB 153	108	80	74 %	0.10	1.20	0.42	42.00	<0.10
	PCB 180	108	73	68 %	0.10	0.76	0.28	27.00	<0.10
	Sum of 7 PCBs (Σ7PCB)	108	81	75 %	0.40	4.90	1.75	210.00	0.11
Phthalates [mg/kg, DM]	Dimethylphthalate (DMP)	108	1	1 %	0.05	<0.05	<0.05	1.40	<0.05
	Diethylphthalate (DEP)	108	0	0 %	0.05	–	–	–	–
	Di-n-propylphthalate (DPP)	108	2	2 %	(0.05–0.50)	<0.05	<0.05	<0.50	<0.05
	Diisobutyl phthalate (DIBP)	108	5	5 %	(0.05–1.00)	<0.05	<0.05	<1.00	<0.05
	Di-n-butylphthalate (DBP)	108	2	2 %	(0.05–0.30)	<0.05	<0.05	<0.30	<0.05
	Di-n-pentylphthalate (DNPP)	108	0	0 %	(0.05–1.00)	–	–	–	–
	Di-n-octylphthalate (DNOP)	108	0	0 %	(0.05–0.25)	–	–	–	–
	Di-(2-ethylhexyl)phthalate (DEHP)	108	50	46 %	0.05	0.26	<0.05	6.10	<0.05
	Butylbenzylphthalate (BBP)	108	4	4 %	(0.05–0.30)	<0.05	<0.05	<0.30	<0.05
	Dicyclohexylphthalate (DCP)	108	0	0 %	0.05	–	–	–	–
	Diisodecyl phthalate (DIDP)	108	0	0 %	2.50	–	–	–	–
	Diisononyl phthalate (DINP)	108	6	6 %	2.50	<2.50	<2.50	6.80	<2.50
	Di-n-hexylphthalate (DNHP)	108	2	2 %	(0.05–0.10)	<0.05	<0.05	0.11	<0.05
Alkylphenols [mg/kg, DM]	4-Tert-octylphenol (OP)	107	1	1 %	(0.01–0.03)	<0.01	<0.01	0.03	<0.01
	4-Nonylphenols (tech.mixture) (NP)	107	19	18 %	(0.10–0.20)	<0.10	<0.10	106	<0.10

pollutants detected in at least 42 % of the samples (the pollutants not included in this analysis were quantified in <23 % of samples).The concentrations of organic pollutants and factors potentially affecting these were also examined using principal components analysis (PCA) performed in the software SIMCA 15 for visualization of the main characteristics and correlations of the analysis results. The PCA included concentrations from the laboratory analysis with the parameters Depth, Location (Fig. 1), specific surface area (SSA), loss on ignition (LOI), total organic carbon (TOC), age, ratio between filter area and catchment area), land use Commercial-, Industrial-, down town urban- and fuel stations areas. The model where UV scaled and log transformed (auto transformed) on skewed variables. For discussion of a practical end use of the data, concentrations of PAH-H, PAH-M, PAH-L and PCB 7 were compared to the Swedish national guidance limits for classification of soil, "soil for sensitive land use" (abbreviated KM) and "soil for less sensitive land use" (abbreviated MKM), published by the Swedish Environmental protection agency (Swedish EPA, 2009).

3. Result and discussion

In total, 32 of the 38 analytes were detected in at least one of the 108 samples while six substances (five phthalates and one PAH) were never detected (Table 2). The most frequently detected pollutants in the study were PAHs and PCBs, while phthalates and alkylphenols were less frequently detected. A summary of results and descriptive statistics are presented in Table 2, while the complete results from the analysis of the sampling campaign are presented in the Supplementary Table 4.1.

3.1. PAHs

PAHs were detected at all twelve sites examined, with at least one type of PAH above the detection limit in 78 % of all samples. Of the 16 analysed PAHs only acenaphthylene was never detected. PAHs were mainly present in the upper layer of the filter material, but were also detected in the deeper layers, though less frequently and at lower concentrations (Fig. 2 and Supplementary Fig. 2.1). The most frequently occurring PAHs, benzo(*b*) fluoranthene and chrysene, were found in 78 % and 76 % of all samples, respectively, followed by fluoranthene, benzo(*a*)pyrene and indeno(1,2,3-*cd*) pyrene, all of which occurred in 71 % of samples. The occurrence and concentrations of PAHs decreased with increased depth from the surface and with increased distance from the inlet (Fig. 2). PAHs with high molecular weights (i.e., PAH-H) and PAHs with medium molecular weights (i.e., PAH-M) were present in at least one sample from all 12 sites, while PAHs with low molecular weights (i.e., PAH-L) were less frequently detected (Table 2). PAH-H and PAH-M appeared in higher concentrations than PAH-L. The concentrations of Σ_{16}PAH ranged from 0.07 mg/kg to

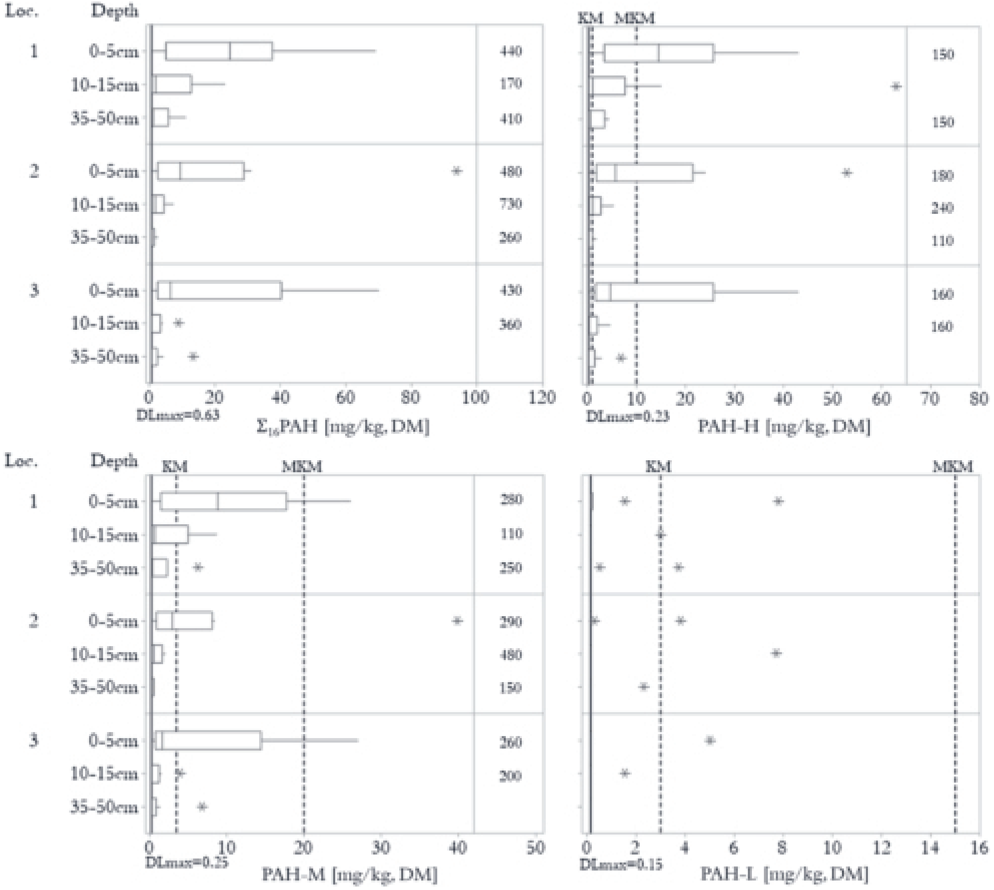

Fig. 2. Boxplots of concentrations of Σ_{16}PAH, PAH-H, PAH-M and PAH-L (mg/kg, DM) for different distances from inlets (Locations, Fig. 1) and distance from surface (Depth, Fig. 1). In addition to those plotted as asterisks (*), outliers above 100 mg/kg, DM are indicated as text to the right for plotting purposes. The concentrations of PAH-H, PAH-M and PAH-L are compared to the Swedish guidelines for pollutant concentrations relating to soil classification (KM (soil for sensitive land use) and MKM (soil for less sensitive land use)). For PAH-H concentrations above MKM are mainly present in the upper layers or close to the inlet and for PAH-M concentrations above KM are mainly present in the upper layers or close to the inlet.

730 mg/kg, with an overall median of 1.9 mg/kg; the median concentration in the top layer was found to be 8 mg/kg (Table 2), significantly higher (Kruskal-Wallis $p < 0.05$) than the layers below (Fig. 2). Also with increased distance from the inlets the median concentrations decreased; however, this trend was not statistically significant. Concentration boxplots for all 16 PAHs are presented in the Supplementary Fig. 2.1. Most of the extreme outliers shown in Fig. 2 were detected at one single facility (site #1) and here in nearly all samples were extraordinarily high (Σ_{16}PAH 273-fold larger, PAH-H 151-fold larger and PAH-M 526-fold larger median concentration compared to the other 11 sites).

3.2. PCBs

PCBs were detected in 75 % of all samples and were the second most frequently observed group of substances in this study. In total, PCBs were not detected at just two of the 12 sites (sites #3 and #7, Table 1). Aside from PCB 28, all PCBs were found in the same 10 sites, while PCB 28 was detected in four out of 12 sites. The most frequently occurring PCBs were PCB 153, detected in 74 % of all samples, followed by PCB 138 (72 %), PCB 180 (68 %), PCB 101 (61 %), PCB 118 (60 %), and PCB 52 (51 %). The least frequent PCB (PCB 28) was detected in just 17 % of all samples.

Although the median concentrations of PCBs were higher in the upper layer, PCBs were also detected in the deeper layers in nearly all facilities (Fig. 3). The median Σ_7PCB concentration of all samples was 1.75 μg/kg, compared with 4.9 μg/kg in the top layer, 1 μg/kg in the middle layer and 0.4 μg/kg in the bottom layer. The top layer (0–5 cm) concentrations were about 5 to 12 times higher than in the deeper layers (depths of 10–15 cm and 35–50 cm), differences which were statistically significant (Kruskal-Wallis, $p < 0.05$). The highest concentrations of PCBs were found in downtown/city center areas with high population density and traffic, while lower concentrations were found in less-densely-populated suburban residential areas with more green space. A trend of decreasing concentrations with increased distance from the inlet was observed; however, due to the large variation of concentrations within and between different sites, ranging from 0.1 μg/kg to 210 μg/kg, no significant

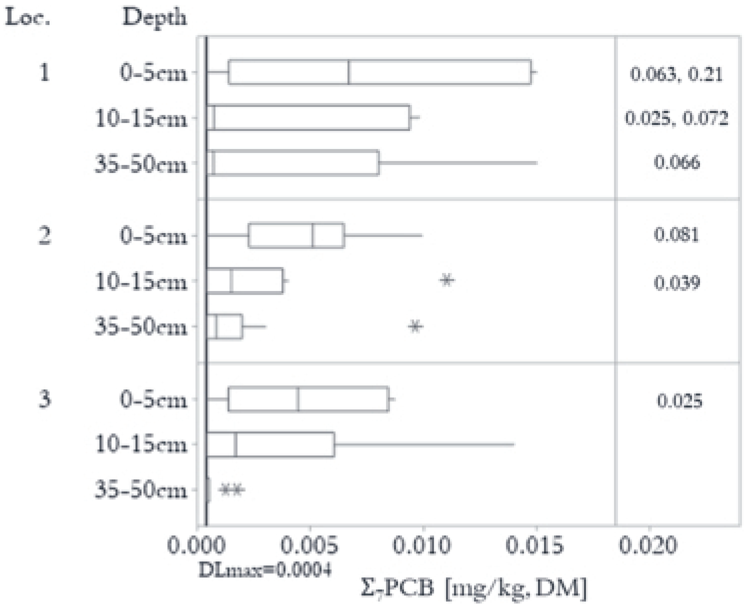

Fig. 3. Box plot of Σ_7PCB for different distances from inlets (Locations, Fig. 1) and distance from surface (Depth, Fig. 1). In addition to those plotted as asterisks (*), outliers above 0.02 mg/kg, DM are indicated as text to the right for plotting purposes.

difference between the concentrations at different distances from the inlet was detected.

3.3. Phthalates

Phthalates were detected in eleven sites and in 52 of 108 samples (48 %). Eight of the 13 different phthalates (Table 1) were detected in at least one sample. The most frequently detected phthalate, di-2-ethylhexyl phthalate (DEHP), was detected in 46 % of samples. The remaining phthalates were only detected occasionally: DINP was found in 6 %, DIBP 5 %, BBP 4 %, DDP 2 %, DBP 2 %, DNHP 2 %, and DMP in 1 % of all samples. When detected, the concentrations of phthalates were significantly higher (Kruskal-Wallis, $p < 0.05$) in the upper layers of the filter material and decreased with increased depth (e.g. DEHP, Fig. 4). The other detected phthalates were only found in few samples from the top layer (e.g. DINP, Fig. 4). Though not statistically significant, concentrations also tended to be higher at locations closer to the inlets and decreased with increased distance from the inlets.

3.4. Alkylphenols

As a group, alkylphenols had the lowest occurrence rate in the study. 4-Nonylphenol (NP) was detected in seven out of 12 sites and in 19 out of a total of 107 samples (18 %) and was mainly identified in the top filter

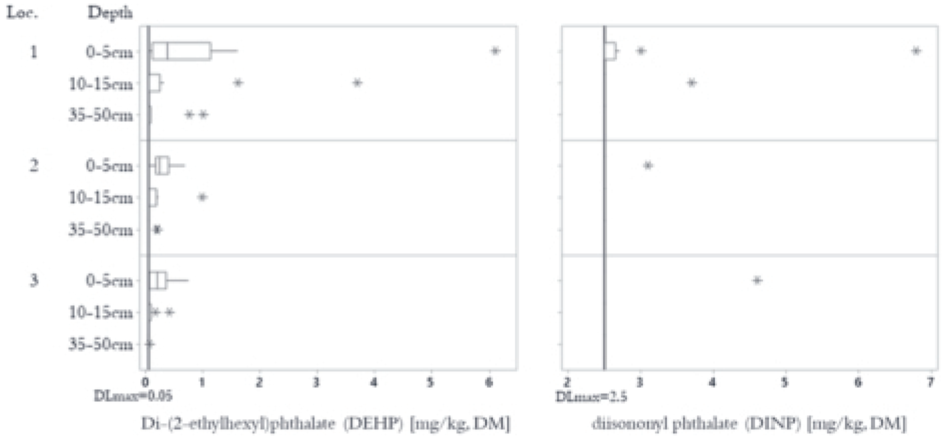

Fig. 4. Concentrations (mg/kg, DM) of di-(2-ethylhexyl)phthalate (DEHP) and phthalate with high occurrence (46 %) in the study and diisononyl phthalate (DINP) and phthalate with lower occurrence (6 %).

layers. 4-Tert-octylphenol was only found above the detection limit in one sample out of 107 (<1 % detection frequency). NP had a higher occurrence rate and higher concentrations in the top layer and at locations closer to the inlet; like other pollutants, concentration of NP rapidly decreased with increased distance from the surface and inlets (Fig. 5).

3.5. Principle component analysis

The PCA had 7 components with $R^2Xcum = 0.90$ (cumulative X-variation modelled after all seven components) and $Q2(cum) = 0.41$ (cumulative overall cross-validated R^2X). However, most variations were explained in the first and second component ($R^2X(p1) = 0.446$ and $R^2X(p2) = 0.124$). A summary of the results from the PCA is shown in the score plots and loading plots in Fig. 6.

In the loading plot, PAHs and PCBs, which were frequently detected, are clustered separately from the other pollutant groups. The less frequently or never-detected phthalates (except DEHP) and alkylphenols (except NP) are located closer to the center of the plot. The most influential parameters on pollutant concentration are Depth, TOC and LOI. Further, there seems to be also some impact from SSA and Location. TOC and LOI are closely correlated to each other but also to PAHs and PCBs. Reasons could be that filter materials with higher TOC contents and/or LOI tend to adsorb more PAHs and PCBs (Björklund and Li, 2017) and/or the commonly-occurring mulch layer at the biofilter surface where many (especially particulate) pollutants are trapped and accumulated. Despite the positive effect of organic matter on adsorption, high contents of organic matter may be disadvantageous for the overall bioretention functionality e.g. due to the risk for nutrient leaching (Hurley et al., 2017).

As already illustrated in the box plots (Figs. 2–5), a strong correlation was also found between depth and concentrations, mainly for the PAH and PCB group. For PAHs the trends are stronger for PAH-H and PAH-M while PAH-L, which was less frequently detected, is close to the center of the plot. A general trend is that the higher occurrence and concentration which can be seen for PCBs that are stretched out from PCB 153 down to PCB 28 but also for the alkylphenol NP and the phthalate DEHP. Age and area ratio have some impact in the weaker second component, mainly connected to PCBs. In general, one would assume that age should have a considerable impact on pollutant concentrations in bioretention due to accumulation over time. One reason that this was not corroborated clearly by the PCA is that the evaluated sites all around 10 years old (Table 1), i.e. age had a relatively little variation. If newly-built sites and/or considerably older sites had been included in the study, age would likely have had a clearer impact. The land use did not have a clear impact either. Also here, one reason might be that the variability and number of sites with the different land uses was too small to identify potential impacts. On the other hand, all land uses (urban, road, industry, fuel station) included numerous potential pollutant sources for OMP. From the score plot one can see that different sites have a tendency of clustering with correlation to certain pollutant groups, especially site 6 which is correlated to PCBs.

In the PCA shown in Fig. 6, site 1 was excluded due to the exceptionally high PAH concentrations at that site which indicate that an extraordinary incident had happened there. That site was included in the PCA shown in supplementary Fig. 3.1, where it becomes clear that the site is a statistical outlier (score plot) and correlated to PAHs (loading plot). That specific site affects the results of the PCA, e.g. residential land use is strongly correlated to PAHs since site 1 was located in a residential area.

The Kendall's-tau (τ) correlation test showed significant ($P < 0.01$) correlations between all of the 18 pollutants detected in a high enough proportion of samples for correlations to be tested (see Table S3.1 in Supplementary data). All correlations were strong ($\tau > 0.27$), though stronger correlations were observed within a given pollutant family (i.e. for PAH with PAH and PCB with PCB, τ ranges from 0.61 to 0.90) than between the pollutant families (i.e. for PAH with PCB, PAH with DEHP and PCB with DEHP, τ ranges from 0.27 to 0.53). This finding corroborates the general observation of the PCA (see also loading plot in Fig. 6) where most PCBs, PAHs and

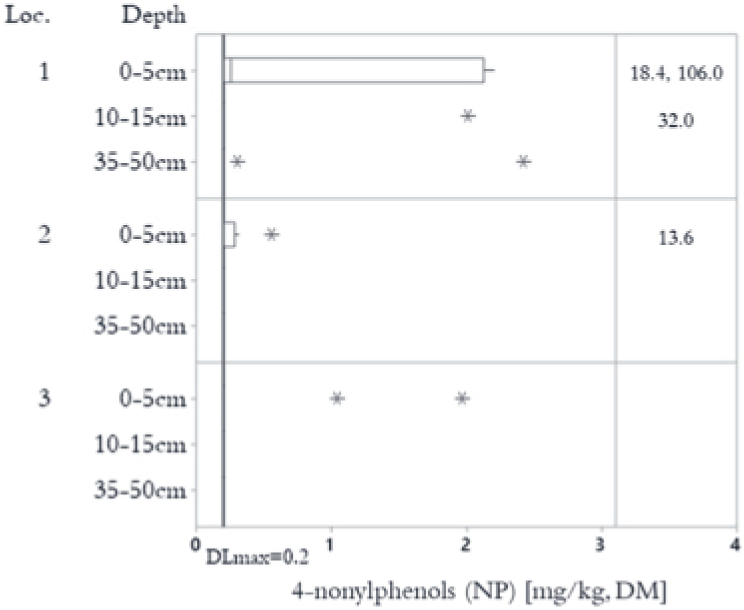

Fig. 5. Boxplot of the alkylphenol 4-nonylphenols (NP). Outliers of greater magnitude are indicated as numbers to the right for easier visualization of boxplots due to the scale.

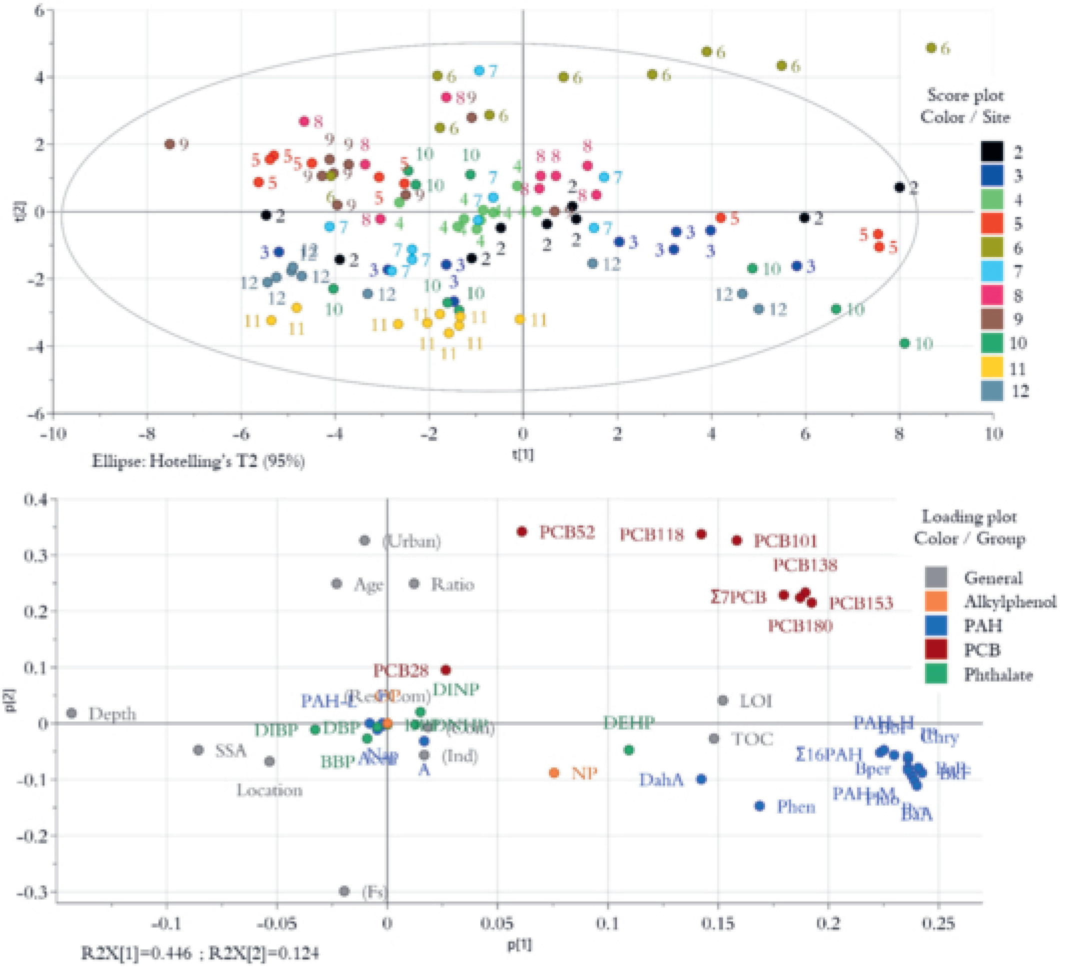

Fig. 6. Score plot (upper) and loading plots (lower) for components 1 and 2. The score plot is colored by site number and the loading plot is colored after the four pollutant groups (alkylphenols, PAHs, PCBs and phthalates) and general parameters. The general parameters include Depth, Specific Surface Area (SSA), Location, Loss On Ignition (LOI), Total Organic Carbon (TOC), Age, Ratio (Filter Area/Catchment Area) and the Land Use parameters Commercial (Com), Industrial (Ind), Down town urban (Urban) and fuel stations (FS). The R^2Xcum = 0.90 (Cumulative X-variation modelled after all seven components) and Q2(cum) = 0.41 (Cumulative overall cross-validated R^2X). R^2X(p1) = 0.446 and R^2X(p2) = 0.124. The model where UV scaled and log transformed (auto transformed on skewed variables). For a PCA including site 1 see Supplementary Fig. 3.1.

DEHP (i.e. the contaminants included in the Kendall's tau-test) are grouped in the same section of the plot, but with specifically strong grouping within the PCB and PAH group.

3.6. Contaminant patterns

The occurrence and concentration patterns of organic contaminants in bioretention filter material are the result of a number of processes, including their emission and mobilization from a given catchment, their retention in the bioretention facility (which depends on their hydrophobicity and solubility), and fate processes occurring in the filter media (biodegradation, volatilization) that may limit their accumulation over time. Hydrophobic compounds are expected to be more readily retained in the filter media than hydrophilic compounds. The compounds studied cover a range from very hydrophobic (log Kow > 6, 5-to-7-ring PAHs, heavy PCBs e.g. PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180 and phthalates e.g. DNOP, DEHP, DCP, DIDP, DINP and DNHP) to moderately hydrophobic (4 < log Kow < 6, 3-to-4-ring PAHs, PCB 28 and PCB 52, phthalates DPP, DIBP, DBP, DNPP and BBP and alkylphenols) and less hydrophobic (log Kow < 4, 2-ring PAHs and phthalates e.g. DMP and DEP).

In the present study, PAH-H and PAH-M were more abundant than PAH-L. Previous studies suggested that high concentrations of PAH-H in runoff could indicate sources such as fossil fuels typically found in high density urban areas (Zgheib et al., 2011a). Studies of organic pollutants in Gothenburg, Sweden also indicated that PAH-H and PAH-M occur in higher concentrations than PAH-L in road and traffic-related runoff (Järlskog et al., 2021; Markiewicz et al., 2017), although they vary over time. The five

PAHs found in the highest concentrations herein (i.e., Fluo, Pyr, Phen, Chry and BbF) were the same as a previous study of 16 PAHs accumulated in the soil of stormwater infiltration facilities (Tedoldi et al., 2017). Heavy PAH molecules are expected to be better retained in filter media since they are more hydrophobic compared to lighter PAHs, they are less soluble, more strongly particle-bound, less biodegradable, and less volatile (Crane, 2014; David et al., 2015; Flanagan et al., 2018; MacKay, 2006a).

Like PAHs, PCBs are highly hydrophobic and often found attached to particles in stormwater (Hwang and Foster, 2008) and are thus effectively treated by bioretention facilities (Gilbreath et al., 2019). PCB concentrations in the bioretention filter media generally followed the order PCB 153 > PCB 138 > PCB 180 > PCB 118 ≈ PCB 101 > PCB 52 > PCB 28. This is similar to the trends observed for particulate concentrations in stormwater in Paris, France by Zgheib et al. (2011a), with the exception of PCB 28, which was much less abundant in the present study. While it is possible that sources of PCBs in the USA and Europe may be different, it may also be explained by the fact that PCB 28 was the least chlorinated of the PCBs in both studies. As the hydrophobicity of PCBs increases with increased chlorination, more chlorinated PCBs tend to be more effectively retained in bioretention facilities than less chlorinated PCBs (David et al., 2015). More chlorinated PCBs are also less biodegradable and less volatile (Mackay, 2006b), making them more susceptible to accumulate within the filter media over time.

While phthalates have been commonly detected in studies of both stormwater (Björklund et al., 2009; Gasperi et al., 2014; Zgheib et al., 2011b) and stormwater pond sediments (Crane, 2019; Flanagan et al., 2021), they were less commonly found in samples of filter material. This may be explained by a decrease in the industrial production and use of phthalates over time (Bergé et al., 2013). According to the PCA no clear trend of phthalate concentration by land use were observed. In addition, due to their more variable hydrophobicity, phthalates are less often found in particulate form in stormwater and are thus less effectively treated in bioretention facilities compared to PAHs (Flanagan et al., 2018). Further, phthalates are more biodegradable than most PAHs and PCBs (Mackay, 2006b), which may decrease their likelihood to accumulate in bioretention facilities over time. DEHP was by far the most frequently detected phthalate in this study. A substance flow analysis of phthalates in an urban catchment showed that DEHP, along with DIDP and DINP, are often present at environmentally relevant concentrations in stormwater (Björklund, 2010). DIDP and DINP were never (i.e., 0 %) and very rarely (6 %) detected in the present study, respectively, likely due to much higher detection limits than those for DEHP (2.5 mg/kg vs. 0.05 mg/kg). Besides its widespread industrial use, the properties of DEHP (i.e., higher hydrophobicity, lower volatility, and lower biodegradability) favor its accumulation in soil as compared with lighter congeners.

Alkylphenols were only rarely detected in the filter media, despite growing evidence illustrating their presence in stormwater (Björklund et al., 2009; Gasperi et al., 2014; Zgheib et al., 2011b). Like phthalates, alkylphenols are less effectively treated in bioretention facilities than PAHs (Flanagan et al., 2018) and are relatively biodegradable as compared with heavy PAHs and PCBs (MacKay, 2006a), which may limit their accumulation in filter media. Nonylphenol was more frequently detected (18 % of samples), and at higher concentrations, than octylphenol (1 % of samples). A major reason for this difference is that nonylphenol ethoxylates have greater industrial use than octylphenol ethoxylates (Bergé et al., 2012). Data from this study adds to previous observations which show concentrations of 4-tert-octylphenol relative to NP in stormwater sediments to be lower in the USA than in Europe (Crane, 2019; Flanagan et al., 2021), possibly reflecting different legislation concerning their use in industrially-produced materials.

Biodegradation, occurring essentially during longer dry periods, is likely to be a major fate process for organic pollutants in biofilters systems that influences the observed contaminant patterns. Indeed, Zhang et al. (2014) performed in-situ column tests on a biofilter system and defined adsorption and biodegradation to be one of the most important treatment processes for organic micropollutants (such as PAHs, phthalates and phenols). However, the present study, which focused on the occurrence and concentrations of pollutants in filter material, does not allow biodegradation to be quantified, both due to the lack of information on the pollutant loads associated with runoff entering and exiting each system and due to the significant uncertainties associated with calculations of pollutant mass accumulated in the filter media of such systems (Flanagan et al., 2019).

3.7. Intra-site variability

The general behavior between the studied groups of pollutants (PAHs, PCBs, phthalates and alkylphenols) is similar in that occurrence frequencies and concentrations are generally higher in the top layers of the filters and decrease rapidly with increased depth from the surface. PAHs and PCBs in stormwater are often associated with suspended solids, (LeFevre et al., 2015; Marsalek et al., 1997; Hwang and Foster, 2008) and are similar to other particle-bound pollutants which are primarily removed in the surface layers through sedimentation and filtration of particles (Blecken et al., 2009b). Alkylphenols and phthalates may have more variable speciation in stormwater, making them more mobile in bioretention facilities (Flanagan et al., 2018), and in turn result in lower concentrations of these pollutants near the surface. In contrast, these compounds have been shown to accumulate in filter media below the surface in a 1-yr-old biofiltration facility, likely due to emissions from construction materials (Flanagan et al., 2019). However, there is no evidence of subsurface accumulation in the present study, which may indicate that such emissions did not occur in the studied facilities or that the emitted contaminants degraded over the 7–13 years of operation since the construction of the facilities studied in this research.

There was an observed trend, albeit not statistically significant, of concentrations and occurrence frequencies being higher close to the inlets and decreasing with increased distance from the inlets. This trend was most obvious in the top layer and less marked than the trend with depth variation. The variation of occurrence and concentration with increased distance from the inlet could be explained as a combination of the effect of pollutants being mainly particle-bound and the long-term effects of filter hydrology and many smaller rainfall events causing a higher pollutant load closer to the inlets (Al-Ameri et al., 2018) and, therefore, also higher pollutant accumulation.

3.8. Inter-site variability

There was a large variation in concentrations between the materials analysed from different sites. This may be the result of different catchment characteristics, the ratio of catchment area to filter area, and land use that contribute different pollutant types and loads (Cao et al., 2019; Crane, 2019). However, the PCA did not show a clear impact of land use and catchment/biofilter ratio on pollutant concentrations. Given the few sites within each land use, variations within each land use group may have contributed to that result.

When considering local and site-specific characteristics, very high concentrations of PAHs at all depths and locations were observed at one site (site 1, Table 1) compared to all other sites. The median concentration of PAH16 in the samples from the outlier site was 410 mg/kg, 273-fold larger than the median PAH16 concentration for the other 11 sites (1.5 mg/kg). Similarly, the difference between site 1 and the other sites was extreme for PAH-M (250 mg/kg compared to 0.57 mg/kg), PAH-H (150 mg/kg compared to 1.3 mg/kg), and PAH-L (4 mg/kg compared to 0.15 mg/kg). These concentrations of PAHs (for example, 186 mg/kg fluoranthene, 138 mg/kg of pyrene and 127 mg/kg of phenanthrene) are very high for samples from a bioretention facility (DiBlasi et al., 2009; Tedoldi et al., 2017), and are also in the range of what would be considered highly PAH-polluted soil. However, no clear explanation was found for the high concentrations at that specific site. In general, the catchment area did not obviously vary from other catchments included in this study. According to the bioretention operator (City of Columbus), possible reasons could be a major car accident that occurred in this area, repaving a stretch of the road or illicit discharge of motor oil.

3.9. Practical implications

Observed PAH-H, PAH-M and PAH-L concentrations were compared with the Swedish guidelines for pollutant concentrations related to soil classification (Swedish EPA, 2009). In that comparison, PAH-H show the greatest exceedance of "soil for sensitive land use" (KM) as compared with PAH-M and PAH-L. It can be seen in Fig. 2 that the PAH-H concentrations are frequently above the limits for KM ($KM_{PAH\text{-}H}$ = 1 mg/kg) and also sometimes above limits for soil classified as "soil for less sensitive land use" (MKM; $MKM_{PAH\text{-}H}$ = 10 mg/kg). Concentrations above the relevant MKM level are classified as hazardous waste (FA) and need certified transportation and disposal at licensed landfill sites. However, concentrations above MKM were mostly present in the upper layer (with a depth 0–5 cm) except for few outliers, where the concentrations were above MKM in the 10–15 cm deep layer, close to the inlet.

Most organic pollutants were generally found in the upper 5 cm of the filter material. This has critical implications for bioretention operators. Removing only the top layer of media periodically may be all that is necessary to ensure that the entire filter media does not saturate and result in discharge of OMPs. Similar guidance has been suggested concerning heavy metals and PAHs (e.g. Al-Ameri et al., 2018; Blecken et al., 2011; Tedoldi et al., 2017). The top media layer is likely to retain the most pollutants and should be managed and prioritized accordingly. Also, the majority of sediment is trapped in that top layer and thus removing it will likely also restore the infiltration capacity of the filter in the event its saturated hydraulic conductivity has decreased due to clogging. According to (Al-Ameri et al., 2018) clogging is more likely to be the limiting factor for bioretention's long term functionality than contamination with high concentrations of pollutants (Al-Ameri et al., 2018) and his study confirms that this could be the case. If the whole filter media needs to be replaced, then it is reasonable to consider managing the filter material close to the surface (which may have to be treated as dangerous waste) differently from material farther below the surface.

Given that most evaluated contaminants in this and other studies (e.g. DiBlasi et al., 2009) were retained in the surface layer of the filters (top 0–10 cm), one could argue that a relatively shallow design filter depth (around 10–20 cm) would be sufficient to ensure pollutant removal. However, other organic micropollutants need to be investigated. While this study mainly focused on particle-bound organic pollutants, studies show that dissolved pollutants (e.g. metals, nutrients) can migrate further down in the system or require a deeper filter depth for sufficient treatment. For instance, Davis et al. (2006) suggested filter depths of 60–80 cm for sufficient removal of nitrogen species and phosphorus. Another relevant factor concerning filter depth is vegetation. Commonly, roots require greater filter depths than 10–20 cm. In summary, the filter depth is not only determined by the removal of particulate or easily adsorbed pollutants, but also other factors.

3.10. Further studies

Further work regarding the long-term function and maintenance needs of bioretention systems is required to better understand the accumulation and distribution of OMPs and other pollutants, both particle-bound and dissolved, in these facilities. Studies which can include a wider age variation than that in the present study could reveal more information on the pollutant accumulation trends which can be expected over the lifetime of these systems, although this likely differs largely depending on site-specific parameters. The impact of different filter materials (e.g., varying particle size distribution, varying composition, use of amendments) should be further explored. Given varying national/regional regulations, use of building materials etc., further studies should also include samples from other countries to capture the geographic variability in these pollutants as well as geographical ambient variations such as temperature, humidity and variation in precipitation hydrographs. Results from field studies are always to some extent site-specific and cannot readily be translated to other geographic locations. Finally, the biodegradation of organic pollutants can involve the formation of potentially-toxic degradation products, which should be a subject of future research.

4. Conclusions

The OMPs included in this study (16 PAHs, 7 PCBs, 13 phthalates and 2 alkylphenols) were commonly found in the filter material of the twelve bioretention facilities across Michigan and Ohio (USA) aged 7–13 years. In total, 32 of the 38 analytes were detected in at least one of the filter material samples while six substances (five phthalates and one PAH) were never detected. The most frequently detected pollutants in the study were PAHs and PCBs, while phthalates and alkylphenols were less frequently detected. Very large variations between the different bioretention sites were observed, most likely due to differences in pollutant sources. In general, the concentrations of most studied OMPs were highest in the upper 5 cm of the filter material and decreased with increased depth in the filter. Further, the highest concentrations tended to be found near the inlet of the facilities and decreased as sample locations increased in distance from the inlet. The overall trend of decreasing concentrations with depth and distance from the inlet are similar for all four studied groups of OMPs (PAHs, PCBs, phthalates, and alkylphenols). Since the results in this study of the behaviors of particle-bound OMPs show similarities in pathways and accumulation with other studies of particle bound pollutants, such as metals, there are likely similarities in long term performance and maintenance needs. Regularly replacing only the top layer of the filter may be all that is necessary to ensure that the entire filter function can be restored, as similarly suggested earlier for metal accumulation and clogging. Safe disposal of polluted filter material must be ensured and, thus, OMP concentrations should be analysed to allow an environmental assessment of the material.

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CRediT authorship contribution statement

Robert Furén: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data curation, Writing – original draft. **Kelsey Flanagan:** Methodology, Formal analysis, Resources, Data curation, Writing – review & editing. **Ryan J. Winston:** Conceptualization, Methodology, Investigation, Resources, Writing – review & editing, Supervision. **R. Andrew Tirpak:** Methodology, Investigation, Resources, Writing – review & editing. **Jay D. Dorsey:** Methodology, Investigation, Resources, Writing – review & editing. **Maria Viklander:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Godecke-Tobias Blecken:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

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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References

Al-Ameri, M., Hatt, B., Le Coustumer, S., Fletcher, T., Payne, E., Deletic, A., 2018. Accumulation of heavy metals in stormwater bioretention media: a field study of temporal and spatial variation. J. Hydrol. 567, 721–731. https://doi.org/10.1016/j.jhydrol.2018.03.027.

Barbosa, A.E., Fernandes, J.N., David, L.M., 2012. Key issues for sustainable urban stormwater management. Water Res. 46, 6787–6798. https://doi.org/10.1016/j.watres.2012.05.029.

Bergé, A., Cladière, M., Gasperi, J., Coursimault, A., Tassin, B., Moilleron, R., 2013. Meta-analysis of environmental contamination by phthalates. Environ. Sci. Pollut. Res. 20, 8057–8076. https://doi.org/10.1007/s11356-013-1982-5.

Bergé, A., Cladière, M., Gasperi, J., Coursimault, A., Tassin, B., Moilleron, R., 2012. Meta-analysis of environmental contamination by alkylphenols. Environ. Sci. Pollut. Res. 19, 3798–3819. https://doi.org/10.1007/s11356-012-1094-7.

Biswal, B.K., Vijayaraghavan, K., Adam, M.G., Lee Tsen-Tieng, D., Davis, A.P., Balasubramanian, R., 2022. Biological nitrogen removal from stormwater in bioretention cells: a critical review. Crit. Rev. Biotechnol. 42, 713–735. https://doi.org/10.1080/07388551.2021.1969888.

Björklund, K., 2010. Substance flow analyses of phthalates and nonylphenols in stormwater. Water Sci. Technol. 62, 1154. https://doi.org/10.2166/wst.2010.923.

Björklund, K., Cousins, A.P., Strömvall, A.-M., Malmqvist, P.-A., 2009. Phthalates and nonylphenols in urban runoff: occurrence, distribution and area emission factors. Sci. Total Environ. 407, 4665–4672. https://doi.org/10.1016/j.scitotenv.2009.04.040.

Björklund, K., Li, L., 2017. Removal of organic contaminants in bioretention medium amended with activated carbon from sewage sludge. Environ. Sci. Pollut. Res. 24, 19167–19180. https://doi.org/10.1007/s11356-017-9508-1.

Blecken, G.-T., Marsalek, J., Viklander, M., 2011. Wat. Air Soil Poll.

Blecken, G.-T., Zinger, Y., Deletić, A., Fletcher, T.D., Viklander, M., 2009a. Impact of a submerged zone and a carbon source on heavy metal removal in stormwater biofilters. Ecol. Eng. 35, 769–778. https://doi.org/10.1016/j.ecoleng.2008.12.009.

Blecken, G.-T., Zinger, Y., Deletić, A., Fletcher, T.D., Viklander, M., 2009b. Influence of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters. Water Res. 43, 4590–4598. https://doi.org/10.1016/j.watres.2009.07.008.

Brown, J.N., Peake, B.M., 2006. Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. Sci. Total Environ. 359, 145–155. https://doi.org/10.1016/j.scitotenv.2005.05.016.

BS ISO, 2010. BS ISO 9277:2010 Determination of the specific surface area of solids by gas adsorption. BET method. [WWW Document]. URL https://www.en-standard.eu/bs-iso-9277-2010-determination-of-the-specific-surface-area-of-solids-by-gas-adsorption-bet-method/.

Cao, S., Capozzi, S.L., Kjellerup, B.V., Davis, A.P., 2019. Polychlorinated biphenyls in stormwater sediments: relationships with land use and particle characteristics. Water Res. 163, 114865. https://doi.org/10.1016/j.watres.2019.114865.

Crane, J.L., 2019. Distribution, toxic potential, and influence of land use on conventional and emerging contaminants in urban stormwater pond sediments. Arch. Environ. Contam. Toxicol. 76, 265–294. https://doi.org/10.1007/s00244-019-00598-w.

Crane, J.L., 2014. Source apportionment and distribution of polycyclic aromatic hydrocarbons, risk considerations, and management implications for urban stormwater pond sediments in Minnesota, USA. Arch. Environ. Contam. Toxicol. 66, 176–200. https://doi.org/10.1007/s00244-013-9963-8.

CSN, 2009. ČSN 72 0103 (720103) Základní postup rozboru silikátů - Stanovení ztráty žíháním (Basic procedure for the analysis of silicates - determination of loss by annealing). [WWW Document]. URL https://www.technicke-normy-csn.cz/csn-72-0103-720103-218183.html.

CSN, 1991. ČSN 46 5735 (465735) Průmyslové komposty (CSN 46 5735 (465735) Industrial composts). [WWW Document]. URL https://www.technicke-normy-csn.cz/csn-46-5735-465735-206692.html.

CSN EN, 2018. ČSN EN 13137 (838021) Charakterizace odpadů - Stanovení celkového organického uhlíku (TOC) v odpadech, kalech a sedimentech (Waste characterisation - determination of total organic carbon (TOC) in waste, sludge and sediment). [WWW Document]. URL https://www.technicke-normy-csn.cz/csn-en-13137-838021-231701.html.

CSN EN, 2014. ČSN EN 12879 (758005) Sludge characterization - determination of loss by annealing (sludge characterization - determination of loss by annealing). [WWW Document]. URL https://www.technicke-normy-csn.cz/csn-en-12879-758005-226751.html.

CSN ISO, 1995. ISO 10694:1995 Soil quality — determination of organic and total carbon after dry combustion (elementary analysis). [WWW Document]. URL https://www.iso.org/standard/18782.html.

David, N., Leatherbarrow, J.E., Yee, D., McKee, L.J., 2015. Removal efficiencies of a bioretention system for trace metals, PCBs, PAHs, and dioxins in a semiarid environment. J. Environ. Eng. 141, 04014092. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000921.

Davis, A.P., Hunt, W.F., Traver, R.G., Clar, M., 2009. Bioretention technology: overview of current practice and future needs. J. Environ. Eng. 135, 109–117. https://doi.org/10.1061/(ASCE)0733-9372(2009)135:3(109).

Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., 2006. Water quality improvement through bioretention media: nitrogen and phosphorus removal. Water Environ. Res. 78, 284–293. https://doi.org/10.2175/106143005X94376.

DiBlasi, C.J., Li, H., Davis, A.P., Ghosh, U., 2009. Removal and fate of polycyclic aromatic hydrocarbon pollutants in an urban stormwater bioretention facility. Environ. Sci. Technol. 43, 494–502. https://doi.org/10.1021/es802090g.

DIN ISO, 2002. Soil quality - determination of organochlorine pesticides and polychlorinated biphenyls - gas-chromatographic method with electron capture detection (ISO 10382:2002). [WWW Document]. URL https://www.iso.org/standard/32422.html.

E DIN, 2014. DIN 19742:2014-08 Soil quality - determination of selected phthalates in sludge, sediment, solid waste and soil after extraction and determination by mass spectrometric gas chromatography (GC-MS). [WWW Document]. URL https://www.beuth.de/de/norm/din-19742/207273179.

Fent, K., 2003. Ecotoxicological problems associated with contaminated sites. Toxicol. Lett. 140–141, 353–365. https://doi.org/10.1016/S0378-4274(03)00032-8.

Flanagan, K., Blecken, G.-T., Österlund, H., Nordqvist, K., Viklander, M., 2021. Contamination of urban stormwater pond sediments: a study of 259 legacy and contemporary organic substances. Environ. Sci. Technol. 55, 3009–3020. https://doi.org/10.1021/acs.est.0c07782.

Flanagan, K., Branchu, P., Boudahmane, L., Caupos, E., Demare, D., Deshayes, S., Dubois, P., Meffray, L., Partibane, C., Saad, M., Gromaire, M.-C., 2019. Retention and transport processes of particulate and dissolved micropollutants in stormwater biofilters treating road runoff. Sci. Total Environ. 656, 1178–1190. https://doi.org/10.1016/j.scitotenv.2018.11.304.

Flanagan, K., Branchu, P., Boudahmane, L., Caupos, E., Demare, D., Deshayes, S., Dubois, P., Meffray, L., Partibane, C., Saad, M., Gromaire, M.-C., 2018. Field performance of two biofiltration systems treating micropollutants from road runoff. Water Res. 145, 562–578. https://doi.org/10.1016/j.watres.2018.08.064.

Fletcher, T.D., Shuster, W., Hunt, W.F., Ashley, R., Butler, D., Arthur, S., Trowsdale, S., Barraud, S., Semadeni-Davies, A., Bertrand-Krajewski, J.-L., Mikkelsen, P.S., Rivard, G., Uhl, M., Dagenais, D., Viklander, M., 2015. SUDS, LID, BMPs, WSUD and more – the evolution and application of terminology surrounding urban drainage. Urban Water J. 12, 525–542. https://doi.org/10.1080/1573062X.2014.916314.

Gasperi, J., Sebastian, C., Ruban, V., Delamain, M., Percot, S., Wiest, L., Mirande, C., Caupos, E., Demare, D., Kessoo, M.D., Saad, M., Schwartz, J.J., Dubois, P., Fratta, C., Wolff, H., Moilleron, R., Chebbo, G., Cren, C., Millet, M., Barraud, S., C Gromaire, M., 2014. Micropollutants in urban stormwater: occurrence, concentrations, and atmospheric contributions for a wide range of contaminants in three French catchments. Environ. Sci. Pollut. Res. 21, 5267–5281. https://doi.org/10.1007/s11356-013-2396-0.

Gilbreath, A., McKee, L., Shimabuku, I., Lin, D., Werbowski, L.M., Zhu, X., Grbic, J., Rochman, C., 2019. Multiyear water quality performance and mass accumulation of PCBs, mercury, methylmercury, copper, and microplastics in a bioretention rain garden. J. Sustain. Water Built Environ. 5, 04019004. https://doi.org/10.1061/JSWBAY.0000883.

Helmfrid, I., Berglund, M., Löfman, O., Wingren, G., 2012. Health effects and exposure to polychlorinated biphenyls (PCBs) and metals in a contaminated community. Environ. Int. 44, 53–58. https://doi.org/10.1016/j.envint.2012.01.009.

Helsel, D.R., 2012. Statistics for censored environmental data using Minitab and R. Wiley Series in Statistics in Practice, 2nd ed. Wiley, Hoboken, N.J.

Hsieh, C.-H., Davis, A.P., 2005. Multiple-event study of bioretention for treatment of urban storm water runoff. Water Sci. Technol. 51, 177–181. https://doi.org/10.2166/wst.2005.0589.

Hwang, H.-M., Foster, G.D., 2008. Polychlorinated biphenyls in stormwater runoff entering the tidal Anacostia River, Washington, DC, through small urban catchments and combined sewer outfalls. J. Environ. Sci. Health A 43, 567–575. https://doi.org/10.1080/10934520801893527.

ISO, 2006. Soil quality — determination of polycyclic aromatic hydrocarbons (PAH) — gas chromatographic method with mass spectrometric detection (GC-MS). [WWW Document]. URL https://www.iso.org/standard/33387.html.

Järlskog, I., Strömvall, A.-M., Magnusson, K., Galfi, H., Björklund, K., Polukarova, M., Garção, R., Markiewicz, A., Aronsson, M., Gustafsson, M., Norin, M., Blom, L., Andersson-Sköld, Y., 2021. Traffic-related microplastic particles, metals, and organic pollutants in an urban area under reconstruction. Sci. Total Environ. 774, 145503. https://doi.org/10.1016/j.scitotenv.2021.145503.

Jones, P.S., Davis, A.P., 2013. Spatial accumulation and strength of affiliation of heavy metals in bioretention media. J. Environ. Eng. 139, 479–487. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000624.

Lamprea, K., Bressy, A., Mirande-Bret, C., Caupos, E., Gromaire, M.-C., 2018. Alkylphenol and bisphenol A contamination of urban runoff: an evaluation of the emission potentials of various construction materials and automotive supplies. Environ. Sci. Pollut. Res. 25, 21887–21900. https://doi.org/10.1007/s11356-018-2272-z.

LeFevre, G.H., Hozalski, R.M., Novak, P.J., 2012. The role of biodegradation in limiting the accumulation of petroleum hydrocarbons in raingarden soils. Water Res. 46, 6753–6762. https://doi.org/10.1016/j.watres.2011.12.040.

LeFevre, G.H., Paus, K.H., Natarajan, P., Gulliver, J.S., Novak, P.J., Hozalski, R.M., 2015. Review of dissolved pollutants in urban storm water and their removal and fate in bioretention cells. J. Environ. Eng. 141, 04014050. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000876.

Li, H., Davis, A.P., 2008. Environ. Sci. Tech. https://doi.org/10.1021/es702681j.

MacKay, D., 2006. 2nd ed. CRC/Taylor & Francis, Boca Raton, Fla rev. ed. ed.

Mackay, D. (Ed.), 2006. Handbook of Physical-chemical Properties And Environmental Fate for Organic Chemicals, 2nd ed. CRC/Taylor & Francis, Boca Raton, Fla rev. ed. ed.

Makepeace, D.K., Smith, D.W., Stanley, S.J., 1995. Urban stormwater quality: Summary of contaminant data. Crit. Rev. Environ. Sci. Technol. 25 (2), 93–193. https://doi.org/10.1080/10643389509388476.

Markiewicz, A., Björklund, K., Eriksson, E., Kalmykova, Y., Strömvall, A.-M., Siopi, A., 2017. Emissions of organic pollutants from traffic and roads: priority pollutants selection and substance flow analysis. Sci. Total Environ. 580, 1162–1174. https://doi.org/10.1016/j.scitotenv.2016.12.074.

Markiewicz, A., Strömvall, A.-M., Björklund, K., 2020. Alternative sorption filter materials effectively remove non-particulate organic pollutants from stormwater. Sci. Total Environ. 730, 139059. https://doi.org/10.1016/j.scitotenv.2020.139059.

Marsalek, J., Brownlee, B., Mayer, T., Lawal, S., Larkin, G.A., 1997. Heavy metals and PAHs in stormwater runoff from the skyway bridge, Burlington, Ontario. Water Qual. Res. J. 32, 815–828. https://doi.org/10.2166/wqrj.1997.044.

Masoner, J.R., Kolpin, D.W., Cozzarelli, I.M., Barber, L.B., Burden, D.S., Foreman, W.T., Forshay, K.J., Furlong, E.T., Groves, J.F., Hladik, M.L., Hopton, M.E., Jaeschke, J.B., Keefe, S.H., Krabbenhoft, D.P., Lowrance, R., Romanok, K.M., Rus, D.L., Selbig, W.R., Williams, B.H., Bradley, P.M., 2019. Urban stormwater: an overlooked pathway of extensive mixed contaminants to surface and groundwaters in the United States. Environ. Sci. Technol. 53, 10070–10081. https://doi.org/10.1021/acs.est.9b02867.

Mastrangelo, G., Fadda, E., Marzia, V., 1996. Polycyclic aromatic hydrocarbons and cancer in man. Environ. Health Perspect. 104, 1166–1170. https://doi.org/10.1289/ehp.961041166.

Müller, A., Österlund, H., Marsalek, J., Viklander, M., 2020. The pollution conveyed by urban runoff: a review of sources. Sci. Total Environ. 709, 136125. https://doi.org/10.1016/j.scitotenv.2019.136125.

Pitt, R., Clark, S., Parmer, K., 1994. Potential Groundwater Contamination From Intentional And Nonintentional Stormwater Infiltration. University of Alabama at Birmingham.

Smith, J.A., Sievers, M., Huang, S., Yu, S.L., 2000. Occurrence and phase distribution of polycyclic aromatic hydrocarbons in urban storm-water runoff. Water Sci. Technol. 42, 383–388. https://doi.org/10.2166/wst.2000.0407.

Søberg, L.C., Al-Rubaei, A.M., Viklander, M., Blecken, G.-T., 2020. Phosphorus and TSS removal by stormwater bioretention: effects of temperature, salt, and a submerged zone and their interactions. Water Air Soil Pollut. 231, 270. https://doi.org/10.1007/s11270-020-04646-3.

Søberg, L.C., Winston, R., Viklander, M., Blecken, G.-T., 2019. Dissolved metal adsorption capacities and fractionation in filter materials for use in stormwater bioretention facilities. Water Res. X 4, 100032. https://doi.org/10.1016/j.wroa.2019.100032.

Stockholm Convention, 2008. URL http://chm.pops.int/TheConvention/ThePOPs/The12InitialPOPs/tabid/296/Default.aspx (accessed 12.21.21).

Swedish EPA, 2009. Riktvärden för förorenad mark Modellbeskrivning och vägledning (Naturvårdsverket publikation No. 5976) Sweden.

Tedoldi, D., Chebbo, G., Pierlot, D., Kovacs, Y., Gromaire, M.-C., 2017. Assessment of metal and PAH profiles in SUDS soil based on an improved experimental procedure. J. Environ. Manag. 202, 151–166. https://doi.org/10.1016/j.jenvman.2017.06.063.

Tedoldi, D., Chebbo, G., Pierlot, D., Kovacs, Y., Gromaire, M.-C., 2016. Impact of runoff infiltration on contaminant accumulation and transport in the soil/filter media of Sustainable Urban Drainage Systems: a literature review. Sci. Total Environ. 569–570, 904–926. https://doi.org/10.1016/j.scitotenv.2016.04.215.

Walsh, C.J., Roy, A.H., Feminella, J.W., Cottingham, P.D., Groffman, P.M., Morgan, R.P., 2005. The urban stream syndrome: current knowledge and the search for a cure. J. N. Am. Benthol. Soc. 24, 706–723. https://doi.org/10.1899/04-028.1.

Zgheib, S., Moilleron, R., Saad, M., Chebbo, G., 2011a. Partition of pollution between dissolved and particulate phases: what about emerging substances in urban stormwater catchments? Water Res. 45, 913–925. https://doi.org/10.1016/j.watres.2010.09.032.

Zgheib, S., Moilleron, R., Saad, M., Chebbo, G., 2011b. Partition of pollution between dissolved and particulate phases: what about emerging substances in urban stormwater catchments? Water Res. 45, 913–925. https://doi.org/10.1016/j.watres.2010.09.032.

Zhang, K., Randelovic, A., Page, D., McCarthy, D.T., Deletic, A., 2014. The validation of stormwater biofilters for micropollutant removal using in situ challenge tests. Ecol. Eng. 67, 1–10. https://doi.org/10.1016/j.ecoleng.2014.03.004.

Paper II

R. Furén, H. Österlund, R. J. Winston, R. A. Tirpak, J. D. Dorsey, M. Viklander, G.-T. Blecken

Concentration, distribution, and fractionation of metals in the filter material of 29 bioretention facilities: A field study

Concentration, distribution, and fractionation of metals in the filter material of 29 bioretention facilities: A field study

R. Furén, H. Österlund, R. J. Winston, R. A. Tirpak, J. D. Dorsey, M. Viklander, G.-T. Blecken

Abstract

Pollutant loads stemming from anthropogenic activities conveyed in urban stormwater runoff contribute to the impairment of downstream water bodies. Cities and municipalities are increasingly turning toward green infrastructure stormwater control measures to treat pollutants at the source of runoff. One example of these technologies is bioretention, which is commonly applied for stormwater treatment in urban areas due to its demonstrated effectiveness in removing various pollutants from water, including sediment, nutrients (e.g., N and P), and metals. As metals are mainly removed by filtration or adsorption to soil particles, the filter media is important for metal removal in bioretention. However, the capacity to remove metals through adsorption by bioretention media is finite; thus, the media may need to be replaced and disposed of after maintenance or at the end of its operational lifespan. Pollutant accumulation in bioretention media has the potential to approach toxicity thresholds, which may introduce complexities for safe handling and disposal. To fully capture the potential challenges associated with metals accumulation in media over time, it is important to understand the accumulation processes and mobility of metals in bioretention facilities as they age. Although several studies have investigated metal accumulation and distribution in bioretention media, few have assessed metal mobility by fractionation using sequential extraction methods in older (i.e., >7 years) facilities. In November 2019, we conducted a comprehensive field study of older facilities in Ohio, Michigan, and Kentucky (USA) to improve the understanding of the accumulation processes and metal mobility in bioretention. In this study, concentrations of several metals (i.e., Cr, Cu, Ni, Pb, and Zn) were analyzed in samples of filter material from 29 bioretention sites in operation for 7-16 years. Except for Cd, all metals were found in all samples. Metals accumulation was clear with highest concentrations found in the top (0-5 cm) layer of the filter material, attributable to the filtration of particles percolating through the media profile. Lower concentrations were observed in deeper (i.e., >10cm) layers of the bioretention media. The fractionation showed that the metals of interest were present at high levels with a risk of leaching over time, among which Cd, Zn, and Pb were suggested to be mobile from the filter material during precipitation. There was also at a potential risk of leaching from filter material or sediments if removed from the bioretention sites during e.g., maintenance. The results of principal component analysis indicated correlations between the metal concentration and the ratio of catchment to filter area and watershed land use. These results assist improved design and operation and suggest regular maintenance and to reduce long-term risks associated with metal accumulation in bioretention or similar facilities for urban stormwater treatment. Since most metals are trapped in the top layer of the filter it may be enough to remove only the top layer. However, metal fractionation should be considered when handling the material.

Introduction

Urban stormwater runoff conveys significant loads of anthropogenic pollutants which lead to the impairment of receiving waters (Müller et al., 2020). Metals (e.g., Cd, Cu, Pb, Zn) are commonly regarded as pollutants of concern in stormwater that contribute to the degradation of aquatic habitats (Göbel et al., 2007). The Nationwide Urban Runoff Program (US EPA, 1983) identified metals, especially Cu, Pb, and Zn, as being toxic in road runoff, while Cd, Cr, Cu, Ni, Pb, and Zn have been identified as contaminants of concern for human and aquatic life in stormwater (Eriksson et al., 2007). Thus, stormwater should be treated to remove metals before being discharged to surface waters (Barbosa et al., 2012).

Bioretention is a commonly applied low impact development practice for stormwater treatment in urban areas (Johnson and Hunt, 2020; Kratky et al., 2017; McGrane, 2016). In these systems, also referred to as biofilters, biofiltration systems or raingardens, stormwater from a contributing watershed is treated vertically through a filter before being released to downstream systems. Bioretention typically consists of a filter media of sand, silt, clay, and organic matter and/or soil often topped with mulch and/or topsoil and planted with a variety of plant species and drained by an underdrain pipe (Figure 1) (Lange et al., 2020b; LeFevre et al., 2015; Tirpak et al., 2021). Research has demonstrated that bioretention provides effective removal of various pollutants such as total suspended solids and metals (Blecken et al., 2009). As most metals are removed by filtration or adsorption to soil particles (Blecken et al., 2009), the filter media is critically important for metal removal in bioretention. Bioretention normally has a filter depth of 0.7-1 m (Davis et al., 2009), although metals are primarily trapped in the upper (0-10 cm) media layers in a fast adsorption process (Al-Ameri et al., 2018; Li and Davis, 2008; Søberg et al., 2019). This has implications for bioretention maintenance, wherein media could potentially become contaminated such that disposal becomes more difficult and costly. Davis et al. (2003) estimated that regulatory limits for biosolids application in the top layer could be reached after 20, 77, 16, and 16 years of bioretention operation for Cd, Cu, Pb, and Zn, respectively (U.S. EPA, 1993). Moreover, based on laboratory results, Hatt et al. (2011) estimated a life span of 12–15 years of operation before the levels of Cd, Cu, and Zn in filter material would exceed guideline values (NEPC, 1999) for human and ecological health and would require special disposal. Al-Ameri et al. (2018) found for highly polluted catchment areas (e.g., industrial areas) that filter material after 9–16 years of operation had high Zn concentrations (Zn >200 mg/kg) and could be classified as contaminated material according to the Victorian EPA criteria's for classification of waste (EPA Victoria, 2007), meaning it would require special disposal if removed. Al-Ameri et al. (2018) also suggested that clogging (e.g., reduced hydraulic function) may be the primary limit to bioretention function for less contaminated areas, rather than high concentrations of metals.

Pollutants captured in the filter material create a pollutant depot (Davis et al., 2003) which carries a risk of metal leaching. To mitigate leaching, Kluge et al. (2018) recommend removal of the top 10 cm of the filter media (with accumulated sediments and associated metals) and replacement after 20-25 years. Further, there is a potential risk of leaching when disposing removed filter material from bioretention. It is essential to better understand the characteristics and behaviors of accumulated metals in the filter media to evaluate and reduce associated risks during the bioretention lifespan or when material is removed during maintenance or decommissioning. Metal fractionation by sequential extraction is one method that can provide information about the mobility and leachability of metals from filter material and may support the evaluation of the risk of metal release during operation, maintenance, and disposal. Other studies (Al-Ameri et al., 2018; Costello et al., 2020; Johnson and Hunt, 2016) have examined metal behavior in bioretention; however, only a few have assessed the availability of metals in *mature* bioretention facilities using sequential extraction methods.

Many previous studies on bioretention have used the sequential extraction method; indeed, Wang et al., (2016) used the sequential extraction method to study Cd in a laboratory-scale bioretention column experiment, while Søberg et al., (2019) used the same method to evaluate the characteristics of adsorbed dissolved metals on different bioretention filter materials. In field-scale bioretention, Li and Davis, 2008 and Jones and Davis (2013) used a five step sequential extraction when studying a quantitative theory for metal capture (Cu, Pb, and Zn) and to evaluate the environmental availability of metals. A recent study by Rommel et al., (2021) involved the use of sequential extraction to assess the mobility of metals (Cr, Cu, Ni, and Zn) in road run-off from roadside bioretention cells. However, the large sample size of this study, which involved field sampling of 29 older (7-16 years of operation) bioretention sites, laboratory analyses of total concentrations and a 5-step sequential extraction of six metals (Cd, Cr, Cu, Ni, Pb, and Zn) make these results and conclusions more impactful as it relates to the potential to glean design and maintenance recommendations for bioretention systems.

Here, we conducted a major field study to increase the knowledge surrounding metal mobility and availability and to improve the understanding and risks associated with metal release from bioretention filter material. The study included filter media sampling and lab analyses of Cd, Cr, Cu, Ni, Pb, and Zn, including fractionation by sequential extraction. The results will assist with improving filter design, operation, and maintenance, which will serve to reduce the long-term risks associated with accumulated metals in bioretention or similar facilities in the context of urban stormwater treatment.

Method

Field sites

Metals accumulation was studied in 29 bioretention facilities, mainly those treating runoff from urban catchments with different land use characteristics, including parking lots, roads, downtown urban areas, and industrial, commercial, and residential areas. The bioretention facilities were located in Ohio, Michigan, and Kentucky (USA). They varied in age from 7 to 16 years old at the time of sampling (2019) and the filter surface areas ranged from approximately 10 m^2 to 1900 m^2. The contributing catchment areas varied in size from approximately 50 m^2 to 125 ha, which results in a variation in the ratio of the filter areas and catchment areas of 0.1% to 20%. The weather and climate in these areas are described as hot-summer humid continental, humid subtropical, and warm-summer humid continental climate with annual precipitation roughly around 760 mm to 1100 mm. Further details are presented in Table 1.

Table 1. Bioretention site characteristics. Ratio is the filter area in percentage of the corresponding catchment area. The site age was the age at sampling in November 2019. Site map in supplementary Figure 1.

Site	Age [yr]	Location	Catchment area usage	Catchment area [m²]	Filter area [m²]	Ratio [%]
1	9	Upper Arlington, OH	Residential	318000	950	0.3
2	9	Upper Arlington, OH	Residential	1250000	1200	0.1
3	9	Upper Arlington, OH	Residential	224000	900	0.4
4	9	Upper Arlington, OH	Residential	146000	1900	1.3
5	8	Upper Arlington, OH	Commercial	750	40	5.3
6	10	Columbus, OH	Industrial	6000	300	5.0
7	8	Westerville, OH	Parking/roads	12000	600	5.0
8	8	Westerville, OH	Parking/roads	2000	50	2.5
9	7	Westerville, OH	Commercial	4000	170	4.3
10	9	Columbus, OH	Parking/roads	4500	580	13
11	9	Columbus, OH	Downtown urban	300	40	13
12	8	Columbus, OH	Downtown urban	50	10	20
13	12	Hamilton, OH	Industrial	4500	200	4.4
14	12	Hamilton, OH	Industrial	4500	300	6.7
15	12	Hamilton, OH	Industrial	4500	200	4.4
16	16	Fort Wright, KY	Commercial	3000	190	6.3
17	9	Toledo, OH	Residential	250	50	20
18	12	Lansing, MI	Downtown urban	600	50	8.3
19	11	Lansing, MI	Downtown urban	500	50	10
20	14	Ann Arbor, MI	Parking/roads	2250	156	6.9
21	11	Seven Hills, OH	Commercial	1200	200	17
22	8	Parma, OH	Fueling station	2500	200	8.0
23	13	Twinsburg, OH	Fueling station	2000	70	3.5
24	10	Orange Village, OH	Residential	250	20	8.0
25	10	Orange Village, OH	Residential	250	20	8.0
26	11	Kent, OH	Fueling station	800	70	8.8
27	13	Akron, OH	Parking/roads	6500	180	2.8
28	12	North Canton, OH	Fueling station	1250	180	14
29	12	North Canton, OH	Fueling station	1000	100	10

Nine samples were collected from each of the 29 bioretention facilities (Figure 1), except for the smaller sites (24 and 25), in which only three samples each were collected; thus, a total of 249 samples were collected. The methodology was a hypothesis-guided sampling similar to that used by Tedoldi et al., (2017), which included three sampling locations along each bioretention filter (i.e., three distances from the inlet) located approximately 1 m, 3 m, and 6 m from the inlet at three different depths. However, for sites 5, 8, 12, which were smaller, these distances were scaled down to fit the three sampling locations within the site and for sites 24 and 25, only one sample point was included. Further, some filters had multiple inlets (sites 5, 16, 23, and 26) or received diffuse flow along one edge (sites 13, 14, 15, 24, and 25); for these sites, the sampling locations were positioned based on the most likely flow path through the system. Therefore, the field work for each site started with mapping and examination of the local site hydrology and topography, before the catchment areas, inlets, deposited sediments, and erosion were studied to define a main inlet from which the sampling points were then measured out. At each of the three sampling locations, samples were taken at three depths (0–5 cm, 10–15 cm, and 30–50 cm from the surface) as illustrated in Figure 1 except for sites 4, 7 and 23, which were sampled to 20-30 cm maximum depth due to shallow filter depth.

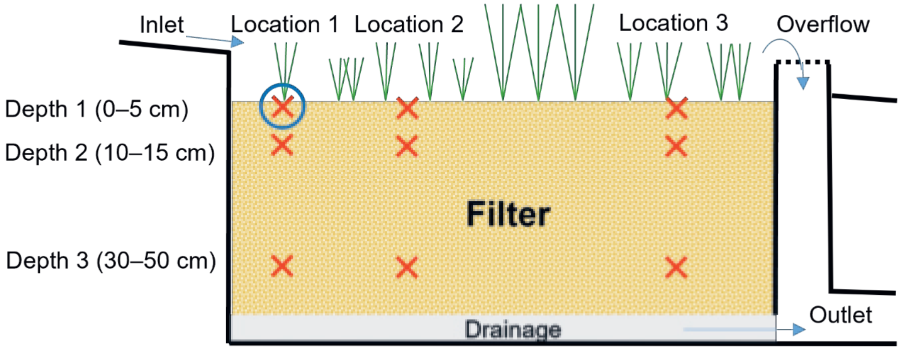

Figure 1. A schematic sketch of the sampling strategy in bioretention filter media with sampling points at three locations and at three depths, as marked by a red "X." The sequential extraction and pH analysis were performed at Location 1 at Depth 1, as marked by a blue circle.

Sampling

Samples in the field were collected by digging a core (approximately 5 cm × 15 cm × 15 cm for layer 1 and 10 cm × 10 cm × 10 cm for layers 2 and 3), with approximately 1–1.5 kg of filter material collected from each of the nine sampling points. The filter material was stored diffusion-tight plastic bags (18 cm × 35 cm), which were sealed shut with cable ties. The outdoor temperature during sampling was between –12 and +6°C and the samples were refrigerated before laboratory analysis, which was conducted within 3 months of sampling.

Laboratory analysis

All samples were sent to an accredited laboratory (ALS Scandinavia AB) for pre-treatment and analysis. To determine the total metal concentration, the samples were dried (50°C) and sieved (2 mm) according to the Swedish standards (SS, 2004a and SS, 2004b). Drying at 105°C was conducted in parallel with sample analysis to correct to a dry matter (DM) concentration. Microwave-assisted digestion was performed on the dried samples in 5 ml of concentrated HNO_3 + 0.5 ml H_2O_2.

To assess the bioavailability of the six metal species of interest (i.e., Cd, Cr, Cu, Ni, Pb, and Zn) in the filter material and to determine to what extent the metals were leachable, a fractionation with a 5-step sequential extraction method was performed in one sample from each sampling site, corresponding to Location 1 and Depth 1 (c.f. Figure 1), probably the most polluted location. This analysis was informed by methodology developed by Hall et al. (1996a, 1996b) for laboratory simulations of leaching.

Analysis of metal leachate water was performed on samples acidified with 1-ml concentrated HNO_3 (Suprapur for trace analysis) per 100 ml. Analysis was performed with Inductively Coupled Plasma

Sector Field Mass Spectrometry (ICP-SFMS) according to Swedish standards (SS-EN ISO, 2016, 2006) and U.S. EPA method 200.8 (U.S. EPA, 1994a). Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES or ICP-AES) was also performed according to Swedish standards (SS-EN ISO, 2009) and U.S. EPA methods (U.S. EPA, 1994b). The detection limits (DLs) were affected in one sample (Site 16, step 2 for Cd, Cr, and Ni) e.g., extra dilution was necessary to reduce matrix effects (For DL see Table 2, Figure 3). Determination of pH was performed according to Swedish standards (SS-EN ISO, 2012) after suspension in water. Loss on ignition (LOI was measured using gravimetric analysis based on CSN EN 12879 (CSN EN, 2014), CSN 72 0103 (CSN, 2009) and CSN 46 5735 (CSN, 1991).

Fraction 1 included adsorbed and exchangeable metals and carbonates; this fraction reflects metals that would potentially leach under acidifying conditions. The leaching was conducted with 1.0 M sodium acetate buffer at pH 5, following which, easily soluble and weakly adsorbed substances are released from material surfaces, including those that are bound to carbonate phases. The exchangeable fractions are released by ion exchange. Easily leached forms that are mobilized during precipitation represent a direct threat to the environment (ALS, 2018).

Fraction 2 measures the potential for metals bound to labile organic forms to leach with 0.1 M Na-pyrophosphate at pH 9, which releases metals bound in humic and fulvic acids. This leaching step serves to simulate what metals will leach and could be bioavailable under oxidizing conditions (ALS, 2018).

Fraction 3 included leaching of metals from amorphous Fe/Mn-oxides and indicates the proportion that can be released if the redox potential in the soil is significantly reduced, and anoxic conditions prevail in the filter material; conditions which might spur this to occur include elevated water levels or at high oxygen consumption due to high levels of organic material. Metals are leached with 0.25 M NH2OH·HCl in 0.10 M HCl at 60°C, pH 1. To some extent, the release of metals in hydroxide form may be due to the acidic environment as opposed to the altered redox potential (ALS, 2018).

Fraction 4 includes metals in crystalline Fe-oxides. Filter material is leached under greatly reduced conditions with 1.0 M NH2OH·HCl in 25% acetic acid at 90°C; this reduces crystalline iron oxides such as ingot, hematite, and magnetite, and releases the metals bound to these phases. The pH of the leachate solution was approximately 1 (ALS, 2018).

Fraction 5 quantifies metals in stable organic forms and sulfides by leaching with KClO3 in 12 M HCl, 4 M HNO3 at 90°C. Upon exposure to air and water, sulfides dissolve to form sulfuric acid and release metals (ALS, 2018).

After every fractionation step, the leachate was analyzed and the extracted concentrations of metals were calculated as mg/kg, DM. Specific surface area (SSA) was measured according to BS ISO 9277:2010 (BS ISO, 2010) gas adsorption - Brunauer, Emmett and Teller (BET) method.

Statistical analysis

For data analyses and to illustrate the metal distribution and concentration in the bioretention filter material, boxplots and stacked bar charts were created in Minitab 18 and principal component analysis (PCA) was performed using Simca 17. As parts of the data were non-normally distributed, the nonparametric Kruskal-Wallis test was used to identify statistically significant differences between examined parameters (i.e., metal concentrations, depth, location, land usage, bioretention age). Censoring of data at the highest reporting limit was performed according to Helse method (Helsel, 2012) for the boxplot of Cd in Figure 2.

Results and Discussion

Concentrations

All analyzed metals (Cr, Cu, Ni, Pb, and Zn) were found in all 249 analyzed samples except for Cd, which was detected in 225 of the samples. The concentration ranges (Figure 2) observed in the filter materials were lower for Cr, Cu, Ni, Pb, and Zn compared to other similar studies while comparable or slightly higher concentrations were found for Cd herein. Indeed, Al-Ameri et al. (2018) reported comparable concentrations for Cu (29 mg/kg), higher concentrations for Pb (30 mg/kg) and Zn (170 mg/kg), and lower concentrations for Cd (0.1 mg/kg) in a study of vegetated biofilters (9–16 years old) with a sandy loam or loamy sand filter medium. Rommel et al. (2021) reported concentrations in filter material from the top layer (0–5 cm) of bioretention cells (<3 years old) treating road runoff from a highly trafficked road in the Munich area, with comparable ranges for Pb (0.7 times higher) and slightly higher ranges for Ni (2.9 times higher), and 8.0–8.9 times higher for Cu, Cr, and Zn.

Moreover, a comparison of the soil background concentrations in England (Cd = 0.29, Cr = 29.2 Cu = 17.3, Ni = 15.8, Pb = 37.4, Zn = 65.9 [mg/kg]) (Alloway, 2013a) showed similar background levels as in the filter materials in the deeper filter layers in this study, indicating that the background metals concentrations in the filters are relatively low; thus, to assess the filter accumulation, it is important to determine the original levels of metals in the filter media. This also confirms the importance of the top layer as a metal's accumulator in bioretention since that is where the investigated metals are concentrated (Figure 2 and table 2, top layer medians; Cd = 0.43, Cr = 13.1 Cu = 26.8, Ni = 14.8, Pb = 23.3, Zn = 146 [mg/kg] and top layer max; Cd = 0.94, Cr = 60.9, Cu = 88.5, Ni = 33, Pb = 122, Zn = 813 [mg/kg]). One study of Cu, Pb, and Zn also showed a high surface accumulation in soil profiles (top 10 cm), while the lower layer concentrations were reported as low as background concentrations (Li and Davis, 2008). In the current study, the metal concentrations in the deeper layers were similar to "possible" background concentrations (Alloway, 2013b), however, the actual original background concentrations in the filter materials are unknown.

Table 2. Metal concentrations, including the total concentration and that in the five steps of fractionation (mg/kg, DM), and occurrence rates (%). ★Indicates for detection limits (DL) that for Cd, Cr, and Ni there was one sample from the analysis with a higher detection limit (double the typical detection limit) than all of the other detection limits (28 samples: CD$_{\mathrm{DL}}$ = 0.3 for 28 samples and Cd$_{\mathrm{DL}}$ = 0.6 for one sample; 27 samples: Cr$_{\mathrm{DL}}$ = 3; 1 sample: Cr$_{\mathrm{DL}}$ = 6; and for Ni, where 26 samples had Ni$_{\mathrm{DL}}$= 3 and one sample had Ni$_{\mathrm{DL}}$ = 6). The values for the total concentrations are taken from lab analyses of total concentration.

Metal	Fraction	Median	Min	Max	DL	Occurance >DL
			[mg/kg, DM]			
Cd	total	0.35	0.10	1.58	0.10	90%
	1	0.20	0.06	0.42	-	100%
	2	-	-	-	0.3★	0%
	3	0.05	0.01	0.10	-	100%
	4	0.05	0.02	0.10	-	100%
	5	0.02	0.01	0.06	-	100%
Cr	total	8.75	2.66	60.9	-	100%
	1	1.02	0.47	3.63	-	100%
	2	<3	<3	3.19	3★	3%
	3	0.41	0.16	4.53	-	100%
	4	5.27	1.84	27.1	-	100%
	5	6.40	1.44	26.8	-	100%
Cu	total	20.7	4.89	93.6	-	100%
	1	1.26	0.19	5.81	-	100%
	2	<8.65	<6	32.8	6	66%
	3	0.42	0.03	9.33	-	100%
	4	13.3	5.22	87.6	-	100%
	5	4.95	2.21	100	-	100%
Ni	total	14.8	3.67	64.0	-	100%
	1	1.37	0.33	3.90	-	100%
	2	<3	<3	4.99	3★	7%
	3	1.25	0.08	6.78	-	100%
	4	6.97	3.35	25.8	-	100%
	5	4.28	1.27	31.4	-	100%
Pb	total	16.0	2.89	122	-	100%
	1	3.51	0.59	22.5	-	100%
	2	<2.50	<1	29.0	1	76%
	3	4.57	0.32	33.8	-	100%
	4	9.24	2.06	36.4	-	100%
	5	1.16	0.32	3.40	-	100%
Zn	total	84.6	16.9	813	-	100%
	1	53.9	4.48	304	-	100%
	2	<13.8	<11	78.6	11	66%
	3	33.6	2.63	330	-	100%
	4	55.9	13.0	214	-	100%
	5	14.5	3.69	26.1	-	100%

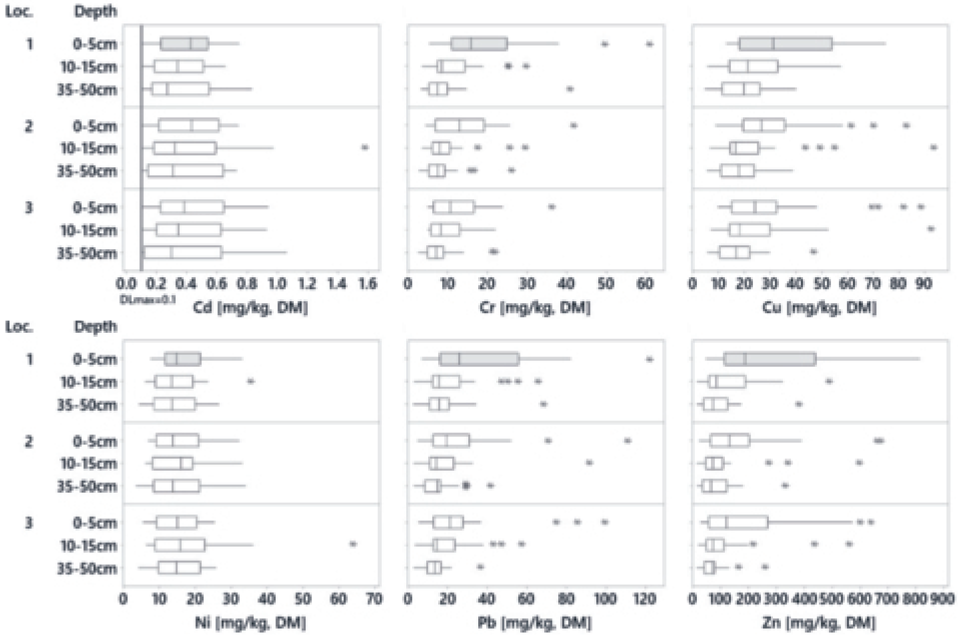

Figure 2. Boxplots showing the total concentration of Cd, Cr, Cu, Ni, Pb, and Zn in bioretention filter material at three depths and at three locations. Sequential extraction analysis was performed on samples at location 1 (close to inlet) at the uppermost depth (0–5 cm), marked grey in the boxplot. Cd, with an occurrence rate of 90%, is in the boxplot censored to DL_{max} = 0.1 mg/kg, DM.

Depth profiles

Metal concentrations tended to decrease with depth in the bioretention media (Figure 2). The concentrations of Cr, Cu, Pb, and Zn were significantly higher (Kruskal–Wallis, $p < 0.05$) in the top layer and decreased with increased depth in the filter. In contrast to the other metals, Ni showed no such trend ($p = 0.635$). Additionally, median Cd concentrations decreased with depth; however, this trend was not statistically significant ($p = 0.29$), likely due to the large variation between sites. For all metals, the concentrations varied considerably between different facilities (4 to 15 times, Figure 2), which is due to the relatively high variation of the data, which affected the statistical significance of the different concentrations between the layers. However, studying all 29 sites separately (Supplementary Figure 3.1), the highest site individual concentration was observed in the top layer at 17 sites for Cd, 25 sites for Cr, 23 sites for Cu, 15 sites for Ni, and 26 sites for both Pb and Zn. The same trend of decreasing metal concentration with depth in bioretention filter material has been shown previously (Blecken et al., 2009; Li and Davis, 2008; Muthanna et al., 2007). This can be explained by the fact that the accumulated metals are associated with particles, which are then removed in the upper soil layers by filtration (Tedoldi et al., 2016). Additionally, Al-Ameri et al. (2018) showed that 70% of dissolved metals were trapped in the top 7 cm of the filter media, mainly explained by metal association to the substrate, which may be caused by fast adsorption of dissolved metals onto the filter material (Søberg et al., 2019).

As for Cr, significantly higher concentrations of Cu were also observed in the top layer, which may be related to a higher content of organic matter in this layer (Figure 5, LOI). This is similar to the background concentrations of Cu in soils, which is normally correlated with the texture and content of organic matter and explains why soils with high amounts of clay minerals and organic matter generally have higher Cu concentrations (Alloway, 2013c). One reason for the higher content of organic matter in the top layer could be the breakdown of the mulch layer often placed on top for the vegetation.

Length profiles

A trend of reduced concentrations with increased distance from the bioretention inlets was also observed for Cr, Cu, and Zn, mainly in the upper layers, although these trends were not statistically significant (Kruskal-Wallis, $p > 0.05$). A similar tendency was observed for Pb, but only in the top layer of the filter. Previous studies have reported variations in concentrations along the top layer of biofilters, which has been explained by hydrology, where the filter media treats more of the runoff closer to the inlets and thus has higher metal concentrations (Jones and Davis, 2013). Additionally, Al-Ameri et al., 2018 conducted a study of stormwater bioretention media and reported that 11 of 19 filters had decreased metal concentrations with increased distance from inlet; 5 of 19 were higher in the middle, while seven filters had lower concentrations close to the inlet. Al-Ameri et al. (2018) and Jones and Davis (2013) suggested that stormwater pathways are not always uniform across a filter meaning that sediments could be carried further into the filter during high flow rates. Furthermore, as was the case in this study, filter designs may vary, resulting in different flow paths into and along each filter. To mitigate this, we conducted an onsite visual investigation in each filter to determine the main inlet and the likely primary flow direction for the filter. However, this approach involves some uncertainty and may explain the insignificant correlation between concentration and distance from the inlet in this study. Some sites (e.g., 5, 10, 13, 14, 15, 16, 22, 23, and 26) had multiple inlets and not one clear main flow path; in these cases, the probable main inlet was defined. Also, local hydrology and filter design, including different shapes, and large variation in the ratio of the catchment to filter areas are factors that could affect the flow patterns in the filter such that the strategic sampling pattern with three sampling points from the inlet may not always describe the actual variation in surface metal concentrations.

Fractionation

The fractionation of metals performed on samples at location 1, depth 1 (Figure 1) showed that all metals appeared in all five fractions with the exception of fraction 2, where several of the 29 analyzed samples were below the DL ($Cd_{<DL} = 29$, $Cr_{<DL} = 28$, $Cu_{<DL} = 10$, $Ni_{<DL} = 27$, $Pb_{<DL} = 7$ and $Zn_{<DL} = 10$, Table 2 and Figure 3). The reason for the non-detection in fraction 2 could be either a result of low concentrations in this fraction and/or due to the relatively high DLs for this fraction. The average distribution between the fractions in this study was as follows: fraction 4 = 36% > fraction 1 = 23% > fraction 5 = 20% > fraction 3 = 13 % > fraction 2 = 8% (were fraction 1 to fraction 4 are potential available), although there were numerous samples below DL in fraction 2. For Cd, Pb, and Zn, most of the detected mass was in the first four fractions (Figures 2 and 4, and Supplementary Table 6.1), while the contents of Cr, Cu, and Ni were greatest in fractions 4 and 5. Cr was the only metal with the highest content in fraction 5 (Figures 3 and 4).

Several studies have used sequential extraction methods to assess metal availability in stormwater. However, these studies have either focused on sediments (Gavrić et al., 2021; Karlsson et al., 2016), been performed as laboratory experiments (Wang et al. [2016] and Søberg et al. [2019]), focused on other applications for stormwater treatment such as coarse surface particles (Borris et al., 2016), or used other sequential extraction methods (e.g., Li and Davis, (2008) and Jones and Davis, (2013), Rauret et al., (1999)), based on those of Ahnstrom and Parker (Ahnstrom and Parker, 1999). The current study was based on field sampling of a material as a mixture of filter material and accumulated sediments analyzed with a sequential extraction based on that described by Hall et al. (1996a, 1996b), and therefore, there are few other comparable studies. As the extent of extraction is method dependent (Ahnstrom and Parker, 1999), one must be aware of these differences when comparing and assessing results from studies using different extraction methods and rather focus on the main trends of mobility rather than the concentrations.

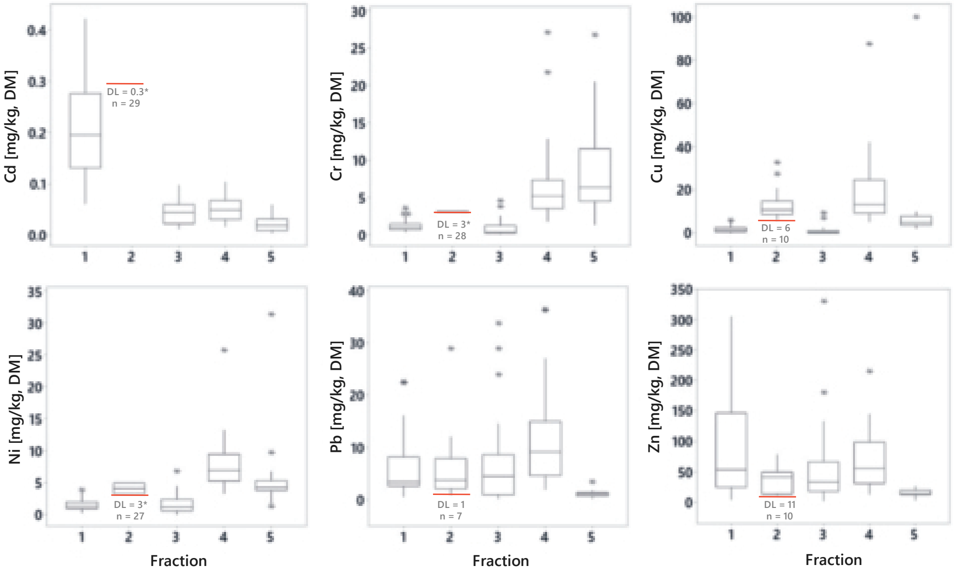

Figure 3. Boxplots of the median concentration of metals in five fractions. For all metals, the detection limit (DL) is indicated in fraction 2 and marked with a red horizontal line. n: Number of values below the DL of 29 samples. ⋆ Indicates that for Cd, Cr, and Ni, there was one sample from the analysis with a higher DL from analysis (double the typical value) than all other DLs (28 samples: CD_{DL} = 0.3 for 28 samples and Cd_{DL} = 0.6 for one sample; 27 samples: Cr_{DL} = 3; 1 sample: Cr_{DL} = 6; and for Ni, where 26 samples had Ni_{DL}= 3 and one sample had Ni_{DL} = 6).

Cd was mainly present in fraction 1 but also in fractions 3, 4, and 5 (Figures 3 and 4). The high presence in fraction 1 indicates that the sampled filter media have low affinity for Cd; the accumulated Cd is easily soluble and may be leached or mobilized from the filter material during normal rainfall or snowfall. Of all the included metals, Cd seemed to be the most mobile, with the highest proportion in fraction 1, as well as from fractions 1 to 4 ($Cd_{\Sigma F1-F4}$ = 93 %). For Cd, although all 29 samples in fraction 2 were below the DL, this does not indicate that Cd was not present in this fraction. With low content in the higher fractions and higher content in the lower fractions, it is most likely that some Cd is present in fraction 2, albeit at concentrations below the DL (DL_{F2}=0.3 mg/kg). These results are in line with those of previous studies that indicate, despite the high removal of total Cd by bioretention (Blecken et al., 2011; Wang et al., 2016), that metals primarily are adsorbed to exchangeable forms rather than permanent, and therefore pose a delayed threat to water resources rather than an immediate (Søberg et al., 2019). Lange et al. (2020) also indicated that salt could have a negative impact on the metal treatment and increase the truly dissolved fractions which then could result in release of Cd from the filter media over time. Cr was found at the highest levels in fraction 5, followed by fraction 4, and to a lesser extent in fractions 1 and 3, while it was only found above the DL in one sample in fraction 2. Of the studied metals, Cr comprised the highest proportion in fraction 5 and the lowest sum in fractions 1 to 4 (i.e., potential available fractions; $Cr_{\Sigma F1-F4}$ = 52%). The high Cr content found in fraction 5 indicates that Cr in the filter material is associated with stable organic forms and may be mobile and bioavailable only under more extreme conditions. Fraction 5 is also associated with sulphides. which, in contact with air, oxygen, and/or water dissolves to form sulfuric acid, which could result in release of metals; however, these conditions are unlikely to occur in bioretention (Søberg et al., 2019).

The high Cr content in fraction 4 indicates that Cr is also is potentially mobile under long-term anoxic conditions, which serve to reduce crystalline iron oxides, releasing the Cr bound to these phases. These conditions are unlikely to occur in the surface layers of a bioretention (i.e., where most metals are captured) but are possible in deeper layers in a saturated zone often implemented in designs to target nitrogen removal via denitrification. The behavior of Cr in soil is complex, controlled by various processes (e.g., biological and chemical redox, sorption, and precipitation) and external conditions (e.g., pH, soil aeration, presence of reductants and oxidants) (Bradl, 2004; Fendorf, 1995). However, as Cr(VI) is soluble in soil, while Cr(III) is more easily adsorbed (Cederkvist et al., 2013; Kimbrough et al., 1999), and with a median pH of 7.2 in the sampled filter material, Cr in fractions 4 and 5 is most likely Cr(III). Taken together, the high Cr content in fractions 4 and 5 ($Cr_{\Sigma F4+F5}$ = 89 %) indicated that Cr was the most stable and least mobile of the studied metals.

Cu was found at the highest levels in fractions 4 and 2, followed by fraction 5, while only low levels were found in fractions 1 and 3. The distribution of Cu in soil is strongly influenced by Mn and Fe oxides (total median Mn = 344 mg/kg and Fe = 13300 mg/kg, Supplementary Figure 3.2) and Cu has a strong affinity to soil organic matter (Bradl, 2004); indeed, the ability to form strong complexes with soluble organic matter (McGrath et al., 1988) is a known mechanism for effective Cu retention in soils. Fraction 2 in the sequential extraction is associated with soil organic matter and described the extraction of metals bound in labile organic forms, such as humic and fulvic acids, which may leach over time if the organic matter in the filter breaks down. These conditions may occur in bioretention, where organic matter (a component of filter media), the top mulch layers, or vegetation degrades over time (Lange et al., 2020b). Therefore, Cu should be regarded as a potentially mobile metal in bioretention filter media and sediments. Fraction 4 indicated that Cu is related to Fe oxides, which also have strong influence on Cu mobility, meaning that Cu may be mobile also after a longer period under anoxic conditions.

Ni was found at the highest levels in fraction 4, followed by fraction 5, with lower levels detected in fractions 1, 2, and 3. In fraction 2, only two of the 29 samples had concentrations above the DL (3.28 and 4.99 mg/kg with DL_{Ni} = 3 mg/kg for all samples but one with DL_{Ni} = 6 mg/kg). Compared to the other metals in the study, after Cr, Ni had the highest content in fraction 5, and the lowest content in the sum of fractions 1 to 4 ($Ni_{\Sigma(F1-F4)}$ = 68%). Ni content was spread across all 5 fractions, indicating that Ni appears to have mobility and bioavailability in the filter medias under study, but was stable compared to the other metals (Cd, Cu, Pb, and Zn) except for Cr.

Pb was found at the highest levels in fractions 4, 3, and 1, while less was found in fractions 2 and 5. Pb had the highest sum of content from fractions 1 to 4 ($Pb_{\Sigma(1-4)}$ = 96%) and the lowest content in fraction 5. The distribution of the Pb content (Figures 3 and 4) indicated that Pb has high potential mobility from bioretention. Many processes and factors affect Pb adsorption or release; these include humic matter, which plays an important role in adsorption in organic rich soil, and Fe oxides, which are more important in mineral soil, while many bioretention facilities contain both. The Pb in fraction 1 is associated with carbonates but also the hydrolysis process that easily adsorbs Pb in the bioretention filter; however, Pb seems to be less mobile than Cd and Zn given the lower content in fraction 1 (Figure 3). This is consistent with the results of previous studies, including Sansalone and Buchberger, (1997), who also reported that Pb was primarily particulate bound in urban roadway stormwater run-off while mainly dissolved for Zn. Also Alloway, (2013d) described the tendency of Pb to concentrate on smaller particle fractions in soil. The content of Pb in fraction 3, and particularly the high content in fraction 4, are most likely effects of Pb-adsorption to Fe- and Mn oxides.

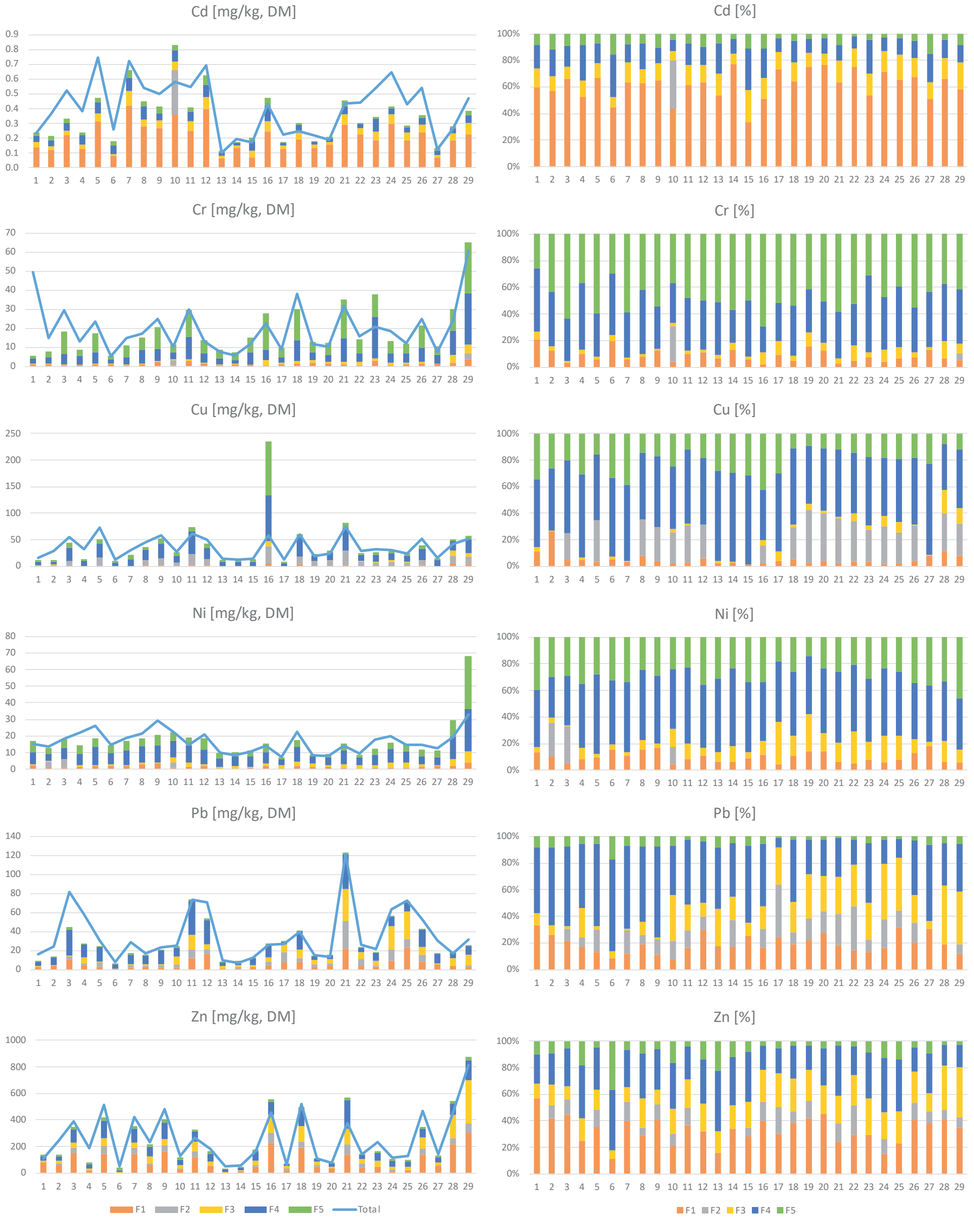

Figure 4. Fractionation of Cd, Cr, Cu, Ni, Pb, and Zn for all sites (1–29). (a) The graphs to the left are reported as total concentrations (mg/kg, DW), while those (b) to the right report the distribution between fractions (%).

The Zn distribution was relatively evenly spread between fractions 1 and 4, with the highest content found in fraction 4 and the lowest in fraction 5. After Pb, Zn had the highest sum of content in fractions 1 to 4 ($Zn_{\Sigma(1-4)}$ = 94%) and the second highest content in fraction 1 (36%) after Cd. The Zn sorption process is mainly influenced by pH, clay mineral content (and clay SSA), cation-exchange capacity, soil organic matter, and soil type, where in alkaline soils Zn sorption easily occurs to carbonates but undergoes wetting or water logging with increased mobility (Alloway, 2013e; Bradl, 2004). This could explain the even spread of Zn observed between fractions 1–4, as well as the high content in fraction 1. Moreover, the sorption of carbonates in the alkaline filter material may explain why Zn seems to have a high potential level of mobility in the filter media.

The metals distribution between fractions in this study is spread over all five fractions in varying degrees (Figure 4). Figure 4 also shows that Cd is mainly present in fraction 1, while Cr is mainly present in fractions 4 and 5, but also that there is a large variation between the different field sites. Despite this local variation, the main characteristic for the different metals is clear. If assessing mobility between the metals in the filter material based on their content in fraction 1 and then ranking them from high to low mobility, the rank will be Cd > Zn > Pb > Ni > Cr > Cu, meaning that Cd is the most mobile, while Cu is the least. Sansalone and Buchberger, (1997) conducted a study of stormwater and reported that Pb and Cr were primarily particulate bound, while Zn, Cd, and Cu were major concerns due to their propensity to be mainly dissolved, bioavailable, and highly mobile. Moreover, Jones and Davis, (2013) found metals as strongly bound to the filter media and to remain immobile since fractionation showed low content in the soluble-exchangeable fraction while the majority of metals was detected in the sorbed-carbonate, oxidizable, reducible and residual fractions. Additionally, Li and Davis (2008), using the same fractionation method, reported low soluble-exchangeable fractions for Zn, Pb, and Cu, where Zn had the highest mobility followed by Cu and Pb. Thus, a comparison of results herein to previous research shows both similarities and differences. However, even in the same study, depending on the expected environmental impact on the filter material, one could also assess the mobility differences. If assessing the sum of fractions 1 to 2, or that of fractions 1 to 3, then the order of mobility would be Cd > Zn > Pb > Cu > Ni > Cr, while if assessing the sum of fractions 1 to 4, the rank would be Pb > Zn > Cd > Cu > Ni > Cr. Therefore, the approach for assessing the potential environmental risks according to the fractionation results is important, and in one way, all five metals are potentially mobile in the filter material depending on which environmental factors (lack of oxygen, changes in pH or decomposition of organic matter) to which the filter material is exposed. Therefore, a risk assessment and or filter sampling is recommended before removing filter material after many years of stormwater treatment.

Principle components analysis

Two PCA models were performed to summarize the data, enable visualization of the main characteristics, and examine correlations between the analyzed parameters.

Model 1 was generated with data from the analysis of total metal concentrations from all samples (Figure 1) and the variables land use type, filter ratio (between catchment and filter surface areas), site age, depth, and location. Model 1 (total concentrations) had two components, with R^2Xcum = 0.452 (cumulative X-variation modeled after all seven components) and Q2(cum) = 0.265 (cumulative overall cross-validated R^2X). Most variations were explained in the first component ($R^2X(p1)$ = 0.325.

Model 2 consisted of data from the fractionation analysis and from the total concentrations in the corresponding samples (Location 1 and depth 1, Figure 1), together with variables for area usage, filter ratio, site age, pH, and LOI. Model 2 (Fractionation) had three components, with R^2Xcum = 0.622 (cumulative X-variation modeled after all seven components) and Q2(cum) = 0.4 (cumulative overall cross-validated R^2X). However, most variations were explained in the first two components ($R^2X(p1)$ = 0.364, $R^2X(p2)$ = 0.154). A summary of the results from the PCA models is shown in the score and loading plots in Figure 5.

In the loading plot of model 1 (Figure 5B) the content from all fractions (fraction 1–5) and total concentrations are located to the right of the origin, in origin (Cr in fraction 2 with only 2 values above the DL or not included as Cd in fraction 2 with no values above the DL). This pattern indicates in the first component (p[1]) that concentrations are positively correlated with each other and to commercial, fueling station and down town urban areas, as well as to LOI, SSA, pH, filter area ratio and site age. In contrast the Industrial, Residential and Parking/Roads land uses were negatively correlated with all concentrations and fractions. Fractions 4 and 5 seem to be most strongly correlated with the total concentrations for all metals. Fraction 1 also showed a strong correlation with total concentrations especially for Zn1 and Cu1 but less strong for Cr1 and Pb1. Fraction 2 showed a weaker correlation, especially for Cr and Ni, although this could partly be explained by the many non-detects in fraction 2, resulting in a weaker model and correlations. However, for Cu and Zn there is a stronger observed correlation between fraction 2 and total concentrations. Fraction 3 is positively correlated with the total concentrations for Cu and Zn, while Cr, Cu, Ni, and Pb are grouped and correlated to filter area ratio in the second component (p[2]); however, the second component is not as well described by the model as p[1]. The model also shows that for Zn, all fractions (1–5) were positively correlated with the total concentrations, which was also true for Cu and Cd, with the exception of fraction 2. In the score plot (Figure 5A), there is a tendency to group in the second component t[2] according to filter area ratio where the observations with higher area ratios are in the upper part of the plot, while those with lower area ratios are in the lower part, which indicated that the area ratio has some impact in p[2].

Figure 5. A. Model 1 of fractionation with the score plot (upper left) of metal concentrations. B. Model 1 loading plot (lower left) with fractions (fraction 1 = F1, fraction 2 = F2, fraction 3 = F3, fraction 4 = F4, and fraction 5 = F5), total concentrations, catchment area characteristics (land use filter area ratio), and filter characteristics (pH, LOI, Site age). C. Model 2 of the metal concentrations in the score plot (upper right). D. Model 2 loading plot (lower right) with total concentrations, depth, location, filter area ratio, and site age. In the plot, the land uses are abbreviated as Residential (Res), Commercial (Com), Industrial (Ind), Parking/roads (P/Rd), Downtown Urban (Urban), and Fueling station (Fuel st.).

In model 2, the score plot for total concentrations (Figure 5C) showed a clear trend of observations clustered in two major groups (an upper larger and a smaller lower group) which are stretched out diagonally through the origin from the lower right to the upper left. A comparison between the groups in the score plot (Figure 5C) with the loading plot (Figure 5D) explained this influence mainly as correlation to filter area ratio and residential land use, where the lower and smaller group in the score plot only contained observations from sites 1–4, which all are residential areas with filter area ratio ≤ 4% (Table 1). A PCA group-to-group comparison (Supplementary figure 4.1) confirmed that the correlated contribution of the two groups is the strong negative correlation between ratio and concentrations. This meant that the lower filter area ratio was correlated to higher concentrations and in this study, this was correlated to the residential area land use. One conclusion of this is that with large catchment areas compared to the bioretention filter areas one could expect higher metals concentrations. Furthermore, the loading plot (Figure 5D) shows a strong negative correlation between the filter area ratio and metals concentrations in the first component, but a negative correlation between Cd and Ni and the filter area ratio. If comparing the score plot with the loading plot (Figure 5C and 5D), one can see that the lower group, with an area ratio ≤ 4%, is positively correlated with metals concentration and residential land use but is negatively correlated with filter area ratio. This indicates that the smaller filter area compared to the catchment area (ratio), the higher the concentrations of metals, and that this is correlated to the residential areas; however, in this study, all the of residential areas in the lower group also had very low area ratios (i.e. might interact statistically). If coloring the score plot after area usage (Supplementary Figure 4.3), one can see that the other three residential sites (sites 17, 24, and 25) are located more in the center of the score plot and had an area ratio between 8% and 20%, which implies that the area ratio is the main influence. However, if looking at the land use of fueling station, one can see that they all seem to be clustered together high up in the upper group, whether they have a filter area ratio ≤ 4% or above (8%–14%). This could indicate that filter area ratio and land use both impact metals concentrations, which may be useful information when predicting metal pollution in bioretention sites given that a lower filter area ratio could indicate a higher degree of pollution. However, catchment land use, filter operation time and quality of performed maintenance are likely also important factors for these predictions.

Another observation in model 2 from the loading plot was that metals concentration was also strongly negatively correlated with depth, meaning that the highest concentrations are located near the surface with lower concentrations at deeper levels in the filter; this was also confirmed in the boxplots in Figure 2. Site age also seems to have some significance according to the loading plots in model 1 and particularly in model 2, where the total concentration is negatively correlated with site age. One would rather assume age to have positive correlation to pollutant concentrations in bioretention due to accumulation over time. However, the hypothesis was not corroborated by the PCA since the evaluated sites with the age spread from 7–16 and mainly around 10 years old (Table 1) have a relatively little variation and no representative age range (e.g. 1-16 years). Model 1 also shows that LOI and SSA are positively correlated with the total concentrations.

Soil guidelines

As an example of the practical implications of this work, the metal concentrations measured herein were compared to the Swedish national guidance limits for the classification of soil, "soil for sensitive land use" (abbreviated KM) and "soil for less sensitive land use" (abbreviated MKM), published by the Swedish Environmental protection agency (Swedish EPA, 2009) and the UK CL:AIRE (UK charity committed for sustainable land reuse) "soil guideline values" (SGVs) for Cd (Martin et al., 2009b) and Ni (Martin et al., 2009a). Soil contaminated above the Swedish EPA class KM and MKM means that if material is removed, special permits are required for transport and disposal. All concentrations were below the UK CL:AIRE SGVs and all metals concentration (Cd, Cr, Cu, Ni and Pb) except Zn were below the Swedish soil guidelines MKM (as illustrated in boxplot in supplementary Figure 5.1). Cr was the only metal below the KM, Ni had one outlier above the KM, while Cd, Cu, Pb, and Zn were more frequently detected above the KM .

Assessing metal mobility and potential environmental risks from old bioretention media is likely to depend on the choice of analysis methods (Ahnstrom and Parker, 1999) and method of data interpretation. If assessing the risk according to detected concentrations above the Swedish SGVs (Swedish EPA, 2009) (Supplementary Figure 5.1 and table 5.1), the order would be Zn > Pb > Cd >Cu > Ni > Cr. However, if assessing the environmental risk as mobility according to the detected metal content in fraction 1, the order would be Cd > Zn > Pb > Ni > Cr > Cu; as the sum of fractions 1 to 2 (and fractions 1 to 3), the order would be Cd > Zn > Pb > Cu > Ni > Cr; and according to the sum of fractions 1 to 4 the rank would be Pb > Zn > Cd > Cu > Ni > Cr. Irrespective of the approach used to assess the risks with accumulated metals in the bioretention filter material, the local environmental sensibility, legislation, and metal mobility should be considered if the filter material and/or sediments are being removed or replaced from a facility.

As the top layer of the filter media is likely to retain the most pollutants and sediments, as a long-term maintenance measure of bioretention technology, the top layer of the filter material could be regularly replaced to restore infiltration capacity of filter materials, reduce surface concentrations of metals, or reduce risk of metal pollutants. In a previous laboratory study, Hatt et al. (2011) estimated that during 12–15 years of operation, the levels of Cd, Cu, and Zn in the filter material would most likely exceed the guidelines for human and ecological health (NEPC, 1999) and therefore may be classified as contaminated soil requiring special disposal. Moreover, Al-Ameri et al., 2018 suggested clogging, rather than high concentrations to limit bioretention function if regularly maintained, given that replacing the top 10 cm of the filter will also remove most accumulated metals. Additionally Hatt et al. (2011) recommended a 2–3-year interval for replacement of top layer to reduce clogging, while Kluge et al., 2018 recommended replacement after 20-25 years as a maintenance routine considering leaching potential. Davis et al., (2003) also estimated that according to US EPA standards (U.S. EPA, 1993) and considering the highest concentrations in the top layer, the accumulation limits could be reached after 20, 77, 16, and 16 years for Cd, Cu, Pb, and Zn, respectively. Thus, filter material removed from older bioretention facilities should be managed and prioritized given that it may have to be treated as a hazardous waste.

Conclusions

All the study metals (Cd, Cr, Cu, Ni, Pb, and Zn) were found in all bioretention filter media samples, except for Cd, which was found in 90% of the samples. The highest metal concentrations were generally found in the top layer (top 5 cm) of the filter material. A comparison of metal concentrations in the filter material using the Swedish national guidance limits for classification of soil showed that Zn is the most significant pollutant in the bioretention filter media, while Cd, Cu, Ni, and Pb were detected at concentration levels of restricted use, suggesting special disposal techniques would be necessary for filter media.

The metal fractionation shows that all study metals (Cd, Cr, Cu, Ni, Pb, Zn) in the top layer of the filter material were present at large extents, with a potential risk of leaching over time. The risk of leaching according to mobility in fraction 1 was highest for Cd, Zn, and Pb, all of which are potentially mobile during precipitation, while Cr followed by Cu and Ni were most stable.

The studied metals are also at a potential risk of leaching from filter material or sediments if removed from the bioretention sites. In that case, the conditions at the new location are of great importance for the risk of metal leaching. For instance, if they are deposited under lack of oxygen the risk of leaching over time would increase for Cr, Cu, and Ni; this may have practical implications for bioretention operators given that removing material from the top layer of media, e.g., in order to reduce clogging, not only carries a risk when handling the material on site but also if the material is placed in a landfill.

The results of PCA indicated a strong correlation between high metal concentrations and low ratio between the filter area and catchment area (filter area ratio). Additionally, the various land uses show correlation with concentrations, which may be useful for predicting the degree of metal pollution at bioretention sites given that a lower filter area ratio could indicate an increased risk of a highly polluted bioretention site. However, the catchment area land use, operation time, and quality of maintenance are likely to be the most important factors for these predictions. In order to maintain function in biofilters over time and reduce the risk of leakage of metals, regular maintenance, including replacement of the top layer, can be recommended.

References

Ahnstrom, Z.S., Parker, D.R., 1999. Development and Assessment of a Sequential Extraction Procedure for the Fractionation of Soil Cadmium. Soil Sci. Soc. Am. J. 63, 1650–1658. https://doi.org/10.2136/sssaj1999.6361650x

Al-Ameri, M., Hatt, B., Le Coustumer, S., Fletcher, T., Payne, E., Deletic, A., 2018. Accumulation of heavy metals in stormwater bioretention media: A field study of temporal and spatial variation. Journal of Hydrology 567, 721–731. https://doi.org/10.1016/j.jhydrol.2018.03.027

Alloway, B.J. (Ed.), 2013a. Heavy Metals in Soils Trace Metals and Metalloids in Soils and their Bioavailability, Table 2.8 p. 38., 3rd ed, Environmental Pollution. Springer, Dordrecht, Department of Soil ScienceUniversity of ReadingReadingUnited Kingdom.

Alloway, B.J. (Ed.), 2013b. Heavy Metals in Soils Trace Metals and Metalloids in Soils and their Bioavailability, Table 17.1 p. 467. with reference (Holmgren et al, 1993), 3rd ed, Environmental Pollution. Springer, Dordrecht, Department of Soil ScienceUniversity of ReadingReadingUnited Kingdom.

Alloway, B.J. (Ed.), 2013c. Heavy Metals in Soils Trace Metals and Metalloids in Soils and their Bioavailability, Table 13.2 p. 371., 3rd ed, Environmental Pollution. Springer, Dordrecht, Department of Soil ScienceUniversity of ReadingReadingUnited Kingdom.

Alloway, B.J. (Ed.), 2013d. Heavy Metals in Soils Trace Metals and Metalloids in Soils and their Bioavailability, p. 397., 3rd ed, Environmental Pollution. Springer, Dordrecht, Department of Soil ScienceUniversity of ReadingReadingUnited Kingdom.

Alloway, B.J. (Ed.), 2013e. Heavy Metals in Soils Trace Metals and Metalloids in Soils and their Bioavailability, p. 478. with reference (Olivie-Lauquet et al, 2001), 3rd ed, Environmental Pollution. Springer, Dordrecht, Department of Soil ScienceUniversity of ReadingReadingUnited Kingdom.

ALS, 2018. Sequential extraction information sheet [WWW Document]. ALS Global. URL https://www.alsglobal.se/miljoanalys/laktester/sekventiella-lakningar (accessed 11.8.21).

Barbosa, A.E., Fernandes, J.N., David, L.M., 2012. Key issues for sustainable urban stormwater management. Water Research 46, 6787–6798. https://doi.org/10.1016/j.watres.2012.05.029

Blecken, G.-T., Marsalek, J., Viklander, M., 2011. Laboratory Study of Stormwater Biofiltration in Low Temperatures: Total and Dissolved Metal Removals and Fates. Water Air Soil Pollut 219, 303–317. https://doi.org/10.1007/s11270-010-0708-2

Blecken, G.-T., Zinger, Y., Deletić, A., Fletcher, T.D., Viklander, M., 2009. Influence of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters. Water Research 43, 4590–4598. https://doi.org/10.1016/j.watres.2009.07.008

Borris, M., Österlund, H., Marsalek, J., Viklander, M., 2016. Contribution of coarse particles from road surfaces to dissolved and particle-bound heavy metal loads in runoff: A laboratory leaching study with synthetic stormwater. Science of The Total Environment 573, 212–221. https://doi.org/10.1016/j.scitotenv.2016.08.062

Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soils constituents. Journal of Colloid and Interface Science 277, 1–18. https://doi.org/10.1016/j.jcis.2004.04.005

BS ISO, 2010. BS ISO 9277:2010 Determination of the specific surface area of solids by gas adsorption. BET method [WWW Document]. URL https://www.en-standard.eu/bs-iso-9277-2010-determination-of-the-specific-surface-area-of-solids-by-gas-adsorption-bet-method/

Cederkvist, K., Ingvertsen, S.T., Jensen, M.B., Holm, P.E., 2013. Behaviour of chromium(VI) in stormwater soil infiltration systems. Applied Geochemistry 35, 44–50. https://doi.org/10.1016/j.apgeochem.2013.05.011

Costello, D.M., Hartung, E.W., Stoll, J.T., Jefferson, A.J., 2020. Bioretention cell age and construction style influence stormwater pollutant dynamics. Science of The Total Environment 712, 135597. https://doi.org/10.1016/j.scitotenv.2019.135597

CSN, 2009. ČSN 72 0103 (720103) Základní postup rozboru silikátů - Stanovení ztráty žíháním (Basic procedure for the analysis of silicates - Determination of loss by annealing) [WWW Document]. URL https://www.technicke-normy-csn.cz/csn-72-0103-720103-218183.html

CSN, 1991. ČSN 46 5735 (465735) Průmyslové komposty (CSN 46 5735 (465735) Industrial composts) [WWW Document]. URL https://www.technicke-normy-csn.cz/csn-46-5735-465735-206692.html

CSN EN, 2014. ČSN EN 12879 (758005) Sludge characterization - Determination of loss by annealing (Sludge characterization - Determination of loss by annealing) [WWW Document]. URL https://www.technicke-normy-csn.cz/csn-en-12879-758005-226751.html

Davis, A.P., Hunt, W.F., Traver, R.G., Clar, M., 2009. Bioretention Technology: Overview of Current Practice and Future Needs. J. Environ. Eng. 135, 109–117. https://doi.org/10.1061/(ASCE)0733-9372(2009)135:3(109)

Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., Winogradoff, D., 2003. Water Quality Improvement through Bioretention: Lead, Copper, and Zinc Removal. Water Environment Research 75, 73–82. https://doi.org/10.2175/106143003X140854

EPA Victoria, 2007. Epa Classification of Wastes (May ed), Victorian Environmental Protection Agency, Victoria, Australia (2007).

Eriksson, E., Baun, A., Scholes, L., Ledin, A., Ahlman, S., Revitt, M., Noutsopoulos, C., Mikkelsen, P.S., 2007. Selected stormwater priority pollutants — a European perspective. Science of The Total Environment 383, 41–51. https://doi.org/10.1016/j.scitotenv.2007.05.028

Fendorf, S.E., 1995. Surface reactions of chromium in soils and waters. Geoderma 67, 55–71. https://doi.org/10.1016/0016-7061(94)00062-F

Gavrić, S., Leonhardt, G., Österlund, H., Marsalek, J., Viklander, M., 2021. Metal enrichment of soils in three urban drainage grass swales used for seasonal snow storage. Science of The Total Environment 760, 144136. https://doi.org/10.1016/j.scitotenv.2020.144136

Göbel, P., Dierkes, C., Coldewey, W.G., 2007. Storm water runoff concentration matrix for urban areas. Journal of Contaminant Hydrology 91, 26–42. https://doi.org/10.1016/j.jconhyd.2006.08.008

Hall, G.E.M., Vaive, J.E., Beer, R., Hoashi, M., 1996a. Selective leaches revisited, with emphasis on the amorphous Fe oxyhydroxide phase extraction. Journal of Geochemical Exploration 56, 59–78. https://doi.org/10.1016/0375-6742(95)00050-X

Hall, G.E.M., Vaive, J.E., MacLaurin, A.I., 1996b. Analytical aspects of the application of sodium pyrophosphate reagent in the specific extraction of the labile organic component of humus and soils. Journal of Geochemical Exploration 56, 23–36. https://doi.org/10.1016/0375-6742(95)00046-1

Hatt, B.E., Steinel, A., Deletic, A., Fletcher, T.D., 2011. Retention of heavy metals by stormwater filtration systems: breakthrough analysis. Water Science and Technology 64, 1913–1919. https://doi.org/10.2166/wst.2011.188

Helsel, D.R., 2012. Statistics for censored environmental data using Minitab and R, 2nd ed. ed, Wiley series in statistics in practice. Wiley, Hoboken, N.J.

Johnson, J.P., Hunt, W.F., 2020. Field Assessment of the Hydrologic Mitigation Performance of Three Aging Bioretention Cells. J. Sustainable Water Built Environ. 6, 04020017. https://doi.org/10.1061/JSWBAY.0000925

Johnson, J.P., Hunt, W.F., 2016. Evaluating the spatial distribution of pollutants and associated maintenance requirements in an 11 year-old bioretention cell in urban Charlotte, NC. Journal of Environmental Management 184, 363–370. https://doi.org/10.1016/j.jenvman.2016.10.009

Jones, P.S., Davis, A.P., 2013. Spatial Accumulation and Strength of Affiliation of Heavy Metals in Bioretention Media. J. Environ. Eng. 139, 479–487. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000624

Karlsson, K., Blecken, G.-T., Öhlander, B., Viklander, M., 2016. Environmental Risk Assessment of Sediments Deposited in Stormwater Treatment Facilities: Trace Metal Fractionation and Its Implication for Sediment Management. J. Environ. Eng. 142, 04016057. https://doi.org/10.1061/(ASCE)EE.1943-7870.0001122

Kimbrough, D.E., Cohen, Y., Winer, A.M., Creelman, L., Mabuni, C., 1999. A Critical Assessment of Chromium in the Environment. Critical Reviews in Environmental Science and Technology 29, 1–46. https://doi.org/10.1080/10643389991259164

Kluge, B., Markert, A., Facklam, M., Sommer, H., Kaiser, M., Pallasch, M., Wessolek, G., 2018. Metal accumulation and hydraulic performance of bioretention systems after long-term operation. J Soils Sediments 18, 431–441. https://doi.org/10.1007/s11368-016-1533-z

Kratky, H., Li, Z., Chen, Y., Wang, C., Li, X., Yu, T., 2017. A critical literature review of bioretention research for stormwater management in cold climate and future research recommendations. Front. Environ. Sci. Eng. 11, 16. https://doi.org/10.1007/s11783-017-0982-y

Lange, K., Österlund, H., Viklander, M., Blecken, G.-T., 2020a. Metal speciation in stormwater bioretention: Removal of particulate, colloidal and truly dissolved metals. Science of The Total Environment 724, 138121. https://doi.org/10.1016/j.scitotenv.2020.138121

Lange, K., Viklander, M., Blecken, G.-T., 2020b. Effects of plant species and traits on metal treatment and phytoextraction in stormwater bioretention. Journal of Environmental Management 276, 111282. https://doi.org/10.1016/j.jenvman.2020.111282

LeFevre, G.H., Paus, K.H., Natarajan, P., Gulliver, J.S., Novak, P.J., Hozalski, R.M., 2015. Review of Dissolved Pollutants in Urban Storm Water and Their Removal and Fate in Bioretention Cells. J. Environ. Eng. 141, 04014050. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000876

Li, H., Davis, A.P., 2008. Heavy Metal Capture and Accumulation in Bioretention Media. Environ. Sci. Technol. 42, 6776–6776. https://doi.org/10.1021/es8019808

Martin, I., Morgan, H., Jones, C., Waterfall, E., Jeffries, J., 2009a. Soil Guideline Values for nickel in soil (Science report No. SC050021). CL:AIRE.

Martin, I., Morgan, H., Waterfall, E., 2009b. Soil Guideline Values for cadmium in soil (Science report No. SC050021). CL:AIRE.

McGrane, S.J., 2016. Impacts of urbanisation on hydrological and water quality dynamics, and urban water management: a review. Hydrological Sciences Journal 61, 2295–2311. https://doi.org/10.1080/02626667.2015.1128084

McGrath, S.P., Sanders, J.R., Shalaby, M.H., 1988. The effects of soil organic matter levels on soil solution concentrations and extractabilities of manganese, zinc and copper. Geoderma 42, 177–188. https://doi.org/10.1016/0016-7061(88)90033-X

Müller, A., Österlund, H., Marsalek, J., Viklander, M., 2020. The pollution conveyed by urban runoff: A review of sources. Science of The Total Environment 709, 136125. https://doi.org/10.1016/j.scitotenv.2019.136125

Muthanna, T.M., Viklander, M., Blecken, G., Thorolfsson, S.T., 2007. Snowmelt pollutant removal in bioretention areas. Water Research 41, 4061–4072. https://doi.org/10.1016/j.watres.2007.05.040

NEPC, 1999. NEPC 1999 Guideline of the Investigation Levels for Soil and Groundwater, Schedule B(1), National Environment Protection Measure. [WWW Document]. URL http://www.nepc.gov.au/system/files/resources/93ae0e77-e697-e494-656f-afaaf9fb4277/files/schedule-b1-guideline-investigation-levels-soil-and-groundwater-sep10.pdf

Rauret, G., López-Sánchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, Ph., 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. J. Environ. Monitor. 1, 57–61. https://doi.org/10.1039/a807854h

Rommel, S.H., Stinshoff, P., Helmreich, B., 2021. Sequential extraction of heavy metals from sorptive filter media and sediments trapped in stormwater quality improvement devices for road runoff. Science of The Total Environment 782, 146875. https://doi.org/10.1016/j.scitotenv.2021.146875

Sansalone, J.J., Buchberger, S.G., 1997. Partitioning and First Flush of Metals in Urban Roadway Storm Water. Journal of Environmental Engineering 123, 134–143. https://doi.org/10.1061/(ASCE)0733-9372(1997)123:2(134)

Søberg, L.C., Winston, R., Viklander, M., Blecken, G.-T., 2019. Dissolved metal adsorption capacities and fractionation in filter materials for use in stormwater bioretention facilities. Water Research X 4, 100032. https://doi.org/10.1016/j.wroa.2019.100032

SS, 2004a. Determination of dry matter and ignition residue in water, sludge and sediment SWEDISH STANDARD · SS 28113 [WWW Document]. URL https://www.sis.se/produkter/miljo-och-halsoskydd-sakerhet/vattenkvalitet/avloppsvatten/ss28113/

SS, 2004b. Determination of dry matter and ignition residue in water, sludge and sediment SWEDISH STANDARD · SS 28113-1 [WWW Document]. URL https://www.sis.se/produkter/miljo-och-halsoskydd-sakerhet/vattenkvalitet/avloppsvatten/ss28113/

SS-EN ISO, 2016. Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of selected elements including uranium isotopes (ISO 17294-2:2016) [WWW Document]. URL https://www.sis.se/produkter/miljo-och-halsoskydd-sakerhet/vattenkvalitet/undersokning-av-vatten-efter-kemiska-substanser/sseniso1729422016/

SS-EN ISO, 2012. Water quality – Determination of pH [WWW Document]. SIS swedish institute for standards. URL https://www.sis.se/api/document/preview/88264/

SS-EN ISO, 2009. Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 11885:2007) [WWW Document]. URL https://www.sis.se/en/produkter/environment-health-protection-safety/water-quality/general/sseniso118852009/

SS-EN ISO, 2006. Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 1: General guidelines (ISO 17294-1:2004) SS-EN ISO 17294-1:2006 [WWW Document]. SIS swedish institute for standards. URL https://www.sis.se/en/produkter/environment-health-protection-safety/water-quality/examination-of-water-for-chemical-substances/sseniso1729412006/

Swedish EPA, 2009. Riktvärden för förorenad mark Modellbeskrivning och vägledning (Naturvårdsverket publikation No. 5976). Sweden.

Tedoldi, D., Chebbo, G., Pierlot, D., Kovacs, Y., Gromaire, M.-C., 2017. Assessment of metal and PAH profiles in SUDS soil based on an improved experimental procedure. Journal of Environmental Management 202, 151–166. https://doi.org/10.1016/j.jenvman.2017.06.063

Tedoldi, D., Chebbo, G., Pierlot, D., Kovacs, Y., Gromaire, M.-C., 2016. Impact of runoff infiltration on contaminant accumulation and transport in the soil/filter media of Sustainable Urban Drainage Systems: A literature review. Science of The Total Environment 569–570, 904–926. https://doi.org/10.1016/j.scitotenv.2016.04.215

Tirpak, R.A., Afrooz, A.N., Winston, R.J., Valenca, R., Schiff, K., Mohanty, S.K., 2021. Conventional and amended bioretention soil media for targeted pollutant treatment: A critical review to guide the state of the practice. Water Research 189, 116648. https://doi.org/10.1016/j.watres.2020.116648

U.S. EPA, 1994a. Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry Revision 5.4. Cincinnati, OH [WWW

Document]. URL https://www.epa.gov/esam/epa-method-2008-determination-trace-elements-waters-and-wastes-inductively-coupled-plasma-mass

U.S. EPA, 1994b. Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry Revision 4.4. Cincinnati, OH [WWW Document]. URL https://www.epa.gov/esam/method-2007-determination-metals-and-trace-elements-water-and-wastes-inductively-coupled-plasma

U.S. EPA, 1993. Standards for the Use or Disposal of Sewage Sludge (40 CFR Part 503). Fed. Regist., Vol 58, No. 32 [WWW Document]. URL https://www.epa.gov/biosolids/biosolids-laws-and-regulations#standards

US EPA, 1983. US-EPA, 1983. Final Report of the Nationwide Urban Runoff Program. U.S. Environmental Protection Agency, Water Planning Division; Washington DC, USA. [WWW Document]. URL https://nepis.epa.gov/Exe/ZyNET.exe/9100JH5T.txt?ZyActionD=ZyDocument&Client=EPA&Index=1981%20Thru%201985&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&UseQField=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5CZYFILES%5CINDEX%20DATA%5C81THRU85%5CTXT%5C00000018%5C9100JH5T.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=1#

Wang, J., Zhang, P., Yang, L., Huang, T., 2016. Cadmium removal from urban stormwater runoff via bioretention technology and effluent risk assessment for discharge to surface water. Journal of Contaminant Hydrology 185–186, 42–50. https://doi.org/10.1016/j.jconhyd.2016.01.002

Paper III

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Occurrence and concentrations of organic micropollutants in bioretention filter media

Presented at NORDIWA 2021

Occurrence and concentrations of organic micropollutants in bioretention filter media

4. Sustainable management and communication

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Introduction

Bioretention is an increasingly implemented stormwater control measure mainly targeting water quality treatment (Davis et al., 2009). Metal and TSS removal and their pathways in the filter are well documented. Although filters normally have a depth of 0.7-1m (Davis et al., 2009) metals are primarily trapped in the top layer (Li et al., 2008). E.g., Al-Ameri et al. found 70% of dissolved metals to be trapped in the top 7 cm of filter media (2018). Recent research has evaluated removal of organic micropollutants by bioretention; Zhang et al. (2014) demonstrated efficient removal for a wide range of organic micropollutants. Diblasi et al (2009) demonstrated PAH mass load reduction of 87 %. Still, only a few studies consider organic micropollutants and in these often only a few micropollutants have been studied.

Regularly, bioretention filter media must be replaced and disposed of as they reach the end of their functional lifespans. Little is known about concentrations and pathways of organic pollutants in the filter material. Diblasi et al (2009) indicated that PAHs accumulate in the top layer, but pointed out the need for further long-term investigation of accumulated PAHs to determine if periodic surface media replacement is required. Alkylphenols and phthalates were shown to also accumulate at greater depths in the filter due to emissions from plastic construction materials (Flanagan et al., 2019). However, it is unclear whether this effect is common or long lasting or if it applies to other pollutants.

Thus, we performed a field study on older bioretention facilities to investigate occurrence, concentrations and pathways of organic pollutants in the filter media. The study is one of the first major field studies of organic pollutant accumulation in bioretention filter media.

Method

Field sites

Filter material samples were collected from 29 bioretention sites in the US, aged 7 to 16 years and treating stormwater from urban catchments. 20 facilities contained forebays for pre-treatment.

Sample collection

From each bioretention site, one sample was taken of the accumulated material in the pre-treatment forebay. From the filter material itself, for each bioretention cell, one sample each was collected at three depths (0-2 cm, 2-10 cm and 40-50 cm) and three distances from the inlet (close to inlet, 1 and 3 meters from the inlet. In total, 268 samples from the 29 sites were collected and analysed.

Lab analysis

The samples were analysed for concentrations of organics (PAHs, PCBs, alkylphenols, phthalates and total organic carbon), particle size distribution, and specific surface area in selected samples.

Results and Discussion

Phthalates were quantified occasionally in the forebay sediments and in the upper layers of the filter media. Bis(2-ethylhexyl)phthalate (DEHP) was quantified in nearly all samples from forebays and upper layers, in some samples from the middle layer, but never in the bottom layer. Thus, a clear depth profile was observed 4-tert-octylphenol was only quantified occasionally, while 4-nonylphenol was found in the majority of the forebay samples and in about 25% of the top layer samples.

PCBs were detected in a majority of the samples, both in the upper, but also in the deeper layers at nearly all facilities. However, concentrations in the filter material were substantial lower than those found in the forebays.

Most PAHs with medium (PAH-M) and high (PAH-H) molecular weight were quantified in nearly all facilities and in the deeper layers. PAHs with low molecular weight (PAH-L) was less regularly quantified. A clear depth profile was observed with highest concentrations in the top layer.

Selected references

Davis A. P., Hunt W. F., Traver R. G., Clar M. (2009). Bioretention Technology: Overview of Current Practice and Future Needs

Blecken G. T., Zinger Y., Deletic A., Fletcher T. D., Viklander M. (2009). Influence of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters

Li H., Davis A. P.,(2008). Heavy Metal Capture and Accumulation in Bioretention Media

Al-Ameri M., Hatt B., Le Coustumer S., Fletcher T., Payne E., Deletic A. (2018). Accumulation of heavy metals in stormwater bioretention media: A field study of temporal and spatial variation

Zhang K., Randelovic A., Page D., McCarthty D.T., Deletic A. (2014). The validation of stormwater biofilters for micropollutant removal using in situ challenge test

Flanagan K., Branchu P., Boudahmane L., Caupos E., Demare D., Deshayes S., Dubois P., Kajeiou M., Meffray L., Partibane C., Saad M., Vitart de Abreu Lima, M., Gromaire M.C. (2019). Stochastic Method for Evaluating Removal, Fate and Associated Uncertainties of Micropollutants in a Stormwater Biofilter at an Annual Scale.

Diblasi C. J., Li H., Davis A. P., Ghosh U. (2009). Removal and Fate of Polycyclic Aromatic Hydrocarbon Pollutants in an Urban Stormwater Bioretention Facility

Søberg L. C., Winston R., Viklander M., Blecken G. T. (2019). Dissolved metal adsorption capacities and fractionation in filter materials for use in stormwater bioretention facilities

El-Mufleh Al Husseini A., Béchet B., Gaudin A., Ruban V. (2013). Trace metal fractionation as a mean to improve on the management of contaminated sediments from runoff water in infiltration basins

Jones P. S., Davis A. P. (2013). Spatial Accumulation and Strength of Affiliation of Heavy Metals in Bioretention Media