DOCTORAL THESIS

Stormwater bioretention systems: Water quality treatment and long-term pollutant accumulation

Robert Furén

Urban Water Engineering

LULEÅ
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Preface

This thesis describes a summary of research work conducted at the Urban Water Engineering Research Group at the Department of Civil, Environmental and Natural Resources Engineering at the Luleå University of Technology. This work was done within DRIZZLE – Centre for Stormwater Management, the Stormwater & Sewers research cluster (Dag & Nät) and also financially supported by NCC R&I, SBUF (Grant no. 13623 and 14197) and VINNOVA (Grant no. 2016-05176 and 2022-03092). I would like to express my sincere gratitude to all these financial supporters.

I would also like to express my deepest gratitude to my supervisors at Luleå University of Technology, professors Godecke Blecken and Maria Viklander for their endless support and guidance through these years. Your insights, encouragement and commitment have made this experience deeply meaningful and rewarding. Your mentorship transformed what could have been a Sisyphean task into a satisfying and enriching endeavour. Thank you for making this journey a truly transformative experience, not only a quest for knowledge. I would like to thank all the inspiring and helpful colleagues at the Urban Water Research Group with special thanks to Alexandra, Ali, Emelie, Haoyu, Lisa and Pär for their help and support. I would also like to extend my deepest gratitude to Katharina Lange for the long-time collaboration, and as an invaluable coauthor on Paper V. Also, a special thanks to the great Peter Rosander for his invaluable help and for fruitful discussions. I would also like to thank our friends and partners at the Ohio State University (U.S.), and particularly Ryan Winston and family for making arrangements and their hospitality during sampling.

I also want to thank all my supervisors, managers and colleagues at NCC, particularly Christina Claeson-Johnsson at NCC R&I for her endless support and encouragement, Birgitta Nyström Berglund and Rasmus Rempling for structure and coaching, and the supportive colleagues at R&I. Furthermore, I want to thank Marie Kruså for support and guidance at Sustainability & Environment, NCC Teknik, Ylva Alfredsson and colleagues at Civil Stockholm for support, interest and patience, and Staffan Hintze and Hans Säll for the NCC initiative of participating in DRIZZLE. Also, I would like to give a special thanks to the SBUF reference group.

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Robert Furén

Abstract

Urban areas are affected by anthropogenic activities and produce pollutants that are transported to receiving waters bodies during precipitation. Greater awareness of pollutants has increased interest in treating stormwater. Organic micropollutants (OMPs, e.g., PAH, PCB, phthalates, and phenols) and metals (e.g. Cd, Cr, Cu, Ni, Pb, Zn) have been identified as potentially harmful to aquatic organisms and humans. Stormwater bioretention systems are popular and considered effective for stormwater treatment. However, there are significant knowledge gaps in bioretention systems' long-term function, performance of stormwater treatment in cold climates, impact of road salt on pollutant treatment, and issues related to operation and maintenance. Furthermore, pollutants have been found to accumulate in the filter material and are also a potential source of pollution. Thus, to understand the long-term function of bioretention systems, it is also important to understand occurrence and mobility of pollutants, and the processes of pollutant accumulation in bioretention systems, particularly in the filter material. To answer these questions, this thesis includes studies of stormwater sampling from 18 bioretention in Malmö, and three bioretention in Sundsvall (both in Sweden), along with a comprehensive field study involving sampling of 29 bioretention systems in the USA (filters that had been in operation for 7–16 years at the time of sampling).

Filter material samples were collected from 31 bioretention facilities (37 filters in total), of which 28 were equipped with a forebay. A total of 277 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 OMPs, including 16 PAHs, 7 PCBs, 13 phthalates, and two alkylphenols. The results from these studies showed that there was a high occurrence of metals (Cr, Cu, Ni, Pb, and Zn) and OMPs (16 PAH, 7 PCB, 13 phthalates, and two alkylphenols). The highest concentrations were detected in the top layer of the filters and in the forebays, particularly of the OMPs. It was also shown that there is a risk of metal leakage from these systems over time, both from the filter material during operation and from filter material and/or sediments removed during maintenance.

The studies in Malmö and Sundsvall was performed on two bioretention systems in with different design and filter configurations, where stormwater was sampled during a period of two years. The results show that stormwater treatment in general is effective in a bioretention system, especially for particle-bound pollutants, but also in filters specifically adapted for cold climates. De-icing with road salt increases the risk of metal leakage from these systems, however continuous maintenance can reduce these risks. A forebay may facilitate operation and maintenance and thus maintain the treatment function over a longer period. Filter materials with high hydraulic conductivity were effective for metal removal in cold climates. Furthermore, filter material with vegetation and with chalk amendments was more efficient for metal removal than filter materials without. In general metal removal is efficient and both metals and OMPs accumulate in the filter material over time. Even if metals can leach the accumulation studies indicated a long-term accumulation of metal in the filter's ant thus, bioretention facilities generally have a positive effect on stormwater treatment over time.

Sammanfattning

Våra städer påverkas av mänskliga aktiviteter vilka producerar föroreningar som vid nederbörd leds till och blir en belastning för sjöar och vattendrag. Ökad förståelse för föroreningar och dess negativa inverkan på miljö har även ökat intresset för att hantera och behandla dagvatten. Organiska föreningar (OMP, t ex PAH, PCB, ftalater och fenoler) samt metaller (t.ex. Cd, Cr, Cu, Ni, Pb, Zn) har identifierats som potentiellt skadliga för vattenlevande organismer och människor. Biofilter är populära och anses effektiva för behandling av dagvatten i stadsmiljöer. Det finns dock betydande kunskapsluckor när det gäller anläggningarnas funktion över tid, i kallt klimat, och reningsfunktion under inverkan av vägsalter. Föroreningar som ackumuleras i filtermaterialet har identifierats som en föroreningsdepå och en potentiell källa till föroreningar. För att förstå biofilters funktion över tid är det viktigt att förstå förekomst och mobilitet av föroreningar, samt de processer som styr ackumulering av föroreningar i biofilter och i filtermaterialet. För att besvara dessa frågor och vidga kunskapen om biofilter innehåller denna avhandling studier med dagvattenprovtagning från 18 biofilter i Malmö och 3 biofilter i Sundsvall (båda i Sverige), samt en omfattande fältstudie med filterprovtagning av 29 biofilter i USA (biofilter som hade varit i drift i 7-16 år vid provtagningstillfället).

Prover har samlats in från 31 olika biofilteranläggningar med 37 filter, varav 28 utrustade med en försedimentering (forebay). Totalt analyserades 277 prover för koncentration av metaller (Cr, Cu, Ni, Pb och Zn), samt en femstegs sekventiell lakning användes för att analysera metallers rörlighet i filtermaterial. Vidare analyserades 116 prover från 12 platser för 38 organiska föreningar (OMPs), inklusive 16 PAH, 7 PCB, 13 ftalater och 2 alkylfenoler. Resultaten från dessa studier visar på hög förekomst av metaller (Cr, Cu, Ni, Pb och Zn) och organiska föroreningar (16 PAH, 7 PCB, 13 ftalater och 2 alkylfenoler). Koncentrationer var högst i det översta lagret av filtermaterialet samt i forebay, i synnerhet för OMPs. Studien visar också att det finns en risk för läckage av metaller över tid, från anläggningarna och/eller från filtermaterial och sediment som avlägsnas vid drift och underhåll.

Studierna i Malmö och Sundsvall utfördes på två större anläggningar med olika design och filterkonfigurationer under två års tid. Resultaten visar att behandling av dagvatten över längre tidsperioder är effektiv i biofilter, och i synnerhet för partikelbundna föroreningar, men även i filter speciellt anpassade för kalla klimat. Avisning med vägsalter ökar risken för läckage av metaller, men kontinuerligt underhåll kan minska dessa risker. En forebay kan underlätta drift och underhåll och ge bibehållen funktionen för behandling av dagvatten över längre tid. Filtermaterial med hög hydraulisk konduktivitet var enligt studien effektiva för rening av metaller även i kallt klimat. Vidare var biofilter med vegetation och de med tillsats av kalk mer effektiva för rening av metaller än filter utan. Generellt sätt renar biofilter metaller bra och metaller likväl som OMPs ackumuleras i filtermaterial över tid. Även om det finns risk för läckage av metaller visar dessa studier att metaller ackumuleras i filtermaterial över tid, varför biofilter generellt sett har en positiv effekt på behandling av dagvatten.

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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, 10 November 2022, Article number 157372.

Paper II Furén, R., Österlund, H., Winston, R. J., Tirpak, R.A., Dorsey, J. D., Smith, J. Viklander, Blecken, G.-T. Fractionation of metals by sequential extraction in bioretention filters for stormwater treatment: Field study. Environmental Science: Water Research & Technology. Volume 9, Number 12, December 2023, pages 3079–3498.

Paper III Furén, R., Winston, R. J., Tirpak, R.A., Dorsey, J. D., Viklander, Blecken, G.-T. Occurrence and Concentration of 6 Metals and 28 Organic Micropollutants in the Forebays of Bioretention Facilities. Journal of Sustainable Water in the Built Environment. Volume 11, Issue 1, February 2025.

Paper IV Robert Furén, Maria Viklander, Godecke-Tobias Blecken. Influence of salt on total and dissolved metal treatment in bioretention: A Field study. Under review in Water Air and Soil Pollution, 2024-09-24.

Paper V Furén, R., Lange, K., Beryani, A., Viklander, M., Blecken, G.-T. Bioretention filter material for cold climate conditions: hydraulic conductivity and metal treatment. Submitted to Journal of Hydrology, 2025-01-27.

Assessment of contribution to the 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	Shared responsibility	Shared responsibility	Responsible	Shared responsibility	Shared responsibility	Responsible	Shared responsibility
II	Shared responsibility	Shared responsibility	Responsible	Shared responsibility	Responsible	Responsible	Shared responsibility
III	Shared responsibility	Shared responsibility	Responsible	Responsible	Responsible	Responsible	Shared responsibility
IV	Contributed	Contributed	Shared responsibility	Shared responsibility	Shared responsibility	Responsible	Shared responsibility
V	Contributed	Contributed	Shared responsibility	Shared responsibility	Shared responsibility	Shared responsibility	Shared responsibility

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. Through surface runoff during precipitation and/or snowmelt, these pollutants are conveyed to receiving water. Thus, untreated urban stormwater and runoff are recognized as main drivers of environmental degradation in receiving water bodies. Commonly occurring contaminants include sediments, metals, organic pollutants, nutrients, bacteria and chlorides (Müller et al., 2020). As awareness of stormwater pollution and its impacts has increased, the interest in stormwater quality treatment has grown.

Bioretention, also referred to as biofilters, biofiltration systems and raingardens, is a commonly implemented best management practice for low impact development (Croft et al., 2024). The typical bioretention system consists of an inlet structure, filter media and an underlying drainage layer (Tirpak et al., 2021). The main treatment occurs as a result of vertical filtration through the filter material, so the filter material is important for pollutant treatment. The filter material is normally an engineered sand or sandy soil, and is often topped with a plant soil and a variety of plant species. The inlet structure of a bioretention system may also be equipped with a forebay for pretreatment (Erickson and Hernick, 2019). Bioretention is considered efficient for removal of total suspended solids (TSS) (Hsieh and Davis, 2005), metals (Blecken et al., 2009a) and a wide range of organic micropollutants (OMPs) (Zhang et al., 2014). Metals (e.g. Cd, Cu, Pb and Zn) are regarded as pollutants of concern in stormwater and contribute to water degradation (Göbel et al., 2007). Previous studies of bioretention systems and metals have mainly focused on removal of particle-bound metals, however, half or more of the metals in stormwater may be related to the dissolved phase (Lange et al., 2020a). Since most metals in bioretention systems are removed by filtration or adsorption to soil particles (Blecken et al., 2009a), the filter medium is important for dissolved and particulate metal removal. The filter materials should ensure sufficient water retention and contact time for adsorption processes, but also have sufficiently high infiltration to avoid overflow and clogging (Fassman-Beck et al., 2015). These requirements are partly conflicting. Thus, to target these conflicting characteristics, an optimizing compromise is necessary. To improve filter characteristics and support pollutant treatment, additives are used, such as organic matter, biochar, pumice and chalk. However, to date, few field studies have assessed filter material with additives at a field-scale and such research is needed to support the previous laboratory studies (Tirpak et al., 2021). Furthermore, few field studies have assessed dissolved metal treatment in bioretention systems. Previous studies have highlighted the importance of increased knowledge of bioretention systems' hydraulic and water quality performance and the need for field studies (Kratky et al., 2017). Further, Kratky et al. (2017) recommended studies of bioretention systems specifically designed for cold climates, with studies of removal of total and dissolved metals and amendments to enhance metal adsorption. Thus, field-scale studies of additives are required, with a particular focus on additives in colder regions and the influence of road salt. A common recommendation for hydraulic conductivity in filter materials is 50–200 mm/hr (Le Coustumer et al., 2009). However, these recommendations do not take cold climates and winter conditions into account and may restrict bioretention implementation when space is very limited (i.e. requiring small facilities). In such cases, better drained filter material is beneficial for infiltration, esp. in low temperatures, since less water stands in the pores between particles during freezing and less untreated overflows are caused from small facilities. However, further field studies of coarser filter materials and pollutant removal (total and dissolved metals) are needed.

Particulate metals are mainly removed from stormwater through filtration (Tedoldi et al., 2016) and primarily accumulated in the top 5–10 cm of the filter (Blecken et al., 2011). Previous research has shown that metals captured in a bioretention system may create a pollutant depot (Davis et al., 2003). Also, studies have shown that even if most metals are bound to smaller fractions which are not efficiently removed by forebays, a significant portion is associated with larger particles (Karlsson and Viklander, 2008) and may still accumulate in the forebay. However, very few studies to date have studied bioretention system forebays (Johnson and Hunt, 2016). Studies of dissolved metal removal in bioretention systems have also reported leaching of metals (Cd, Cu and Zn) from filter materials (Søberg et al., 2019). Characterization of pollutant accumulation, occurrence, and mobility in bioretention filter materials and forebays is important for understanding pollutant removal and long-term pollutant removal. Also, few studies have assessed accumulation, characteristics, and behaviour of accumulated metals in the filter material. Thus, to understand the accumulation and distribution processes of metals in bioretention systems better, further studies are needed. Recent studies have shown that OMPs are a pollutant group of concern due to their environmental persistence and ability for bioaccumulation, which may have long-term harmful effects on receiving waters, aquatic life and also humans (Markiewicz et al., 2017). Field studies have demonstrated high removal (>90%) of PCBs (Gilbreath et al., 2019) and PAHs (87%) (DiBlasi et al., 2009). However, very limited research has been carried out on the pathways and accumulation of OMPs (PAHs, PCBs, phthalates and alkylphenols) in filter materials. Thus, also here further studies of the accumulation processes and distribution of OMPs in bioretention filter materials and forebays are needed.

1.1 Aim and research objectives

The overall aim of the work described in this thesis was to study pollutant occurrence, accumulation, and concentration in various bioretention filter materials and forebays after long-term stormwater treatment in urban areas and to assess pollutant treatment functionality in field facilities with specific focus on the effects of cold climate and the use of de-icing salts for road maintenance. The findings of this study contribute to knowledge and understanding of the requirements for design, long-term operation, maintenance, and waste management, with the intention of improving pollutant treatment and reducing environmental impact and risks that may occur when using bioretention or similar technologies for treating stormwater in urban areas.

The specific objectives of the study were as follows:

1) How do design parameters (filter configuration, chalk and pumice additives and infiltration capacity) affect metal treatment in bioretention systems?
2) What is the effect of salt on total and dissolved metal treatment in bioretention systems?
3) What is the occurrence, concentration, distribution and/or availability of organic micropollutants and metals in bioretention filter materials and forebays after long-term operation of stormwater treatment facilities in urban areas?

1.2 Thesis structure

This thesis is based on research carried out over a five-year period and includes three major field sampling campaigns. The research resulted in the five appended papers, referred to as Papers I–V. Papers I–III are based on field studies of pollutant accumulation in bioretention filter materials and sediments. Papers IV and V are based on studies of pollutant removal from stormwater in bioretention systems with various filter configurations.

Paper I describes a study of accumulation, occurrence and concentration for assessment of pathways of OMPs (PAHs, PCBs, phthalates and alkylphenols) in bioretention filter materials 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 filter materials after long-term operation. The study included an evaluation of distribution of metals in the filter medium, and a fractionation using a five-step sequential extraction method for assessing metal availability. Paper III is based on a broader study of bioretention facilities where the occurrence, distribution, and concentrations of OMPs in forebays and filter materials were examined. Paper IV presents a study of total and dissolved metal (Cd, Cr, Cu, Ni, Pb and Zn) treatment in bioretention systems under the influence of chlorides for different filter configurations. Paper V presents the results from a study of metal removal by bioretention facilities in cold climates. The study assessed the efficiency of filter materials especially adapted to winter conditions.

For understanding the long-term function of bioretention systems treating pollutants, knowing how design features, filter materials, ageing and maintenance affect the pollutant accumulation and removal over time is essential. Separately, the papers describe different elements of processes and design that affect accumulation and removal of pollutants in a bioretention system. Papers I, II and III, based on filter material sampling, describe accumulation of OMPs and metals in filter material and forebays of 37 bioretention sites operating for 2 to 16 years at the time of sampling. Papers IV and V are based on stormwater sampling from test sites and describe metal removal in various filter designs (vegetated, non-vegetated, sand, use of amendments and a submerged zone) with and without impact of chlorides from road maintenance in a cold climate. The additional value of the thesis is mainly created when Papers I–V are combined (Figure 1). Overall, this thesis, with all the subtopic papers, describes the function and performance of a whole bioretention system for the treatment of metals in stormwater runoff, taking into account long-term accumulation processes om metals and OMPs and the effects of cold climate and road maintenance using de-icing salts.

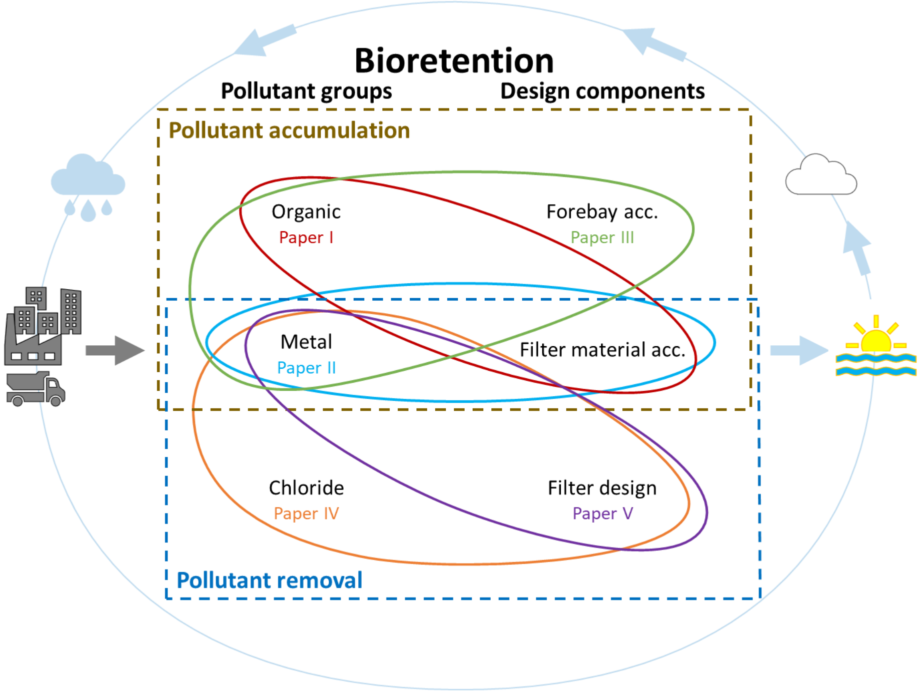

Figure 1. Synthesis of papers included in this thesis. Paper I, II and III are based on studies of pollutant treatment and Paper IV and V are based on studies of pollutant removal.

The thesis consists of seven chapters and starts with an introduction followed by a background chapter which summarizes the state-of-the-art and identifies and describes the research gaps. In chapter three follows a summary of the methods and the results from the appended studies are presented in chapter four. The thesis is completed with a discussion in chapter five and the conclusions in chapter six. References cited in the thesis are listed in chapter seven.

2 Background

This review of sustainable urban stormwater treatment focuses on stormwater bioretention systems. The increased implementation of stormwater management technologies all over the world, such as bioretention systems, makes it important to understand their performance and long-term function (Blecken et al., 2017; Davis et al., 2009; Kratky et al., 2017; Pitt et al., 2021). The aim of the review was to motivate the need for increased knowledge and the research conducted in this thesis both on bioretention systems and their role in water quality treatment and long-term pollutant accumulation.

2.1 Urban stormwater

Due to increased urbanization in combination with a growing global population, it has become apparent that urban areas affect the natural hydrological cycle. For example, increased urbanization (UN-Habitat, 2020) has transformed vegetated areas into impervious surfaces such as roads, car parks and rooftops. These impermeable surfaces prevent infiltration, leading to increased surface runoff and therefore more rapid runoff with higher flow peaks (Walsh et al., 2005). Furthermore, due to the impact of numerous sources and anthropogenic activities (e.g. vehicular transportation, roads, building materials and atmospheric deposition), urban stormwater contains a variety of contaminants such as sediments, metals, organic pollutants, nutrients, bacteria, and chlorides (Eriksson et al., 2007; Makepeace et al., 1995). These are transported by runoff and/or snowmelt to receiving waters where they can affect the local environment and ecosystems (Barbosa et al., 2012; Müller et al., 2020). Untreated stormwater runoff is recognized as one main driver of environmental degradation which can affect environmental and public health (Walsh et al., 2005). Ecological degradation, including changed flow patterns and pollution load 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). This concept embodies an important part of the challenges in urban water management and thus stormwater should be treated before being discharged (Barbosa et al., 2012; Göbel et al., 2007; Markiewicz et al., 2017; McGrane, 2016). Furthermore, climate change is affecting precipitation patterns, resulting in more frequent and intense rain events, increased runoff, and elevated concentrations of nutrients and contaminants that carry larger volumes of pollutants into water bodies (Calvin et al., 2023; Walsh et al., 2005). As the awareness of these negative effects has increased (Moazzem et al., 2024; Sharma et al., 2016), stormwater is now being considered to be one major source of pollutant dispersion causing environmental degradation of urban waters (Walsh et al., 2005). Thus, interest in quality treatment of urban stormwater has also increased (Fletcher et al., 2015).

2.2 Pollutants in stormwater

Previous research on stormwater quality treatment in urban areas has identified a number of pollutants that could pose a potential hazard to humans and aquatic life (Eriksson et al., 2007; Ma et al., 2019, 2016; Novotny and Witte, 1997). The European Water Framework Directive (WFD, 2014) lists, in Directive 2013/39/EU 45 priority substances in the field of water policy for which environmental quality standards have been set. These priority substances include the pollutant groups metals, PAHs, PCBs, phthalates, and phenols. Numerous studies have evaluated the occurrence and concentrations of these contaminants in stormwater, such as TSS, PAHs, metals (Cd, Cu, Pb and Zn) and nutrients (N, P) (Biswal et al., 2022; Gasperi et al., 2014; Göbel et al., 2007; Zgheib et al., 2012, 2011). There are also previous studies of less documented, emerging pollutants of concern, such as phenols and phthalates (Bergé et al., 2013; Björklund et al., 2009; Gasperi et al., 2014; Järlskog et al., 2021; Markiewicz et al., 2017; Müller et al., 2021; Zgheib et al., 2011), PCBs (Cao et al., 2019; Gilbreath et al., 2019), PFAS (Kali et al., 2025) and microplastics (Österlund et al., 2023). This indicates that stormwater can be highly contaminated and thus needs to be treated before being discharged.

2.2.1 Metals

Metals naturally occur in the environment (Alloway, 2013). However, in urban areas, they are also a major source of contamination of stormwater (Müller et al., 2020), and are considered as contaminants of concern for human and aquatic life (Pitt et al., 1994). Eriksson et al. (2007) proposed the use of a list of selected priority pollutants in stormwater, including the metals Cd, Cr, Cu, Ni, Pb, Pt and Zn. Furthermore, in road runoff, the Nationwide Urban Runoff Program (NURP) has classified metals (especially Cu, Pb and Zn) as toxic in stormwater (US EPA, 1983). In stormwater, metals either occur in particulate forms or as dissolved fractions (Lange et al., 2020a). Huber et al. (2016) discussed the importance of stormwater treatment strategies from the perspective that, in general, for Zn, Cu, Ni and Cd the largest fractions are in the dissolved phase, whereas Pb and Cr are mainly particle-bound. Particulate as well as dissolved metals are of concern in stormwater, and contribute to the degradation of receiving waters (Al-Ameri et al., 2018; Göbel et al., 2007).

2.2.2 Organic micropollutants (OMPs)

OMPs are large groups of numerous pollutants with different chemical characteristics, highlighted as a cause for concern since they are often persistent in the environment and tend to bioaccumulate, which can have long-term negative effects on receiving waters (Barbosa et al., 2012; Markiewicz et al., 2017). Common sources that contribute OMPs in stormwater include coal tar sealants, traffic, construction materials and those from industrial use (Bergé et al., 2013; Brown and Peake, 2006; Crane, 2014; Lamprea et al., 2018; LeFevre et al., 2012; Markiewicz et al., 2017). Previous field studies have detected OMPs in urban runoff e.g. polycyclic aromatic hydrocarbons (PAHs) (Smith et al., 2000), polychlorinated biphenyls, PCBs (Cao et al., 2019; Hwang and Foster, 2008), phthalates

(Björklund et al., 2009) and alkylphenols (Lamprea et al., 2018). PCBs, alongside alkylphenols, are considered as an important class of persistent organic pollutant (POP) chemicals (Jones and de Voogt, 1999; Stockholm Convention, 2008). In previous studies, samples of stormwater have contained up to 80 times higher levels of PCBs than base flow (Hwang and Foster, 2008). The main sources of PCBs include oil-filled cables, paints, pesticides, insecticides transformer oils, small capacitors, heat transfer fluids and hydraulic fluids. Studies of sediments in urban lakes have revealed that there are still active sources contributing to PCBs, and that stormwater is the main pollutant pathway (Andersson et al., 2015). In a study of 1100 compounds to identify priority pollutants, Markiewicz et al. (2017) listed PAHs, alkylphenols and phthalates among the four highest ranked priority pollutants. Also, Eriksson et al. (2007) included PAHs, phenols, di(2-ethylhexyl) phthalate and PCB28 in the list of selected priority pollutants. 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).

2.3 Bioretention

For stormwater quality treatment, different treatment methods are commonly used, such as bioretention, ponds, (bio-)swales, permeable pavements, infiltration basins, and wetlands (Dietz, 2007; Kaur and Gupta, 2022). Stormwater bioretention is one of the most commonly used techniques and increasingly popular for treatment of urban stormwater (Croft et al., 2024; Davis et al., 2009; Kratky et al., 2017; McGrane, 2016; Vijayaraghavan et al., 2021). Numerous sstudies have also shown that bioretention systems can be effective for reduction of runoff volumes, peak flows and improving water quality (Davis et al., 2009; Hatt et al., 2008; Yang et al., 2024).

Bioretention systems treat the water by percolating it vertically through a filter material, before the water is released through a drain layer to the downstream system (receiving water, stream, or stormwater drainage system). A typical bioretention system (Figure 2) consists of an inlet structure, commonly vegetated bioretention soil media, often a sand-based filter substrate, with an underlying drainage layer (Davis et al., 2009; Hunt et al., 2012; Tirpak et al., 2021). A ponding zone on top of the filter material allows for temporary storage of stormwater as stormwater inflows often exceed the infiltration capacity of the filter material. Some facilities are also equipped with a pre-sedimentation forebay by the inlet for pretreatment and settling of suspended sediments (Blecken et al., 2017; Erickson and Hernick, 2019; Kallin et al., 2004). The bioretention 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) which has positive effects on the bioretention system's long-term function e.g. reducing clogging, (Le Coustumer et al., 2012) which is beneficial for removal of metals (Lange et al., 2020b) and also increases infiltration rates (Valtanen et al., 2017). To enable bypassing of the filter when there are high flows during high intensity rain events that exceed designed flows, the bioretention system is normally equipped with an overflow device (Erickson and Hernick, 2019).

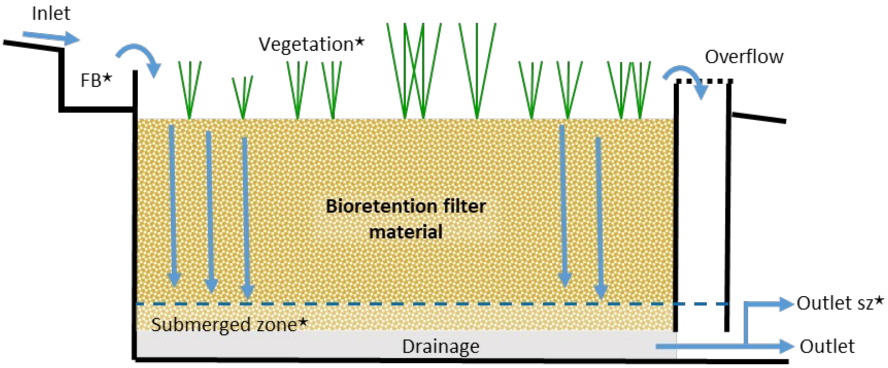

Figure 2. Schematic of a bioretention system. *Forebay (FB), vegetation and submerged zone (sz) where applicable.

2.4 Pollutant removal in stormwater bioretention systems

Bioretention is considered to be an efficient method for removal of various pollutants, e.g. total suspended solids (TSS) (Hsieh and Davis, 2005), metals and particulate pollutants (Blecken et al., 2009a; Dietz, 2007) as well as for a wide range of (mainly hydrophobic) OMPs (Zhang et al., 2014). Studies have shown significant removal of suspended solids and metals (mainly particle-bound metals), with pollutant removal that often exceeds 70–90% (Blecken et al., 2009b; Chapman and Horner, 2010; David et al., 2015; Davis et al., 2003; Flanagan et al., 2018; Glass and Bissouma, 2005; Hatt et al., 2009; Hsieh and Davis, 2005; Hunt et al., 2008; Jafarzadeh et al., 2024; Lange et al., 2022; LeFevre et al., 2015; Li and Davis, 2009). Furthermore, previous studies have also reported correlations between particulate metals and TSS. This occurs since most particulate metals are removed by filtration (Blecken et al., 2009a; Tedoldi et al., 2016).

While most studies of stormwater treatment have focused on particles and particle-bound pollutants, few studies have assessed dissolved metals, despite the environmental relevance of the dissolved phase (Lange et al., 2020a; LeFevre et al., 2015). Previous laboratory studies have showed that total metal removal, in general, is more efficient (Blecken et al., 2009a; Hatt et al., 2007; Sun and Davis, 2007) than removal of dissolved metals (Hatt et al., 2007; Søberg et al., 2017) and truly dissolved metals (Lange et al., 2022, 2020b). Studies of dissolved metal removal by bioretention systems have reported removal as well as leaching (Hatt et al., 2007; Muthanna et al., 2007; Paus et al., 2014a; Søberg et al., 2017, 2014). For the dissolved metal fractions, sorption processes are important for the removal mechanism (Dean et al., 2005; Maniquiz-Redillas and Kim, 2016). The main processes of dissolved metals treatment in bioretention systems are precipitation/dissolution, and sorption processes of dissolved metals (Alloway, 2013; Davis et al., 2003; LeFevre et al., 2015). Further, LeFevre et al. (2015) stated in a review study that there was a need to study dissolved metal treatment in bioretention systems but that, at that point, only a few studies had included the measurement of dissolved metals (Lange, 2021).

Compared to metals, there are fewer studies and limited data available on removal of OMPs by bioretention systems. Most studies of OMPs in bioretention facilities have focused on hydrocarbons, and particularly on PAHs. However, some studies have indicated efficient removal of a wide range of OMPs (K. Zhang et al., 2014), with high concentration reductions (>90%) for PCBs and PAHs (both hydrophobic, often particulate OMPs) (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). Beryani et al. (2023) reported removal of OMPs in stormwater from 50% for phenolic substances to 50–80% for PAHs. Thus, these high concentrations of various pollutants (OMPs and metals) that accumulate in the filter material indicate the importance of the filter material for stormwater treatment.

2.4.1 Sand-based filter material

The filter material is probably the most important factor for pollutant removal in a bioretention facility (Blecken, 2010; Blecken et al., 2011; Muthanna et al., 2007; Sun and Davis, 2007). The main function of the filter is, besides retaining or delay flow, to improve stormwater quality with various bio/chemical and physical processes including adsorption, precipitation, ion-exchange, and filtration (Fassman-Beck et al., 2015; Hsieh and Davis, 2005; Søberg et al., 2019; Tirpak et al., 2021). There are a number of filter material configurations, typically refined sand-based (sandy loam or loamy sand) with a low organic matter content, and/or a mixture of sand with additives such as organic matter, biochar, chalk or vegetation soils, that support e.g. plant growth or metal treatment (Davis et al., 2009; Hatt et al., 2011; Hunt et al., 2012; Søberg et al., 2019). The filter material has to ensure adequate retention of the water to ensure sufficient contact time for treatment processes, but also provide relatively high infiltration to avoid overflow and also to support plant life and avoid clogging (Fassman-Beck et al., 2015; Tirpak et al., 2021). The different requirements in the bioretention filter are partly conflicting e.g. while small particle size distribution increases water retention and pollutant removal, a coarser grain size increases infiltration and prevents clogging (Tirpak et al., 2021). Thus, to target the conflicting characteristics, an optimizing compromise is desirable and beneficial for best performance. In general, filter materials classified as sand with naturally high pH, low organic matter content and large specific surface area are recommended, particularly for dissolved metals (Søberg et al., 2019) since finer particles have a greater surface area per unit mass, and metals are adsorbed more effectively to a finer filter material (Li et al., 2013). However, previous research has recommended that future research should focus on optimizing bioretention systems for treatment of dissolved metals and there should be more field studies to generate more data on the effect of different environmental conditions (Lange et al., 2022).

Another feature for improving the characteristics of the filter materials is the use of additives and amendments, such as organic matter, biochar, pumice and chalk, to support pollutant treatment. For instance, a chalk additive (e.g. $CaCO_3$) in filter materials, as described in the German water manual DWA M-187 (DWA, 2005), may improve the metal adsorption, especially of dissolved metals (Søberg et al. 2019). Such a chalk additive may increase pH in the filter media and thus improve the metal adsorption (Hatt et al., 2011; Søberg et al., 2019). To support the previous laboratory studies of filter material additives and amendments, field-scale studies are needed (Tirpak et al., 2021). To date, there have been very few studies on the effect of chalk additives in bioretention media.

Cheng et al. (2018) carried out a laboratory study of pumice bioretention and removal of phosphorus, nitrogen and TSS, with successful results. Fassman-Beck et al. (2015) and Liu and Fassman-Beck (2018) also carried out studies using pumice and showed that filter material with pumice can retain more water. Fassman-Beck et al. (2015) explained this increase in water holding capacity as being because pumice can store water within intraparticle pores. However, so far no field studies have assessed pumice and hydraulic conductivity and the effects on metal treatment. Narayanasamydamodaran et al. (2024) also carried out laboratory-scale studies of nitrogen removal and showed that a pumice additive could have a positive effect. Both Cheng et al. (2018) and Narayanasamydamodaran et al. (2024) identified a need for further research on bioretention with pumice amendments, and particularly field studies of pumice additives and total and dissolved metal removal.

Kratky et al. (2017) undertook a large review study, and specifically pointed out the importance of better understanding of bioretention facilities' hydraulic and water quality performance and the need of both laboratory and field studies. Further, Kratky et al. (2017) also recommended studies of bioretention systems specifically designed for cold climates, removal of both total and dissolved metals and studies of amendments to enhance metal adsorption and TSS. Thus, larger-scale field studies of additives are required, with a particular focus on additives in colder regions and the influence of road salt.

2.4.2 Infiltration and hydraulic conductivity

Particle size distribution is considered to be one of the most important properties to consider when optimizing hydraulic conductivity (K_{sat}), contaminant removal and maintenance frequency, as increased particle size increases hydraulic conductivity and reduces clogging (Liu and Fassman-Beck, 2018; Muthanna et al., 2007; Stoeckeler and Weitzman, 1960). A common recommendation for hydraulic conductivity in filter materials is that it is 50–200 mm/hr K_{sat} (Le Coustumer et al., 2009). Fassman-Beck et al. (2015) suggested an acceptable target range of 12.5–150 mm/hr, and Hunt et al. (2012) suggested up to 150 mm/hr for best particulate removal.

A coarser filter material lacking fines (e.g. sand) increases infiltration rates as a result of increased K_{sat}, thus increasing the volume of stormwater percolating through the material, while finer materials (e.g. silt and clay) reduce infiltration rates but increase removal of pollutants (Funai and Kupec, 2017; Hunt et al., 2012; Kandra et al., 2014; Tirpak et al., 2021). Despite potentially less adsorption, a higher hydraulic conductivity could also contribute to more efficient pollutant treatment by reducing number and amount of high flow overflows (Tirpak et al., 2021). Further, higher infiltration also means that a larger volume of runoff is treated for a specific filter area, and is thus beneficial for urban areas where space for facilities is scarce. Finally, filter materials with low hydraulic conductivity may increase risk of clogging (Kandra et al., 2014).

Further, recommendations for infiltration capacities around 50-200 mm/hr do not account for cold climate and winter conditions, with temperatures below or fluctuating around zero degrees Celsius. Here, coarser materials may have benefits: a more well-drained and coarser filter material is beneficial for infiltration at low temperatures, because less water will stand in the pores between particles during freezing (Caraco and Claytor, 1997). Thus, in colder regions and where winter conditions are expected, a coarser and better drained material, with higher hydraulic conductivity than normally recommended (50–200 mm/hr) could be beneficial (Blecken et al., 2011; Zhao and Gray, 1999). However, further field studies of coarser filter materials and pollutant removal (total and dissolved metals) specially adapted for cold climates are needed.

2.4.3 Submerged zone

A submerged zone, also known as a saturated zone or internal water storage has been used to improve pollutant removal, especially of nitrogen in bioretention facilities, (Blecken et al., 2009b; Kim et al., 2003; Li et al., 2014). Several laboratory-based studies have reported improved nitrogen removal due to submerged zone (Blecken et al., 2009b, 2009a; Kim et al., 2003; Søberg et al., 2017; Z. Zhang et al., 2014). This is mainly due to the anaerobic conditions created in the submerged zone that stimulates denitrification (Li et al., 2014). Previous studies have also shown improved metal removal (Cu and Pb) with a submerged zone (Blecken et al., 2009a; Z. Zhang et al., 2014). However, to date, few field studies have assessed the effect of a submerged zone on metal treatment in bioretention facilities in a cold climate using filter materials with higher hydraulic conductivity. Further studies of vegetation and submerged zones under field conditions have been recommended in previous research (Z. Zhang et al., 2014).

2.4.4 Chloride influence

Relatively few studies to date have evaluated the effect of cold climate and de-icing salt on bioretention facilities' ability to treat metals (Kratky et al., 2017). Marsalek (2003) reported an increased potential impact on the environment from road salting (1972–2000). Previous studies have shown that concentration of fine particles (< 10 μm) increases under the influence of salts (Behbahani et al., 2021). Further, elevated salinity can negatively impact stormwater treatment by reducing the ability to capture pollutants through alteration of the stability of suspended particles. Higher salinity also results in increased desorption of exchangeable Cr, Cu, Zn and Pb, likely due to cation exchange and formation of aqueous metal complexes (Behbahani et al., 2021). Paus et al. (2014a) carried out a laboratory study of temperature and NaCl impact on metal retention in bioretention columns. The study reported effective capture of Cd and Zn but reduced removal of particulate Cu. Furthermore, Paus et al. (2014a) also noted that NaCl caused already accumulated metals to leach since the salt changed the distribution of metals towards the dissolved phase. In a laboratory study of temperature and salt influence on metal removal in bioretention facilities, Søberg et al. (2014) detected significant removal of dissolved Zn and Cd (> 90%), while removal of dissolved Cu and Pb was less efficient (-1345% to 71%) due to the presence of salt. Géhéniau et al. (2015) reported significantly increased effluent chloride concentrations during the cold season due to the use of de-icing salt in rain gardens, and observed effective removal of total Pb and Zn while no removal or release of total Cu and Ni. However, that study lacked evaluation of the dissolved metal fractions, which are relevant when looking at metals and salt. Although already Blecken et al. (2011) identified the need for future research and the effects of road salt on stormwater biofiltration during the winter period, to date, there have been few studies, especially field studies, on that topic. Lange et al. (2022) and Kratky et al. (2017) recommended future research should focus on bioretention facility treatment of dissolved metals, and more field experiments including road salt application. In a field study of metal treatment in a bioretention system, Lange et al. (2020a) observed that total metals were efficiently removed, while there was a less effective removal of dissolved metals and increased metal concentrations under the influence of salt application from road maintenance. Previous laboratory studies that assessed the effects of low temperature on bioretention facilities (Søberg et al., 2017) also addressed a need for further studies of the effect of road salt on metal treatment. In particular, Géhéniau et al. (2015), in a study of rain gardens, addressed the need for further research on metal treatment (Cu, Ni, and Zn) in cold climates. Previous studies on the effect of vegetation mainly focused on TSS, metal, and nutrient removal (e.g. Dagenais et al., 2018), and did not include the impact of cold climate nor the influence of de-icing salt. Thus, there is a need for field studies of chloride influence on total and dissolved metal removal.

2.5 Pollutant accumulation in bioretention facilities

2.5.1 Accumulation of metals

Filtration of suspended material is the main treatment process for removal of particulate metals (Blecken et al., 2009b, 2009a; David et al., 2015; Li and Davis, 2008a). Consequently, many metals (and other particulate pollutants) are mainly trapped and retained in the top layer of the filter (Al-Ameri et al., 2018; Blecken et al., 2009a; Li and Davis, 2008b). Studies have shown high reductions of metals (mainly particle-bound metals) that often exceed 70–90% (Blecken et al., 2009b; Chapman and Horner, 2010; David et al., 2015; Davis et al., 2003; Flanagan et al., 2018; Glass and Bissouma, 2005; Hatt et al., 2009; Hsieh and Davis, 2005; Hunt et al., 2008; Jafarzadeh et al., 2024; Lange et al., 2022; LeFevre et al., 2015; Li and Davis, 2009). Due to this accumulation in the top layer of the filter material, understanding the accumulation processes in addition to stormwater treatment is also important for understanding the long-term function of a bioretention facility. Previous studies of bioretention filter materials have estimated that the time for metal accumulation to reach environmental and health regulatory limits for concentrations in the filter material is highly varying, e.g. 20, 77, 16 and 16 years for Cd, Cu, Pb and Zn respectively (Davis et al., 2003), and 12–15 years of operation to exceed ecological guideline values requiring special disposal processes for Cd, Cu and Zn (Hatt et al., 2011). Leaching and desorption potentials also affect long-term function (Okaikue-Woodi et al., 2020). This is because of the potential risk of leaching of previously accumulated pollutants from the filter material, and during disposal of material removed from polluted facilities. Due to the leaching potential, regular replacement of sediment and pollutant accumulated filter material has been recommended after 20–25 years (Kluge et al., 2018). There have been few studies of bioretention filter material (Søberg et al., 2019) and, for metals, there are knowledge gaps in respect of long-term retention, risks for leaching of adsorbed metals and accumulation processes (Hatt et al., 2008; Søberg et al., 2017). 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.

For assessment of metal leaching from filter materials, fractionation studies can provide information about the leaching potential and long-term behaviour of metals in a bioretention facility. Although several studies have investigated metal behaviour in bioretention facilities, few studies have assessed the availability of metals using sequential extraction methods. Previous laboratory studies using sequential extraction have studied metals (Cd) in a laboratory bioretention column experiment (Wang et al., 2016) and evaluated adsorbed dissolved metals in bioretention filter materials (Søberg et al., 2019). In a laboratory study, Søberg et al. (2019) also found metals were primarily adsorbed to exchangeable forms. Another laboratory study found that 88–97% of Zn, Cu, Pb was captured in the filter material while only 0.5–3.3% was captured in the plants, and thus accumulation in the filter media played an important role in long-term metal removal (Sun and Davis, 2007). Two field studies used five-step sequential extraction methods to study metal capture (Cu, Pb and Zn) and environmental availability (Jones and Davis, 2013; Li and Davis, 2008b). Jones and Davis (2013) found metals to be strongly bound to the filter media and largely immobile. Li and Davis (2008a) found that most captured metals were anthropogenic with correlations between soluble-exchangeable forms with dissolved metals, while the more stable forms were associated with runoff and particulate metals. A field study used sequential extraction to assess metal (Cr, Cu, Ni and Zn) mobility of road runoff in bioretention facilities (Rommel et al., 2021). However, there have been only a few previous larger studies assessing older field sites using sequential extraction methods, so further research is needed.

2.5.2 Accumulation of organic micropollutants (OMPs)

Compared to other pollutants (e.g. metals, nutrients and TSS), there has been limited previous research assessing accumulation of OMPs by bioretention facilities in the filter material and its effect on long-term function (K. Zhang et al., 2014). While there have been several studies of metal distribution in filter media (Al-Ameri et al., 2018; Jones and Davis, 2013), less is known about OMP pathways and accumulation in the filter material. Previous studies have shown that the main removal of particulate metals by a bioretention facility occurs in the top layer of the filter material (Davis et al., 2009; Hatt et al., 2008). However, OMPs, particularly those with high molecular weights and/or high hydrophobicity (e.g. Bper, IP, PCB180 and PCB153, see Table 17), tend to accumulate in the top layer of soil, sometimes reaching concentrations above regulatory limits (DiBlasi et al., 2009; Flanagan et al., 2018; Tedoldi et al., 2017). Previous studies have also shown that there is less efficient accumulation of the more hydrophilic and soluble substances e.g. phthalates, bisphenol A, and polyfluorinated alkyl substances (PFAS) (Beryani et al., 2024b, 2023; Boehm et al., 2020; Spahr et al., 2020; Zhang et al., 2016). Collectively, this highlights the need for further studies of long-term accumulation and distribution of OMPs in bioretention facilities. Better knowledge of pollutant pathways and filter accumulation of both metals and OMPs is needed to enable improved design and assessment of bioretention facility long-term performance (Davis et al., 2009). Kratky et al. (2017) also recommended further research into long-term performance and disposal requirements of polluted filter media. Understanding accumulation processes, and the occurrence, concentration, and distribution of OMPs in the filter material is important for the understanding of bioretention facilities' long-term OMP treatment.

2.5.3 Forebay

A forebay is often implemented to provide pre-sedimentation at the bioretention facility (Figure 2) inlet to minimize sediment transport to the filter surface and thus prevent clogging, or as an energy dissipator (Tirpak et al., 2021). Its technical function is to reduce flow velocities and thus promote sedimentation and large debris removal (Al-Ameri et al., 2018; Erickson and Hernick, 2019; Maniquiz-Redillas et al., 2014; McNett and Hunt, 2011; Winston et al., 2023). When bioretention is implemented e.g. in a swale, the side slope serves as a buffer strip reducing the amount of sediment entering the filter surface. In environments where such a buffer strip cannot be installed, e.g. due to space restrictions, often a forebay, which comprises of a small settling or sediment basin, is placed at the inlet as a velocity dissipator and/or for erosion protection but may also be a rock structure with a pooling function. The size of bioretention facility forebays is often approximately 10% of the design surface area (City of Portland, 2020; Minesota Pollution Control Agency, 2022), however the design can vary depending on local statutes, policies, and practices. From a study of biofilter wetlands, Kallin et al. (2004) suggested that an efficient design should incorporate a forebay for settling of large suspended sediments.

To date, few studies have examined forebay sediments and performance for pretreatment of stormwater. Previous studies on sedimentation basins have shown that a large proportion of particle-bound pollutants accumulate in sediments (German, 2003; Grottker, 1990) and that sediments accumulate in forebays. In studies of ponds and wetlands, McNett and Hunt (2011) assessed the toxicity of 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 their study) may restrict potential land applications. Wetlands and wet ponds are commonly larger than bioretention, and since forebays in wetlands and wet ponds (10–20% of total area) are larger than in bioretention facilities (10% of a smaller total area) (Maniquiz-Redillas et al., 2014; Schaad et al., 2008; Winston et al., 2013), the comparison between bioretention facility forebays and ponds is not always meaningful. While most metals are bound to small particle fractions that are not efficiently removed by small forebays, a significant portion of metals may be associated with larger particles (Karlsson and Viklander, 2008; Stone and Marsalek, 1996) and thus may accumulate in the forebays of bioretention cells. Previous studies have emphasized the need for frequent maintenance and removal of accumulated sediments in pretreatment devices to restore storage volume and prevent contamination of downstream facilities and/or waterbodies (Blecken et al., 2017; Grimm et al., 2023; McNett and Hunt, 2011).

Regular maintenance is also needed to maintain the long-term performance of a bioretention facility (Johnson and Hunt, 2016). In a review of stormwater control measures maintenance by Blecken et al. (2017), they described the key maintenance needs for a bioretention facility which included vegetation upkeep, inspecting and cleaning the inlet structure including the forebay and preserving the surface infiltration. Lange et al. (2022) recommended that future studies of bioretention systems should focus on optimizing them for the treatment of dissolved metals, and development of better pretreatment facilities. Thus, further field studies of bioretention facility forebays and the accumulation of OMPs, total and dissolved metals in the forebay are required.

2.6 Research gaps

In summary, this review shows that stormwater bioretention is increasingly popular and one of the most commonly used techniques for management of urban stormwater. Bioretention is considered effective for removal of a variety of pollutants including OMPs and metals from urban stormwater. Numerous studies have been carried out to evaluate bioretention treatment functionality, however many of these previous studies have been limited to laboratory studies or smaller field-scale studies, in warmer climate conditions or with a shorter time scale perspective. In general, there is a need for increased knowledge of water quality treatment and pollutant accumulation in bioretention facilities for improved stormwater treatment in urban areas. Three areas covered by these research gaps have been identified in this review of stormwater bioretention systems:

- Design parameters, such as filter configuration, including additives of chalk and pumice, and infiltration characteristics and their effect on metal treatment.
- The effect of de-icing salt on total and dissolved metal treatment
- The occurrence, concentration, distribution and/or availability of organic micropollutants and metals in bioretention filter materials and forebays.

Thus, the work for this thesis focused on bridging these knowledge gaps. There is a need for more large full-scale field studies with a longer time perspective. As the use of different engineered additives and amendments becomes more common, there is a need for field studies assessing their actual function. The effects of chalk and pumice additives on total and dissolved metal treatment need to be evaluated in field studies. Also, the impact of higher infiltration capacities and their effect on total and dissolved metal removal need to be clarified in full scale tests. This is particularly true for colder regions with longer periods of temperatures around zero degrees Celsius. Also, the effect of an increased ratio of dissolved metals e.g. due to road salt application during winter needs to be assessed. Furthermore, understanding the distribution of pollutants (OMPs and metals) is essential for better understanding accumulation processes and for understanding the long-term performance of a bioretention facility for stormwater quality treatment. Previous research has highlighted the need for further studies to understand accumulation and distribution of metals and OMPs in the bioretention filter material and forebays. Studies of older facilities have been suggested to gain a longer-term perspective on maintenance needs and measures, and help characterize them. Characterizing the accumulation of pollutants in bioretention facility filters and forebays is essential for evaluating the function associated with managing bioretention facility media throughout its life cycle.

This increased knowledge would contribute to a better understanding of how bioretention technology can contribute to the development of better methods for stormwater management and, thus, a more sustainable development of urban areas.

3 Methods

Three major field studies were carried out to collect the data presented in this thesis. One study focused on pollutant accumulation in bioretention filter media and included sampling of filter material in the U.S. The other two studies focused on pollutant accumulation using the results of stormwater sampling from two field sites in Sweden.

3.1 Pollutant accumulation (studies I, II and III)

3.1.1 Field sites and site characteristics

The field work for the study of pollutant accumulation (studies I, II and III) was carried out in November 2019 on stormwater bioretention systems located in Ohio, Michigan, and Kentucky (USA). Pictures of some of these sites are shown in Figure 3. Filter material was sampled from 29 bioretention sites, where 20 were equipped with a forebay (FB) (Figure 2). All bioretention sites were located in urban areas, with contributing catchments a mixture of urban, high urban, residential and industrial/commercial areas, mainly treating road runoff and urban stormwater, as summarised in Table 1. The studied sites had been treating stormwater for 7–16 years at time of sampling. The studies of FB sediments also included samples from eight younger (approximately 2–4 years of operation) bioretention FBs in Sweden (a description of the Swedish sites is presented in section 3.2 Pollutant removal (studies IV and V)).

Figure 3. Selected bioretention sites from field sampling of filter material for studies of pollutant accumulation in Ohio, Michigan, and Kentucky in November 2019. Upper left: site #18. Upper right: site #27. Lower left: site #22. Lower right: site #26 (Table 1).

Table 1. Field sites and site characteristics from studies of pollutant accumulation. *Indicates sites only included in FB sediment analysis (Paper III). Analyses of organic micropollutants (omp) and metals (me), forebay (FB) and filter area/catchment area (FA/CA).

Site	Analyse	FB	Age [yr]	Location	Catchment area characteristics	Catchment Area [m²]	Filter Area [m²]	FA/CA [%]
1	omp/me	Yes	9	Upper Arlington, OH	Residential	318000	950	0.3
2	me	Yes	9	Upper Arlington, OH	Residential	1250000	1200	0.1
3	me	Yes	9	Upper Arlington, OH	Residential	224000	900	0.4
4	me	Yes	9	Upper Arlington, OH	Residential	146000	1900	1.3
5	omp/me	No	8	Upper Arlington, OH	Commercial	750	40	5.3
6	omp/me	No	10	Columbus, OH	Industrial	6000	300	5.0
7	me	Yes	8	Westerville, OH	Parking/Roads	12000	600	5.0
8	me	Yes	8	Westerville, OH	Parking/Roads	2000	50	2.5
9	omp/me	Yes	7	Westerville, OH	Commercial	4000	170	4.3
10	me	Yes	9	Columbus, OH	Parking/Roads	4500	580	12.9
11	omp/me	Yes	9	Columbus, OH	Downtown Urban	300	40	13.3
12	omp/me	Yes	8	Columbus, OH	Downtown Urban	50	10	20.0
13	me	Yes	12	Hamilton, OH	Industrial	4500	200	4.4
14	omp/me	Yes	12	Hamilton, OH	Industrial	4500	300	6.7
15	me	Yes	12	Hamilton, OH	Industrial	4500	200	4.4
16	me	No	16	Cincinatti, KY	Commercial	3000	190	6.3
17	me	No	9	Toledo, OH	Residential	250	50	20.0
18	omp/me	No	12	Lansing, MI	Downtown Urban	600	50	8.3
19	omp/me	Yes	11	Lansing, MI	Downtown Urban	500	50	10.0
20	me	Yes	14	Ann Arbor, MI	Parking/Roads	2250	156	6.9
21	me	No	11	Seven Hills, OH	Commercial	1200	200	16.7
22	omp/me	Yes	8	Parma, OH	Fueling station	2500	200	8.0
23	omp/me	No	13	Twinsburg, OH	Fueling station	2000	70	3.5
24	me	No	10	Orange Village, OH	Residential	250	20	8.0
25	me	No	10	Orange Village, OH	Residential	250	20	8.0
26	me	Yes	11	Kent, OH	Fueling station	800	70	8.8
27	me	Yes	13	Akron, OH	Parking/Roads	6500	180	2.8
28	omp/me	Yes	12	North Canton, OH	Fueling station	1250	180	14.4
29	me	Yes	12	North Canton, OH	Fueling station	1000	100	10.0
30*	omp/me	Yes	2	Stockholm, SWE	Road	340	20	5.9
31*	omp/me	Yes	2	Stockholm, SWE	Parking	340	20	5.9
32*	omp/me	Yes	2	Stockholm, SWE	Road	370	20	5.4
33*	omp/me	Yes	2	Stockholm, SWE	Parking	340	20	5.9
34*	omp/me	Yes	2	Malmö, SWE	Downtown Urban	350	20	5.7
35*	omp/me	Yes	2	Malmö, SWE	Downtown Urban	350	20	5.7
36*	omp/me	Yes	2	Malmö, SWE	Downtown Urban	350	20	5.7
37*	omp/me	Yes	2	Malmö, SWE	Downtown Urban	350	20	5.7

3.1.2 Soil sampling

The methodology used for sampling of filter material was a hypothesis-guided sampling regime for mapping the dispersion of contaminants along, and at depth in, the filter material. Similar methods have previously been used by e.g. Tedoldi et al. (2017), as illustrated in Figure 4. The main aim using this methodology was to determine length/depth profiles of pollutant accumulation in the filter material. Samples were collected at three locations along each filter, located at 1 m, 3 m and 6 m from the inlet. For shorter sites (#5, #8, #12), the distances between sampling points were scaled to fit three locations within each site. Due to the small size of sites #24 and #25, only samples from one location were taken. Further, some filters either had multiple inlets (sites #5, #16, #23 and #26) or inlets stretched out along one of the sides of the filter (sites #13, #14, #15, #24 and #25). For these sites, the sampling locations were selected on site by judging the likely main flow path, based on topography and sediments. Therefore, prior to sampling, mapping and examination of the local topography and hydrology were carried out. Catchments, inlets, sediments and erosion were studied to define the main inlet of stormwater to the filter. The sampling points were then measured from the defined main inlet.

From each of the sampling locations (Figure 4), filter material was collected from three different depths (0–5 cm, 10–15 cm, and 30–50 cm). Samples from the two shallower depths were always taken at 0–5 and 10–15 cm, while the sample from the deeper depth in some facilities (i.e. at sites #6, #7, #8, #23 and #27) due to their design was taken from less than 50 cm. From these sites, the deeper sample was collected from the filter layer between 35 cm and the bottom of the filter. In general, nine samples were collected from each bioretention filter (except at sites #24 and 25, where only 3 samples were taken), and one sample from each of the 20 forebays, resulting in a total of 269 samples (Table 1). Also, eight samples of FB sediments were collected from two test sites located in Sweden (Sundsvall and Malmö).

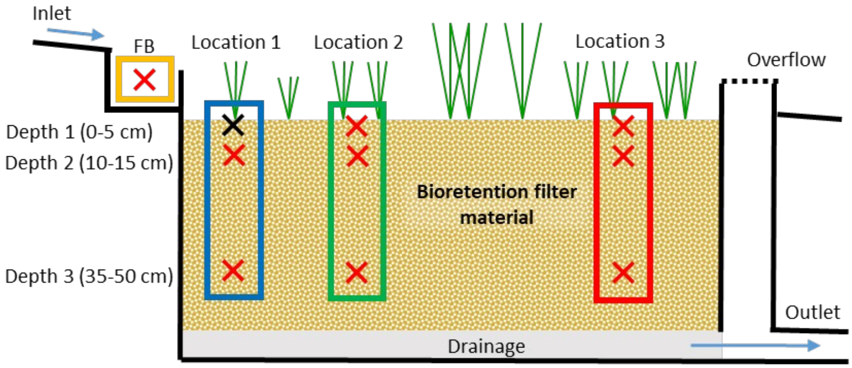

Figure 4. Cross section of a bioretention facility illustrating the 10 sampling points (forebay, three locations in the filter and at three depths) all illustrated with a red "X" except "Depth 1" and "Location 1" marked with a black "X" indicating that a sequential extraction was also carried out on the sample. The coloured rectangles indicate different locations in the filter.

Samples were collected by cutting/digging out a core of filter material (5 cm x 15 cm x 15 cm for depth 1 and 10 cm x 10 cm x 10 cm for depth 2 and 3). The filter material (about 1 to 2 kg) was placed into diffusion-tight plastic bags (18 cm x 35 cm) that were sealed with cable ties. At the time of sampling (November 2019), the outdoor temperature varied between -12 and +6°C. After sampling, the samples were refrigerated prior to laboratory analysis. The forebay samples consisted of sediments collected from sites with a forebay (Table 1), or a forebay structure with a similar function i.e. a pre-treatment facility of steel, concrete or larger stones or rock structures with a pooling function where the stormwater sediment was deposited (Figure 5).

Figure 5. Left: sampling of filter sand in a bioretention facility covered with a mulch layer (site #22). Right: sampling of sediments in a forebay (site #22).

3.2 Pollutant removal (studies IV and V)

3.2.1 Field sites and site characteristics

Two major field study sites were used for collecting data of pollutant removal in bioretention facilities for studies IV and V.

In September 2020, a field study for stormwater sampling (study IV) was set up outside Sundsvall, Sweden. The study focused on metal removal and chloride impact in a cold climate. The Sundsvall study was carried out on a larger bioretention facility treating highway runoff from a bridge and associated traffic areas located along the European highway E4 in Sweden with a traffic load of 13000 vehicles a day. Filter configuration and site characteristics are described in Table 2 and Table 3. The Sundsvall site is located in an area with a continental subarctic climate (Köppen climate zone Dfb). The facility was designed according to the German guidelines for bioretention systems treating stormwater from motorways (DWA, 2005) and had been in operation for 2–4 years at the time of sampling. The total catchment area for the site was 8.2 ha and consisted of 4.7 ha of hard surfaces (with the bridge accounting for 1.9 ha) and 3.5 ha of green areas. During precipitation or snowmelt, stormwater (SW) was conveyed from the bridge through a 100 m long stormwater pipe (d=800 mm) to the bioretention facility.

Table 2. Filter configuration and Test factors.

Site	Test factors	Filter type	Forebay	Year built
Sundsvall	Filter material	Sand filter (S)	Gross Pollutant Tank (GPT)	2017
	Filter material and, vegetation	Sand filter, vegetated (SV)		
	Filter material, vegetation and chalck	Sand filter, vegetated with chalck (SVc)		
Malmö	Filter material and, hydraulic conductivity	Sand filter, vegetated (SV)	Forebay FB	2018
		Sand filter, vegetated with pumice (SVp)		
	Submerged zone	Sand filter, vegetated with a submerged zone (SVsz)		

Table 3. Table of site characteristics for Sundsvall and Malmö.

Site	Filter type	Sampling		Filter depth	Area			Main land use in catchment
		Start	Finished	[mm]	Filter [m^2]	All filters [m^2]	Catchment [m^2]	
Sundsvall	S	2020	2022	500	235	705	47000	Highway (E4)
	SV				235			
	SVc				235			
Malmö	SV	2021	2022	650	6 x 15	270	1900	Down town streets
	SVp				6 x 15			
	SVsz				6 x 15			

The Sundsvall bioretention system (Figure 6) consists of a Gross Pollutant Trap Tank (GPT) where coarser particles are separated out before the water is discharged to the filters. The water is then spread out between three parallel filters with different configurations: a sand filter (S), a vegetated sand filter (SV) and a vegetated sand filter with chalk additive (SVc) (Table 2). The experiment was designed to assess the effect of vegetation and addition of chalk in the sand-based filter material. The approximate area of each filter section is 230 m^2 and water is spread over the filters using a spreader pipe. The filter material in SVc contains 10% (weight) CaCO$_3$ as a pH buffer (DWA 2005). The vegetation in SVc and SV is planted in a 3–4 cm soil layer.

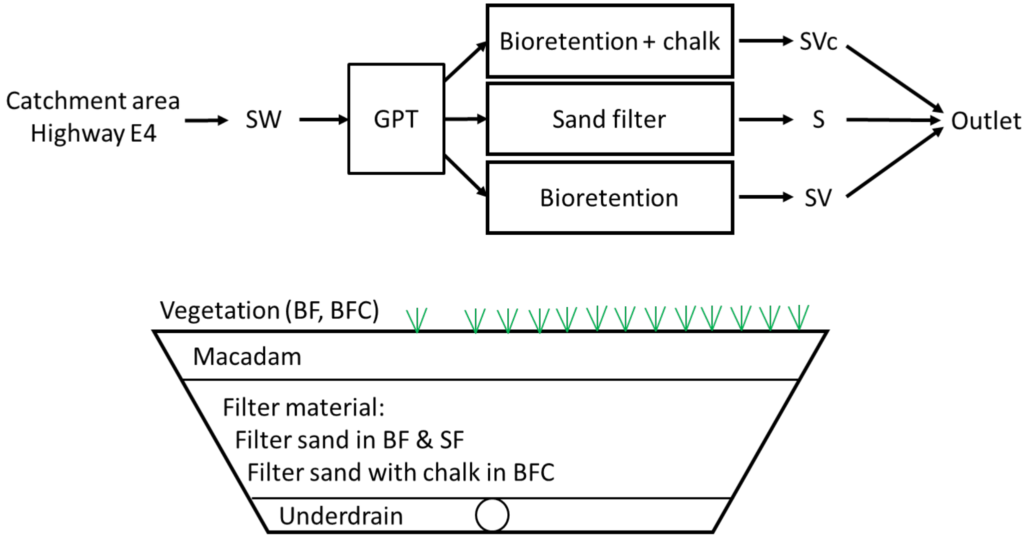

Figure 6. Diagram of the studied bioretention facility and filter configuration from study IV. Numbers with a name indicate sampling locations i.e. SW incoming stormwater, GPT sampled by outlet from GPT tank, SVc, S and SV are the locations of the sampling points after the three parallel filters. Top: view from above; bottom: cross section

Another field study of pollutant removal in bioretention started at the Malmö bioretention facility in spring 2019 and was finished in December 2022. The study was carried out on a larger system consisting of three sections of bioretention along a busy road in central Malmö, Sweden. Each of the three sections consisted of six series-connected bioretention (Figure 7), built according to three different filter configurations (Table 2 and Table 3): vegetated sand filters (SV), sand filters with peat (SVp) and sand filters with a submerged zone (SVsz).

The study focused on metal removal, with the aim of assessing metal removal in filter material with a high hydraulic conductivity in a cold climate, and thus a high infiltration capacity. The filter materials in Malmö (study V) were designed with a specific particle size distribution (Table 4) to create a very high hydraulic conductivity (K_{sat}) (Table 5).

Table 4. Particle size distribution for filter materials with very high K_{sat} investigated for study V.

Filter	Material	Particle size	SV/SVsz	SVp
		[mm]	[%]	
Malmö	Sand	0.063 – 0.15	4	2
		0.15 – 0.25	8	4
		0.25 – 0.5	28	14
		0.5 – 1.0	25	12.5
		1.0 – 2.0	25	12.5
		2.0 – 4.0	10	5
	Pumice	2.0 – 8.0	-	50
			S/SV	SVc
Sundsvall	Sand	0.06 – 0.20	4	2
		0.20 – 0.60	8	4
		0.60 – 2.00	28	14
	CaCO3	-	-	10

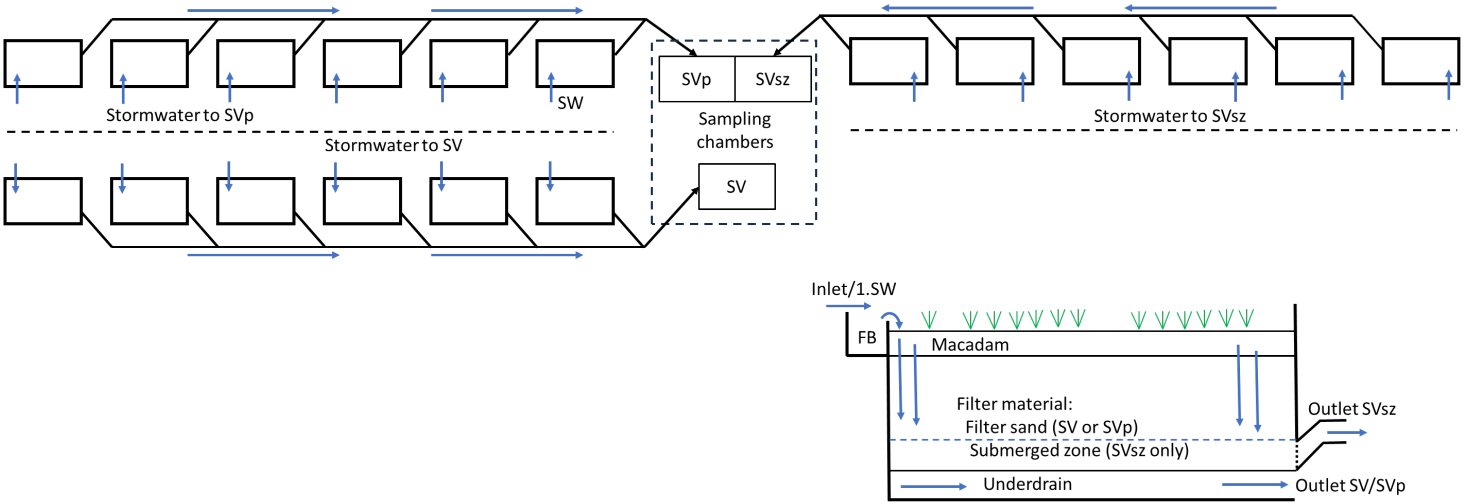

Figure 7. Malmö facilities and test setup. Stormwater was sampled at inlet SW, and in the FB. The treated water was sampled in sampling chambers after the filters at SVp, SVsz and SV. Top: view from above; bottom: cross section

The infiltration measured as saturated hydraulic conductivity K_{sat} was generally very high (Table 5 and Figure 8) in all three filter materials compared to what is normally recommended (<150–200 mm/hr) (Fassman-Beck et al., 2015; Le Coustumer et al., 2009). The median K_{sat} in the studied filters was highest in SVp (2834 mm/hr), lower in SV (1885 mm/hr) and lowest in SVsz (1517 mm/hr), and thus approximately 10 to 15 times higher than normally recommended in previous literature. The first infiltration measurement was carried out in spring 2019, a few months after installation of the filters, with the last measurement in December 2022. No time dependent trend was observed i.e. no significant clogging of the filter surface had occurred over those three years and nine months of operation.

Table 5. Hydraulic conductivity K_{sat} for three different filter materials estimated using infiltrations tests in Malmö for study V.

	SV		SVp		SVsz	
Date	Ksat	St.dev	Ksat	St.dev	Ksat	St.dev
2019-03-19	1352	± 650	2985	± 1069	1896	± 467
2019-11-12	2603	± 789	1758	± 3718	2299	± 845
2020-06-16	1428	± 508	2977	± 2394	1384	± 250
2020-12-09	1733	± 330	-	-	1523	± 813
2021-08-31	2916	± 1294	-	-	1500	± 2341
2022-12-09	1473	± 1726	3634	± 1918	1213	± 1111

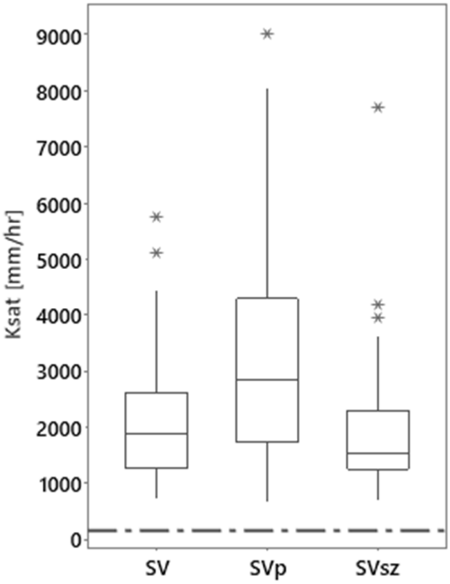

Figure 8. Hydraulic conductivity K_{sat} in three different filter materials. Reference line at 150 mm/hr indicates the highest recommended hydraulic conductivity according to Fassman-Beck et al. (2015).

3.2.2 Stormwater sampling

At the Sundsvall site, stormwater was sampled from 12 rain events with varying characteristics (Table 6) from autumn 2020 to summer 2022. All samples were collected volume-proportionally using ISCO6712 automatic samplers. For the first six rain events (A–F), each sampler was equipped with 24 acid washed plastic bottles, and sub-samples were collected and analysed separately (Lange et al., 2022b). Event mean concentrations were calculated based on data from events A–F. Composite samples were taken for each event G–L. The volume-proportional sampling at SW and GPT was controlled by valves in the GPT, opening when the water reached a maximum level. Pulses from the valve opening were used for calculations of inflow and outflow to/from the GPT. Samples taken from the outlets of the filters (S, SV and SVc) were controlled by in-pipe electromagnetic flowmeters in the outflow pipes of the bioretention systems (MAG 5100 Siemens AG, München, Germany). Rain characteristics (Table 6) were determined using a tipping bucket rain gauge (ISCO 674), installed by the treatment facility. For rain event C, precipitation data from a local weather station (0.2 km away) were used, due to technical problems with the rain gauge on site. In total, samples were collected at five different sampling points: SW, GPT, S, SV and SVc (Figure 6).

Table 6. Rain characteristics of 12 sampled events at Sundsvall sampling site. ★Indicates precipitation event with higher chloride concentration. ★★Warm weather season ★★★Days without rain i.e. without rainfall runoff, however period includes snowmelt of accumulated snow during the period.

		precipitation					
Rain	Date	Duration [hr]	Total [mm]	Max. intensity [mm/min]	day before [mm]	ADD [days]	**Cl$^-$** in SW [mg/l]
A	2020-09-17	8	6.4	1.4	0	3	9.65
B	2020-09-29	11	31	6.3	0	8	3.18
C	2020-10-07	9	13	≥1.8	0	7	4.7
D	2020-10-26	7	3	0.6	17	0	37.4
E	2020-11-05	22	18	4.7	1	0	21.8
F★	2020-12-07	34	7.6	1	0	8	1380
G	2021-10-28	5	6	1.2	0	7	86.8
H	2021-11-04	12	5	12.1	0	2	33.9
I★	2021-12-13	33	15	26	0	17	2390
J★	2022-01-14	<48	<35	Snowmelt	0	22★★★	3330
K★	2022-06-01★★	13	30	90	1	1	210
L	2022-06-20★★	7	4	18	0	1	47.8

At the Malmö site, water was collected from the influent (i.e. stormwater) and from the effluent of each filter section (SVc, SV and S) to investigate the treatment performance in the different filter materials. Event mean composite samples were collected from 19 rain events (labelled as rain events A–S, Table 7), covering different seasons and rain intensities and/or depths. The flow-proportional sampling used automatic samplers (ISCO6712). Samples were then analysed by an accredited laboratory for TSS, TOC, DOC, chlorides, total and dissolved metals using standard methods (see section 3.3 sample analysis below), while pH and infiltration were determined in the field. Infiltration measurements for determination of K_{sat} (Table 5) were carried out using a modified Phillip Dunne Infiltrometer (Upstream technologies, Minneapolis, USA).

Table 7. Precipitation data and rain characteristics. ★indicates data provided from the Swedish Metrological and Hydrological Institute (SMHI, 2024) from the closest weather and climate station Malmö 2 (SMHI 53370), located 300–350 m from the bioretention cells. These data do not have the same accuracy and precision as data measured on site.

		Temp		Precipitation			ADD		
Event	Date	Low	High	Total	Max intencity	Duration	>0	>0.2	>1
		[C°]		[mm]	[mm/hr]	[hr]		[d]	
A	2021-04-30	4.2★	13.1★	5.4★	2★	6.8★	7★	7★	17★
B	2021-09-16	11.1★	20.2★	14.2★	5.2★	11★	2★	17★	17★
C	2021-10-20	0.5	15.0	27.9	9.2	22	3	4	4
D	2021-11-06	3.2	11.6	3.3	3.2	5	1	1	8
E	2021-11-17	4.8	7.7	3.1	2.4	3	2	3	10
F	2021-11-25	4.8	9.3	5.1	1.6	8	4	4	5
G	2021-12-10	0.1	1.1	5.5	1.2	8	5	6	6
H	2022-01-20	-1.8	5.3	2	2.8★	2★	2	2	2
I	2022-01-27	-2.8	8.2	6.2	16.4	9	1	2	2
J	2022-01-29	1.3	8.3	6.3	2	7	0	0	0
K	2022-02-03	-2.4	6.0	14.3	2.4	15	1	1	1
L	2022-02-06	1.2	6.5	12.9	13.6	11	0	0	0
M	2022-02-16	2.8	9.0	20.3	4.8	12	2	4	4
N	2022-02-18	0.7	8.3	18.1	6	12	0	0	0
O	2022-02-22	1.0	3.0	21.9★	3.6★	19.3★	0	0	0
P	2022-05-13	9.6★	15.2★	4.8★	6★	2.5★	1★	1★	1★
Q	2022-05-20	12.5★	24.9★	0.4★	1.6★	0.3★	5★	5★	5★
R	2022-05-24	11.6★	18.7★	3.4★	4★	2.5★	1★	1★	3★
S	2022-05-30	8.4★	18.5★	40.1★	16.4★	16.3★	0★	0★	0★

3.3 Soil sample analysis (studies I, II and III)

Samples of bioretention filter media (studies I, II and III) were analysed by accredited conventional laboratories from which data were obtained on the occurrence and concentration of OMPs (16 PAHs, 7 PCBs, 14 phthalates and 2 alkylphenols) and metals (Cd, Cr, Cu, Ni, Pb and Zn) in the filter media and the forebays. Also, a fractionation of metals was carried out using a five-step sequential extraction method. All collected samples were analysed for the concentration of six metals (Cd, Cr, Cu, Ni, Pb and Zn), total organic carbon (TOC) content and pH. The fractionation of metals was carried out using a five-step sequential extraction method for all samples from location 1 at depth 1 (Figure 4) for 29 sites in the U.S. Further, the concentrations of 38 organic pollutants from four pollutant groups (16 PAHs, 7 PCBs, 13 phthalates and 2 alkylphenols) were measured for 12 sites, of which eight had a forebay (Table 1). For these 12 sites, TOC and loss on ignition (LOI) were also analysed. In two samples from each site (location 1, depth 1 and depth 2), specific surface area (SSA) was also analysed. All samples were sent to an external accredited laboratory ALS Scandinavia AB (ALS Global, 2022) for pretreatment and analysis.

For the analysis of OMP concentration, gas chromatography-mass spectrometry was used (GC-MS). Analyses of 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 (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).

Concentrations of total organic carbon (TOC) were 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, 2004). Drying at 105°C was carried out in parallel to the analysed samples to calculate the DM concentration. Microwave assisted digestion was carried out on the dried samples in 5 ml concentrated HNO_3 and 0.5 ml H_2O_2.

The sequential extraction method used for analysis in this study was a fractionation method developed for laboratory simulations of leaching (Table 8). The method 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 can leach to the environment, and hence be a potential pollutant. This method for analysis in our 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 various metals. The 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, 2016a, 2016b) (mod) and U.S. EPA method (U.S. EPA, 1994a) (mod). Inductively Coupled Plasma Optica Emission Spectrometry (ICP-OES or ICP-AES) was also carried out 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 8. Fractionation steps of the five-step sequential extraction method (ALS, 2018).

Fraction	Form	Leaching solution	Description/comments
1	Adsorbed, exchangeable metals and carbonates	1.0 M sodium acetate buffer, pH 5	Mimic 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	Release of 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 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	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 that, on exposure to air and water, dissolve to form sulphuric acid, which can then release metals.

3.4 Stormwater analysis (studies IV and V)

All stormwater samples (studies IV and V) were analysed for total and dissolved (<0.45 µg) concentrations of Cd, Cr, Cu, Ni, Pb, and Zn. Also, concentrations of chloride (Cl^-), total organic carbon (TOC), dissolved organic carbon (DOC), total suspended solids (TSS), and pH were determined. Total metal analyses samples were pretreated with nitric acid and autoclaved according to Swedish standard SS 28150 (SS, 1993). Samples were analysed using inductively coupled plasma-sector field mass spectrometry ICP-SFMS according to Swedish standard SS-EN ISO 17294-2:2016 (SS-EN ISO, 2016) and U.S. EPA Method 200.8:1994 (US EPA, 1983). Limits of quantification (LOQ) for total metal analysis were for Cd 0.05 µg/L, Pb 0.5 µg/L, Cu 1 µg/L and Zn 4 µg/L. Dissolved metal fractions were filtered according to SS-EN ISO 5667-3:2018 (SS-EN ISO, 2018), before being acidified (1 ml HNO_3/100 ml). Analysis of dissolved metals was carried out using ICP-SFMS, according to SS-EN ISO 17294-2:2016 (SS-EN ISO, 2016b) and US EPA Method 200.8:1994 (US EPA, 1983). LOQ for analysis of dissolved metals were for Cd 0.002 μg/L, Pb 0.01 μg/L, Cu 0.1 μg/L and Zn 0.2 μg/L. Chlorides were measured using ion chromatography according to method CSN EN ISO10304-1 (CSN-EN ISO, 2009) and CSN EN 16192 (CSN EN, 2012). TOC and DOC were determined with IR detection based on CSN EN 1484 (CSN EN, 1998), CSN EN 16192 (CSN EN, 2012) and SM 5310 (SM, 1998). TSS were determined by filtration with 1.6 μm filters using method SS-EN 872-2:2005 (SS-EN, 2005). pH was measured on site using the handheld WTW pH 330 (WTW GmbH, Weilheim, Germany).

3.5 Data analysis

The data and statistical analyses are further described in detail in the appended papers (I–V). In general, to interpret the data, Minitab® 20.4 software was used for descriptive statistics, statistical tests and boxplots. For visualization of the main characteristics and identification of correlations in analysis results, the multivariate data analysis software SIMCA 17 was used. Since most of the datasets were non-normally distributed, a nonparametric method (Kruskal-Wallis test with significance level for $\alpha=0.05$) 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 in filter material in studies I and II, or for determination of statistical significance between median concentrations in different stages in studies IV and V. For testing the statistical significance of correlation between chloride and metal concentrations in study IV, the pairwise spearman correlation test was used.

4 Results

Metals occurred both in particulate and dissolved form in the stormwater inflow in Malmö and Sundsvall, as shown in Table 9 (Malmö) and Table 10 (Sundsvall). Precipitation data for the sampled rain events are given in Table 6 (Sundsvall) and Table 7 (Malmö). In Sundsvall, concentrations of total Cd, Cr, Cu, Ni and Zn were higher than in Malmö, but lower for Pb. Concentrations of dissolved Cd, Cr Ni and Zn were higher than in Malmö, but lower for Cu and Pb. Further, median Cl^- concentration was, on average, 50% higher in Sundsvall than in Malmö. The analysed metals detected in the stormwater from sampled rain events and metal concentrations with descriptive statistics are presented in Table 9. The average percentages of dissolved metals were: Cd=10.4%, Cr=7.7%, Cu=17.4%, Ni=16.6%, Pb=1.4%, and Zn=15.7%, respectively in Malmö, and Cd=21.6%, Cr=4.8%, Cu=15.1%, Ni=15.0%, Pb=0.8%, and Zn=28.0% in Sundsvall. Further, median TSS and DOC were higher in Sundsvall than in Malmö, while TOC was higher in Malmö (Table 9 and Table 10). Median pH was 7.6 in Malmö and 7.5 in Sundsvall in the stormwater inflow.

The metal concentrations in untreated stormwater in both Sundsvall and Malmö are presented in Table 9 and Table 10, and corresponding previous data of studied stormwater (Pamuru et al., 2022), stormwater quality data (Makepeace et al., 1995) and the StormTac Database (2023) for residential and downtown areas are presented in Table 11. The median TSS concentration (86 mg/L) was higher than reported by Pamuru et al. (2022), see Table 11. The median Cl^- concentration in the stormwater was higher than data in the StormTac Database (2023), but varied between different rain events (Table 6). Due to road salt application during the cold weather season, chloride concentrations increased in winter.

Table 9. Descriptive statistics for concentrations of all examined substances in sampled stormwater (SW) and at the effluent after treatment in three different filters (SV, SVp and SVsz).

			Total concentrations				Dissolved concentrations			
Substance		Variable	SW	SV	SVp	SVsz	SW	SV	SVp	SVsz
[µg/L]	Cd	N	16	19	16	18	16	18	16	17
		Min	0.025	0.025	0.025	0.025	0.001	0.001	0.002	0.002
		median	0.070	0.025	0.054	0.025	0.007	0.013	0.022	0.016
		max	0.350	0.133	0.344	0.210	0.063	0.121	0.279	0.126
	Cr	N	16	19	18	17	16	18	17	16
		Min	1.13	0.45	1.57	0.045	0.09	0.23	0.20	0.086
		median	5.85	2.52	7.20	3.08	0.44	0.50	0.78	0.40
		max	28.8	11.3	151	52.2	1.4	1.0	3	1.6
	Cu	N	16	19	16	18	16	18	16	17
		min	7.71	2.33	2.80	2.09	1.01	1.27	1.59	1.34
		median	32.7	4.19	8.99	4.16	6.2	2.55	3.36	2.09
		max	114	20.0	21.2	33.5	16	5.3	6.4	4.4
	Ni	N	16	19	16	18	16	18	16	17
		Min	0.30	0.30	2.77	0.30	0.50	0.23	0.63	0.29
		median	4.96	2.39	5.76	2.61	1.014	0.936	2.3	1.92
		max	25.8	21.3	21.1	18.1	2.63	20.4	14	16
	Pb	N	16	19	16	18	16	18	16	17
		Min	1.24	0.25	0.75	0.25	0.028	0.005	0.02	0.005
		median	10.8	0.25	2.40	0.44	0.11	0.026	0.05	0.04
		max	57.1	4.72	14.1	12.1	0.678	0.082	0.183	0.1
	Zn	N	16	19	16	18	16	18	16	17
		Min	37.3	2.00	9.56	2.00	10	0.41	1.52	0.36
		median	176	10.0	38.0	9.33	27.6	2.2	5.7	2.46
		max	792	84.7	94.6	195	78.5	17	23.5	11.5
[mg/l]	Cl-	N	16	18	16	18	-	-	-	-
		min	2.28	2.42	18.5	4.08	-	-	-	-
		median	19.9	130	141.5	93.0	-	-	-	-
		max	1850	5650	4540	6500	-	-	-	-
	TSS	N	16	18	15	16	-	-	-	-
		min	6.90	1.00	1.10	1.65	-	-	-	-
		median	86.0	6.15	16.0	6.30	-	-	-	-
		max	370	20.0	160	24.0	-	-	-	-
TOC/DOC		N	16	18	15	17	16	18	15	17
		min	2.29	2.65	3.25	3.55	1.28	1.59	2.01	2.18
		median	15.65	5.54	6.08	6.04	5.08	4.45	4.17	5.69
		max	112	10.3	9.40	17.2	16.4	9.78	7.43	16.4
	pH	N	16	18	16	18	-	-	-	-
		min	6.80	7.80	7.90	7.70	-	-	-	-
		median	7.60	8.00	8.00	8.00	-	-	-	-
		max	8.10	8.30	8.20	8.10	-	-	-	-

In Sundsvall between April and September (i.e. spring and summer), Cl^- concentrations were lower, with no large variations between the six sampled rain events (Table 6). During winter events (October–March), Cl^- concentrations in runoff increased considerably. It also showed that, between these 6 rain events (winter sampling), there were large variations in chloride concentrations (Table 6 and Figure 9), unlike in the samples between April and September. Also in Malmö, Cl^- concentrations were higher during and after the cold season than during the warmer season. This was caused by the use of road salt (commonly NaCl) for winter road maintenance. Previous studies have found chloride concentrations to be lower in warmer regions than in the colder (northern) regions during winter, with clearly larger chloride loads in urban rather than in rural areas (Beom et al., 2021; Gavrić et al., 2021; Marsalek, 2003).

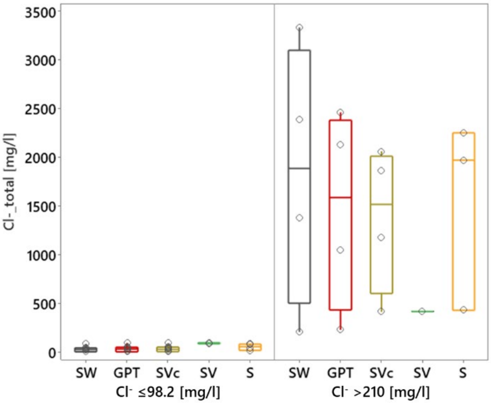

Figure 9. Chloride concentrations for all rain events in SW, GPT, SVc, SV and S for low chloride concentrations (Cl-≤98.2 mg/l) and high chloride concentrations (Cl->210 mg/l).

Further, median TSS and DOC were higher in Sundsvall than in Malmö, while TOC was higher in Malmö (Table 9 and Table 10). Median pH was 7.6 in Malmö and 7.5 in Sundsvall in the incoming stormwater.

Table 10. Descriptive statistics of metals in different components of the studied stormwater treatment system in Sundsvall. Mean metal concentrations are in µg/l, mean concentrations of Cl⁻, TOC, DOC, TSS are in mg/l and Removal is in %.

Substance		Cl⁻	SW	GPT		SVc		SV		S	
			Mean	Mean	Removal	Mean	Removal	Mean	Removal	Mean	Removal
Cd	Tot	≤98.2	0.10 ± 0.08	0.11 ± 0.12	-5.56 ± 20.2	0.05 ± 0.00	30.9 ± 28.8	0.06 ± 0.03	23.6 ± 83.9	0.07 ± 0.04	13.9 ± 25.5
		>210	0.15 ± 0.04	0.11 ± 0.04	26.1 ± 19.1	0.10 ± 0.06	20.3 ± 63.3	0.11 ± 0.06	68.1 ± ⋆	0.13 ± 0.05	-8.5 ± 59.8
	Diss.	≤98.2	0.02 ± 0.01	0.01 ± 0.01	15.3 ± 36.0	0.01 ± 0.00	25.7 ± 53.4	0.03 ± 0.04	-286 ± 90.5	0.02 ± 0.01	-25.8 ± 56.1
		>210	0.05 ± 0.03	0.05 ± 0.02	4.70 ± 25.5	0.09 ± 0.08	-53.9 ± 97.0	0.10 ± 0.07	-123 ± ⋆	0.11 ± 0.05	-99.0 ± 26.5
Cr	Tot	≤98.2	25.4 ± 36.1	29.9 ± 48.7	-3.72 ± 17.9	1.59 ± 1.03	84.1 ± 17.1	1.37 ± 0.72	96.7 ± 1.54	11.9 ± 17.5	45.2 ± 9.8
		>210	31.5 ± 28.8	29.0 ± 15.8	-14.5 ± 33.6	1.31 ± 0.82	94.4 ± 3.03	1.13 ± 0.32	98.1 ± ⋆	8.01 ± 4.79	58.2 ± 18.5
	Diss.	≤98.2	1.48 ± 1.20	1.35 ± 1.16	12.1 ± 10.7	0.79 ± 0.68	41.9 ± 36.2	0.75 ± 0.57	-13.8 ± 140	1.09 ± 0.90	26.7 ± 7.48
		>210	0.76 ± 0.73	0.65 ± 0.59	17.6 ± 20.2	0.43 ± 0.24	14.9 ± 52.6	0.55 ± 0.52	48.2 ± ⋆	0.53 ± 0.41	16.5 ± 33.0
Cu	Tot	≤98.2	51.8 ± 54.3	56.3 ± 75.2	4.21 ± 18.3	7.63 ± 6.74	81.3 ± 11.8	13.0 ± 14.6	79.6 ± 1.34	27.0 ± 32.9	31.7 ± 11.3
		>210	63.1 ± 48.6	58.7 ± 29.3	-4.10 ± 22.6	13.0 ± 9.02	77.2 ± 10.0	20.6 ± 21.7	73.4 ± ⋆	27.5 ± 18.5	43.5 ± 15.3
	Diss.	≤98.2	5.38 ± 1.11	4.93 ± 0.86	6.58 ± 14.5	5.45 ± 5.59	4.90 ± 78.8	11.1 ± 13.3	-207 ± 302	5.84 ± 2.19	-18.1 ± 23.8
		>210	9.73 ± 4.95	9.82 ± 6.82	4.26 ± 16.4	10.6 ± 7.61	-2.50 ± 20.6	19.8 ± 20.8	-105 ± ⋆	10.3 ± 6.86	-3.5 ± 15.0
Ni	Tot	≤98.2	12.7 ± 16.6	14.9 ± 22.8	-6.52 ± 26.4	1.03 ± 0.58	78.2 ± 22.8	1.72 ± 0.96	86.3 ± 12.3	6.30 ± 8.29	31.6 ± 21.8
		>210	18.6 ± 14.2	16.4 ± 7.22	-3.00 ± 31.0	2.12 ± 0.89	84.3 ± 10.8	3.90 ± 1.28	92.4 ± ⋆	7.73 ± 2.31	34.7 ± 34.2
	Diss.	≤98.2	1.16 ± 0.75	1.11 ± 0.69	3.17 ± 8.99	0.47 ± 0.33	56.4 ± 17.3	1.70 ± 0.87	-42.0 ± 96.8	1.20 ± 0.75	-4.91 ± 7.46
		>210	3.21 ± 1.11	3.00 ± 1.13	7.78 ± 9.19	1.58 ± 0.58	49.7 ± 13.2	4.17 ± 2.23	33.8 ± ⋆	3.57 ± 0.35	-0.52 ± 17.2
Pb	Tot	≤98.2	9.04 ± 11.6	10.7 ± 17.0	-0.95 ± 21.9	6.41 ± 15.7	-66.0 ± 406	0.90 ± 0.72	93.1 ± 1.34	5.25 ± 7.05	23.7 ± 21.0
		>210	12.1 ± 11.6	11.4 ± 6.82	-19.8 ± 35.6	0.90 ± 0.80	90.9 ± 4.29	1.02 ± 0.7	94.7 ± ⋆	4.51 ± 3.87	42.7 ± 20.2
	Diss.	≤98.2	0.09 ± 0.10	0.07 ± 0.07	21.7 ± 19.8	0.10 ± 0.17	-5.20 ± 66.9	0.30 ± 0.50	-258 ± 3.37	0.12 ± 0.22	-17.0 ± 67.4
		>210	0.07 ± 0.10	0.09 ± 0.15	-3.40 ± 28.8	0.16 ± 0.12	-476 ± 445	0.43 ± 0.48	-253 ± ⋆	0.10 ± 0.17	-36.1 ± 47.1
Zn	Tot	≤98.2	429 ± 368	498 ± 570	-4.28 ± 17.2	24.0 ± 19.2	94.1 ± 2.07	106 ± 102	62.9 ± 39.4	272 ± 270	21.4 ± 19.8
		>210	671 ± 601	609 ± 352	-5.80 ± 25.4	150 ± 99.3	63.1 ± 35.2	202 ± 98.3	82.7 ± ⋆	412 ± 155	-2.00 ± 61.0
	Diss.	≤98.2	80.2 ± 49.2	81.5 ± 56.5	4.86 ± 23.9	14.9 ± 10.1	68.2 ± 34.2	97.4 ± 104	-337 ± 90.6	78.0 ± 47.1	-40.4 ± 52.7
		>210	99.5 ± 38.6	106 ± 44.9	-5.90 ± 24.6	116 ± 87.0	-11.8 ± 76.8	174 ± 73.5	-111 ± ⋆	205 ± 98.0	-96.1 ± 59.9
TOC		≤98.2	20.9 ± 48.6	25.6 ± 61.6	-4.23 ± 14.5	4.11 ± 5.31	40.0 ± 35.1	12.0 ± 14.2	74.1 ± 14.5	21.4 ± 33.5	23.2 ± 17.6
		>210	35.0 ± 38.2	28.7 ± 25.7	10.6 ± 24.7	9.24 ± 10.2	72.7 ± 5.01	21.7 ± ⋆	76.3 ± ⋆	14.7 ± 7.18	55.2 ± 17.9
DOC		≤98.2	4.78 ± 2.94	4.64 ± 2.81	3.07 ± 9.69	4.04 ± 4.85	28.7 ± 35.5	11.3 ± 13.4	-13.7 ± 112	6.63 ± 4.28	6.31 ± 15.7
		>210	9.91 ± 4.23	11.4 ± 9.02	-6.10 ± 36.4	9.03 ± 9.89	21.0 ± 52.0	0.73 ± ⋆	95.4 ± ⋆	9.29 ± 4.91	10.7 ± 6.81
TSS		≤98.2	215 ± 364	244 ± 470	-6.30 ± 30.0	12.3 ± 18.4	47.1 ± 128	11.0 ± ⋆	99.0 ± ⋆	199 ± 263	30.3 ± 39.8
		>210	359 ± 358	303 ± 189	-11.1 ± 38.2	4.42 ± 4.39	98.5 ± 0.70	4.00 ± ⋆	99.5 ± ⋆	79.3 ± 45.2	62.8 ± 19.4
pH		≤98.2	7.20 ± 0.27	7.20 ± 0.27	0.00 ± 0.00	7.97 ± 0.15	-10.7 ± 3.74	7.45 ± 0.07	-4.20 ± ⋆	7.20 ± 0.20	-0.03 ± 1.35
		>210	7.63 ± 0.25	7.60 ± 0.20	0.43 ± 0.75	7.70 ± 0.46	-1.07 ± 9.25	7.60 ± ⋆	-2.70 ± ⋆	7.50 ± 0.10	1.67 ± 3.98

Table 11. Reference values for concentrations of contaminants in stormwater (Makepeace et al., 1995; Pamuru et al., 2022; StormTac Database, 2023).

		Pamuru et al.				Makepeace et al.				StormTac	
Type		Min	Median	Mean	Max	Min	Mean min	Mean max	Max	Res.	Downt.
Cd		0.009	0.34	1	275	0.05	0.3	0.011	13730	0.5	1
Cr		0.2	3.9	6.1	559	1	10	230	2300	5.8	5
Cu	Total	0.1	13	45.3	7270	0.06	635	150	1410	20	32
Ni	[µg/l]	0	4.4	6.6	281	1	6	150	49000	6	8.5
Pb		0.1	7.3	22.3	2300	0.57	20.9	1558	26000	12	18
Zn		0.1	75.7	144	27500	0.7	16.6	580	22000	80	160
Cd		-	-	-	-	-	-	-	-	-	-
Cr		0.1	1.4	2.4	41	-	-	-	-	-	-
Cu	Diss	0.3	6.5	51.6	3540	-	-	-	-	-	-
Ni	[µg/l]	0	2	3.1	82	-	-	-	-	-	-
Pb		-	-	-	-	-	-	-	-	-	-
Zn		0.1	29	76.4	25800	-	-	-	-	-	-
Cl^-		-	-	-	-	0.3	-	-	25000	35	40
TS		12	124	198	2910	76	481	1440	36200	-	-
TSS		0.1	47	104	6900	1	4	1223	36200	45	100
TDS	[mg/l]	0.2	72	283	113860	75.9	178	178	2792	-	-
TOC		-	-	-	-	-	-	-	-	-	-
DOC		-	-	-	-	-	-	-	-	10	24
pH		3.5	7.1	7.1	11	-	-	-	-	7	17

4.1 Metal treatment

4.1.1 Sand-based filters

In the outflow from the sand-based filters both in Malmö (SV, SVp and SVsz) and Sundsvall (S, SV and SVc, all analyzed metals were detected in most samples (before and after treatment in the filters), except for total Cd in Malmö (5 of 16 samples had total Cd below DL, 2 of 16 samples had dissolved Cd below DL), and Cd and Pb in Sundsvall (2 of 12 samples had total Cd below DL, and 1 of 12 samples had dissolved Pb below DL). The results from analyses of metal concentrations after the different filter configurations and descriptive statistics for Malmö are shown in Table 9, Figure 10, and Figure 11, For Sundsvall, metal concentrations and descriptive statistics are presented in Table 10, Figure 12, and Figure 13.

4.1.2 Filter materials, additives, and submerged zone

In Malmö, three factors (high infiltration, pumice additive and a submerged zone) were tested using three different filter designs. These factors affect treatment of metals since higher infiltration reduces removal of pollutants (Funai and Kupec, 2017; Hunt et al., 2012; Kandra et al., 2014; Tirpak et al., 2021), chalk additives may improve the metal adsorption (Søberg et al., 2019), pumice affects water holding capacity and hydraulic conductivity which influence metal treatment (Fassman-Beck et al., 2015; Narayanasamydamodaran et al., 2024), and the submerged zone may also have an impact on metal behaviour (Blecken et al., 2009b). In general, total Cu, Pb and Zn were removed efficiently by all three filters at the Malmö site (SV, SVp and SVsz), while removal of total Cd, Cr and Ni was less efficient (Figure 10). Of the dissolved metals, in Malmö, Cu, Pb and Zn were treated mostly efficiently, while a release of dissolved metals was observed for Cd, Cr and Ni (Figure 11, Table 12). Dissolved Zn had the highest median removal (SV = 93%, SVp = 80% and SVsz = 93%) followed by Pb (SV = 78.0%, SVp = 54% and, SVsz = 78%) and then Cu (SV = 59%, SVp = 49% and SVsz = 61%). The highest median removal of total metals was for Cu, Pb and Zn in SV (Cu=87%, Pb=92% and Zn=94%) and in SVsz (Cu=87%, Pb=91% and Zn=96%). For Cd and Cr, median removal by SVp was around 0% while it varied between 35% and 63% for the two other filter designs. The metal removal was statistically significant (Kruskal-Wallis test $P<0.05$) for Cu, Pb and Zn for all filters. For dissolved Cd, Cr and Ni in SVp, the increase in concentration after the filter was statistically significant (Kruskal-Wallis test $P<0.05$) i.e. indicating a release of metals. Also, for dissolved metals as for total metals, removal was less efficient in SVp compared to the other two filters (Figure 11). The difference in median concentrations between the filter outlets was statistically significant (Kruskal-Wallis test $P<0.05$) for Cr, Cu, Pb and Zn, while not for Cd and Ni. This indicates lower removal of Cu, Pb and Zn as well as higher release of Cr, as seen in Figure 11. The Kruskal-Wallis test showed that concentrations of total Cu, Pb and Zn were significantly lower ($P<0.05$) after treatment in all filters in Malmö (SV, SVp and SVsz) compared to concentrations in incoming stormwater. Total Ni also showed significantly ($P<0.05$) lower concentrations after treatment in SV and SVsz, and both Cd and Cr had significantly lower concentrations after treatment of total metals in SV. There was a significant difference (Kruskal-Wallis test, P<0.05) in median total concentrations between the filters after treating the stormwater, where the filter with pumice SVp was less efficient than SV and SVsz for removal of total Cr, Cu, Ni, Pb and Zn. Cd removal in SVp (Figure 10). was less efficient compared to the other two filters, however not statistically significant i.e. P>0.05.

Table 12. Min, median and max removal [%] of Cd, Cr, Cu, Ni, Pb and Zn from SW by the three different filters SV, SVp and SVsz in the Malmö study.

		Total					Dissolved		
Substance	Filter	N	N*	Min	Median	Max	Min	Median	Max
Cd	SV	16	2	-120	63	86	-500	-38	86
	SVp	16	3	-1276	0	93	-2436	-208	62
	SVsz	15	4	-476	35	86	-1263	-125	71
Cr	SV	16	2	-39	54	90	-556	-30	64
	SVp	16	3	-1814	-6	80	-2173	-54	54
	SVsz	15	4	-1949	60	90	-526	-9	88
Cu	SV	16	2	63	87	98	-26	59	86
	SVp	16	3	3	76	98	-115	49	88
	SVsz	15	4	63	87	97	-33	61	91
Ni	SV	16	2	-57	38	82	-688	-24	67
	SVp	16	3	-1080	5	72	-653	-134	36
	SVsz	15	4	-640	46	77	-518	-82	57
Pb	SV	16	2	68	92	100	11	78	96
	SVp	16	3	-106	64	99	-150	54	91
	SVsz	15	4	63	91	100	-3	78	96
Zn	SV	16	2	83	94	99	63	93	98
	SVp	16	3	11	82	99	23	80	94
	SVsz	15	4	82	96	99	46	93	98
TOC/ DOC	SV	16	2	-65	67	96	-85	17	64
	SVp	16	3	-124	62	100	-314	36	100
	SVsz	15	4	-168	64	97	-229	-23	63
TSS	SV	16	2	73	93	99	-	-	-
	SVp	16	3	-13	75	100	-	-	-
	SVsz	15	4	72	94	100	-	-	-
Cl-	SV	16	2	-9400	-208	24	-	-	-
	SVp	16	3	-23280	-291	-52	-	-	-
	SVsz	16	3	-10182	-271	34	-	-	-
pH	SV	16	2	-16	-7	2	-	-	-
	SVp	16	3	-18	-6	0	-	-	-
	SVsz	16	3	-16	-5	1	-	-	-

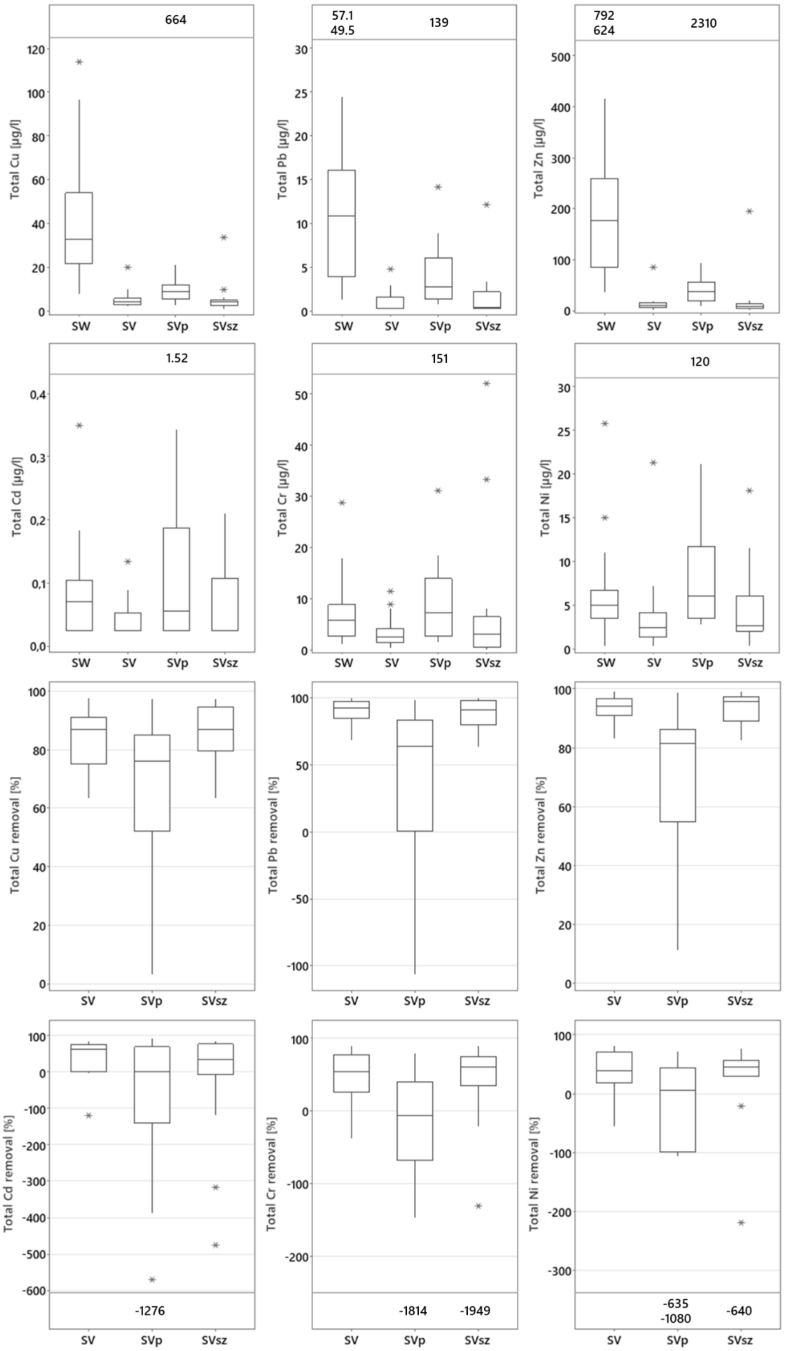

Figure 10. Boxplots of total metal concentrations in Malmö for Cu, Pb, Zn, Cd, Cr and Ni and Zn in SW, in the three different filter configurations (SV, SVsz, SVp) and of removal by filters SV, SVp and SVsz. Numbers above boxplots of total concentrations of metals and below boxplots of removal are outliers not plotted on the graphs for clearer visualization of boxplots.

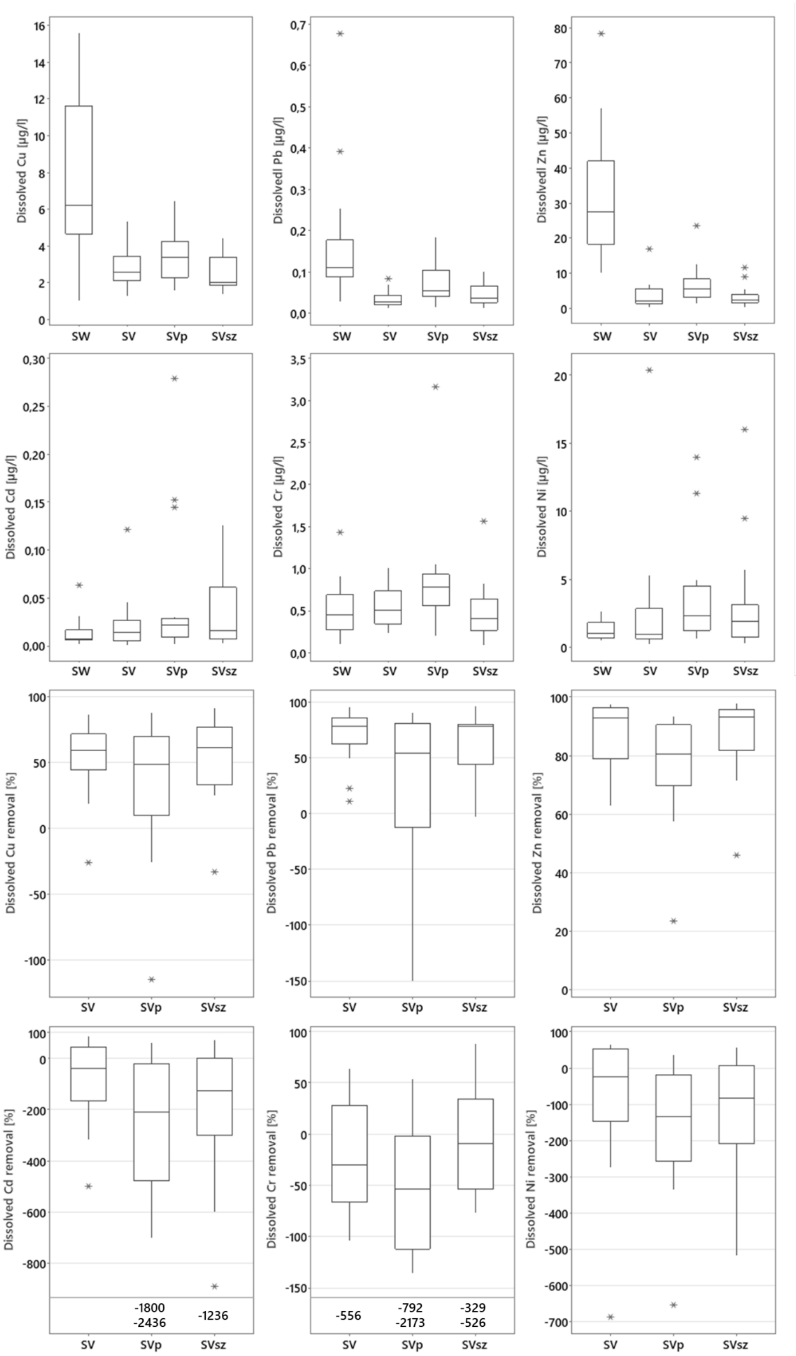

Figure 11. Boxplots of dissolved metal concentrations in Malmö for Cu, Pb, Zn, Cd, Cr and Ni and Zn in SW, in the three different filter configurations (SV, SVsz, SVp) and of removal in filters SV, SVp and SVsz. Numbers below removal boxplots represent outliers not plotted on the graphs for clearer visualization of boxplots.

4.1.1 Chlorides and metal removal

At the Sundsvall bioretention site, the clear variations in salinity in stormwater and runoff between summer and winter were used to evaluate the effect of chlorides on metal treatment in the three different filter configurations (S, SV and SVc) and the pre-sedimentation GPT (Figure 6). There was an observed variation over time for all total metal concentrations and for dissolved Cd, Ni and Zn, with this variation positively correlated to the variation in chloride concentrations (Figure 9, Figure 12, and Figure 13).

A pairwise spearman correlation test was used for testing statistical significance of the correlation between chloride and metal concentrations (Table 13). In general, there was observed correlations between chloride concentrations and most dissolved metal concentrations (Cd, Cu, Ni, Pb and Zn) in SVc, while less correlations for total metals. Statistical significance ($p<0.05$) was identified for total Zn in SVc, and for Cd the p-value was 0.053 in SVc (ρ =0.57). Further statistical significance ($p>0.05$) was also identified in SVc for dissolved Cd, Pb and Zn, and in S for dissolved Cd, Ni and Zn and for Cu the p-value was 0.051 (ρ =0.573).

The total metal concentrations observed in Sundsvall are presented in boxplots in Figure 12 a–f, before and after treatment by the different filters (S, SV and SVc) and for low ($Cl^- \leq 98.2$ mg/l) and high ($Cl^- > 210$ mg/l) chloride concentrations. The GPT pre-sedimentation system did not show any significant (Kruskal-Wallis test, $P<0.05$) removal of metals from stormwater (Table 10 and Figure 12), but all filters removed metals at least to some extent.

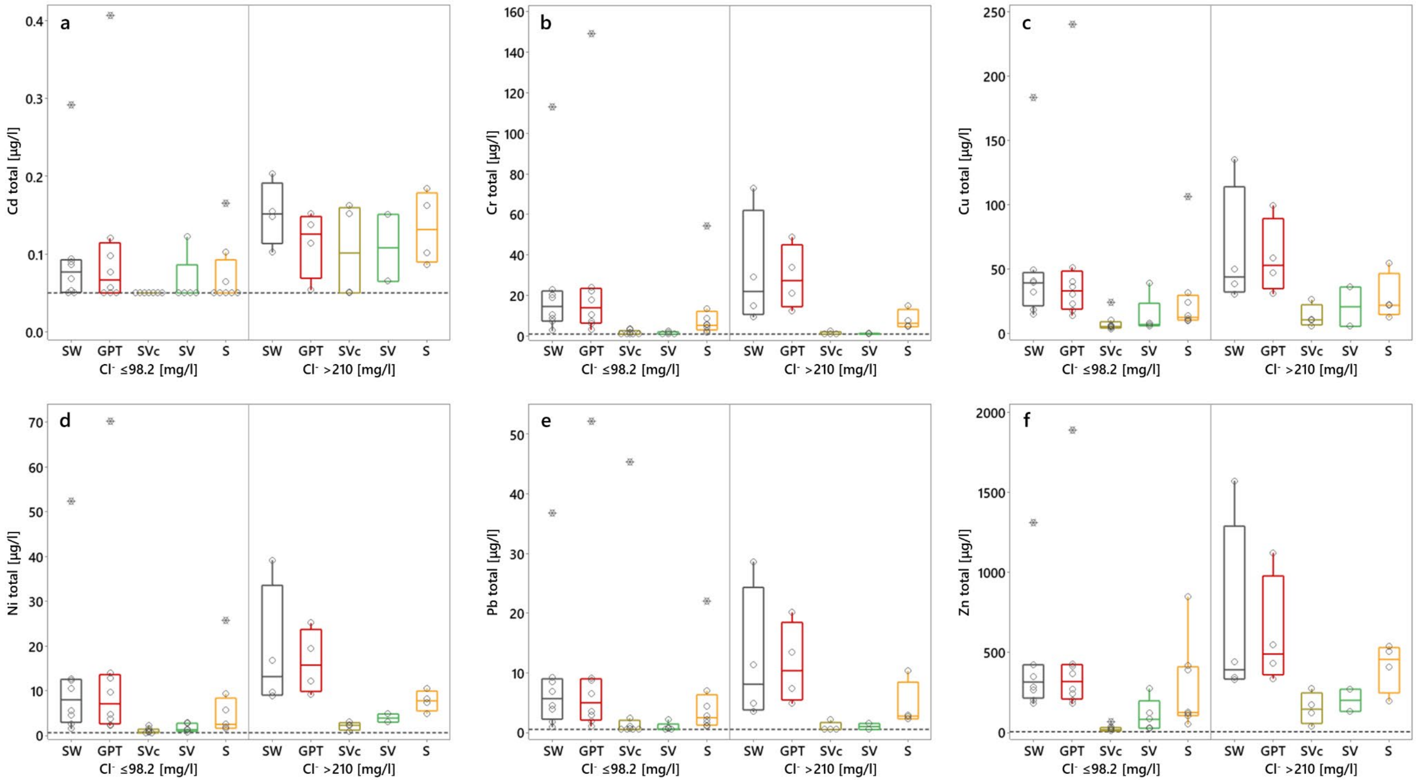

Figure 12. Total metal concentrations for low (Cl$^-$≤98.2 mg/l) and high (Cl$^-$>210 mg/l) chloride concentrations for all parts of the studied bioretention site.

Table 13. Pairwise Spearman correlation for Cl^- verses total and dissolved metals in Sundsvall. The Spearman's rank correlation coefficient (ρ) assesses how well a correlation between the metals and Cl^- is described by the monotonic function. ★Indicates no data due to too few samples i.e. for SV. ★★Indicates significant negative correlation for dissolved Cr.

Variable vs Cl-			Total			Dissolved		
	Type	N	Correlation ρ	95% CI for ρ	P Value	Correlation ρ	95% CI for ρ	P Value
Cd	SW	12	0.715	(0.163; 0.926)	0.009	0.734	(0.199; 0.932)	0.007
	GPT	12	0.592	(-0.028; 0.883)	0.043	0.874	(0.524; 0.972)	0
	SVc	12	0.57	(-0.057; 0.874)	0.053	0.93	(0.705; 0.985)	0
	SV	3	0.5	(★; ★)	0.667	0.5	(★; ★)	0.667
	S	7	0.607	(-0.347; 0.944)	0.148	0.964	(0.674; 0.997)	0
Cr	SW	12	0.385	(-0.265; 0.794)	0.217	-0.706	(-0.923; -0.148)	0.01★★
	GPT	12	0.483	(-0.163; 0.839)	0.112	-0.664	(-0.909; -0.079)	0.018★★
	SVc	12	-0.398	(-0.800; 0.252)	0.2	-0.469	(-0.833; 0.178)	0.124
	SV	3	-0.5	(★; ★)	0.667	-0.5	(★; ★)	0.667
	S	7	-0.071	(-0.783; 0.721)	0.879	-0.107	(-0.797; 0.704)	0.819
Cu	SW	12	0.301	(-0.343; 0.752)	0.342	0.469	(-0.178; 0.833)	0.124
	GPT	12	0.545	(-0.088; 0.865)	0.067	0.455	(-0.193; 0.826)	0.138
	SVc	12	0.399	(-0.251; 0.801)	0.199	0.573	(-0.052; 0.876)	0.051
	SV	3	-0.5	(★; ★)	0.667	-0.5	(★; ★)	0.667
	S	7	-0.071	(-0.783; 0.721)	0.879	0	(-0.753; 0.753)	1
Ni	SW	12	0.497	(-0.147; 0.845)	0.101	0.874	(0.524; 0.972)	0
	GPT	12	0.524	(-0.114; 0.856)	0.08	0.804	(0.344; 0.953)	0.002
	SVc	12	0.368	(-0.281; 0.786)	0.24	0.867	(0.504; 0.970)	0
	SV	3	1	(★; ★)	★	0.5	(★; ★)	0.667
	S	7	0.107	(-0.704; 0.797)	0.819	0.893	(0.270; 0.989)	0.007
Pb	SW	12	0.378	(-0.272; 0.791)	0.226	-0.566	(-0.873; 0.061)	0.055
	GPT	12	0.524	(-0.114; 0.856)	0.08	-0.545	(-0.865; 0.088)	0.067
	SVc	12	-0.405	(-0.804; 0.244)	0.191	0.846	(0.447; 0.964)	0.001
	SV	3	-0.5	(★; ★)	0.667	-0.5	(★; ★)	0.667
	S	7	-0.071	(-0.783; 0.721)	0.879	-0.393	(-0.892; 0.538)	0.383
Zn	SW	12	0.566	(-0.061; 0.873)	0.055	-0.126	(-0.654; 0.485)	0.697
	GPT	12	0.65	(0.057; 0.904)	0.022	-0.042	(-0.602; 0.545)	0.897
	SVc	12	0.916	(0.656; 0.982)	0	0.972	(0.870; 0.994)	0
	SV	3	0.5	(★; ★)	0.667	0.5	(★; ★)	0.667
	S	7	0.321	(-0.586; 0.871)	0.482	0.821	(0.028; 0.980)	0.023
TOC/DOC	SW	12	0.699	(0.136; 0.921)	0.011	0.566	(-0.061; 0.873)	0.055
	GPT	12	0.65	(0.057; 0.904)	0.022	0.552	(-0.079; 0.868)	0.063
	SVc	12	0.364	(-0.285; 0.784)	0.245	0.322	(-0.324; 0.763)	0.308
	SV	3	-0.5	(★; ★)	0.667	-1	(★; ★)	★
	S	7	0.286	(-0.608; 0.860)	0.535	0.214	(-0.649; 0.836)	0.645
TS	SW	12	0.643	(0.046; 0.902)	0.024	-	-	-
	GPT	12	0.678	(0.101; 0.914)	0.015	-	-	-
	SVc	12	-0.324	(-0.764; 0.322)	0.304	-	-	-
	SV	2	-1	(★; ★)	★	-	-	-
	S	7	-0.071	(-0.783; 0.721)	0.879	-	-	-
pH	SW	6	0.6	(-0.490; 0.958)	0.208	-	-	-
	GPT	6	0.6	(-0.490; 0.958)	0.208	-	-	-
	SVc	6	-0.429	(-0.928; 0.620)	0.397	-	-	-
	SV	3	1	(★; ★)	★	-	-	-
	S	6	0.493	(-0.577; 0.940)	0.321	-	-	-

After treatment by all three filters, there was a decreased concentration of Cr, Cu, Ni, Pb and Zn, but not for Cd. In general, removal of metals from incoming stormwater was most efficient in filter SVc, followed by SV and then S. Furthermore, the metal concentrations were higher when there were higher concentrations of chlorides ($Cl^- > 210$ mg/l). Median concentration of total Cd showed a significant difference (Kruskal-Wallis test, $p < 0.05$) between the different parts of the plant SW, GPT and the three filters (SVc, SV and S), where Cd concentrations (boxplot in Figure 12a) were higher with higher chloride concentrations. Furthermore, Cd was treated by all three filters (SVc, SV and S) at lower chloride concentrations ($Cl^- \leq 98.2$ mg/l) but by SVc and SV only when chloride concentrations were higher ($Cl^- > 210$ mg/l). On two occasions (rain events A and B, Table 6), the concentrations of Cd in incoming stormwater were below the detection limit (DL=0.05). Total Cu concentrations were significantly lower (Kruskal-Wallis test, $p < 0.05$) after treatment by each of the three filters compared to the incoming SW. This was seen both with higher chloride concentrations ($Cl^- > 210$ mg/l), as well as with low chloride concentrations ($Cl^- \leq 98.2$ mg/l). This, for Cu as for Cd, was particularly clear for filter SVc, followed by filter SV, while less obvious in S (Figure 12 a and c). Total Pb concentrations also showed significant differences (Kruskal-Wallis test, $p < 0.05$) between concentrations in the inflow and outflow water from the filters, again mainly for filters SVc and SV, while less so for S. Also, for total Pb, there were higher concentrations with increasing concentrations of chlorides both in the SW and after treatment through the filters. The median total Zn concentration showed significant differences (Kruskal-Wallis test, $p < 0.05$) between the treatment steps (SW, GPT and the filters). Zn was efficiently treated, with a high removal percentage, by all three filters when at lower chloride concentrations ($Cl^- \leq 98.2$ mg/l), and by filters SVc and SV with high chloride concentrations ($Cl^- > 210$ mg/l) in the stormwater. Also, the median concentrations of total Ni (Figure 12d) showed significant differences (Kruskal-Wallis test, $p < 0.05$) between the different treatment steps. Total Ni was treated and showed removal by all filters both with low chloride concentrations ($Cl^- \leq 98.2$ mg/l) and high chloride concentrations ($Cl^- > 210$ mg/l), although less so by S than by SV and SVc (S>SV>SVc). Further, Ni concentrations were higher with higher chloride concentrations ($Cl^- > 210$ mg/l). The median concentrations of total Cr (Figure 12b) in the stormwater (SW and GPT) compared to the effluent (SVc, SV and S) indicate treatment by all three filters, however less so by S. Cr concentrations were also higher with higher chloride concentrations ($Cl^- > 210$ mg/l).

To assess differences between median concentrations in the different parts of the bioretention system (SW, GPT, SVc, SV and S) and statistical significance under different conditions (high or low chloride concentrations), the Kruskal-Wallis test was used (Z values, Table 14). The general conclusion from the Z values is that there was a removal of total metals with lower chloride concentrations, except for Cr and Pb, by filter S. This test shows that treatment by removal was most efficient by SVc, followed by SV, while there was less efficient or no removal (Cr and Pb) by S. For total metals with high chloride concentrations, all metals were treated except Cd by SVc and SV, and not by S. For dissolved metals, there was slight treatment of Zn with low chloride concentrations and, for Pb, with high chloride concentrations, by filter SVc.

Table 14. Z values, P values and H values from Kruskal-Wallis test for metal concentrations before and after filters in Sundsvall. Null hypothesis H_0: All medians are equal and, the Alternative hypothesis H_1: At least one median is different. Cl- concentration (mg/l).

				Cd		Cr		Cu		Ni		Pb		Zn	
Parameter	Type	Cl impact	N	Tot.	Diss.	Tot.	Diss.	Tot.	Diss.	Tot.	Diss.	Tot.	Diss.	Tot.	Diss.
H-Values	Not adj. for ties		-	22.3	33.3	39.0	8.26	30.5	17.8	33.3	35.9	28.0	13.9	34.7	25.8
	Adj. For ties		-	24.1	33.3	39.3	-	30.6	17.8	33.3	36.0	28.2	13.9	-	25.8
P-Values	Not adj. for ties		-	0.01	0.00	0.00	0.51	0.00	0.04	0.00	0.00	0.00	0.13	0.00	0.00
	Adj. For ties		-	0.00	0.00	0.00	-	0.00	0.04	0.00	0.00	0.00	0.13	-	0.00
Z-Values	SW	≤100	8	0.24	-1.34	2.03	1.77	2.08	-0.72	1.42	-1.05	1.50	0.64	1.48	0.02
	GPT		8	0.05	-2.10	2.03	1.17	1.58	-1.48	1.46	-1.23	1.46	-0.31	1.41	-0.17
	SVc		8	-3.06	-2.91	-3.06	-0.41	-3.68	-2.72	-3.99	-3.93	-2.27	-0.29	-4.34	-4.13
	SV		5	-1.46	0.50	-2.63	-0.20	-1.82	0.40	-2.02	0.44	-2.31	1.35	-1.84	-0.35
	S		8	-1.11	-1.10	0.29	0.62	-0.49	-0.25	-0.36	-0.81	0.24	-0.41	-0.36	-0.14
	SW	>100	4	2.32	1.85	2.11	-0.49	1.91	1.65	2.20	2.43	1.85	-1.35	1.91	0.68
	GPT		4	1.39	1.72	2.33	-0.62	2.20	1.26	2.30	2.01	2.17	-1.51	2.30	0.96
	SVc		4	0.66	1.99	-2.46	-1.46	-1.38	1.52	-1.39	0.52	-2.35	1.88	-1.10	0.94
	SV		2	0.81	1.80	-1.66	-0.67	-0.49	0.94	0.04	1.80	-1.42	1.75	-0.27	1.66
	S		4	1.93	2.71	0.39	-1.00	0.32	1.46	1.09	2.79	0.65	-1.30	1.59	2.61

An efficient removal of total metals at low chloride concentrations is also indicated by removal percentages, which exceeded 78% by SVc for Cr, Cu, Ni and Zn, and 79% by SV for Cr, Cu, Ni and Pb. The removal percentages were significantly lower ($P<0.05$) for S, which were in a range between 23.7 and 45.2% (Table 10). Also, with higher chloride concentrations, the removal was higher by SVc and SV, still exceeding 77% (Cr, Cu, Ni and Pb), than by S (around 40%).

There was also an observed difference in concentrations between treatment of total (Figure 12 a–f) and treatment of dissolved (Figure 13 a–f) metals. For total metal concentrations (Figure 12 a–f), there was an efficient removal (Kruskal-Wallis test, $p<0.05$) by all three filters (SVc, SV and S), while there was no significant difference in concentrations before and after the filters for dissolved metals (no removal in the filters). However, dissolved metal concentrations (Cd, Cu, Ni, Pb and Zn) were higher both in stormwater and after the filters, when the chloride concentrations were higher ($Cl^->210$ mg/l), except for Cr concentrations that instead decreased with higher chloride concentrations. The increased concentrations in the effluent (after the filters SVc, SV and S) with higher chloride concentrations could indicate release of previously accumulated metals from the filter materials.

Dissolved Cd concentrations in effluent water after the filters (Figure 13a) indicate that there was no removal of Cd from incoming stormwater with low chloride concentrations ($Cl^-\leq98.2$ mg/l) in the stormwater. However, there was a significant difference (Kruskal-Wallis test, $p<0.05$) for Cd concentrations, which were higher in effluent than in stormwater (release of Cd) with higher chloride concentrations ($Cl^->210$ mg/l). For dissolved Cu, there was no observed removal from stormwater by all three filters. However, there was an increase in concentration in effluent after filter SV compared to incoming stormwater. The boxplot in Figure 13c shows higher Cu concentrations after the filters with higher chloride concentrations ($Cl^->210$ mg/l) compared to when lower chloride concentrations were present ($Cl^-\leq98.2$ mg/l). This is particularly clear for filter SVc, which removed dissolved Cu comparatively well with low chloride concentrations but not at all with high chloride concentrations. Furthermore, the median dissolved Cu concentration in the effluent from SV was much higher when there was higher chloride concentrations compared to lower ones. However, due to the small number of samples ($N=3$) for SV, it is difficult to draw any general conclusions about the high dissolved Cu concentrations. Dissolved Pb concentrations did not show any significant difference (Kruskal-Wallis test, $p<0.05$) between incoming stormwater (SW) and after the filters (SVc, SV and S). When there were low chloride concentrations ($Cl^-\leq98.2$ mg/l), all medians were in a similar range for all three filters (Table 10) and all stages of the treatment facility, i.e. no treatment of dissolved Pb at all. The dissolved Pb concentrations were also relatively low in incoming stormwater (Table 10) and close to the DL of 0.01 mg/l (two samples, one each in SW and in GPT were below the detection limit). As a result of high chloride concentrations ($Cl^->210$ mg/l), there was a release of Pb from the filters, and particularly from filters SVc and SV, likely of previously accumulated Pb, a phenomenon previously described by Søberg et al. (2017). Boxplots of dissolved Zn concentrations in Figure 13f show higher concentrations with higher chloride concentrations ($Cl^->210$ mg/l) in stormwater, particularly after the filters. As a result of low chloride concentrations ($Cl^-\leq98.2$ mg/l), SVc removed Zn from the stormwater, whereas SV and S did not. For higher chloride concentrations, the boxplots show no removal of dissolved Zn by SVc Figure 13f, while there was a release from SV and S. Dissolved Ni concentrations shown in the boxplots in Figure 13d indicate removal from stormwater by SVc, but not by S, while the increased concentrations after SV may indicate release of previously accumulated Ni. Ni concentrations were higher (Kruskal-Wallis test, $p<0.05$) as a result of higher chloride concentrations ($Cl^{-}>210$ mg/l) in all parts of the system (SW, GPT, SVc and S). The concentrations of dissolved Cr showed a large variation in SW and the GPT, as well as in the outflow from all three filters, particularly when there were lower chloride concentrations. However, for dissolved Cr there was no significant difference between median concentrations (Kruskal-Wallis test, $p<0.05$) in the different parts of the system (SW, GPT, SVc and S). A tendency was observed for lower median concentrations in all SVc and S (Figure 13b) when there were higher chloride concentrations ($Cl^{-}>210$ mg/l) in the stormwater, but these were not statistically significant (Kruskal-Wallis, $p<0.05$).

For the dissolved metal concentrations measured in Sundsvall, the Kruskal-Wallis test (Table 14; $p<0.05$ and Z values) confirmed the observations of chloride impact as seen in boxplots (Figure 13a–f). The dissolved metal concentrations shown in Figure 13a–f are clearly higher in the stormwater when there were lower chloride concentrations for all metals except Cr. For example, in Table 14, the Z values for Zn in the filters SVc, SV and S all are negative when $Cl^{-}\leq 98.2$ mg/l, whereas Z values in filters for $Cl^{-}>210$ mg/l are all positive. Thus, this indicates that median Zn concentrations were higher in effluent water after the filters than in stormwater, when there were higher chloride concentrations (also observed in boxplot Figure 13f). Further, the result of the Kruskal-Wallis test (Z values and $p<0.05$) indicates that there was a reduction in dissolved Zn concentration, and a smaller reduction in Cr, Cu and Ni concentrations by SVc, with low chloride concentrations in the stormwater. These effects are less clear for SV and S. The Z values in Table 14 indicate that when there were high chloride concentrations, there was only a reduction in the concentration of Pb by filters SVc and SV. Removal percentages for dissolved metals were mainly negative (Table 10), except by SVc when there were low chloride concentrations in SW. Further, removal of dissolved Cd (25.7%), Cu (4.9%) and Zn (68.2%) were only seen after stormwater had been treated by SVc and when there were low chloride concentrations. After treatment of stormwater by SV and S, there was an increase in concentrations. Further, dissolved Cr was removed by filter SVc (41.9%) and SV (26.7%), and Ni by SVc, while Pb was not removed at all. For high chloride concentrations, only Cr was removed by all three filters (14.9–48%), and Ni by SVc (49.7%) and SV (39.8%). All the other concentrations increased after all three filters.

To summarize the impact of chloride concentration, metal concentrations were higher in stormwater as well in the filter effluent when chloride concentrations were higher. Removal of total metals was, in general, efficient by all three filters, but most efficient by SVc, then SV and S (removal efficiency SVc>SV>S). For the dissolved metals, removal from stormwater was less effective and, when there were high chloride concentrations, there was a release of previously accumulated metals from the filters.

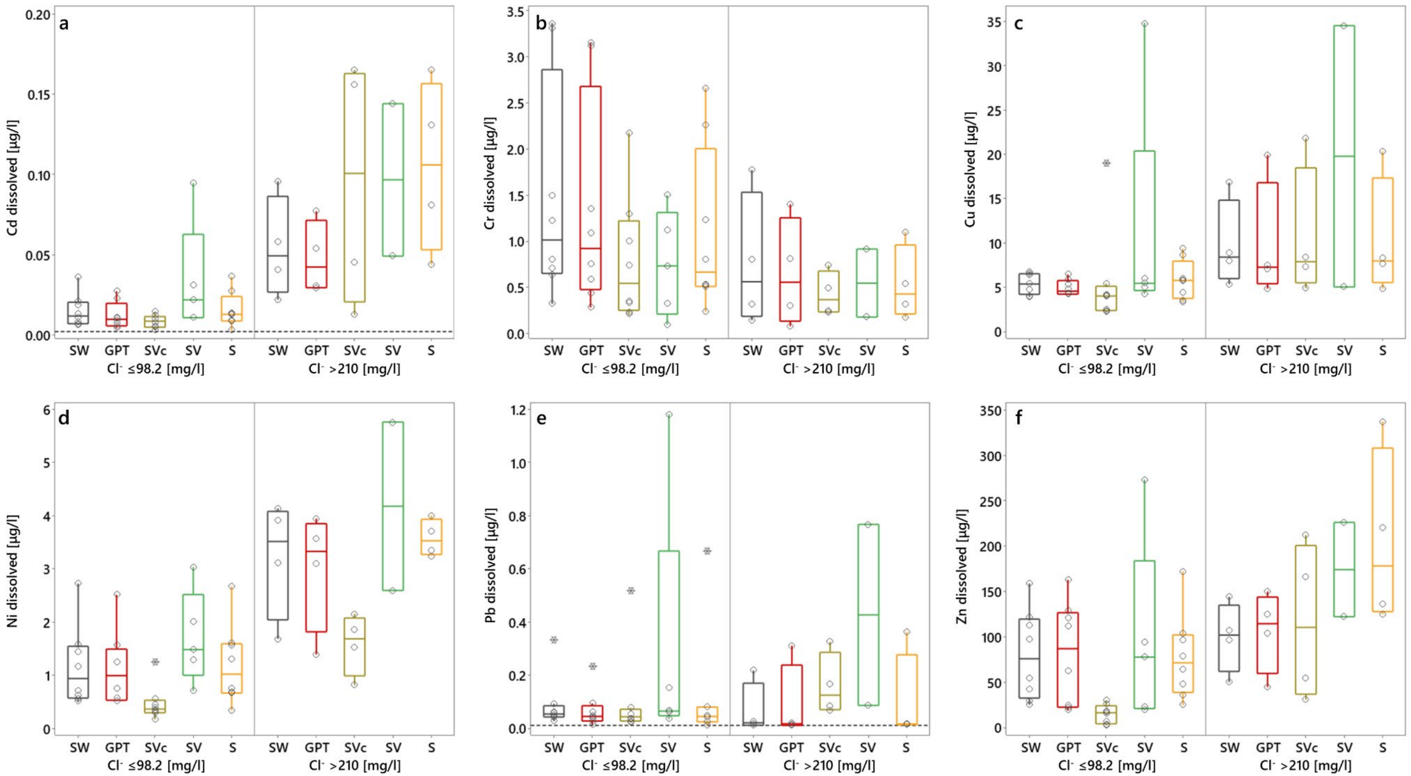

Figure 13. Dissolved metal concentrations for low (Cl^{-}≤98.2 mg/l) and high (Cl^{-}>210 mg/l) chloride concentrations for different stages in the studied bioretention site.

4.2 Pollutant accumulation

4.2.1 Accumulation of metals

All metals except Cd (i.e. Cr, Cu, Ni, Pb and Zn) were found in all 269 analysed samples (Table 15). Cd was detected in 245 of 269 samples (91%), and 21 of the 24 non-detects were from the four sites with the lowest concentrations (sites 13, 14, 15 and 27) in the study.

It was observed that concentrations decreased with increased depth in the filter material, for Cd, Cr, Cu, Pb and Zn but not Ni (Figure 14). This was statistically significant for Cr, Cu, Pb and Zn (Kruskal-Wallis, $p<0.05$), whereas only observed as a trend in boxplots for Cd (Figure 14). However, looking at each site separately reveals that all metals at most sites showed a decrease in concentration with increased depth in the filter material. Further, it was also observed that concentrations decreased with increased distance from the inlet for Cr, Cu, Pb and Zn in the top layer of the filters (Kruskal-Wallis, $p<0.05$). A similar tendency was also observed for Cd, but it was not statistically significant.

In the forebay for Cr, Cu and Zn, there was a tendency for slightly higher concentrations in the samples (20 of the sites 1–29, Table 1) compared to the samples from the filter materials (Figure 4). In contrast, Ni did not exhibit any difference in concentration while Cd and Pb had lower concentrations in the forebay than in the top layer of the filters. However, these trends were not statistically significant (Kruskal-Wallis, $p<0.05$).

Table 15. Metal concentrations, total concentrations and occurrence after each step (1–5) of fractionation (mg/kg, DM) and occurrence rates (%). ⋆Indicates that 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	Occurrence >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%

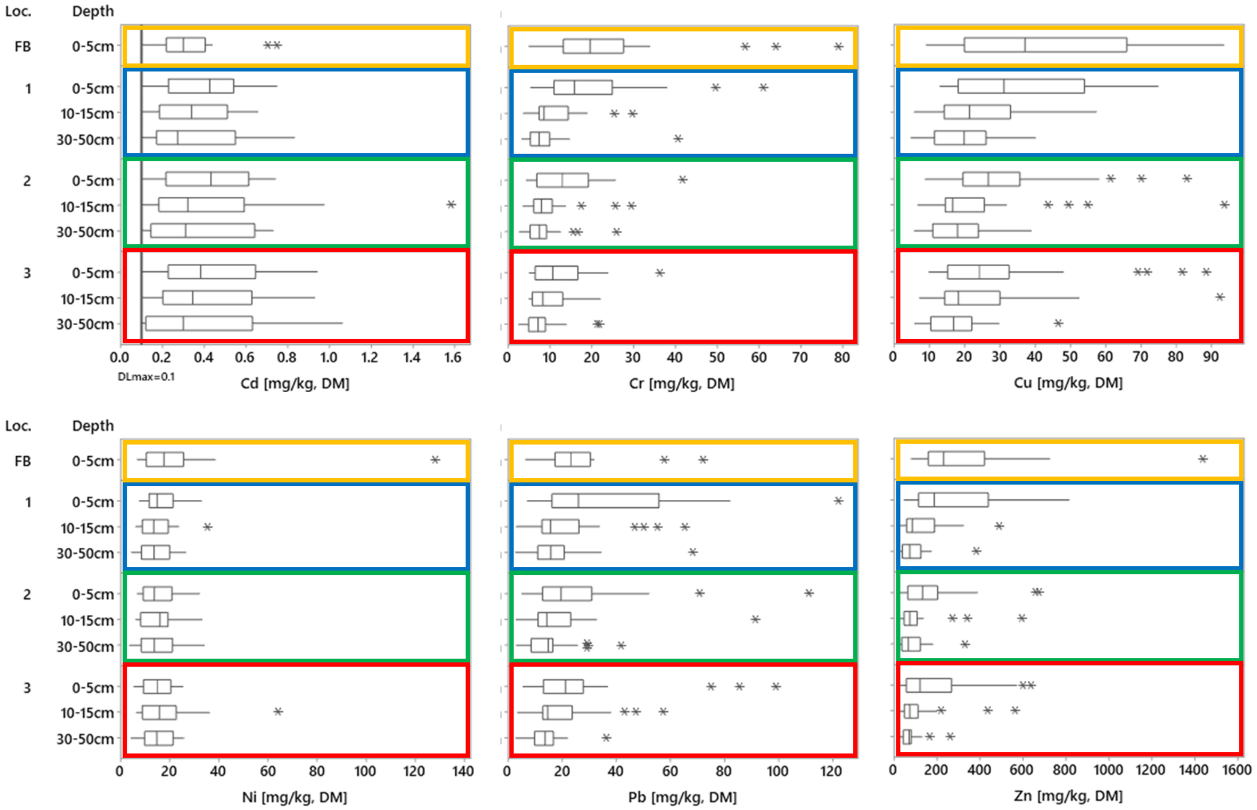

Figure 14. Boxplots with total concentration of Cd, Cr, Cu, Ni, Pb and Zn at three different locations and three depths for each location. Fractionation with sequential extraction was carried out on samples from location 1 (close to inlet) at the first depth (0–5 cm). Data for Cd with a 90% occurrence were censored to DL_{max}=0.1 mg/kg, DM. Each location is marked with a coloured rectangle.

Metal fractionation

To study the accumulated metals (Cd, Cr, Cu, Ni, Pb, Zn) and their potential to leach from filter material and sediments, a fractionation of the metals was carried out on the samples collected closest to the inlets in the top layer (Figure 4, location 1, depth 1). These are, in most cases, the samples with the highest metal concentrations. The fractionation method used for this study was a five-step sequential extraction, where the most soluble metals are extracted in step 1, and the least soluble in step 5 (Table 8).

The results showed that all studied metals were present in all five fractions, and, thus, that all analysed metals (Cd, Cr, Cu, Ni, Pb, Zn) were available in potentially mobile forms in the filter material, albeit to varying degrees. From the fractionation, the most mobile metal in the studied bioretention filters and sediments was Cd, while Cr was the most stable.

The general observation (Figure 15) was that there were high metal content in fraction 4 (except for Cd) and low metal content in fraction 2. For all metals, most mass was detected in the first four fractions (Table 16 and Figure 15). Cr was the only metal in the study with its highest concentration in fraction 5 (very stable form, Table 8) and Cd the only metal with its highest concentration in fraction 1 (easily soluble form, Table 8). Cu, Ni and Pb all had their highest concentrations detected in fraction 4 (Table 16 and Figure 15).

Table 16. Distribution between fractions in percentage of detected metal concentration (for each metal), calculated from median concentrations, with detection limits reported by the external accredited laboratory.

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

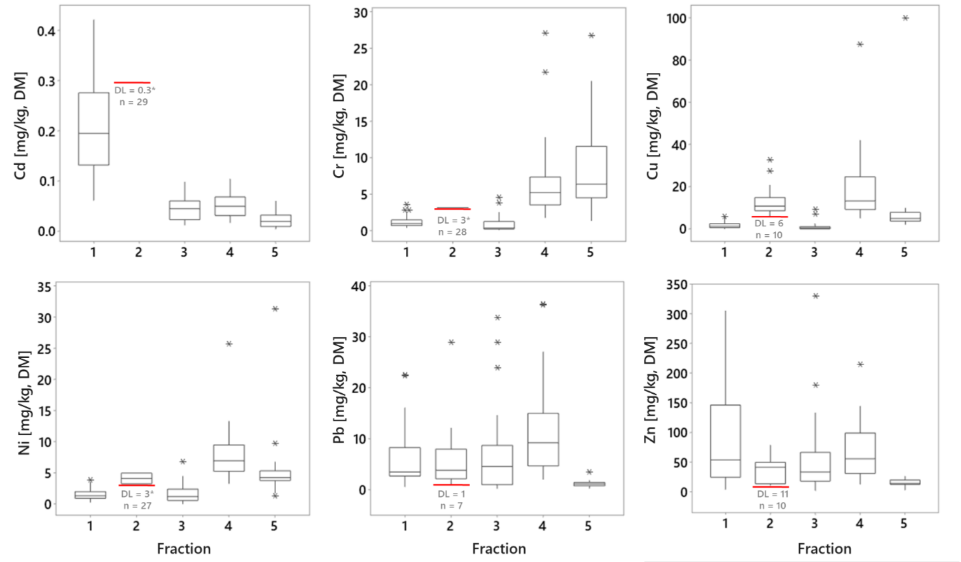

Figure 15. Boxplots of median concentration for metals in five different fractions. For all metals, the detection limit (DL) is indicated in fraction 2 and marked with a horizontal line. "n" indicates the number of values below DL out of a total of 29 samples. ⋆ Indicates that, for Cd, Cr and Ni, one sample in the analysis had a higher DL (double value) than the other DLs (i.e. $\mathrm{Cd}_{\mathrm{DL}}$=0.3 for 28 samples and $\mathrm{Cd}_{\mathrm{DL}}$=0.6 for one sample, $\mathrm{Cr}_{\mathrm{DL}}$=3 for 27 samples and $\mathrm{Cr}_{\mathrm{DL}}$=6 for one sample, $\mathrm{Ni}_{\mathrm{DL}}$=3 for 26 samples and $\mathrm{Ni}_{\mathrm{DL}}$=6 for one sample).

Cd was mainly present in fraction 1 (Table 16), with its highest concentration in fraction 1, and highest sum of concentrations from fractions 1–4 ($\mathrm{Cu}_{\Sigma \mathrm{F1\text{-}F4}}$=93 %). Cr was mainly found in fraction 5 and fraction 4: $\mathrm{Cr}_{\mathrm{F1}}$ = 7%, $\mathrm{Cr}_{\mathrm{F2}}$ = 1%, $\mathrm{Cr}_{\mathrm{F3}}$ = 5%, $\mathrm{Cr}_{\mathrm{F4}}$ = 38%, $\mathrm{Cr}_{\mathrm{F5}}$ = 48%. Cr had the highest concentration in fraction 5, which was also the highest concentration compared to the other metals. Cu had the highest detected metal concentration in fractions 4 and 2, but was also present in fraction 5 ($\mathrm{Cu}_{\Sigma(2+4+5)}$ = 92%). Cu distribution between different fractions was: $\mathrm{Cu}_{\mathrm{F1}}$ = 4%, $\mathrm{Cu}_{\mathrm{F2}}$ = 22%, $\mathrm{Cu}_{\mathrm{F3}}$ = 4%, $\mathrm{Cu}_{\mathrm{F4}}$ = 48%, $\mathrm{Cu}_{\mathrm{F5}}$ = 22%. The total sum of Cu in fraction 1 to fraction 4 ($\mathrm{Cu}_{\Sigma 1\text{-}4}$) was 78%, and the sum in fraction 2 and fraction 4 was 70 % ($\mathrm{Cu}_{\Sigma \mathrm{F2+F4}}$=70%). Ni was found with the high concentration in fraction 4 and fraction 5, and the distribution between fractions was: $\mathrm{Ni}_{\mathrm{F1}}$ = 9%, $\mathrm{Ni}_{\mathrm{F2}}$ = 2%, $\mathrm{Ni}_{\mathrm{F3}}$ = 10%, $\mathrm{Ni}_{\mathrm{F4}}$ = 47%, $\mathrm{Ni}_{\mathrm{F5}}$ = 32%. After Cr, Ni had the highest concentration in fraction 5. Pb had a high concentration in fractions 1, 3 and 4, and the highest sum of concentration of all the metals from fraction 1 to fraction 4 ($\mathrm{Pb}_{\Sigma(1\text{-}4)}$ = 96%). Zn showed a relatively even spread between fractions, with its highest concentration in fraction 4 and lowest in fraction 5. The Zn distribution between fractions was: $\mathrm{Zn}_{\mathrm{F1}}$ = 31%, $\mathrm{Zn}_{\mathrm{F2}}$ = 8%, $\mathrm{Zn}_{\mathrm{F3}}$ = 20%, $\mathrm{Zn}_{\mathrm{F4}}$ = 33%, $\mathrm{Zn}_{\mathrm{F5}}$ = 8%. Zn had the second highest (after Pb) sum of concentration in fractions 1–4 ($\mathrm{Zn}_{\Sigma(1\text{-}4)}$ = 94%) and the second highest (after Cd) concentration in fraction 1 (36%). In fraction 2, several of the 29 analysed samples were below the detection limit ($\mathrm{Cd}_{<\mathrm{DL}}$ = 29, $\mathrm{Cr}_{<\mathrm{DL}}$ = 28, $\mathrm{Cu}_{<\mathrm{DL}}$ = 10, $\mathrm{Ni}_{<\mathrm{DL}}$ = 27, $\mathrm{Pb}_{<\mathrm{DL}}$ = 7 and $\mathrm{Zn}_{<\mathrm{DL}}$ = 10, Table 15 and Figure 15). Of the 29 samples, all Cd samples were below DL, with Cr detected in one sample, Cu in

19 and Ni in two. A reason for the non-detects in fraction 2 was either low concentrations of metal in the samples and/or a combination of the level of detection limits in the method.

4.2.2 Accumulation of organic micropollutants

Of 116 filter material samples from 12 sites (Table 1), 34 of the 38 organic analytes were detected in at least one sample. Only four substances were not detected at all, one of the PAHs (acenaphthalene) and three phthalates (diethylphthalate (DEP), di-n-octylphthalate (DNOP) and dicyclohexylphthalate (DCP)).

PAH was detected above the detection limit in 79% of all 116 samples. The PCBs were, together with PAHs, the most frequently observed group of organic micropollutants, detected in 77% of all samples. All PCBs except PCB28 were detected at all 12 sites except two (sites 3 and 7). PCB 153 occurred most frequently, being detected in 76% of all samples. PCB28, the least frequently occurring PCB, was detected at four sites (5, 19, 22 and 23) and in 17% of all samples. Phthalates were detected at 11 of 12 sites and in 59 of 108 samples (51%) Of 13 studied phthalates, 12 were detected in at least one sample. Di-2-ethylhexylphthalate (DEHP) was the most frequently quantified phthalate detected in 49% of the samples, whereas the other phthalates together were only detected occasionally (≤7% of all samples). Alkylphenols had the lowest occurrence rate of the OMPs in this study. NP was most frequently detected, being found at 10 of 12 sites, and in 26 out of 107 samples (23%). OP was only detected in one sample out of 107. Furthermore, PAHs and PCBs with higher molecular weights occurred more frequently than those with lower molecular weights. PAHs with high and median-high molecular weights (PAH-H and PAH-M) occurred in higher concentrations than PAHs with lower molecular weights (PAH-L). Further information of the occurrence and concentration of OMPs in the bioretention facility soil samples are shown in Table 17.

Table 17. Descriptive statistics for OMPs in bioretention facility soil samples with abbreviations, detection limit (DL) and concentrations.

Group/ Units	Substance name	No. of samples	Occurance >DL		DL	Concentrations			
						Top layer	All data		
			Nr	%		Median	Median	Max	Min
PAH	Naphthalene (Nap)	107	13	12%	0.10	<0.10	<0.10	1.49	<0.10
[mg/kg, DM]	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

Continuation of Table 17.

Group/ Units	Substance name	No. of samples	Occurance >DL		DL	Concentrations			
						Top layer	All data		
			Nr	%		Median	Median	Max	Min
PCB	PCB 28	108	18	17%	(0.20-0.40)	<0.10	<0.10	18.00	<0.06
[µg/kg, DM]	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 153	108	80	74%	0.10	1.20	0.42	42.00	<0.10
	PCB 138	108	78	72%	0.10	1.05	0.37	36.00	<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	dimethylphthalate (DMP)	108	1	1%	0.05	<0.05	<0.05	1.40	<0.05
[mg/kg, DM]	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	4-tert-octylphenol (OP)	107	1	1%	(0.01-0.03)	<0.01	<0.01	0.03	<0.01
[mg/kg, DM]	4-nonylphenols (tech.mixture) (NP)	107	19	18%	(0.10-0.20)	<0.10	<0.10	106	<0.10

The boxplots in Figure 16 show that pollutant concentrations of PAHs, PCBs and phthalates were higher in the surface layers, although those pollutants were also detected in the deeper layers, albeit less frequently and at lower concentrations. The detected alkylphenols were mainly found in the top layer close to the inlet and forebay. Concentrations decreased considerably with depth (Figure 16) for the three studied groups of OMPs (PAHs, PCBs, phthalates) and for the more frequently detected alkylphenol 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 (Kruskal-Wallis, $p<0.05$). Furthermore, for all four OMP groups, a large variation in concentrations within, as well as between, different sites were observed, particularly in the forebay but also for PAHs in all surface layers.

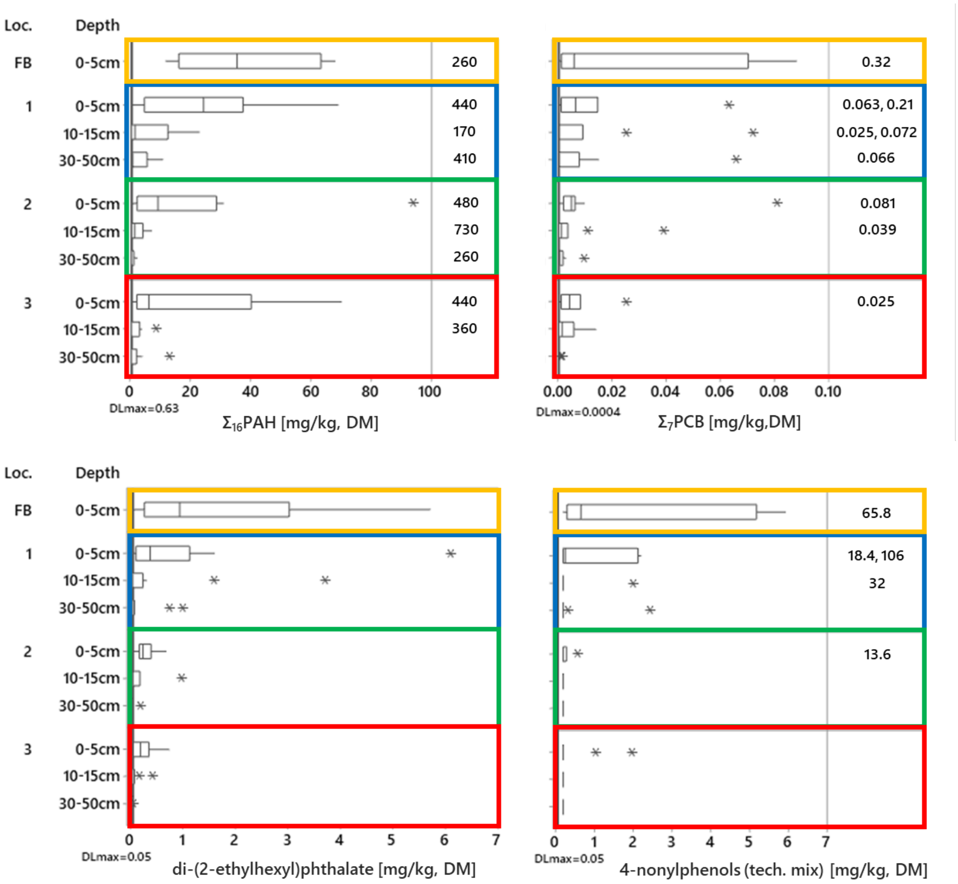

Figure 16. Boxplots of concentrations for Σ_{16}PAH, Σ_7PCB, di-2-ethylhexyl phthalate and 4-nonylphenols (Tech Mix) for different locations, forebay (FB), three locations in the filters (1, 2 and 3) and at three depths (0–5 cm, 10–15 cm and 30–50 cm). Different locations are marked with coloured rectangles.

Of twelve sites examined for concentrations of OMPs, eight were equipped with a forebay (sites 1, 9, 11, 12, 14, 19, 22 and 28, Table 1). For those sites, NP was detected in seven forebays (sites 9, 11, 12, 14, 19, 22 and 28) but only in four of the corresponding filters materials (sites 11, 12, 19 and 28). PAHs, phthalates and NP concentrations were statistically higher (Kruskal-Wallis, $p<0.05$) in the forebay than in surface locations in the filters (locations 1, 2 and 3). Also, for PCBs, higher concentrations were observed in the forebay (Figure 16). Two phthalates (di-n-pentylphthalate (DNPP) (site 11) and diisodecyl phthalate (DIDP) (site 22)) were only detected in one sample each, and then in the forebay. NP (Tech Mix) was only detected in three of the forebays (sites 9, 14 and 22) and OP was detected in two samples, one in a forebay (site 22) and one in a top layer sample (Site 5). For further information of occurrence and concentrations of OMPs in forebays, see Table 18.

In general, the pollutant concentrations in forebays (Table 18) were higher compared to the concentrations in the filter material (Table 15 and Table 17), and also when compared to the top layer (0–5 cm) where the predominant removal of pollutants occurs (Blecken et al., 2009a). An estimation of accumulated pollutant mass in the top 5 cm in the filter material in this study (Table 19) showed that, despite higher concentrations in the forebay, only a small proportion of pollutants were accumulated in the forebay. However, the size of bioretention facility forebays in this study was approximately 1.2 % of the filter area, whereas the normal recommendation is 10% of the design surface area (City of Portland, 2020).

Table 18. Descriptive statistics for OMPs in bioretention forebay soil samples.

Group/ Units	Substance name	No. of samples	Occurence >DL		All data			DL
			Nr	%	Min	Median	Max	
PAH [mg/kg, DM]	Naphthalene (Nap)	16	6	38%	<0.05	<0.10	0.30	(0.05-0.30)
	Acenaphthylene (Acyl)	16	3	19%	<0.05	<0.10	0.30	(0.05-0.30)
	Acenaphthene (Acen)	16	4	25%	<0.05	<0.10	1.72	(0.05-0.30)
	Fluorene (F)	16	7	44%	<0.05	<0.10	2.01	(0.05-0.30)
	Phenanthrene (Phen)	16	12	75%	<0.10	0.65	35.7	(0.10-0.30)
	Anthracene (A)	16	10	63%	<0.09	0.20	4.06	(0.10-0.30)
	Fluoranthene (Fluo)	16	14	88%	<0.10	1.92	60.7	(0.10-0.30)
	Pyrene (Pyr)	16	15	94%	<0.16	1.51	45.6	0.30
	Benzo(a)anthracene (BaA)	16	13	81%	<0.05	0.66	17.0	(0.05-0.15)
	Chrysene (Chry)	16	15	94%	<0.05	0.79	22.8	0.15
	Benzo(b)fluoranthene (BbF)	16	16	100%	0.18	1.31	25.7	0.05
	Benzo(k)fluoranthene (BkF)	16	10	63%	<0.05	<0.63	9.63	(0.05-0.70)
	Benzo(a)pyrene (BaP)	16	15	94%	<0.08	0.75	16.6	0.15
	Dibenzo(a,h)anthracene (DahA)	16	13	81%	<0.05	0.18	1.86	(0.05-0.15)
	Benzo(g,h,i)perylene (Bper)	16	15	94%	<0.18	0.73	11.5	0.30
	Indeno(1,2,3-cd)pyrene (IP)	16	15	94%	<0.11	0.76	9.12	0.15
	PAH sum Low weight (PAH-L)	16	7	44%	<0.08	<0.15	1.90	(0.08-0.45)
	PAH sum medium-weight (PAH-M)	16	15	94%	<0.19	4.45	150	(<0.19-0.75)
	PAH sum high-weight (PAH-H)	16	16	100%	0.26	5.55	110	<0.26
	PAH 16 sum (Σ16PAH)	16	13	81%	<1.30	9.95	260	(1.30-3.80)

Continuation of Table 18.

Group/ Units	Substance name	No. of samples	Occurence >DL		All data			DL
			Nr	%	Min	Median	Max	
PCB	PCB 28	16	2	13%	<0.10	<0.15	3.60	(0.10-0.50)
[µg/kg, DM]	PCB 52	16	15	94%	<0.10	0.32	27.0	0.10
	PCB 101	16	15	94%	<0.10	1.10	61.0	0.10
	PCB 118	16	15	94%	<0.10	0.75	64.0	0.10
	PCB 153	16	16	100%	0.16	1.60	62.0	0.10
	PCB 138	16	16	100%	0.14	1.60	54.0	0.10
	PCB 180	16	16	100%	0.11	1.45	47.0	0.10
	sum of 7 PCBs (Σ7PCB)	16	16	100%	0.41	6.85	320	<0.40
Phthalates	dimethylphthalate (DMP)	16	-	0%	-	-	-	0.05
[mg/kg, DM]	diethylphthalate (DEP)	16	-	0%	-	-	-	0.05
	di-n-propylphthalate (DPP)	16	-	0%	-	-	-	(0.05-2.00)⋆
	diisobutyl phthalate (DIBP)	16	3	19%	<0.05	<0.05	0.09	(0.05-0.10)
	di-n-butylphthalate (DBP)	16	1	6%	<0.05	<0.05	1.10	(0.05-0.10)
	di-n-pentylphthalate (DNPP)	16	1	6%	<0.05	<0.05	0.051	(0.05-0.30)
	di-n-octylphthalate (DNOP)	16	-	0%	-	-	-	(0.05-0.30)⋆⋆
	di-(2-ethylhexyl)phthalate (DEHP)	16	15	94%	<0.05	1.50	5.70	0.05
	butylbenzylphthalate (BBP)	16	-	0%	-	-	-	(0.05-1.00)⋆⋆⋆
	dicyclohexylphthalate (DCP)	16	-	0%	-	-	-	0.05
	diisodecyl phthalate (DIDP)	16	2	13%	<2.50	<2.50	5.10	2.50
	diisononyl phthalate (DINP)	16	6	38%	<2.50	<2.50	11.0	2.50
	di-n-hexylphthalate (DNHP)	16	-	0%	-	-	-	(0.05-0.07)⋆⋆⋆⋆
Alkylphenols	4-tert-octylphenol (OP)	16	5	31%	<0.01	<0.02	0.10	(0.01-0.03)
[mg/kg, DM]	4-nonylphenols (tech.mixture) (NP)	16	9	56%	0.06	<0.10	65.8	0.10

⋆ Of 16 samples, 14 nondetects were <0.05, 1 was <0.08 and, 1 was <2.00

⋆⋆ Of 16 samples, 10 nondetects were <0.05, 1 was <0.15, 2 were <0.20, 1 was <0.25 and, 1 was <0.30

⋆⋆⋆ Of 16 samples, 14 nondetects were <0.05, 1 was <0.10 and, 1 was <1.00

⋆⋆⋆⋆ Of 16 samples, 15 nondetects were <0.05 and, 1 was <0.07

Table 19. Approximate estimates of pollutant mass accumulation in the top 5 cm of filter material and Forebay (FB).

	Area	PAH16		PCB7		Cu		Pb		Zn	
Location	m^2	mg/kg	kg	mg/kg	kg	mg/kg	kg	mg/kg	kg	mg/kg	kg
Filter	128	8.0	102	4.9	0.1	21	265	16	205	85	1083
FB	1.5	10	1.5	6.9	0.0	51	7.6	24	3.6	243	36
FB/Filter	1.2%		1.5%		1.6%		2.9%		1.7%		3.4%

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

4.2.3 Pollutant accumulation and correlations

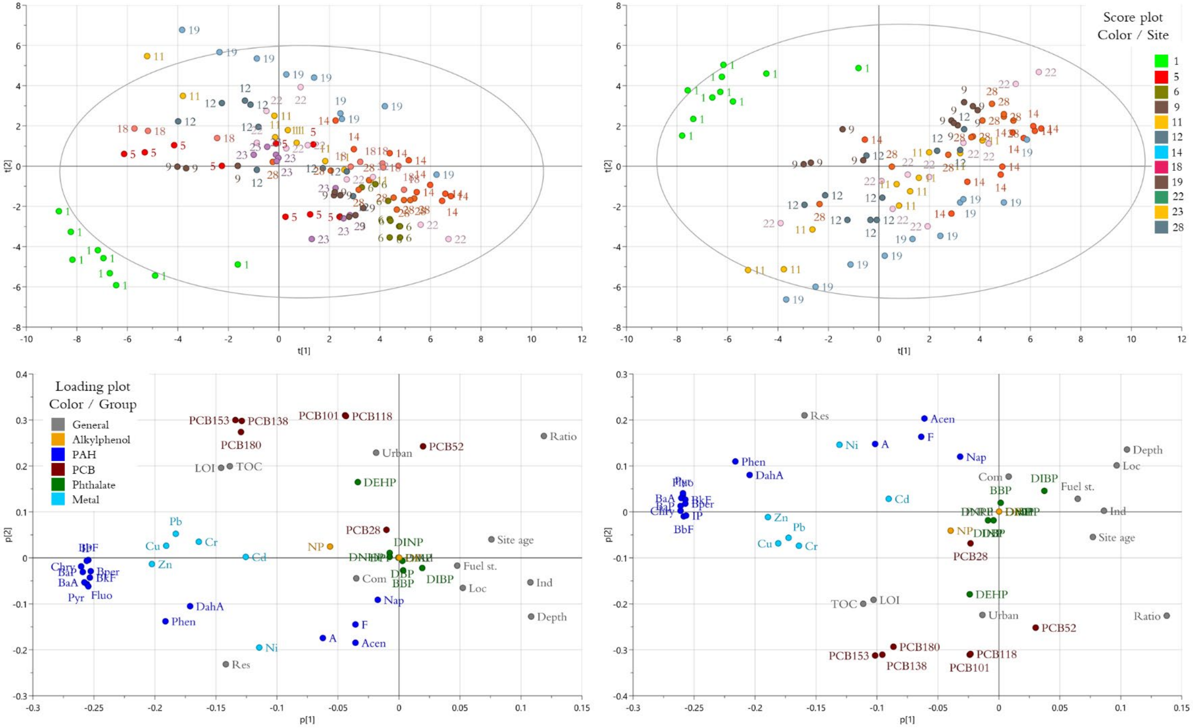

Figure 17. PCA of OMPs and metals at 12 sites without a forebay (left plots) and eight sites with a forebay (right plots). Score plots (upper) and loading plots (lower) for principal components 1 and 2. The score plot is coloured according to the site number and the loading plot according to pollutant 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%.

The main observation identified in the score plot (Figure 17) was the clustered groups site by site, where 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 corresponded to the observations in the loading plot between area ratio (between catchment area size and filter area) and land use, but also between depth and concentration. This indicates a large variation in concentrations between sites, as well as within sites. In the loading plot, the main observation was that concentrations of PAHs, metals, PCBs, NP, DEHP and general parameters (TOC and LOI) were located towards the left. Depth, ratio, industrial, location and site age, on the other hand, were located on the right side of the plot. Thus, there is a negative correlation between the concentrations, the general parameters and land use parameters. The variables for catchment characteristics (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. PAHs with high 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 PCB138, PCB 153 and PCB180 located to the far left, PCB101 and PCB118 also to the left, while PCB28 and PCB52 were located closer to the origin in p[1]. TOC and LOI show correlation to PCBs, phthalates and DEHP but also 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 reveals correlation between some sites and certain pollutant groups, e.g. site 1 to PAHs, sites 11 and 19 to PCBs, and site 5 to metals. From the score plot, a pattern of sites stretched out from lower left to upper right can also be seen. This seems to correspond to a diagonal from left to right in the loading plot with a relationship 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 were grouped, shows a negative correlation between area ratio and residential land use, especially for the PAH group and site 1. For example, a lower ratio between filter area and catchment area i.e. larger catchment area compared to filter area at sites 1, 2 and 3 (Table 1) is correlated to higher concentrations of PAHs. Urban/downtown areas show correlation to PCBs. Otherwise, there was no clear correlation between land usage and concentrations. All pollutants with high occurrences showed stronger negative correlation to ratio and depth, but also to location and age.

5 Discussion

5.1 Stormwater

In general, the metal concentrations of untreated sampled stormwater SW in both Malmö (Table 9) and Sundsvall (Table 10) were within the typical ranges that could be expected for urban stormwater/road runoff e.g. corresponding to previous studies of stormwater data (Pamuru et al., 2022), stormwater quality data (Makepeace et al., 1995) and the StormTac Database (2023) for residential and downtown areas (Table 11). The stormwater concentrations in Sundsvall (i.e. road runoff from a larger highway carrying around 13,000 vehicles per day) were compared with previous studies of road runoff (Göbel et al., 2007; Davis and Birch, 2010). Concentrations of Cd and Pb were generally lower, Ni within the same range or lower, and Cr, Cu, and Zn had higher maximum and lower minimum concentrations than reported by Göbel et al. (2007). Compared to Davis and Birch (2010), the Sundsvall study also had similar levels of Cu, lower concentrations of Pb and similar or higher concentrations of Zn.

In summary, the metal concentrations (Cd, Cr, Cu, Ni, Pb and Zn) in stormwater from the Sundsvall and Malmö studies were in comparable ranges to previous studies of highway runoff, thus representing typical highway runoff. Therefore, the sampled stormwater in the studies included in this thesis is considered as representative of a typical road runoff and/or urban stormwater. Consequently, the presented dataset, results and conclusions are not only specific for these study sites but also in ranges expected in urban stormwater and/or road runoff, and so results can be generalized further. A comparison of stormwater between the different sites (Sundsvall and Malmö) shows that Sundsvall generally has higher concentrations for all metals except Pb and dissolved Cu.

5.2 Metal treatment

5.2.1 Effect of bioretention design on metal treatment

Sand based filters

As with previous laboratory scale studies, removal of total metals in Malmö and Sundsvall was generally more efficient (Blecken et al., 2009a; Hatt et al., 2007; Sun and Davis, 2007) than removal of dissolved (Hatt et al., 2007; Søberg et al., 2017) and truly dissolved metals (Lange et al., 2022, 2020b). Also, compared to previous field studies, there were similar removals e.g. for total metals in Malmö, Cu and Pb and dissolved Cu and Zn, while reduction of dissolved Cd was lower compared to David et al. (2015) and Hatt et al. (2009) (Table 20). Previous studies have also reported that filtration of suspended material (i.e. TSS and associated metals) is the main treatment process for the more efficient removal of particulate metals (Blecken et al., 2009a; Li and Davis, 2008a) compared to the less efficient adsorption of dissolved metals (Davis et al., 2009). Further, previous studies have shown that e.g. Cu, Pb and Zn occur mainly in particulate form in stormwater (Flanagan et al., 2018; Lange, 2021; Lindfors et al., 2020). For these particulate metals, often correlated to TSS, a generally high removal often exceeding 85% has previously been reported (Blecken et al., 2009b, 2009b; David et al., 2015). This may explain the overall efficient reduction in total concentrations of the more particulate Cu, Pb and Zn observed both in Malmö and Sundsvall. Concerning dissolved metals, leaching of e.g. Cu and Pb has also been reported in laboratory studies (Søberg et al., 2017), and this is different to that observed in the filters in Malmö while similar to Sundsvall for Pb in all filters and for Cu in filters S and SV.

When comparing the mean removal in the two sand-based filters (SV) in Malmö and Sundsvall, the Malmö filter (Table 20) showed higher removal of total Cu and Zn, while Sundsvall showed a higher removal of total Cr, Ni and Pb. For Cd, they both had a mean removal of 38%. Removal of dissolved metal concentration was higher in Malmö for Cu and Pb, but higher in Sundsvall for Cr. For dissolved Cd and Ni, there was a release (negative removal in Table 20) rather than accumulation. However, differences in results between the two sites may be affected by different area usage and operators for the catchment areas. While the street along the Malmö bioretention system is in a downtown area and operated by Malmö municipality, the catchment area in Sundsvall is a national highway operated by road authorities. The national highway, with a higher speed limit than in the downtown area, has other requirements for road maintenance e.g. use of de-icing salt during the winter when temperatures reach a specific value. Also, the intervals between maintenance may differ between the different sites, which may impact the metal removal in treated stormwater.

Table 20. Mean metal removal [%] in Malmö and Sundsvall, and reported removal in previous field studies of bioretention performance. References: Davis et al. (2003), Li and Davis (2009), Hatt et al. (2009), Chapman and Horner (2010), David et al. (2015), (Glass and Bissouma (2005), Hunt et al. (2008), Lange et al. (2022) and Jafarzadeh et al. (2024). Field sites were located in Sweden (SWE), United States (U.S.) and Australia (AUS).

			Removal %							
Site	Filter		Cd	Cr	Cu	Ni	Pb	Zn	Reference	Location
Malmö	SV	Total	38	46	84	37	89	93	Paper V	SWE
	SVp		-127	-126	66	-112	43	71		
	SVsz		-24	-88	86	-19	88	93		
	SV	Dissolved	-84	-53	53	-78	70	88		
	SVp		-430	-219	34	-162	30	77		
	SVsz		-249	-52	54	-118	60	88		
Sundsvall	S	Total	4	51	37	33	32	11	Paper IV	SWE
	SV		38	97	78	88	94	70		
	SVc		27	88	80	80	-14	84		
	S	Dissolved	-57	22	-12	-3	-25	-64		
	SV		-232	7	-173	-17	-256	-262		
	SVc		-1	33	2	54	-162	42		
Greenbelt		Total	–	–	97	–	>95	>95	Davis et al., (2003)	U.S.
Largo			–	–	43	–	70	64		
–		Total	–	–	81	–	75	79	Glass and Bissouma, (2005)	U.S.
–		Total	–	–	–	–	–	76	Hunt et al., (2008)	U.S.
College Park		Total	–	–	65	–	83	92	Li & Davis (2009)	U.S.
Silver spring			–	–	100	–	96	100		
Monash		Total	–	–	67	–	80	84	Hatt et al., (2009)	AUS
McDowall			91	–	98	–	98	99		
–		Total	–	–	80	–	86	80	Chapman & Horner (2010)	U.S.
–		Dissolved	–	–	58	–	–	72		
–		Total	84	–	83	–	51	93	David et al., (2015)	U.S.
–		Total	–	–	79	–	>76	94	Lange et al., (2022)	SWE
–		Total	–	–	–	–	–	67	Jafarzadeh et al., (2024)	U.S.

Vegetation and chalk

There have been few previous studies that have assessed bioretention and the impact of chalk and pH on metal treatment. Søberg et al. (2019) carried out a batch test study of (dissolved) metal adsorption to bioretention filter materials and concluded that chalk additives may improve metal adsorption, but that further full-scale studies were needed. When comparing the results of metal removal (Table 12, Figure 13) by the three filters in Sundsvall, the results show that SVc treats dissolved metals better when compared to SV and S, i.e. the difference being the chalk additive ($CaCO_3$). This is likely due to pH being an important factor controlling the balance between adsorbed and soluble metal fractions. If the chalk additive increases pH in the filter, the concentrations of soluble and extractable metals (Zn, Pb, Ni, Cd, and Cu) will decrease (Alloway, 2013; Gray et al., 2006). Previous studies have also shown that the pH of stormwater (road runoff) is nearly 7 (Sansalone and Buchberger, 1997), but lower in soil, with a clear trend of decreasing with depth (Li and Davis, 2008b). Thus, metals and associated complexes become more stable and particle-bound, explaining why more particles then accumulate in the filter material. Muthukrishnan and Oleske (2008) described an example of this when they used limestone in a laboratory study to increase the pH in soil and to improve the sorption of metals in the bioretention filter material. Furthermore, previous studies (Hamedani et al., 2019; Muthukrishnan and Oleske, 2008) have shown that a filter with chalk additives and vegetation (e.g. SVc) exhibits, in general, better treatment of metals in stormwater.

Previous studies of the impact of vegetation on water quality treatment in bioretention have mainly been carried out in laboratories with a focus on nutrients. A beneficial effect of vegetation in bioretention filters has been observed for nutrient removal, and particularly for nitrogen, whilst phosphorus removal seems to be less affected by vegetation (Bratieres et al., 2008; Lucas and Greenway, 2008). There have been few field studies of metal removal and vegetation impact. While Zhang et al. (2014) did not observe a difference between planted and nonplanted filters in laboratory, Lange (2021) observed positive effects on total metals removal. This was explained by enhancement of soil structure, reduced clogging and improved infiltration, which are critical for capture of particulate metal removal. Further in a vegetated filter, there is less risk of clogging as the plants break up fine sediments accumulated on the surface, thus maintaining infiltration capacity (Muerdter et al., 2018). Thus, this positive observed effect of vegetation on metal treatment in bioretention filters may be related to increased infiltration, and particularly for maintaining the infiltration capacity in biofiltration systems over time due to reduced surface clogging (Le Coustumer et al., 2009; Técher and Berthier, 2023).

Coarse filter materials and effect of pumice

The results obtained from the bioretention systems in Malmö for coarse filter materials show that the sand-based filter materials with very high hydraulic conductivity (>1500 mm/hr) remove total metals relatively well (Table 12). The sand filters (SV) and similar material equipped with a submerged zone (SVsz) were most efficient in removal of total metals (mainly particulate), while the filter material with the pumice amendment (SVp) was less efficient. A review of bioretention filter materials assessing effects of properties and performance (Tirpak et al., 2021) described the effect of coarser particle size distributions to be increased infiltration, decreased retention capacity, reduced risk of clogging with reduced number of overflows, and decreased pollutant removal. The larger volume capture created by increased infiltration also increases the yearly treated runoff volume in a bioretention facility and may thus increase the yearly total pollutant removal from the stormwater. On the other hand, lower infiltration increases the percentage of pollutant (metal) removal from the treated stormwater. Thus, two of the main objectives (runoff volume capture and pollutant removal) of a bioretention facility are to some extent in conflict. Consequently, for the best performance, infiltration needs to be optimized between the yearly treated volume of stormwater and the corresponding removal percentages. A recommended range for bioretention filter materials is between 50–200 mm/hr (Fassman-Beck et al., 2015; Le Coustumer et al., 2009; WSUD, 2024). Using results from a laboratory study, Hsieh and Davis (2005) suggested 72–324 mm/hr for removal of TSS (>96%), Pb (>98%), total phosphorus (24–70%) and nitrates (6–9%).

However, the Malmö study shows that filter materials with a higher hydraulic conductivity of approximately 1500-1800 mm/hr can also still remove total Cu, Pb, Zn relatively efficiently and, to some extent, Cd, Cr and Ni, while they are less efficient for dissolved contaminants. Previous studies of more traditional finer graded filter materials with lower infiltration have shown similar effects of less effective removal of dissolved metals (Croft et al., 2024; Lange et al., 2022, 2020a; Søberg et al., 2017). Furthermore, this study also showed that removal percentages were higher for particulate than for dissolved metal fractions in these filter materials. Since Cu, Pb and Zn are metals expressly identified as potentially toxic in road runoff by The Nationwide Urban Runoff Program (US EPA, 1983), the efficient removal by filters SV and SVsz with coarser filter materials could be used for bioretention facilities when (total) metal removal is targeted. Together, this indicates that filters with high hydraulic conductivity can be similarly effective for particle removal in a bioretention facility as finer materials.

These results are also promising for bioretention implementation in regions with cold/winter climates since a coarser material could still be an option. Such materials are better suited for infiltration when temperatures fluctuate around zero degrees Celsius, and there is a risk of ground frost (e.g. day above zero, night below) (Caraco and Claytor, 1997; Muthanna et al., 2007; Stoeckeler and Weitzman, 1960). A higher hydraulic conductivity offered by a coarser filter material could then increase the total yearly volume of treated runoff due to the higher volume capture (Tirpak et al., 2021). Furthermore, Søberg et al. (2014) described a laboratory study of temperature influence on bioretention performance, and found that coarse filter materials did not impair performance. Also, Blecken et al. (2011) did not see any deterioration in metal adsorption when assessing coarse filter materials in a laboratory study.

Another factor related to higher hydraulic conductivity is that there will likely be fewer overflow events. Therefore, a coarser filter material could also be an option in (compared to the catchment area) small filters e.g. in densely built areas where space is limited as they can treat a larger amount of water, and there is less overflow in a given area each year. Thus, even if a filter containing higher hydraulic conductivity material does not treat all metals as efficiently as a filter containing material with lower hydraulic conductivity, the high infiltration capacity filter may result in treatment a larger ratio of the annual runoff, and thus still protect receiving water bodies well.

One aspect limiting the operational life of a stormwater infiltration system (including bioretention facilities) is clogging due to accumulation of fines on top of the filter material, especially when maintenance and/or pretreatment are insufficient. Le Coustumer et al. (2009) carried out bioretention column experiments and found that infiltration decreased over time (mainly due to clogging), from an initial median of 186 mm/hr to one of 51 mm/hr after 72 weeks. Also, Carpenter and Hallam (2010) used a field study and measured infiltration rates in 13 established rain gardens, finding that the mean infiltration rates varied between 43–368 mm/hr. Kendra et al. (2014) showed that filters with smaller particle sizes exhibited better TSS removal but also had a shorter lifespan than filters with larger particle sizes. Furthermore, Al-Ameri et al. (2018)

described a study of metal accumulation and suggested that metal concentrations may become an issue in some systems while, for most systems, clogging rather than accumulation would determine long-term performance. Hence, filter materials with a larger particle size distribution and higher hydraulic conductivity could increase the operational time between maintenance and still retain a particle removal function over a longer period as they are less prone to clogging (Tirpak et al., 2021).

Pumice

The filter with pumice additives, SVp, showed less efficient metal removal (Table 20) compared to the other two filter materials in SV and SVsz. An explanation for this is likely the very high hydraulic conductivity caused by the coarse filter material in SVp and, probably, the large pumice pores. In SVp, 50% of the filter material was a mixed pumice (Table 4) with a particle size of 2–8 mm and, therefore, much coarser than the filter sand in the study (0.063–4 mm). Thus, the infiltration capacity and hydraulic conductivity K_{sat} was higher in SVp and was, perhaps, too high for efficient metal removal. Probably preferential flow paths have been created, as reported by Carpenter and Hallam (2010) who observed high infiltration rates (460 mm/h) from a full-scale field experiment due to preferential flow paths, created in filter materials from the surface directly to the underdrain. Thus, the very high K_{sat} creates shorter hydraulic retention time, which may explain the less efficient metal treatment by SVp, something thus related to physical properties such as particle size and soil texture, rather than chemical properties such as cation exchange.

Submerged zone

A submerged zone, such as in the SVsz filter, is commonly implemented in bioretention facilities to improve, in particular, nitrogen removal (Kim et al., 2003; Li et al., 2014). Previous studies have shown that metal removal can also be enhanced to some extent in filters by using a submerged zone (Blecken et al., 2009b, 2009a; Søberg et al., 2017) although for metals, most removal occurs in the top layers of the filter material (Blecken et al., 2009a; Furén et al., 2023). Blecken et al. (2009b) concluded that it was likely not the submerged zone itself that increased the metal removal, but that the intermixed carbon source (sawdust) contributed with additional adsorption of metals (especially Cu due to OM-Cu-complexation). Similarly, (Zhang et al., 2014) investigated the effect of a submerged zone with carbon addition in a bioretention column study, and concluded that removal of Cu and Pb was significantly increased in biofilters with a submerged zone and carbon source. This was partly explained by the carbon source having a major impact, particularly on Cu removal, due to Cu and Pb having a high affinity for carbon. Further, Zhang et al. (2014) also suggested that the reducing conditions in bioretention facilities with a submerged zone may cause complexation of metals which reduces their mobility in the filter material. In the Malmö study, where unfortunately no carbon source (such as sawdust, shredded newspaper or similar) was added to the submerged zone, there was no significant difference between the sand filter configuration in SV compared to the sand filter equipped with a submerged zone in SVsz, which likely corroborates the hypothesis by Blecken et al. (2009b) and Zhang et al. (2014) concerning the role of the embedded organic matter. This, together with the very high hydraulic conductivity with less potential for adsorption of metals in the submerged zone, may explain the non-significant effect of the submerged zone in this study. It is worth noting that the submerged zone does not affect the metal removal negatively so can be implemented to enhance nutrient removal without compromising metal removal.

5.2.2 Impact of ambient conditions

For investigation of road salt impact, the runoff events in Sundsvall were divided into two groups (Figure 9, Figure 12, and Figure 13). In general, the highest removal of total metals was observed in filter SVc followed by SV and then S. There was less efficient removal of dissolved metals in the filters. In some cases, under higher chloride concentrations, the dissolved metal concentrations increased after the filters compared to concentrations in the untreated SW. This indicates a release of Cd, Cu, Ni, Pb and Zn from the filter SV rather than accumulation.

Previous studies of chlorides and bioretention systems have shown that there is a negative effect of chlorides on removal of metals from stormwater. A previous laboratory study by Nelson et al., (2006) indicated that road salts have an effect on metal mobility in soil, resulting in metal release (e.g. of Cu and Cd) and organic matter. Also, McManus and Davis, (2020) described the removal of metals (Cu and Zn) in a bioretention mesocosm study of NaCl influence on metals. Their findings (McManus and Davis, 2020) were that even though Cu and Zn showed high effluent peaks (particularly at the beginning of storms) also when higher concentrations of NaCl, a net accumulation of Cu and Zn were still present in the bioretention system. Also, Paus et al. (2014) and Søberg et al. (2017) showed that salt could cause increased mobility of metals, and Lange et al. (2020a) found that metal removal from stormwater was reduced in a bioretention facility when salt was added. A review study (Kratky et al., 2017) suggested that de-icing salts increased salinity in spring runoff, causing increased metal solubility, and thus cause leaching of previously accumulated metals (Cd, Zn and Cu) from a bioretention facility, creating increased dissolved fractions in receiving waters. An explanation for increased concentration of Cr, Cu, Pb and Zn under the influence of high chloride concentrations in stormwater (inflow and outflow) is that chlorides (e.g. NaCl, KCl, $MgCl_2$, and $CaCl_2$), due to cation exchange and formation of aqueous metal complexes, lead to increased desorption of exchangeable Cr, Cu, Pb and Zn, (Amrhein et al., 1992; Bäckström et al., 2004; Behbahani et al., 2021; Paus et al., 2014b; Søberg et al., 2017). This could also explain the negative effect of salt on metal removal in bioretention facilities. Further, Lange, (2021) studied bioretention facilities and metal treatment and concluded that Cd and Zn were more affected by salt than Cu and Pb, as the former less strongly associate to minerals and organic matter.

5.3 Pollutant accumulation

Pollutant treatment, accumulation, occurrence and concentration of metals and OMPs in the filter over time (Figure 16 and Figure 16) are the result of various processes in a bioretention facility's filter materials and are affected by material properties, filter characteristics, hydrology and other site specific and/or local conditions. Pollutant substance properties, such as hydrophobicity, solubility, ability to biodegrade, and volatilization, are also important processes that affect accumulation over time. Also, local, geographical and seasonal conditions have a large impact on pollutant accumulation e.g. temperature, precipitation intensity and patterns (dry and wetting periods), pollutant load and emissions from catchment areas, and global and local sources. Other aspects influencing occurrence and concentration of pollutants in a bioretention facility are filter design, filter material, maintenance, road maintenance with de-icing salts and local hydrology.

5.3.1 Occurrence and concentration

OMPs were frequently detected in the filter material samples (Table 17). PAHs and PCBs showed a higher occurrence than alkylphenols and phthalates, while metals showed an overall high occurrence. There is a difference in occurrence between metals and OMPs, where metals, in general, more commonly occurred than OMPs. This may partly be explained since metals are naturally occurring, and thus more widely spread, whereas OMPs are anthropogenic, and therefore more localized.

Total metal concentration ranges observed in the soil (Table 15) were generally lower for Cr, Cu, Ni, Pb and Zn compared to previous studies, but were comparable or slightly higher for Cd (Al-Ameri et al., 2018; Rommel et al., 2021). The concentrations in our study varied greatly between different facilities, where the deeper layers of the filter material had similar levels to soil background concentrations (England, USA and median global average) (Alloway, 2013). OMP concentrations also varied largely but were within similar ranges as reported in previous studies. Between various sites, large differences in concentrations and occurrence were observed for both metals and OMPs. However, this trend was not as clear for metals as for OMPs. Specifically, in comparison to studies such as DiBlasi et al. (2009) and Tedoldi et al. (2017), extremely high PAH concentrations were detected at one particular site (site #1, Table 1). This large variation in concentrations between the different sites may be explained by local variations e.g. in catchment characteristics such as the ratio between catchment area to filter area and/or different land use, potential point sources etc. and local hydrology, all of which may contribute to different pollutant types and loads (Cao et al., 2019; Crane, 2019).

A PCA demonstrated that the observations from different sites were often grouped together and correlated to a certain group of pollutants (Figure 17). For example, the PCA showed that the highest PCB concentrations were detected in urban areas in downtown/city centres, areas characterized by high population density and traffic. The lower concentrations were also detected in the less densely populated areas with more green space. Thus, differences in sources related to area use may play an important role in the occurrence and concentrations detected in the bioretention facility, and this is especially true for OMPs, since these pollutants are mainly anthropogenic. This idea was also supported by the result showing that nonylphenol was more frequently detected and at higher concentrations than octylphenol, since 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 also reported that concentrations may be lower in USA than in Europe (Crane, 2019; Flanagan et al., 2021), related to the different legislation concerning the use of phthalates in industry.

5.3.2 Spatial distribution within the filters

The main observation for detected pollutants in the filter material, especially for OMPs (i.e. PAHs, PCBs, phthalates and alkylphenols e.g. DEHP and NP) was the higher occurrence frequencies and concentrations in the top layers of the filters, decreasing with increasing depth from the surface (Figure 16). The main explanation for the decrease in pollutant concentrations with depth could be that both OMPs and metals (Al-Ameri et al., 2018; Blecken et al., 2009a; Li and Davis, 2008b; Muthanna et al., 2007; Tedoldi et al., 2016) accumulate in the filter material as particle-bound pollutants, due to their ability to attach to particles. The explanation for a clearer trend for PAHs and PCBs could then be that these pollutants are often associated with suspended solids in the stormwater (LeFevre et al., 2015; Marsalek et al., 1997; Hwang and Foster, 2008), and thus have similar properties to other particle-bound pollutants. Therefore, they are primarily removed in surface layers through sedimentation and filtration of particles (Blecken et al., 2009a). Alkylphenols and phthalates are more mobile (Flanagan et al., 2018) and exhibit more variable speciation in the stormwater, and therefore also occur in lower concentrations near the surface. Another example of more mobile OMPs is PFAS. A study of PFAS on the same sites using samples from the same sampling campaign as described here showed a less clear concentration decrease with depth, with most PFAS being more evenly distributed (Beryani et al., 2024b), likely to their hydrophilicity and less or less quick adsorption by the filter material.

In general, the metal concentrations also decreased with increasing depth in the filter material (Figure 14), with the decrease significant for Cr, Cu, Pb and Zn (Kruskal-Wallis, $p<0.05$), and such decreases were also observed for Cd and Ni. Similar results have also been reported by previous studies (Blecken et al., 2009a; Li and Davis, 2008b; Muthanna et al., 2007). An explanation for this could be that accumulated metals, similar to OMPs, are associated with particles, and thus removed from stormwater by filtration of sediments in the top layers, reducing the concentration with depth from the surface (Al-Ameri et al., 2018; Tedoldi et al., 2016). Similarly, for these facilities, Lange et al. (2023) showed a similar pattern of microplastics in the filter material as observed for metals, PAHs, and PCBs.

For OMPs, concentrations and occurrence frequencies decreased with increasing distance from the inlet (Figure 16). For metals (PCA papers I and II), this trend was less clear, and observed only for Cr and Zn, partly for Cu and to some extent for Pb in the top layer (Figure 14). For OMPs, this trend was most clear for PAHs and PCBs and, to a lesser extent, for alkylphenols and phthalates. For the more regularly occurring alkylphenols

(NP) and phthalates (DEHP), this trend was also clearer. This variation of occurrence and concentration with distance from the inlet may be explained by pollutants being mainly particle-bound, and thus also associated with sediments together with the long-term effects of filter hydrology. For example, the more frequently occurring smaller rainfall events could, over time, cause a higher sediment and thus pollutant load closer to inlets, resulting in higher pollutant accumulation. However, higher rain events may then move sediments further in from the inlet (Al-Ameri et al., 2018; Jones and Davis, 2013).

The reason that these trends are less clear for metals than OMPs could be the effect of a lower pollutant load of metals, and thus lower concentrations. However, metals may also occur either as particle-bound or dissolved, depending on local environmental conditions. For example, pH, concentration, organic matter, and the presence of other metals (Fe, Mn), as well as the effect of de-icing salts, may affect or reduce accumulation over time. Furthermore, OMPs with higher molecular weight (such as PAH-H and heavier PCBs) were retained at higher concentrations in the filter medium and were more frequently detected than substances with lower molecular weight (such as PAH-L and lower weight PCBs). This is most likely because heavier molecules are generally more hydrophobic than lighter molecules, and are thus retained in the filter material to a higher degree, are less soluble, are more strongly particle-bound, and are less biodegradable and volatile (Crane, 2014; David et al., 2015; Flanagan et al., 2018; MacKay, 2006). These explanations are supported by the work described in Paper I, which showed that the highest PAH concentrations were detected for Fluo, Pyr, Phen (PAH-M), Chry and BbF (all PAH-H). These results are similar to the findings of a previous study of accumulated PAHs in stormwater infiltration facilities (Tedoldi et al., 2017). Also, for PCBs, the concentrations showed a trend of decreasing with decreased molecular weight in the order PCB 153 > PCB 138 > PCB 180 > PCB 118 ≈ PCB 101 > PCB 52 > PCB 28. However, for PCBs, this may also be related to the degree of chlorination, since hydrophobicity of PCBs also increases with increasing chlorination. Thus, the more chlorinated PCBs tend to be more effectively retained in filter material than the less chlorinated ones (David et al., 2015). Furthermore, the highly chlorinated PCBs are also less biodegradable and less volatile (MacKay, 2006). Phthalates and alkylphenols were less frequently detected in the filter materials, which may reflect their lesser industrial use (Bergé et al., 2013) and, also, that they are less effectively removed by the filter materials than, for example, PAHs (Flanagan et al., 2018). It may also be because they are more biodegradable compared to heavier PAHs and PCBs (Mackay, 2006), which then may reduce the filter accumulation over time. Biodegradation is considered to be one of the most important treatment processes for OMPs (K. Zhang et al., 2014) and, since this predominantly occurs during longer dry periods, it is likely to be a major factor in determining the fate of contaminants in long-term contaminant patterns.

5.3.3 Forebay

The occurrence and concentration of OMPs in the forebay showed an overall higher occurrence and higher concentrations compared to the filter material. However, it is important not to confuse the high concentration in the forebay with a large amount, which is demonstrated in Table 19. In contrast, for metals, the concentrations were more similar in the forebay to those in the rest of the filters, especially in the top layer. There were variations in concentrations between various metals; e.g., Cr, Cu and Zn had slightly higher concentrations in the forebay, Ni concentration was similar to the rest of the filter, and Cd and Pb exhibited lower concentrations in the forebay. However, when comparing concentrations in a forebay to those in the filter material, it is important to consider that forebay samples in a bioretention facility consist mainly of stormwater sediments (Blecken et al., 2017; McNett and Hunt, 2011), whereas a sample from the filter consists both of sediments and filter material. Thus, in the FB, stormwater sediment accumulates over time (Johnson and Hunt, 2016; McNett and Hunt, 2011; Merriman and Hunt, 2014), resulting in a larger quantity than in the filter while, in the filter, the material accumulation of sediments due to incoming pollutants leads to increased concentrations over time (Al-Ameri et al., 2018; Blecken et al., 2011; LeFevre et al., 2012). This could then be an explanation for the higher observed concentrations of OMPs in the forebays and top layer close to the inlet, compared to samples from the rest of the filter (Study I). For metals, this may also have an impact since metals are naturally occurring and widespread (Alloway, 2013). Filter media could also be a source of metals, while the OMPs (anthropogenic) are expected to be found in stormwater sediments. The similarities and variations in concentrations in forebay samples between OMPs and metals as a group, as well as within metals, may also be affected by different substance properties e.g. ability to attach to particles, hydrophobicity, and mobility and, for metals, their ability to dissolve (David et al., 2015; Flanagan et al., 2018; Mackay, 2006).

5.3.4 Fractionation of metals

When assessing risks of metal leaching (Cd, Cr, Cu, Ni, Pb and Zn) from bioretention filter materials and sediments, 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). A fractionation by sequential extraction is one way of assessing metal leaching potential (Gleyzes et al., 2002; Stone and Marsalek, 1996; Tessier et al., 1979).

One important observation from the sequential extraction was that metals were found over all five fractions. This indicates that all examined metals (Cd, Cr, Cu, Ni, Pb and Zn) are (potentially), to some extent, mobile in the assessed filter materials, and therefore could pose a risk of leaching from the filters or disposed filter material over time. Leaching could then cause negative environmental impact (Barbosa et al., 2012; Göbel et al., 2007). The results from the fractionation also indicated that the properties of different metals affect the potential risk of leaching. In the sequential extraction, a high metal content in fraction 1 indicated an easily soluble metal (Table 8), potentially leached or easy mobilized from the filter materials during normal precipitation. Cd had the highest metal content in fraction 1, and hence was the most mobile and available metal in the study (Table 15, Table 16 and Figure 15). This indicates that Cd in filters or used filter material could pose a threat to Cd-sensitive recipients or environments. A high metal content in fraction 5 indicates that a substance could be associated with stable organic forms, and therefore only potentially mobile and bioavailable under more 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. Cr had the highest metal content in both fractions 4 and 5 ($Cr_{\sum F4+F5}$ = 89 %), which indicates that Cr was the most stable metal in the study, and therefore the least mobile and bioavailable. Also, the more extreme conditions for leaching of metals simulated in fraction 5 indicate that Cr is very stable in the filter material. Fraction 2 indicates release of metals associated to soil organic matter and showed extraction of metals bound in labile organic forms, such as humus and fulvic acids. This indicates a form which can potentially leach over time if organic matter in the filter breaks down. Such conditions are possible in bioretention facilities, involving the breakdown of organic matter in the filter medium and top mulch layers, or degradation of vegetation over time. Cu had the highest content in fractions 2 (highest in the study, Cu_{F2} = 22%) and 4 from the sequential extraction. 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. This indicates that Cu may become mobile under anoxic conditions after a longer time and should be regarded as a potentially mobile metal in filter materials and sediments. Both Cu and Cr had significantly higher concentrations in the top layer of the filters, which could be related to the higher concentration of organic matter in the top layers (Figure 4 and Figure 14). Ni was distributed within all five 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 of metal content in fractions 1, 3 and 5 and the highest proportion in fraction 4. Therefore, Ni may be potentially mobile under certain conditions. Ni, similar to Cu, has a high affinity for organic matter in soil (Alloway, 2013). Pb was primarily distributed between fractions 1 to 4, with the highest proportion in fraction 4 and the lowest in fraction 5. Therefore, it may be mobile to some extent in most bioretention environments. Zn was present in fractions 1 to 4, with a 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.

In summary, the order of the total metal content in fraction 1 from high to low was Cd>Zn>Pb>Ni>Cr>Cu and the total content in fraction 1 to fraction 4 was Pb>Zn>Cd>Cu>Ni>Cr. This indicates that Cd, Pb and Zn were very mobile in the filter medium, and Cr, Cu and Ni were mobile to some degree. Cd was probably the most mobile metal analysed in the study, whereas Cr was the least.

5.4 Practical implications

The results from these studies of pollutant accumulation and pollutant treatment for different bioretention facility configurations could contribute to improvement of the design and maintenance of bioretention facilities. As the results of the studies herein are for different filter configurations and various infiltration capacities, they help in the understanding of the effects of chlorides and the design of long-term sustainable bioretention facilities. This is of particular importance when designing facilities adapted to colder climate conditions e.g. where temperatures fluctuate around zero degrees Celsius. The data on pollutant accumulation facilitates designing proper maintenance processes to preserve filter function during long-term treatment of stormwater, but also help with understanding of the risks associated with used filter material and sediments.

5.4.1 Metal treatment

The choice of filter material is a crucial parameter when designing bioretention facilities. Particularly in cold climate areas, filter material with a higher hydraulic conductivity could facilitate infiltration during winter into (partly frozen) ground (Zhao and Gray, 1999), reduce the risk of clogging in general and minimize overflows. Previous studies have recommended that the top (2–5 cm) of the filter material is removed every two years to avoid hydraulic failure due to clogging. However, with a coarser filter material on top, this time may be extended. Especially in denser urban areas with space restrictions, space-efficient bioretention systems with higher hydraulic capacity can be an advantage. Thus, a higher hydraulic conductivity is not only relevant for cold climate regions but generally for bioretention system implementation in very dense urban areas.

To choose the “ideal” filter material, an optimization must be made by weighing various parameters against each other, such as days with temperatures around zero degrees Celsius, available surface area, risk of clogging and the recipient's need for protection, after which the filter material with the desired hydraulic conductivity, additives and vegetation can be selected.

Table 21 The Sundsvall bioretention system to guide line values from the Swedish Agency for Marine and Water Management (SwAM) which describe the national implementation of the environmental quality criteria for status evaluation within the EU Water Framework Directive, the Swedish target value group (STVG) 2009 (Jacobs et al., 2009), and target values from the environmental management department of Gothenburg (EMDG) (Landström et al., 2020).

								SwAM					STVG		EMDG	
			SW	GPT	SVc	SV	S	Bioavailable	Stream		Lake		Lakes		Ref.	Limit
Substance		Cl-	Mean concentrations					⋆Generic	5-percentil	Median	5-percentil	Median	Small	Large	value	2020
Cd	Total	≤100	0.10	0.11	0.05	0.06	0.07	0.08⋆	-	-	-	-	0.4	0.45	0.45	0.9
		>100	0.15	0.11	0.10	0.11	0.13									
	Diss	≤100	0.02	0.01	0.01	0.03	0.02									
		>100	0.05	0.05	0.09	0.10	0.11									
Cr	Total	≤100	25.4	29.9	1.59	1.37	11.9	3.4⋆	-	-	-	-	10	15	3.4	7
		>100	31.5	29.0	1.31	1.13	8.01									
	Diss	≤100	1.48	1.35	0.79	0.75	1.09									
		>100	0.76	0.65	0.43	0.55	0.53									
Cu	Total	≤100	51.8	56.3	7.63	13.0	27.0	0.5	3.3	12	2.4	12	18	30	10	10
		>100	63.1	58.7	13.0	20.6	27.5									
	Diss	≤100	5.38	4.93	5.45	11.1	5.84									
		>100	9.73	9.82	10.6	19.8	10.3									
Ni	Total	≤100	12.7	14.9	1.03	1.72	6.30	4	8.2	16	8.4	19	15	20	34	68
		>100	18.6	16.4	2.12	3.90	7.73									
	Diss	≤100	1.16	1.11	0.47	1.70	1.20									
		>100	3.21	3.00	1.58	4.17	3.57									
Pb	Total	≤100	9.04	10.7	6.41	0.90	5.25	1.2	2.8	12	2.4	13	8	10	14	28
		>100	12.1	11.4	0.90	1.02	4.51									
	Diss	≤100	0.09	0.07	0.10	0.30	0.12									
		>100	0.07	0.09	0.16	0.43	0.10									
Zn	Total	≤100	429	498	24.0	106	272	5.5	6.8	19	7	20	75	90	30	30
		>100	671	609	150	202	412									
	Diss	≤100	80.2	81.5	14.9	97.4	78.0									
		>100	99.5	106	116	174	205									
Mean metal concentrations in [µg/l] and Cl- in [mg/l]								(Jacobs et al., 2009)					(Landström et al., 2020)			

Also, the results of metal concentrations and treatment by the various bioretention filter materials in Sundsvall (Table 10) were compared to local guideline limit values for the protection of waters, lakes, and streams (Table 21). Most metal concentrations in the stormwater before treatment were already below the guideline values except for Zn and partly Cr and Cu Table 21. In most cases, these concentrations (Zn, Cr and Cu) were below the guideline values after treatment by the filters. Compared to the SwAM threshold, the concentrations of Cu and Zn in the effluent were still higher than bioavailable concentrations. However, dissolved metal concentration cannot be directly compared with the bioavailable guideline values. The bioavailable guideline value can provide a reference, provided one takes into account that any specific metal most likely has a lower bioavailability, and that bioavailabilities are higher in truly dissolved metals than in both dissolved metals and particulate metals that are not directly bioavailable (Lange et al., 2020a). The Sundsvall study showed that a filter with vegetation has positive effects and could be recommended, since it reduces the risk of clogging as the plants break up fine sediments accumulated on the surface thus maintaining infiltration capacity (Muerdter et al., 2018). Filters with chalk additives and vegetation exhibit, in general, better treatment of metals in stormwater (Hamedani et al., 2019; Muthukrishnan and Oleske, 2008). However, such filters are less efficient at treating dissolved metals and under high chloride concentrations. Despite this, these two features are recommended to be implemented in bioretention systems.

5.4.2 Pollutant accumulation

The fact that most pollutants are accumulated in the top 5–10 cm of the filter materials and that these concentrations exceed guidelines e.g. Swedish EPA (2009) is of great importance for bioretention facility operators, as it implies that removing only the top layer of the filter medium periodically instead of all the filter material might be sufficient to enhance the operational lifetime. This has also been suggested previously by Al-Ameri et al. (2018), Blecken et al. (2011) and Tedoldi et al. (2017). However, studies have also shown different behaviour of PFAS (Beryani et al., 2024b) which may be soluble to a higher extent than other OMPs, and thus further research is needed. Also, when removing material from a bioretention facility e.g. forebay sediments or top layer filter material during maintenance work due to clogging (Al-Ameri et al., 2018), these materials have to be assessed since they are potentially hazardous waste, especially for material that is found close to the surface and inlets. To optimize operation and maintenance further, one should consider the impact of the 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 those of OMPs.

5.5 Further studies

For future work, further studies of short-term and long-term function, pollutant accumulation and maintenance are required. This would improve understanding of treatment processes, accumulation and distribution of metals, OMPs and other particle-bound and dissolved pollutants. Also, studies of other pollutants are needed. For instance, studies have shown that PFAS, although having the highest concentrations in the top 5 cm of filter material, can migrate into deeper layers. Thus, only managing the top media layer may not suffice for more complex and mobile contaminants such as PFASs (Beryani et al., 2024b). Concerning treatment, the focus of this thesis was on metals. Also treatment of organic pollutants (which only were regarded in this thesis concerning their accumulation) in these filters should be investigated. This was outside the scope of this work but has been done for the filter in Sundsvall (Beryani et al., 2024a, 2023).

Results from field studies are site-specific and dependent on the choice of specific analysis and methods used. Since the nature of the filter medium affects dissolved 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. Continuous studies of filter materials with high hydraulic conductivity are also needed for better understanding of the long-term function of filter materials. These studies should also include other pollutants e.g. organic micropollutants (for example PAHs, PCBs, alkylphenols, phthalates and PFAS), phosphorus and nitrogen. Here, mass balance measurements and calculations are required to improve the comparison of function with traditional filter materials, and the optimization between pollutant removal and captured removal. Mass balance measurements could also be combined with studies of forebay function and accumulation studies.

For accumulation studies, one parameter not included in many accumulation studies is biodegradation of OMPs, along with uncertainties associated with calculations of pollutant mass (Flanagan et al., 2019). Pollutant mass calculations could include measurements of stormwater quality and quantity in and out at sampled bioretention cells. Further mass balance calculations in forebays and filter material could provide information on the number of pollutants in forebays but, for OMPs, also about leaching and biodegradation processes. Previous studies have shown variations in emissions over time (Markiewicz et al., 2017), so continued sampling of filter material from previous sampled sites and targeted sampling campaigns over yearly cycles and over longer periods could enable a broader understanding of time perspectives.

Also, studies including a broader age variation of new filters and those in operation for a longer time would complement information on pollutant accumulation trends and pollutant treatment performance expected over a bioretention system's lifetime. Due to the different national/regional regulations and use of different building materials etc. studies should also include samples from other countries for evaluation of geographic variabilities of pollutants, as well as geographical ambient variations in temperature, humidity and precipitation hydrographs.

6 Conclusions

This thesis describes a study of stormwater bioretention systems in respect to water quality treatment and long-term pollutant accumulation. The aim of the study was to advance knowledge in (i) design parameters, such as different filter material configurations (including vegetation, chalk, pumice) and characteristics (infiltration capacity), and how they affect total and dissolved metal treatment in these systems, (ii) the influence of salt on total and dissolved metal treatment and, (iii) the long-term fate of OMPs and metals in bioretention filter materials and forebays including their occurrence, concentration, distribution and/or availability.

In general, the results showed that, in those bioretention systems with sand-based filter materials, removal was generally good for total metals in stormwater, although treatment of dissolved metals was less effective. Removal was most efficient for total Cu, Pb and Zn, metals that are, to a greater extent, particle-bound.

Filter materials with high infiltration capacity specially adapted to cold climates and/or use in (relative to the catchment) smaller facilities e.g. in dense environments with space restrictions, showed, in general, high removal of total metals and less efficient removal of dissolved metals, likely due to lacking adsorption sites. Metal removal in the filters with high infiltration capacity was highest for Cu, Pb and Zn, while less efficient for Cd, Cr and Ni.

Of the studied design parameters, chalk had a positive effect on metal treatment and increased removal, particularly of the dissolved fractions. The pumice additive in this study decreased both total and dissolved metal removal likely due to preferential flows caused by the larger particle size distribution of the pumice and, consequently, preferential flow paths. Vegetation showed an overall positive effect on total metal removal, but not for dissolved metal removal. The submerged zone did not show any effect on metal treatment in this study, likely due to the lacking carbon amendment. However, such a water saturated zone is primarily implemented due to its positive effect on nitrogen removal.

Further, chlorides from the use of de-icing salts for road maintenance during cold temperatures had a negative impact on metal removal in the filters. This was particularly clear for the dissolved metal fractions, while most total metals (Cr, Cu, Ni, Pb and Zn) still experienced high removal, but not Cd. Also, the chlorides increased the metal concentrations both in influent stormwater as well as effluent water after treatment in the filters. Furthermore, higher chloride concentrations ($Cl^->210$ mg/l) increased the proportion of dissolved metals in the stormwater, and thus also reduced metal removal. However, a filter with chalk additives was more effective for removal, particularly of dissolved metals, when there were higher chloride concentrations in the stormwater.

Long-term accumulation studies showed that all metals (Cd, Cr, Cu, Ni, Pb, and Zn) and most OMPs (16 PAHs, 7 PCBs) analysed in this study were commonly detected in (nearly) all samples. In contrast, phthalates and alkylphenols were detected least. For both metals and OMPs, there was a large variation in concentrations between the different bioretention sites. The (mostly hydrophobic) detected OMPs were found at the highest concentration in the forebay and the upper 10 cm of the filter material, but their concentrations then decreased with increasing depth in the filter. For metals, a similar, but less clear trend was observed for Cr, Cu, Pb, and Zn. Also, 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. Metal fractionation of the filter material top layers showed that all studied metals have a potential risk of leaching over time. The metals with the highest risk of leaching according to metal mobility were Cd, Zn, and Pb, while Cr, Cu and Ni were more stable. It is important to note that these metals are also at a potential risk of leaching from filter material or sediments if removed from the bioretention sites.

Combining the results of studies of stormwater treatment and pollutant accumulation in larger bioretention systems showed that metal removal is efficient and that both metals and OMPs accumulate in the filter material over time, mainly in the top layer. However, even if metals can leach during cold weather (when temperatures fluctuate around freezing) e.g. when de-icing salts are used for road maintenance, the accumulation studies indicated that there was a long-term accumulation of metal in the filters.

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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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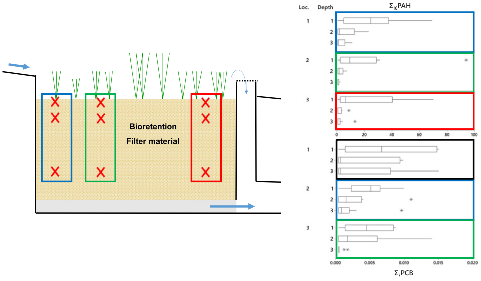
HIGHLIGHTS

- 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 nonparametric Kendall's-tau (τ) correlation test, applicable for the analysis of censored data, was performed using the NADA package in R for

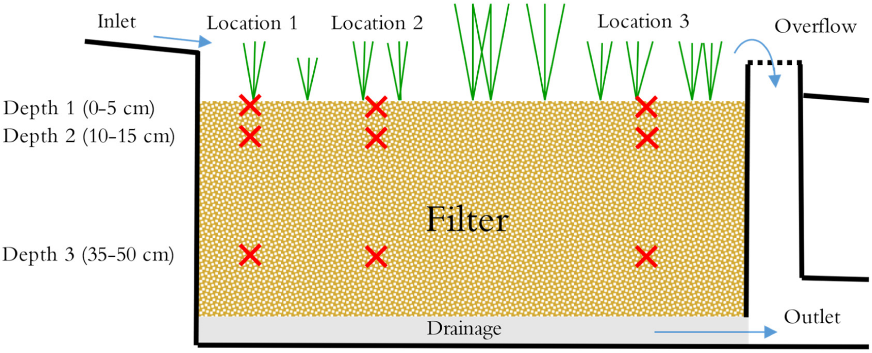

Fig. 1. Cross-section of a bioretention facility illustrating the nine sampling points (at three locations and at three depths) used in this study.

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

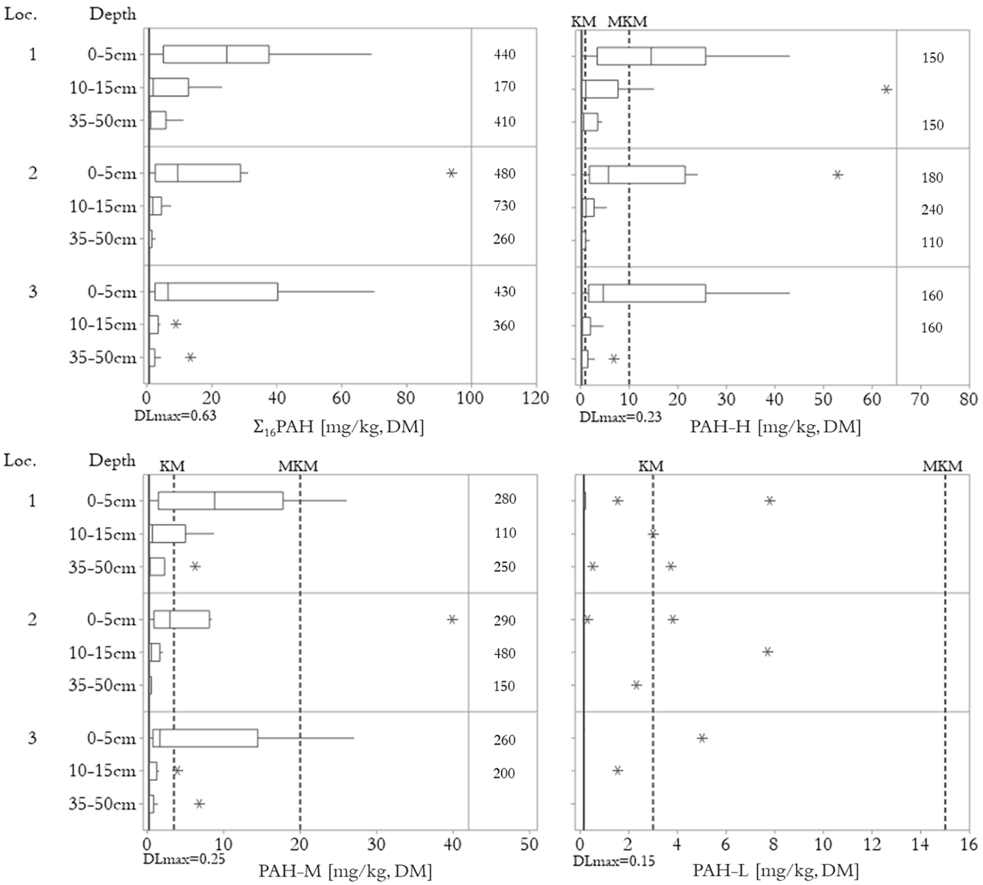

Fig. 2. Boxplots of concentrations of Σ_{16}PAH, PAH-H, PAH-M and PAH-L (mg/kg, DM) for different distances from inlets (Locations, Fig. 1) and distance from surface (Depth, Fig. 1). In addition to those plotted as asterisks (*), outliers above 100 mg/kg, DM are indicated as text to the right for plotting 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

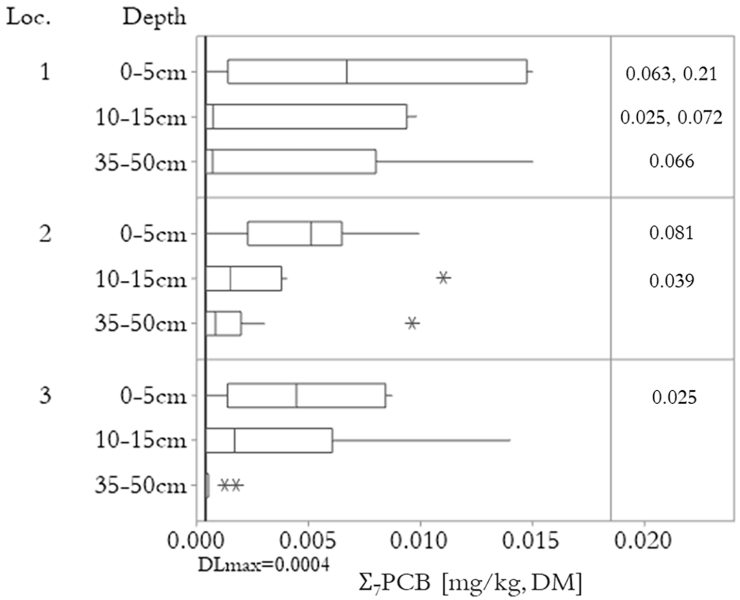

Fig. 3. Box plot of Σ_7PCB for different distances from inlets (Locations, Fig. 1) and distance from surface (Depth, Fig. 1). In addition to those plotted as asterisks (*), outliers above 0.02 mg/kg, DM are indicated as text to the right for plotting purposes.

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

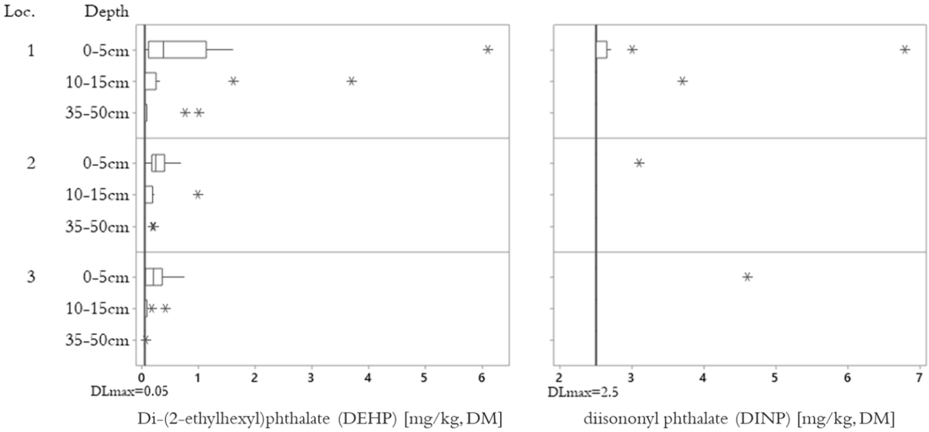

Fig. 4. Concentrations (mg/kg, DM) of di-(2-ethylhexyl)phthalate (DEHP) and phthalate with high occurrence (46 %) in the study and diisononyl phthalate (DINP) and phthalate with lower occurrence (6 %).

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

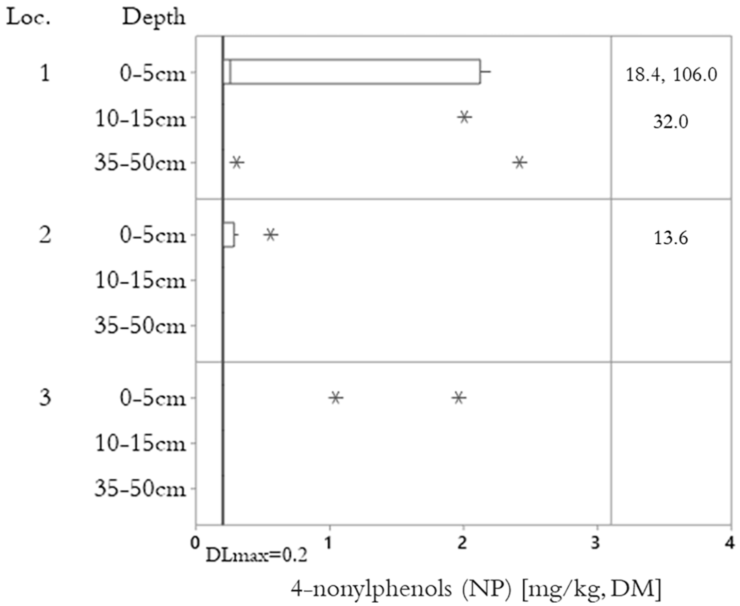

Fig. 5. Boxplot of the alkylphenol 4-nonylphenols (NP). Outliers of greater magnitude are indicated as numbers to the right for easier visualization of boxplots due to the scale.

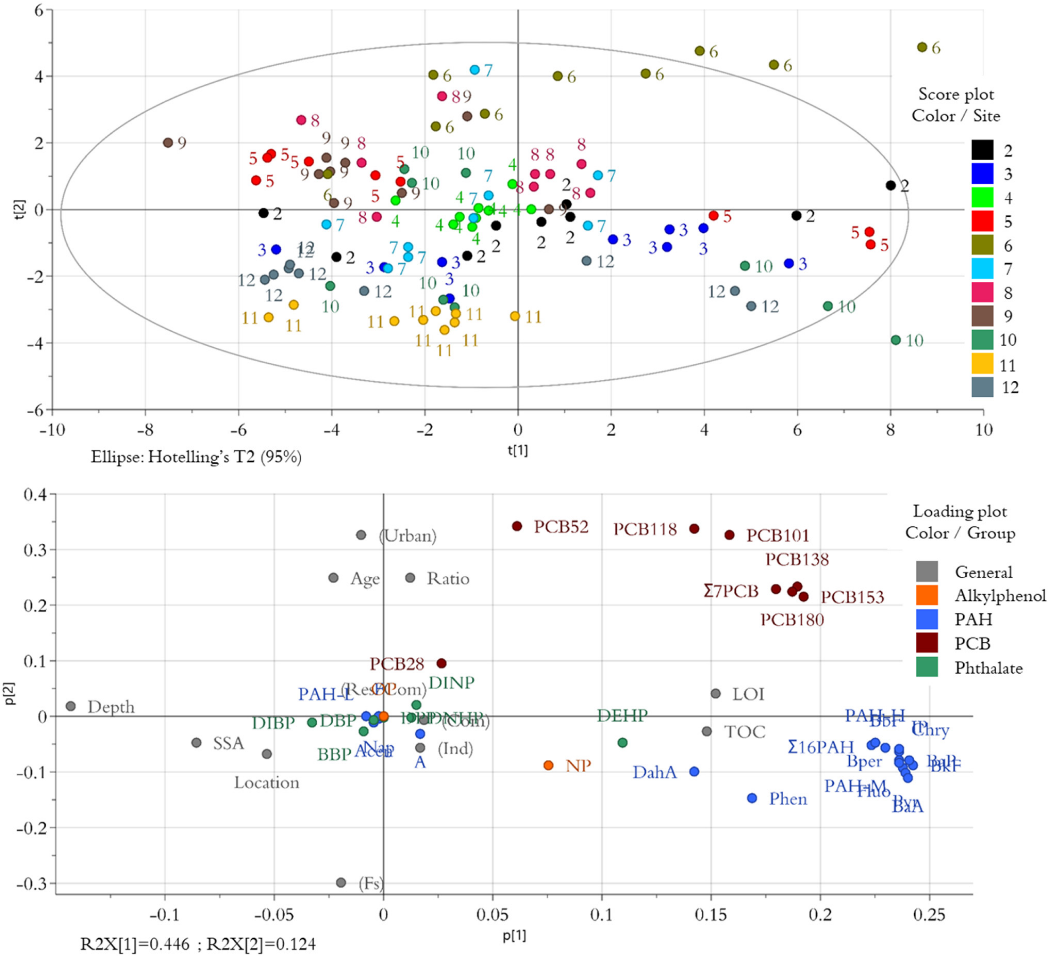

Fig. 6. Score plot (upper) and loading plots (lower) for components 1 and 2. The score plot is colored by site number and the loading plot is colored after the four pollutant groups (alkylphenols, PAHs, PCBs and phthalates) and general parameters. The general parameters include Depth, Specific Surface 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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Paper II

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

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

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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 metals removal capacity of 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. All the study metals (Cd, Cr, Cu, Ni, Pb, and Zn) were found in all samples, except for Cd. Metals accumulation was 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 already during precipitation. There was also at a potential risk of leaching from filter material or sediments if removed from the bioretention sites. The results of principal component analysis indicated correlations between the metal concentration and the ratio of catchment, filter area, and land usage. These results assist improved design, operation, and maintenance for reduced long-term risks associated with metal accumulation in bioretention or similar facilities for urban storm water treatment.

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). US-EPA in the 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). As these are transported by stormwater to the receiving water bodies, they could affect public health and the environment; thus, stormwater should be treated to remove metals before being discharged (Barbosa et al., 2012).

Bioretention technology 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 a bioretention, also referred to as biofilter, biofiltration system or raingarden, stormwater from surrounding areas is treated vertically through a filter before being released to downstream systems. A bioretention typically consist of a filter medium of sand 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). 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 (Al-Ameri et al., 2018; Li and Davis, 2008). Davis et al. (2003) estimated that regulatory limits for biosolids application (U.S. EPA, 1993) could be reached after 20, 77, 16, and 16 years for Cd, Cu, Pb, and Zn, respectively. 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 for human and ecological health. At this point the filter material would be classified as contaminated soil requiring special disposal. Al-Ameri et al. (2018) found for highly polluted catchment areas e.g., industrial areas that filter material due to high Zn concentrations 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 clogging for less contaminated areas, rather than high concentrations of metals, to limit the bioretention function and therefor regularly suggested maintenance by replacing the top 10 cm of bioretention media.

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 the bioretention. It is essential to better understand the characteristics and behaviors of accumulated metals in the filter to evaluate and reduce associated risks during the bioretention lifespan or when material is removed from the filters. 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. Several other studies (Al-Ameri et al., 2018; Costello et al., 2020; Johnson and Hunt, 2016) have examined metal behavior in bioretention areas; however, only a few have assessed the availability of metals in mature bioretention facilities using sequential extraction methods. Many previous laboratory studies have used the sequential extraction method; indeed, Wang et al., (2016) used the sequential extraction method to study Cd in a bioretention column lab-scale experiment, while Søberg et al., 2019 used the same method to evaluate the characteristics of adsorbed dissolved metals on different bioretention filter materials. In the field, 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 in a bioretention. 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 road side bioretention cells. However, the large 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 general compared to previous studies. As a larger field study could provide more general conclusions compared to smaller or more site-specific studies, they complement each other well.

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 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 work, which will serve to reduce the long-term risks associated with accumulated metals in bioretention or similar facilities in the context of urban storm water treatment.

Method

Field sites

Metals accumulation was studied in 29 bioretention facilities, mainly those treating road runoff from dense urban catchment areas with different land use characteristics, including parking lots, roads, downtown urban areas, and industrial, commercial, and residential areas, located in Ohio, Michigan, and Kentucky (USA). The facilities varied in age from 7 to 16 years old at the time of sampling (2019) and the filter area sizes 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 rate between 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 a 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. The site age was the age at sampling in November 2019. Site map in supplementary Figure 3.

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	Cincinnati, 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 sampling sites (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 (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, sediments, and erosion were studied to define a main inlet from which the sampling points were then were 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 due to shallow filter depth.

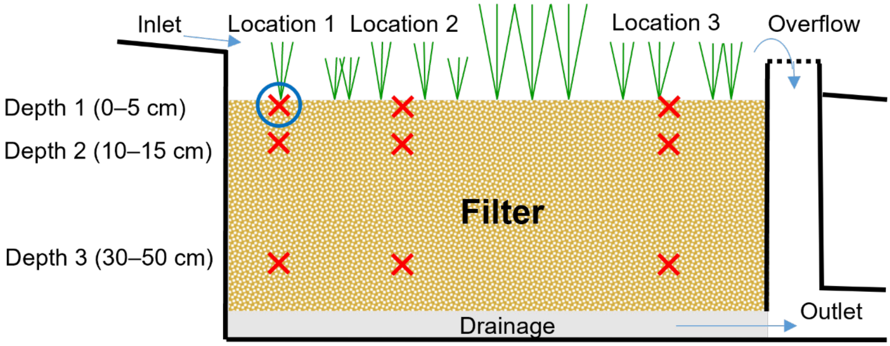


Figure 1. A schematic sketch of the sampling strategy in bioretention filter media with sampling points at three locations and at three depths, as marked by a red "X." The sequential extraction and pH analysis were performed at Location 1 at Depth 1, as marked by a blue circle.

Sampling

Samples in the field were collected by digging out 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 analyses

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). 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 nitric acid (Suprapur for trace analysis) HNO_3 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 (U.S. EPA, 1994a). Inductively Coupled Plasma Optica Emission Spectrometry (ICP-OES or ICP-AES) was also performed according to Swedish standard (SS-EN ISO, 2009) and U.S. EPA method (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 standard (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 and refers to mimicking the effects of 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 estimates labile organic forms by leaching with 0.1 M Na-pyrophosphate at pH 9, which releases metals that are bound in labile organic forms, such as humic and fulvic acids. This leaching step serves to simulate what could be bioavailable and will degrade and release the captured metals under oxidizing conditions (ALS, 2018).

Fraction 3 included 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 material; for example, at elevated groundwater levels, when covering results in reduced oxygen uptake, or at high oxygen consumption due to high levels of organic material. The material is 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 crystalline Fe-oxides. The 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 leachant solution was approximately 1 (ALS, 2018).

Fraction 5 estimate 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 amount of metal was 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

Table 2. Metal concentrations, including the total concentration and that in the five steps of fractionation (mg/kg, DM), and occurrence rates (%). ★Indicates that for Cd, Cr, and Ni there was one sample from the analysis with a higher detection limit (double value) than all of the other detection limits (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 $Ni_{DL} = 6$). The values for the total concentrations are taken from lab analyses 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	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%

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. 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 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 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 layers in this study, indicating that the 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 in a bioretention since that is where the investigated metals seem to accumulate (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 was 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.

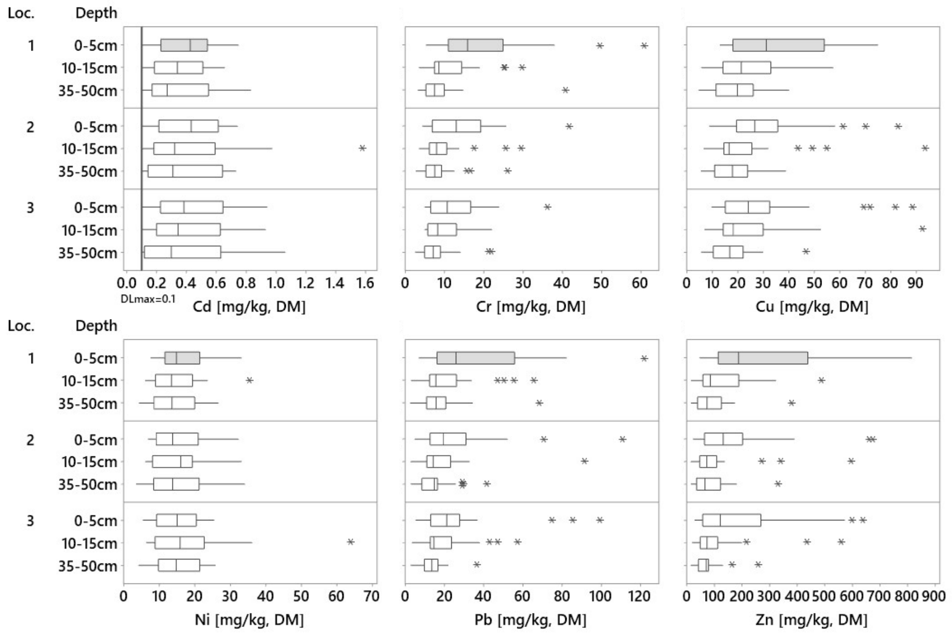


Figure 2. Boxplots showing the total concentration of Cd, Cr, Cu, Ni, Pb, and Zn at three depths and at three locations. Sequential extraction analysis was performed on samples at location 1 (close to inlet) at the uppermost depth (0–5 cm), marked grey in the boxplot. Cd, with an occurrence rate of 90%, 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 reducing the statistical significance of the different concentrations between the layers. However, studying all 29 sites separately (Supplementary Figure 2.1), 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, we also observed significantly higher concentrations of Cu 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 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 more often receives run-off closer to the inlets and thus has higher metal concentrations (Jones and Davis, 2013). Additionally, Al-Ameri et al., 2018 conducted a study of storm water bioretention medium 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 given that sediments could be carried further into the filter during high flow rates over the filter surface. Furthermore, as was the case in this study, filter designs may vary, resulting in different flow paths 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 between the catchment and 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 concentration.

Fractionation

The fractionation of metals performed on samples at location 1, depth 1 (Figure 1) shows 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 masking the presence of Cd. 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%, although there were several 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, such as Li and Davis, (2008) and Jones and Davis, (2013) or the Rauret et al., (1999), based on the Ahnstrom and Parker method (Ahnstrom and Parker, 1999). The current study was based on field sampling of a material as a mixture of filter material and 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.

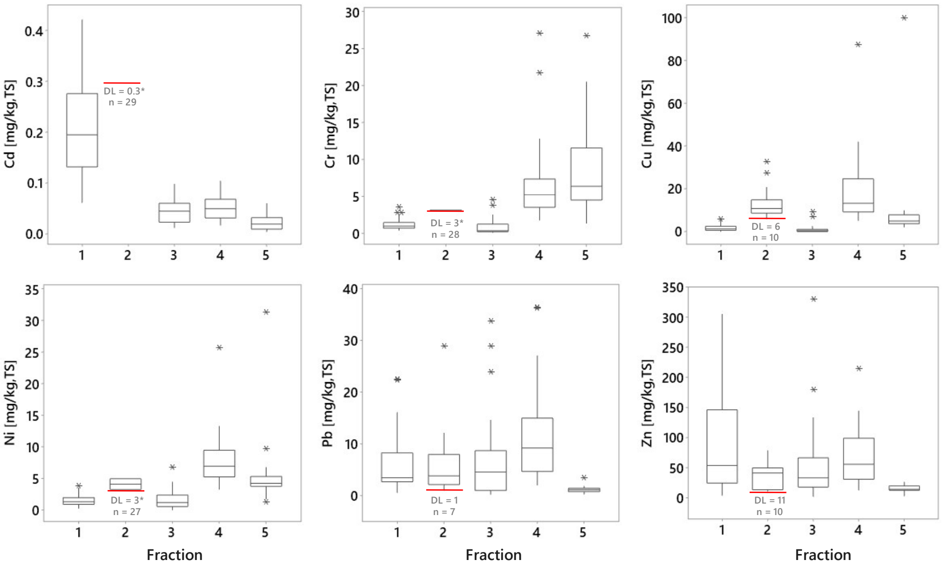


Figure 3. Boxplots of the median concentration of metals in five fractions. For all metals, the detection limit (DL) is indicated in fraction 2 and marked with a red horizontal line. n: Number of values below the DL of 29 samples. * Indicates that for Cd, Cr, and Ni, there was one sample from the analysis with

a higher DL from analysis (double 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 medium has low affinity for Cd; the accumulated Cd is easily soluble and may be leached or mobilized from the filter material during normal precipitation. 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 the recipient 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 dissolve 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 of content 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 under more extreme conditions. Fraction 5 is also associated with sulphides. which, in contact with air or oxygen, and/or water dissolves to form sulphuric 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 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 %) indicates that Cr is 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 2.2) and 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 and described the extraction of metals bound in labile organic forms, such as humus and fulvic acids, which may leach over time if the organic matter in the filter breaks down. These conditions may occur during bioretention, where organic matter, as a component of filter media, in the top mulch layers or from vegetation, could degrade over time (Lange et al., 2020b). Fraction 4 indicate that Cu is related to Fe oxides, which also have strong influence on the Cu mobility, meaning that Cu may be mobile after a longer period under anoxic conditions. Therefore, Cu should be regarded as a potentially mobile metal in bioretention filter media and sediments.

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%). There was a spread of Ni content between 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.

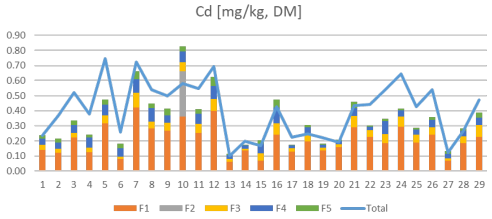
Pb was found at the highest levels in fractions 4, 3, and 1, while less was found in fractions 2 and 5. Pb had the highest sum of content from fractions 1 to 4 ($Pb_{\Sigma(1-4)}$ = 96%) and the lowest content in fraction 5. The distribution of the Pb content (Figures 3 and 4) indicated that Pb has potential mobility in biofilters. 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).

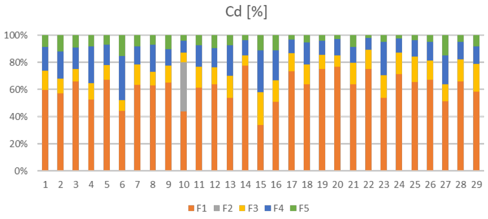
This is consistent with the results of previous studies, including Sansalone and Buchberger, (1997), who also reported that Pb was primarily particulate bound in urban roadway stormwater run-off while mainly dissolved for Zn. Also Alloway, (2013d) described the tendency of Pb to concentrate on smaller 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.

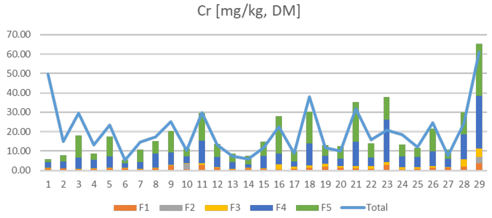
The Zn distribution was relatively evenly spread between fractions 1 and 4, with the highest content found in fraction 4 and the lowest in fraction 5. After Pb, Zn had the highest sum of content in fractions 1 to 4 ($Zn_{\Sigma(1-4)}$ = 94%) and the second highest content in fraction 1 (36%) after Cd. The Zn sorption process is mainly influenced by pH, clay mineral content (and clay SSA), cation-exchange capacity (CEC), soil organic matter, and soil type, where in alkaline soils Zn sorption easily occur to carbonates but also undergoes wetting or water logging following precipitation (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.

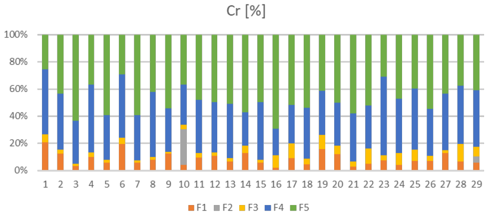
The major trend in the distribution between fractions in this study is that the metal content is spread over all five fractions in varying degrees (Figure 4). Figure 4 also shows that Cd is mainly present in fraction 1, while Cr is mainly present in fractions 4 and 5, but also that there is a large variation 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.

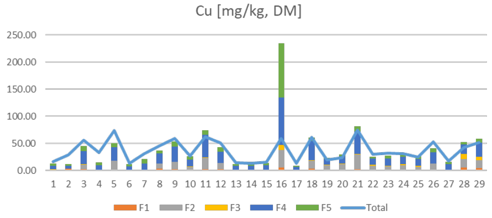
Sansalone and Buchberger, (1997) conducted a study of stormwater and reported that Pb and Cr were primarily particulate bound, while Zn, Cd, and Cu were major concerns due to their propensity to be mainly dissolved, bioavailable, and highly mobile. Moreover, Jones and Davis, (2013) found metals as strongly 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. A comparison between previous results 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 results of 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) filter material is exposed. Therefore, a risk assessment and or filter sampling is recommended before removing filter material after a longer period for stormwater treatment.

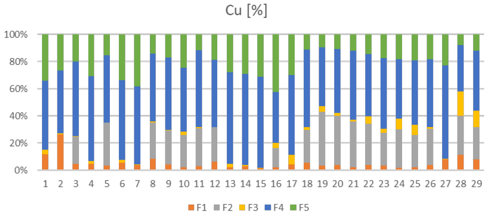


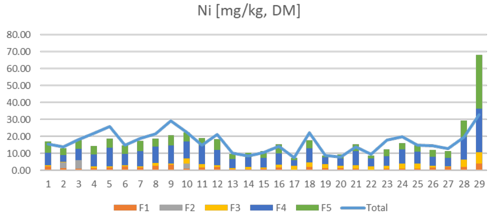


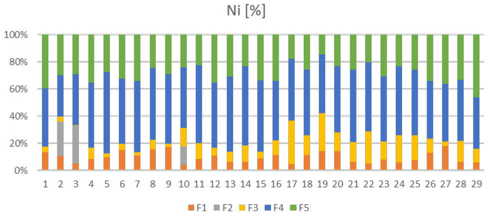


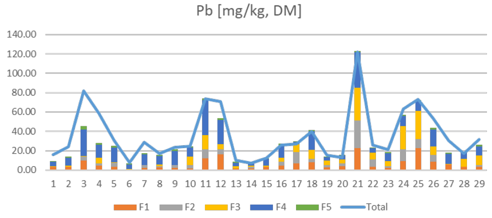


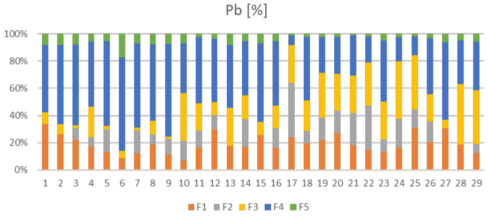


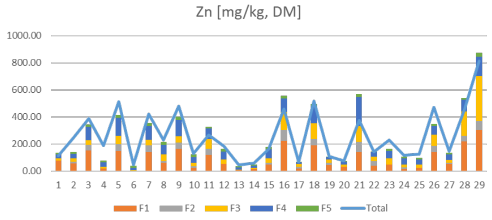












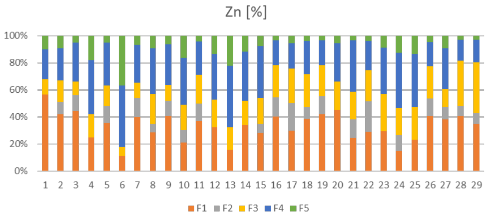


Figure 4. Fractionation of Cd, Cr, Cu, Ni, Pb, and Zn for all sites (1–29). (a) The graphs to the left are reported as total concentrations (mg/kg, DW), while those (b) to the right report the distribution between fractions (%).

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), together with the variables for area usage, filter ratio (between catchment area and filter are), 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.

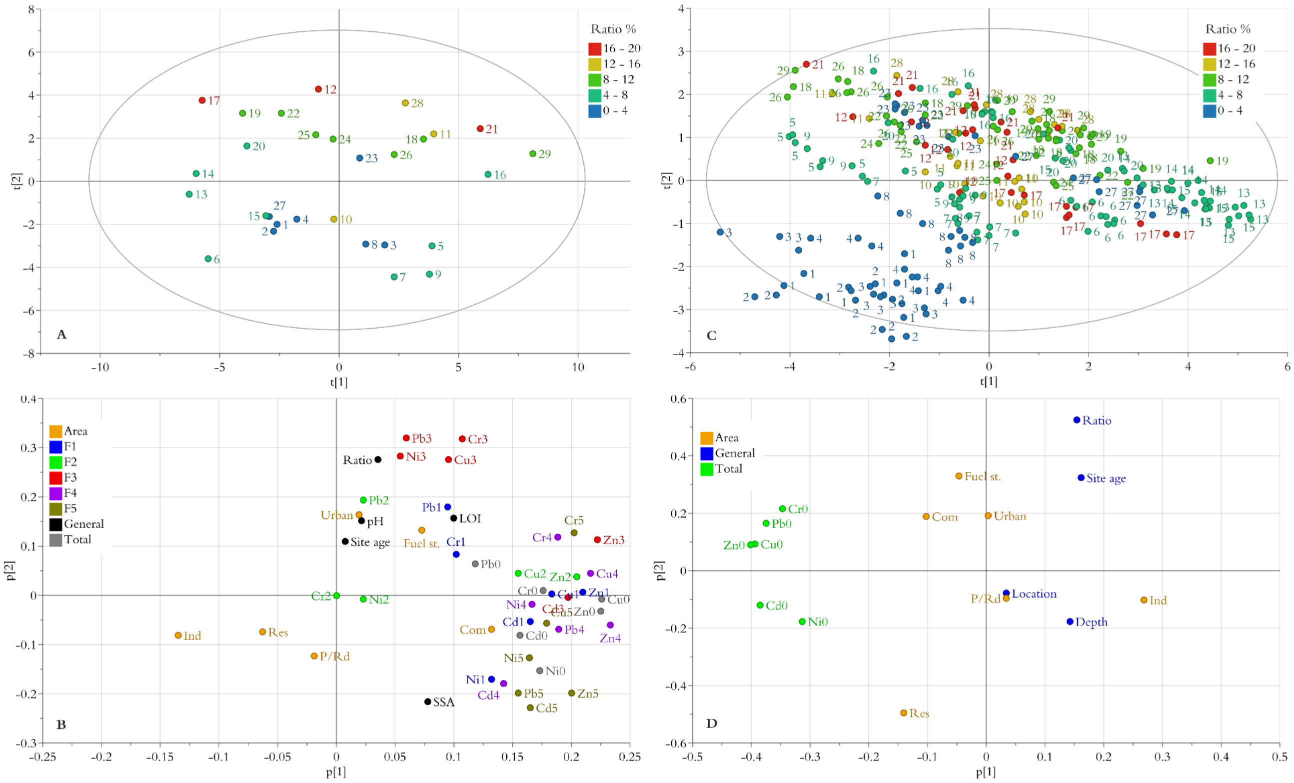


Figure 5. A. Model 1 of fractionation with the score plot (upper left) of metal concentrations. B. Model 1 loading plot (lower left) with fractions (fraction 1 = F1, fraction 2 = F2, fraction 3 = F3, fraction 4 = F4, and fraction 5 = F5), total concentrations, catchment area characteristics (area usage, 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 usages are abbreviated as Residential (Res), Commercial (Com), Industrial (Ind), Parking/roads (P/Rd), Downtown Urban (Urban), and Fueling station (Fuel st.).

In the loading plot of model 1 (Figure 5B), the content from all fractions (fraction 1–5) and the total concentrations are located to the right of the origin or in the origin, as for Cr in fraction 2 (with only 2 values above the DL), or not included, as for Cd in fraction 2 (values not above the DL). This pattern indicates in the first component (p[1]), that concentrations are positively correlated with each other and to the area usage of Commercial, Fueling station and Urban areas, as well as to LOI, SSA, pH, Ratio and Site age. In contrast, the area usages of Industrial, Residential and Parking/Roads are negatively correlated with all concentrations and fractions. The fractions 4 and 5 seem to be most strongly correlated with the total concentrations for all metals. Fraction 1 showed a strong correlation with total concentrations but with a spread 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 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 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) was positively correlated with the total concentrations, which was also true for Cu and Cd, with the exception in fraction 2. In the score plot (Figure 5A) there is a tendency to group in the second component t[2] according to area ratio were 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 indicate that the area ratio seems to have some impact in p[2].

In model 2, the score plot for total concentrations (Figure 5C) show a clear trend of observations clustered in two major groups (an upper larger and a smaller lower group), that are stretched out diagonal 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) explain this influence mainly as correlation to area ratio and residential area usage, where the lower and smaller group in the score plot only contained observations from sites 1–4, which all are residential areas with area ratio ≤ 4% (Table 1). A PCA group-to-group comparison (Supplementary figure 4.1) confirm that the correlated contribution of the two groups is the strong negative correlation between ratio and concentrations. This mean that the lower area ratio is correlated to higher concentrations and in this study, this is correlated to the residential area usages. One conclusion of this is that with large catchment areas compared to the bioretention filter areas one could expect higher concentrations. Furthermore, the loading plot (Figure 5D) shows a strong negative correlation between the area ratio and concentrations in the first component, but a negative correlation between Cd and Ni and the 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 concentration and residential area use, but is negatively correlated with 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. 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 have an area ratio between 8% and 20%, which implies that the area ratio is the main influence. However, if looking at the area usage of fueling station, one can see that they all seem to be clustered together high up in the upper group, if they have an area ratio ≤ 4% or above (8%–14%). This could indicate that area ratio and area usage both impact the 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 area usage, operation time and quality of performed maintenance is most likely also important factors for these predictions.

Another observation in model 2 from the loading plot is that concentration also is strongly negatively correlated with depth, meaning that the highest concentrations are located near the surface while 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 reason this was not corroborated by the PCA is that 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, the metal concentrations 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 (Supplementary Figure 5.1) were below the UK CL:AIRE SGVs and all metals (Cd, Cr, Cu, Ni and Pb) except Zn were below the Swedish soil guidelines MKM. 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 in bioretention 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 medium 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 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 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, removing filter material 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 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.

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 deposition 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/catchment area). Additionally, the various land usages 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 usage, 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.

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Paper III

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

Occurrence and Concentration of 6 Metals and 28 Organic Micropollutants in the Forebays of Bioretention Facilities

Journal of Sustainable Water in the Built Environment

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Occurrence and Concentration of 6 Metals and 28 Organic Micropollutants in the Forebays of Bioretention Facilities

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Maria Viklander[5]; and Godecke-Tobias Blecken[6]

Abstract: Pollutant loads in urban runoff from anthropogenic sources contribute to degradation of downstream waters. Cities are turning toward green infrastructure to manage urban stormwater. Bioretention is popular as green infrastructure and is commonly installed to remove runoff pollutants. A significant proportion of pollutants in urban runoff are particulates or particulate-bound and are effectively removed in bioretention cells. Pollutants accumulate in concentrated areas of the bioretention (e.g., forebays, inlets, surficial filter layers), which require maintenance to restore effective treatment and to increase the operational lifespan. Particles trapped in forebays risk diminished effectiveness of the pretreatment, which may eventually lead to filter clogging and leaching of toxic pollutants. Studies have examined pollutant accumulation and distribution in bioretention filter media, but less is known about processes in bioretention forebays. In this study, 28 bioretention forebays were examined in urban areas of Ohio and Michigan (United States) as well as Stockholm and Malmö (Sweden) to investigate the occurrence and accumulation of metals (i.e., Cd, Cr, Cu, Ni, Pb, and Zn) and 38 analytes of organic micropollutants [OMPs, i.e., alkylphenols, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and phthalates]. Investigated metals were present in all 28 samples, except Cd detected in 27 samples. Of 38 OMP analytes, 31 were detected in at least one sample. PAHs and PCBs were the most frequently detected pollutants found at all examined sites. In general, high concentrations of pollutants were detected in all forebay sediments. Cu, Ni, Zn, PAHs with high molecular weight, and PCBs were detected at concentrations above US and Swedish soil quality guidelines. It was concluded that forebays regularly need to be excavated to maintain their function, and excavated sediments must be handled safely during maintenance work and disposal. **DOI: 10.1061/JSWBAY.SWENG-583.**

Practical Applications: High pollutant concentrations in forebay sediments have critical implications for bioretention operators and regulators. Previous studies indicate clogging as a limiting factor for long-term function of bioretention systems, and sedimentation forebays are used to reduce the sediment load reaching the filter surface. However, operators should consider that removed sediment may be contaminated, exceeding guidelines and soil screening levels, and that removed material should be handled accordingly. Zn was the metal most commonly exceeding the Eco-SSL and Swedish EPA guidelines, followed by Cu and Ni. PAH-H exceeded the US EPA Eco-SSL and Swedish EPA standards, PAH-M and Σ7PCBs exceeded Swedish EPA. Concentrations exceeding Swedish EPA may be classified as hazardous waste, need certification for transportation, and must be disposed of at licensed landfill. The large variation between the different forebays (land use, catchment characteristics) underlines that sediment removal frequency and disposal are site-specific and difficult to generalize. However, the recommendation for bioretention operators is regular monitoring and sampling to inform forebay maintenance procedures.

Introduction

Urban stormwater carries large amounts of anthropogenic pollutants, including nutrients, heavy metals, bacteria, hydrocarbons, and other emerging pollutants of concern, which contribute to degradation of receiving waters and pose risks to human health and safety (Müller et al. 2020). For example, metals in stormwater (e.g., Cd, Cr, Cu, Ni, Pb, Zn) have been recognized as contaminants of concern for humans and aquatic life (Eriksson et al. 2007) and are present at toxic levels (Cu, Pb, and Zn) in road runoff

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(USEPA 1983). Recently, studies have identified organic micropollutants (OMPs) as a pollutant group of concern in urban runoff that may have negative impacts on humans and aquatic habitats (Barbosa et al. 2012; Markiewicz et al. 2017). OMPs such as alkylphenols, phthalates, and polycyclic aromatic hydrocarbons (PAHs) are considered genotoxic substances (Markiewicz et al. 2020) while phthalates and nonylphenols as endocrine disruptors (Björklund et al. 2009). Similarly, petroleum hydrocarbons are suspected carcinogens (Fent 2003; LeFevre et al. 2012; Mastrangelo et al. 1996), while polychlorinated biphenyls have been shown to increase the risk of certain cancers and have adverse effects on human reproduction (Helmfrid et al. 2012).

Bioretention cells, also referred to as biofilters, biofiltration systems, or raingardens, are a common technique implemented by cities worldwide to treat urban stormwater (Kratky et al. 2017; McGrane 2016; Winston et al. 2020). Bioretention systems are landscape depressions backfilled with engineered soil media, generally topped with mulch, and planted with native plants (Tirpak et al. 2021). Paus et al. (2014) showed that a properly designed bioretention can maintain key functions such as infiltration and metal removal. Thus, many filtering systems are equipped with a sedimentation device or forebay to settle out pollutants before runoff reaches the filter (Maniquiz-Redillas et al. 2014). Kallin et al. (2004) and Blecken et al. (2017) recommended that biofilter design should incorporate a forebay for settling large suspended sediments.

A forebay (e.g., Figs. S1.1–S1.22) is an energy dissipation and sedimentation device (e.g., settling or sediment basin, inlet lined with large rocks, etc.) placed near the inlet to the bioretention cell that slows flow velocities and promotes sedimentation and large debris removal to minimize sediment transport into the filter, erosion, and clogging (Al-Ameri et al. 2018; Erickson and Hernick 2019; Maniquiz-Redillas et al. 2014; McNett and Hunt 2011; Winston et al. 2023). The size of bioretention forebays is often approximately 10% of the design surface area (City of Portland 2020; Minnesota Pollution Control Agency 2022); however, the design can vary depending on local statutes, policies, and practices. Scientific studies on the performance of forebays for pretreatment of stormwater are rare. Previous studies on large sedimentation basins have shown that a large proportion of particle-bound pollutants accumulate in sediments (German 2003; Grottker 1990) and sediments accumulate in forebays. Another study of stormwater wetlands and wet ponds (McNett and Hunt 2011) assessed concentrations of metals in forebay sediments and found potentially toxic levels of Cu, Ni, and Zn that may pose a threat to aquatic health. However, when comparing these concentrations with US EPA 40 CFR503 (USEPA 1993), they are below threshold values and thus would not pose a threat to the environment after subsequent excavation and land application. Nevertheless, potential presence of PAHs and PCBs [not assessed in the McNett and Hunt (2011) study] may make land application more difficult. However, since wetlands and wet ponds are commonly larger than bioretention, the forebays in wetlands and wet ponds (10%–20% of total area) are also larger than in bioretention facilities (10% of a smaller total area) (Maniquiz-Redillas et al. 2014; Schaad et al. 2008; Winston et al. 2013). While most metals are bound to small particle fractions that are not efficiently removed by small forebays, a significant portion of metals may be associated with larger particles (Karlsson and Viklander 2008b; Stone and Marsalek 1996) and thus may accumulate in the forebays of bioretention cells. Previous studies have emphasized the need for frequent maintenance and removal of accumulated sediments in pretreatment devices to restore storage volume and prevent contamination of downstream facilities and/or waterbodies (Blecken et al. 2017; Grimm et al. 2023; McNett and Hunt 2011). Since forebays regularly need to be excavated to maintain their function, it is important to know what contaminants and substances are present in the sediments to handle and dispose of them safely.

To date, several studies have focused on pollutant retention in the filter material; however, only a few studies have examined forebays in bioretention systems and little is known about the characteristics of forebay sediments. Given the potential risks to human health and aquatic ecosystems as well as possible impacts to bioretention performance associated with sediment accumulation in forebays, it is important to understand the pollutant composition in forebays and evaluate how sediments can be handled safely during maintenance and disposal. In the present study, we examined 28 bioretention forebays located in the United States (Ohio and Michigan) and Sweden (Stockholm and Malmö) to investigate the pollutant concentrations and characteristics of the sediments, targeting metals commonly occurring in stormwater (i.e., Cd, Cr, Cu, Ni, Pb, and Zn) and four groups of organic micropollutants (OMPs) (i.e., alkylphenols, PAHs, phthalates, and PCBs). Concentrations were compared with various regulatory guidelines to determine the environmental risks posed by pollutants accumulating in bioretention forebays.

Materials and Methods

Field Sites and Sampling Methods

In total, 28 bioretention cell forebays were included in this study: 18 in Ohio and two in Michigan (United States) and eight in Sweden (Fig. 1). The bioretention sites were located in urban areas with various land uses in their catchment areas (e.g., residential, parking/roads, downtown urban, industrial, fuel station; Table 1).

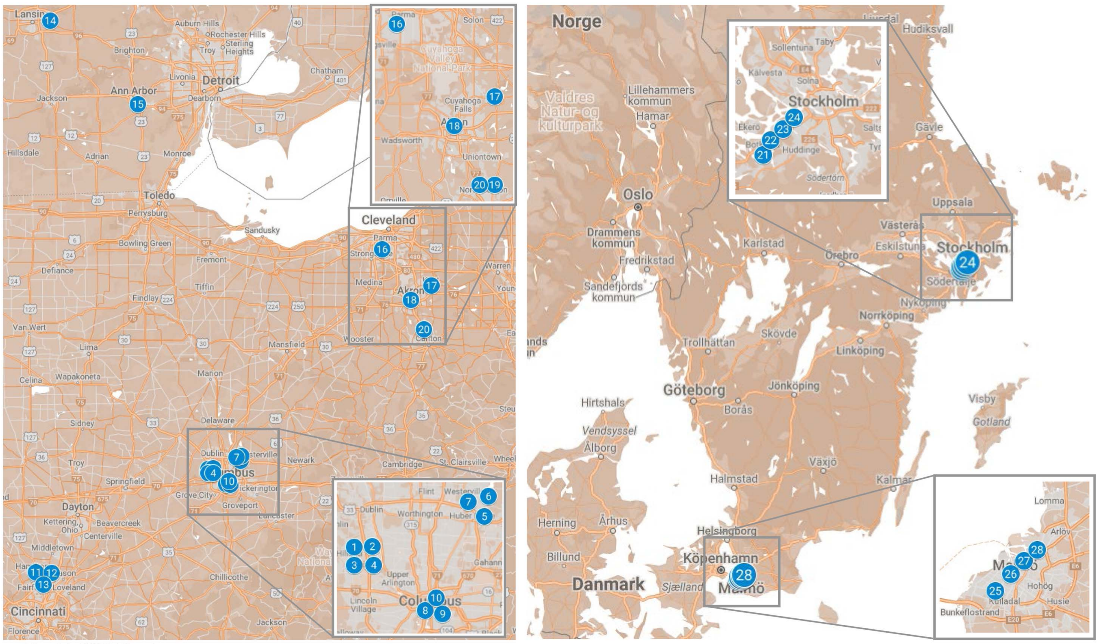
The examined forebays had surface areas that varied from 0.002% to 2% of the catchment area, while the filter areas varied from 0.3% to 20% of the catchment area (Table 1). At some sites, the forebay was comprised of a small (e.g., sites 5, 6, 8) or large (e.g., sites 1–4) settling basin by the inlet that only filled up during precipitation events. At other sites, the forebay was comprised of a small steel (e.g., sites 10, 21, 22, 23, 24) or concrete (e.g., sites 25, 26, 27, 28) settling basin or rock structure (e.g., sites 7, 14, 15, 16, 17, 18, 19, 20) by the inlet to reduce inflow velocity and prevent erosion. In some instances, other structures that allowed the settling and accumulation of sediments were used (e.g., sites 9, 11, 12, 13; see Figs. S1.1–S1.22).

Sediment samples were collected from the forebays in November 2019–April 2021. Samples were collected using a steel spade to dig or scrape approximately 1 kg of accumulated sediment from each forebay, which was subsequently placed in diffusion-tight plastic bags (18 cm × 35 cm) that were sealed shut with cable ties. The outdoor temperature during sampling was approximately −12°C to +6°C, and the samples were refrigerated prior to laboratory analysis.

Analysis

All samples were sent to an accredited laboratory for pre-treatment and analysis. Sediment samples from all 28 sites were analyzed for concentrations of Cd, Cr, Cu, Ni, Pb, and Zn. To determine the total metal concentration, samples were dried at 50°C and sieved (2 mm) according to Swedish standards (SS 2004, 1993). Drying at 105°C was conducted in parallel with sample analysis to correct to the dry matter (DM) concentration. Microwave-assisted digestion was performed on dried samples using 5 mL of concentrated HNO_3 and 0.5 ml of H_2O_2.

Sediment samples from 16 sites (marked with "a" in Table 1) were also analyzed for concentrations of four groups of OMPs



Map data ©2024 Google

(a)

(b)

Fig. 1. Map of bioretention cells in: (a) Ohio and Michigan, USA, and in (b) Malmö and Stockholm, Sweden. (Map data ©2024 Google.)

(i.e., 16 PAHs, 7 PCBs, 13 phthalates, and 2 alkylphenols) 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 analyzed according to US EPA 8270 (Pitt et al. 1994) and ISO 18287 (ISO 2006). Σ16PAHs was calculated as the sum of the concentrations of all 16 PAHs. The total PAHs with low molecular weights (PAH-L) was calculated as the sum of the concentrations of naphthalene, acenaphthylene, and acenaphthene; total PAHs with medium molecular weights (PAH-M) as the sum of the concentrations of fluorene, phenanthrene, anthracene, fluoranthene, and pyrene; and total PAHs with high molecular weights (PAH-H) as the sum of the concentrations 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 PCB indicator congeners, i.e., PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, and PCB 180, were analyzed following DIN ISO 10382 (DIN ISO 2002). Σ7PCBs 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 analyzed following E DIN19742 (DIN 2014). The concentrations of two alkylphenols, i.e., 4-tert-octylphenol (OP) and 4-nonylphenol (NP), were also analyzed.

Besides the metals and 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 72 0103 (CSN 2009), and CSN 46 5735 (CSN 1991). Dry matter (DM) was measured using appropriate methods for each pollutant group.

For data analyses, comparisons, and to illustrate pollutant distribution and concentrations in bioretention forebays, boxplots and descriptive statistics (median, min, max) were created in Minitab 20.4.

Results and Discussion

Metals

Occurrence

All analyzed metals were detected in all 28 examined forebay samples (Table 2), except Cd (detected in 27 of 28 samples). The nondetectable levels of Cd were from Bioretention Site #23 (Table 1) located in Sweden. This site had only been in operation for two years and was among the youngest of the facilities included in the study. Maintenance of the forebay with removal of sediment had been performed at sites #21–#23 after one year of operation. In a previous review study of micropollutants in stormwater outlets, Mutzner et al. (2022) presented a top-10 list of pollutants with high

Table 1. Bioretention site, age, site location, catchment area characteristics, catchment area, forebay area, and filter area

Site	Age (year)	Site location	Catchment area characteristics	Catchment area (Ca; m^2)	Forebay area (FbA; m^2)	Filter area (FA; m^2)	FbA/Ca (%)	FbA/FA (%)	FA/Ca (%)
1[a]	9	Upper Arlington, Ohio	Residential	318,000	20	950	0.01	2.11	0.30
2	9	Upper Arlington, Ohio	Residential	1,250,000	20	1,200	0.00	1.67	0.10
3	9	Upper Arlington, Ohio	Residential	224,000	10	900	0.00	1.11	0.40
4	9	Upper Arlington, Ohio	Residential	146,000	10	1,900	0.01	0.53	1.30
5	8	Westerville, Ohio	Parking/roads	12,000	1.5	600	0.01	0.25	5.00
6	8	Westerville, Ohio	Parking/roads	2,000	1	50	0.05	2.00	2.50
7[a]	7	Westerville, Ohio	Commercial	4,000	8	170	0.20	4.71	4.30
8	9	Columbus, Ohio	Parking/roads	4,500	2	580	0.04	0.34	13.0
9[a]	9	Columbus, Ohio	Downtown urban	300	1.5	40	0.50	3.75	13.0
10[a]	8	Columbus, Ohio	Downtown urban	50	1	10	2.00	10.00	20.0
11	12	Hamilton, Ohio	Industrial	4,500	10	200	0.22	5.00	4.40
12[a]	12	Hamilton, Ohio	Industrial	4,500	10	300	0.22	3.33	6.70
13	12	Hamilton, Ohio	Industrial	4,500	10	200	0.22	5.00	4.40
14[a]	11	Lansing, Michigan	Downtown urban	500	1	50	0.20	2.00	10.0
15	14	Ann Arbor, Michigan	Parking/roads	2,250	3	156	0.13	1.92	6.90
16[a]	8	Parma, Ohio	Fueling station	2,500	10	200	0.40	5.00	8.00
17	11	Kent, Ohio	Fueling station	800	1	70	0.13	1.43	8.80
18	13	Akron, Ohio	Parking/roads	6,500	1	180	0.02	0.56	2.80
19[a]	12	North Canton, Ohio	Fueling station	1,250	8	180	0.64	4.44	14.0
20	12	North Canton, Ohio	Fueling station	1,000	4	100	0.40	4.00	10.0
21[a]	2	Stockholm, Sweden	Road	340	1.5	20	0.44	7.50	5.90
22[a]	2	Stockholm, Sweden	Parking	340	1.5	20	0.44	7.50	5.90
23[a]	2	Stockholm, Sweden	Road	370	1.5	20	0.41	7.50	5.40
24[a]	2	Stockholm, Sweden	Parking	340	1.5	20	0.44	7.50	5.90
25[a]	2	Malmö, Sweden	Downtown urban	350	1	20	0.29	5.00	5.70
26[a]	2	Malmö, Sweden	Downtown urban	350	1	20	0.29	5.00	5.70
27[a]	2	Malmö, Sweden	Downtown urban	350	1	20	0.29	5.00	5.70
28[a]	2	Malmö, Sweden	Downtown urban	350	1	20	0.29	5.00	5.70

Note: FbA/Ca is the forebay area as a percentage of catchment area, FbA/FA is the forebay area as percentage of the filter area and, FA/Ca is the filter area in percentage of catchment area. The site age was determined at the time of sampling (i.e., November 2019 for sites 1–20 and April 2021 for sites 21–28). All forebay sediment samples were analyzed for metals content.

[a] Sites were also analyzed for OMP content.

Table 2. Occurrence, concentration, and detection limit (DL) of metals

Group/units	Metal	No. of samples	Occurrence >DL No.	Occurrence >DL %	All data Min	All data Median	All data Max	DL
Metals (mg/kg, DM)	Cd	28	27	96	<0.10	0.29	0.75	0.1
	Cr	28	28	100	5.06	21.2	78.9	—
	Cu	28	28	100	9.22	50.9	95.2	—
	Ni	28	28	100	6.89	18.4	128	—
	Pb	28	28	100	6.48	23.7	72.2	—
	Zn	28	28	100	80.6	243	1,440	—

occurrence and risk for surface waters, which included Cu, Zn, and Hg. In our study, two (i.e., Cu and Zn) of these high occurrence and risk metals were found in all samples of forebay sediments.

Concentrations

Few previous studies have examined metals in bioretention forebays (for data of previous studies, see Supplemental Materials Tables S1 and S2), and only two assessed concentrations of metals accumulated in forebay sediments of stormwater wetlands, ponds, and bioretention (McNett and Hunt 2011; Johnson and Hunt 2016). Compared with the forebays sampled herein (Fig. 2 and Table 2), McNett and Hunt (2011) report similar concentrations for Cr (20.0–28.3 mg/kg) and Ni (13.0–15.9 mg/kg) as well as lower concentrations for Cu (15.1–23.0 mg/kg), Pb (11.4–13.0 mg/kg), Zn (44–75 mg/kg), and Cd (below DL). There is no clear reason to

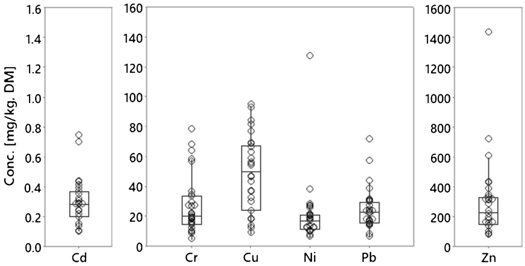


Fig. 2. Boxplots of concentrations of Cd, Cr, Cu, Ni, Pb, and Zn with the concentration of each sample should as an open symbol.

explain these generally lower concentrations in the McNett and Hunt (2011) study; however, sites were mainly younger in the their study (1–10 years) and the sites (draining institutional, commercial, and residential land uses) may have lower traffic intensity compared with a greater proportion of roads in our study. However, we cannot be certain of the reason for the differences.

Similarly, Johnson and Hunt (2016) found two to four times lower metal concentrations in the forebay of an 11-year-old bioretention facility (e.g., Cu mean: 11.16 mg/kg; Zn mean: 157 mg/kg).

Sediment from other stormwater treatment facilities, like ponds and sedimentation tanks, has been evaluated in other studies. Commonly, such larger facilities (e.g., evaluated by Karlsson et al. 2010), often trap finer sediments compared with the smaller forebays in this study. Metal concentrations are often inversely proportional to particle diameter; thus, the highest concentrations are found in the finest fractions (German and Svensson 2002). Consequently, Karlsson et al. (2010) in a study of sediments from stormwater ponds and sedimentation tanks report Cr (ca. 65–70 mg/kg), Cu (230–250 mg/kg), and Ni (28–34 mg/kg) concentrations of which were 2.5 times higher than the bioretention forebays herein. Cd (1.0 and 0.4 mg/kg in pond and tank sediments, respectively), Pb (80 mg/kg), and Zn (950–1,400 mg/kg) concentrations, however, were in the same range as in this study.

In contrast with ponds, catch basins (also referred to as gully pots) may be similar in size to forebays but are located underground. In a study of metal concentrations in sediments from stormwater catch basins, Karlsson and Viklander (2008b) concluded that most metals were associated with particles and dissolved) and reported median concentrations of Cd, Cr, Cu, Ni, and Zn similar or lower than those found in our study. Pun et al. (2019) reported that elevated Zn concentrations (267–3,700 mg/kg) were commonly found in road catch basin sediments, and high concentrations of Cu (27–1,020 mg/kg), Pb (21–332 mg/kg) and Cr (14–439 mg/kg) were also found), suggesting the possibility of sediment pollution with an ecological risk classified as considerable/moderate to high. In runoff sediments from stormwater traps in Bergen, Norway, concentrations were reported in a wide range between 0.02–11.1 mg/kg for Cd, 9–675 mg/kg for Pb, and 51.3–4,670 mg/kg for Zn (Jartun et al. 2008). Compared with these previous studies, metal concentrations in our study were found at lower levels than in Jartun et al. (2008), similar to levels in Karlsson et al. (2010), or higher levels than Johnson and Hunt (2016) and McNett and Hunt (2011). This underlines that variation between catchments and/or facilities can be high, which makes a generalized characterization of sediment from a specific type of sediment-trapping facility difficult.

OMPs

Occurrence

OMPs were detected in all samples (Table 3). In total, 31 of the 38 investigated OMP analytes were detected in at least one sample, including all 16 PAHs, all seven PCBs, both alkylphenols (i.e., OP and NP) and six of 13 phthalates (i.e., DIDP, DBP, DNPP, DEHP, DIDP, and DINP). PCBs were the most frequently detected OMPs and were found at all bioretention forebays with an average of 85% occurrence for the seven analyzed compounds. PCB analytes with high molecular weight (i.e., PCB138, 153, and 180) were detected in all samples, while PCB118, PCB101, and PCB52 were detected in 94% and PCB28 in 13% of all samples. PAHs were the second most frequently detected OMPs, and all samples contained at least one of 16 PAH compounds. The 16 PAH analytes (Table 3) were on average detected in 71% of samples, and the most frequent (BbF) was detected in all samples. OP was detected in 31% of samples and NP in 56% of samples. DEHP was the most commonly occurring phthalate, detected in 94% of samples, followed by DINP (38% of samples), DIBP (19%), DIDP (13%), and DBP and DNPP (both 6%). On average, the phthalates analyzed were detected in 13% of all samples.

Mutzner et al. (2022) presented a top-10 list of pollutants of high occurrence and risk for surface waters, including seven PAHs and three metals (i.e., BaP, Fluo, Pyr, Cu, Zn, Hg, BbF, Chry, Bper, DahA). In our study, these seven PAHs also had a high occurrence in forebay sediments (81%–100%, Table 3), underlining their importance for stormwater management as suggested by Mutzner et al. (2022). According to Σ16PAHs, analytes with high molecular weight (PAH-H) were detected in all samples (Table 3), PAHs with medium molecular weight (PAH-M) were detected in 94% of samples, and PAHs with low molecular weight (PAH-L) were detected in 44% of samples. Further, when comparing the 16 PAH analytes to those identified by Mutzner et al. (2022), similar trends were evident, i.e., PAHs with a larger number of molecular rings and higher molecular weight had a higher occurrence than PAHs with a low number of molecular rings and molecular weight. A similar tendency was also observed in our study regarding PCBs with high molecular weight (e.g., PCB180, PCB138, and PCB153), which were detected in all samples. Similarly, PCB118, PCB101, and PCB52 were detected in 94% of samples, while PCB28 was only present in 13% of samples. Flanagan et al. (2021) measured organic micropollutants in stormwater pond sediments and found a similar relationship between increased occurrence and decreased molecular weight, e.g., PAHs occurred in 53% of samples, phthalates, including DEHP in 66%, DiNP in 33%, DBP in 31%, and DiDP in 28% of samples, alkylphenols in 38% of samples, PCB101, 118, 138, 153, and 180 in 69%–75%, and PCB28 and PCB53 in 53% of samples. Also, in a study of catch basin sediments, Karlsson and Viklander (2008a) observed that PAHs with low molecular weight were more highly dissolved (<0.45 μm), whereas PAHs with high molecular weight were mainly associated with particulate matter. In contrast, in our study, the occurrence of phthalates and alkylphenols seemed to be related to catchment land use, with industrial land use driving higher concentrations rather than molecular weight, e.g., nonylphenol was more frequently detected than octylphenol, possibly because nonylphenols are more widely used in industry than octylphenols (Bergé et al. 2012). Despite the observed trend between molecular weight and concentration for OMPs, the occurrence and concentration of OMPs in forebay sediments may be influenced by other factors (e.g., discharge and mobilization from catchment areas and affinity of pollutants for particles), including hydrophobicity and solubility. For example, hydrophobic substances may accumulate more extensively in the sediments than more hydrophilic species (Flanagan et al. 2021; Furén et al. 2022), which is supported by results herein.

Concentrations

OMP concentrations in the forebays showed a wide variation between different bioretention cells (Table 3). Only a few previous studies have analyzed OMPs in of bioretention forebay sediments, whereas sediments in sedimentation tanks, catch basins, and bioretention filter material have been evaluated more frequently. Compared with a previous study of bioretention filter materials (Furén et al. 2022), median concentrations of OMPs in forebay sediments in this study were generally higher (Table 3, Fig. 3). However, top layer concentrations in filter material were closer to those in forebay sediments. Furén et al. (2022) reported median Σ16PAHs, PAH-H, PAH-M, and PAH-L in filter material of 1.90 mg/kg (8 mg/kg in top layer), 1.30 mg/kg (5.90 mg/kg in top layer),

Table 3. Occurrence, concentration, and detection limit (DL) of OMPs

Group/units	Substance name	No. of samples	Occurrence > DL		All data			DL
			No.	%	Min	Median	Max	
PAH (mg/kg, DM)	Naphthalene (Nap)	16	6	38	<0.05	<0.10	0.30	(0.05–0.30)
	Acenaphthylene (Acyl)	16	3	19	<0.05	<0.10	0.30	(0.05–0.30)
	Acenaphthene (Acen)	16	4	25	<0.05	<0.10	1.72	(0.05–0.30)
	Fluorene (F)	16	7	44	<0.05	<0.10	2.01	(0.05–0.30)
	Phenanthrene (Phen)	16	12	75	<0.10	0.65	35.7	(0.10–0.30)
	Anthracene (A)	16	10	63	<0.09	0.20	4.06	(0.10–0.30)
	Fluoranthene (Fluo)	16	14	88	<0.10	1.92	60.7	(0.10–0.30)
	Pyrene (Pyr)	16	15	94	<0.16	1.51	45.6	0.30
	Benzo(a)anthracene (BaA)	16	13	81	<0.05	0.66	17.0	(0.05–0.15)
	Chrysene (Chry)	16	15	94	<0.05	0.79	22.8	0.15
	Benzo(b)fluoranthene (BbF)	16	16	100	0.18	1.31	25.7	0.05
	Benzo(k)fluoranthene (BkF)	16	10	63	<0.05	<0.63	9.63	(0.05–0.70)
	Benzo(a)pyrene (BaP)	16	15	94	<0.08	0.75	16.6	0.15
	Dibenzo(a,h)anthracene (DahA)	16	13	81	<0.05	0.18	1.86	(0.05–0.15)
	Benzo(g,h,i)perylene (Bper)	16	15	94	<0.18	0.73	11.5	0.30
	Indeno(1,2,3-cd)pyrene (IP)	16	15	94	<0.11	0.76	9.12	0.15
	PAH sum Low weight (PAH-L)	16	7	44	<0.08	<0.15	1.90	(0.08–0.45)
	PAH sum medium-weight (PAH-M)	16	15	94	<0.19	4.45	150	(<0.19–0.75)
	PAH sum high-weight (PAH-H)	16	16	100	0.26	5.55	110	<0.26
	PAH 16 sum (Σ16PAH)	16	13	81	<1.30	9.95	260	(1.30–3.80)
PCB (μg/kg, DM)	PCB 28	16	2	13	<0.10	<0.15	3.60	(0.10–0.50)
	PCB 52	16	15	94	<0.10	0.32	27.0	0.10
	PCB 101	16	15	94	<0.10	1.10	61.0	0.10
	PCB 118	16	15	94	<0.10	0.75	64.0	0.10
	PCB 153	16	16	100	0.16	1.60	62.0	0.10
	PCB 138	16	16	100	0.14	1.60	54.0	0.10
	PCB 180	16	16	100	0.11	1.45	47.0	0.10
	Sum of 7 PCBs (Σ7PCB)	16	16	100	0.41	6.85	320	<0.40
Phthalates (mg/kg, DM)	Dimethylphthalate (DMP)	16	—	0	—	—	—	0.05
	Diethylphthalate (DEP)	16	—	0	—	—	—	0.05
	Di-n-propylphthalate (DPP)	16	—	0	—	—	—	(0.05–2.00)*
	diisobutyl phthalate (DIBP)	16	3	19	<0.05	<0.05	0.09	(0.05–0.10)
	Di-n-butylphthalate (DBP)	16	1	6	<0.05	<0.05	1.10	(0.05–0.10)
	Di-n-pentylphthalate (DNPP)	16	1	6	<0.05	<0.05	0.051	(0.05–0.30)
	Di-n-octylphthalate (DNOP)	16	—	0	—	—	—	(0.05–0.30)**
	Di-(2-ethylhexyl)phthalate (DEHP)	16	15	94	<0.05	1.50	5.70	0.05
	Butylbenzylphthalate (BBP)	16	—	0	—	—	—	(0.05–1.00)***
	Dicyclohexylphthalate (DCP)	16	—	0	—	—	—	0.05
	Diisodecyl phthalate (DIDP)	16	2	13	<2.50	<2.50	5.10	2.50
	Diisononyl phthalate (DINP)	16	6	38	<2.50	<2.50	11.0	2.50
	Di-n-hexylphthalate (DNHP)	16	—	0	—	—	—	(0.05–0.07)****
Alkylphenols (mg/kg, DM)	4-tert-octylphenol (OP)	16	5	31	<0.01	<0.02	0.10	(0.01–0.03)
	4-nonylphenols (tech.mixture) (NP)	16	9	56	0.06	<0.10	65.8	0.10

Note: Occurrence is reported as number (No.) above DL. *Of 16 samples, 14 nondetects were <0.05, 1 was <0.08 and, 1 was <2.00; ** of 16 samples, 10 nondetects were <0.05, 1 was <0.15, 2 were <0.20, 1 was <0.25 and, 1 was <0.30; *** of 16 samples, 14 nondetects were <0.05, 1 was <0.10 and, 1 was <1.00; and **** of 16 samples, 15 nondetects were <0.05 and, 1 was <0.07.

0.57 mg/kg (2.10 mg/kg in top layer), and <0.15 mg/kg, respectively. However, when comparing concentrations in stormwater sediments with different configurations, e.g., forebay versus filter material, care should be taken since filter samples consist of trapped sediments and filter material, whereas forebays contain only sediment from external sources.

Flanagan et al. (2021) investigated OMPs in stormwater pond sediments. Here, Σ16PAHs medians were 20 times lower (0.64 mg/kg), and median Σ7PCBs concentration of 3.2 μg/kg were about half the median concentration compared with the forebay sediments herein (Table 3). This is somewhat surprising given that ponds often remove smaller sediment fractions, which commonly carry a greater fraction of pollutants. However, in Flanagan et al. (2021), some ponds were included, which received runoff from nonurban land uses and which likely resulted in lower median concentrations. In studies of catch basin sediments, median Σ16PAHs was 4.0 mg/kg DM (Karlsson and Viklander 2008a) and 0.6–24.7 mg/kg (Pun et al. 2019), which is also lower compared with our study. Finally, for sediments from stormwater traps (catch basins) in Norway, Jartun et al. (2008) reported similar PAH (0.2–80 mg/kg) and Σ7PCBs (0.0004–0.704 mg/kg) concentrations to those observed in our study (Table 3, Fig. 4).

Studies on phthalates in stormwater sediment remain limited. Flanagan et al. (2021) reported phthalate DEHP concentrations of 0.05–33 mg/kg (median of 1.3 mg/kg) and concentrations of DiNP of ≤430 mg/kg, DBP of 0.79 mg/kg, and DiDP of 22 mg/kg, thus higher or comparable with those in the bioretention forebay sediments (Table 3, Fig. 5). Liu et al. (2018) assessed

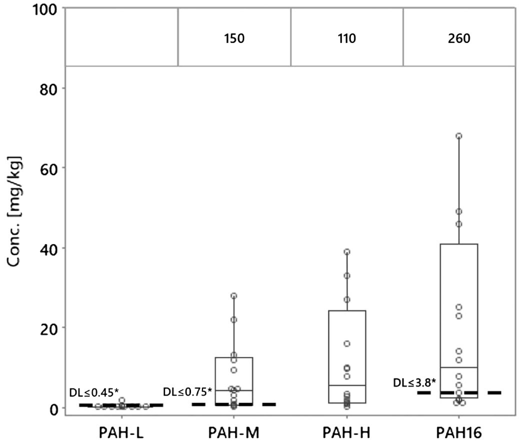


Fig. 3. Individual value plot and boxplot of PAH-L, PAH-M, and PAH-H, Σ16PAHs (mg/kg DM). *Highest DL for PAH-L, PAH-M, and Σ16PAH (Table 3). Outliers above 100 mg/kg DM are indicated as text above each boxplot for plotting purposes.

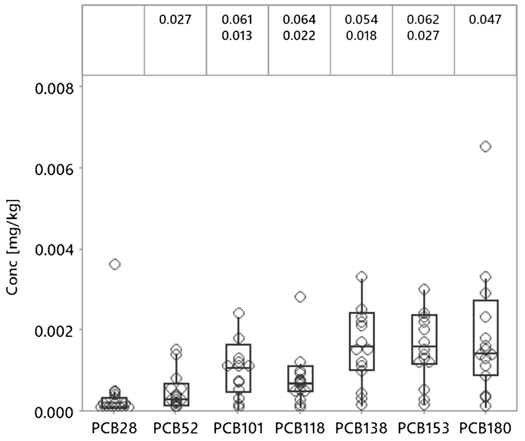


Fig. 4. Individual value plot and boxplot of concentrations of seven PCBs (DL in Table 3). Outliers above 0.008 mg/kg DM are indicated as text above each boxplot for plotting purposes.

removal of phthalates in a bioretention system and concluded that the main treatment of phthalates occurred due to filtration in the filter material rather than through sedimentation in the forebay. In general, concentrations vary with hydrophobicity (Flanagan et al. 2021), also correlated to molecular weight (i.e., heavier molecules showed higher accumulation and were better retained in the sediments), which could explain the high concentrations of PAH-H, PCBs with high molecular weight, DEHP, and NP in forebay sediments.

Comparison to Guidelines

To further assess the forebay sediments, concentrations were compared with national guidance limits. Comparison with the US EPA ecological soil screening levels (Eco-SSL), (USEPA 2023) showed that median concentrations of Cd, Cr, and Pb (Table 2) in the studied forebay sediments were lower than the limits (Table 4) for plants, and those of Cd, Ni, and Pb were lower than the limits for soil invertebrates (USEPA 2005a, b, 2007b). The median concentrations of Cu and Zn exceeded the Eco-SSL (USEPA 2007a, d) guidelines for plants and soil invertebrates.

Sweden has national guidelines (Swedish EPA 2022, 2009) for the classification of soils (Table 4), including “Soil for Sensitive Land Use” (abbreviated SLU) and “Soil for Less Sensitive Land Use” (abbreviated LessSLU). Cd and Cr concentrations did not exceed these limits in any of the forebay samples. Cu exceeded the limit for SLU in four samples and Pb in two samples. Ni exceeded the limits for SLU and LessSLU in one sample, while Zn exceeded the limits for SLU in 13 samples and LessSLU in three samples. A comparison with guidance from the Australian Government National Environment Protection Council (NEPC) and the Measure for Site Contamination (ASC NEPM 2013) in residential areas with garden/accessible soil showed that all concentrations in our study (Table 2; Fig. 2) were lower than the guideline values (Table 4). Similar conclusions were drawn when comparing with UK CL:AIRE (UK charity committed for sustainable land reuse) “Soil Guideline Values” (SGVs) for allotment, residential, and commercial areas (Martin et al. 2009a) and the US 40CFR503 land application standards (USEPA 1993). Thus, according to the US EPA Eco-SSL (USEPA 2023) and Swedish Environmental Protection Agency, Zn was the most concerning metal in the analyzed forebay sediments, i.e., leading to classification that may require disposal of the forebay materials and transport as hazardous waste.

OMP concentrations in forebay sediments were compared to US EPA Eco-SSL (USEPA 2007c) limits for soil invertebrates, which showed that PAH-H exceeded the limit in four samples, whereas PAH-L never exceeded these guideline values. Compared with Swedish national guidance limits for classification of soil (Swedish EPA 2022), PAH-H and PAH-M frequently exceeded the limits for SLU and LessSLU, whereas PAH-L did not exceed these limits. Σ7PCBs exceeded the LessSLU limit in one sample and SLU in seven samples. Thus, according to Swedish EPA guidelines (Swedish EPA 2022), there are environmental risks associated with bioretention forebay sediments.

Conclusions

This study investigated the occurrence and concentration of heavy metals and OMPs in forebays of 28 bioretention cells in the United States and Sweden. Most pollutants considered in this study (i.e., all metals and many OMPs) showed high occurrence and concentrations in the sampled forebay sediments. Compared with previous studies, concentrations of these pollutants were found at similar or higher levels herein. However, when comparing concentrations in forebay sediments with results from previous studies, it is important to distinguish between those in filter material, stormwater sediments, and pond/bottom sediments. Forebay samples mainly consisted of accumulated stormwater sediments, whereas samples of bioretention filter material consist of both of sediments and filter material. Therefore, it is likely that higher concentrations of particulate OMPs are present in forebay sediments compared with the mixture of filter material and accumulated sediments in the top layer of bioretention filter material, which may be one explanation for the high concentrations observed in this study. Moreover, larger stormwater treatment facilities (e.g., ponds and wetlands) often trap finer sediments compared with smaller forebay devices, which makes it difficult to compare the sediment

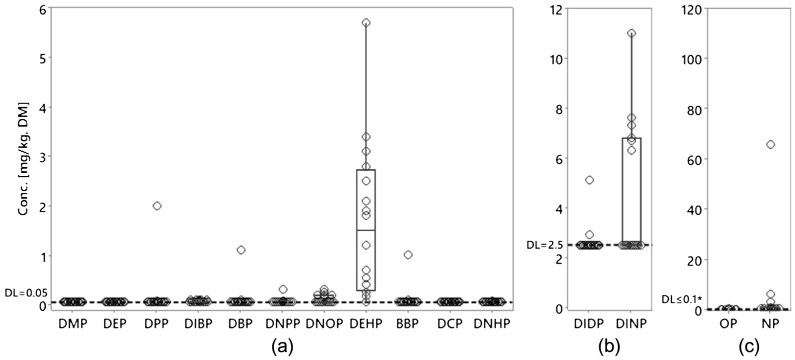


Fig. 5. Individual value plots and boxplots of concentrations of: (a and b) phthalates; and (c) alkylphenols (OP, NP). *Highest $DL_{OP} = 0.03$ mg/kg and $DL_{NP} = 0.1$ mg/kg (Table 3).

Table 4. Guideline limits of the US EPA Eco-SSL, Swedish EPA, Australian NEPC 1999, UK CL:AIRE and US EPA CFR503 together with the number of forebay samples in excess of each standard

Guideline	Classification	Unit	Cd	Cr	Cu	Ni	Pb	Zn	PAH-H	PAH-M	PAH-L	PCB7
US EPA Eco-SSL[a]	Plants	(mg/kg)	32	—	70	38	120	160	—	—	—	—
	Detection	(No)	0	0	5	2	0	23	—	—	—	—
		(%)	0	0	18	7	0	82	—	—	—	—
	Soil invertebrates	(mg/kg)	140	—	80	280	1,700	120	18	—	29	—
	Detection No.	(No)	0	—	4	0	0	25	4	—	0	—
	Detection %	(%)	0	—	14	0	0	89	25	—	0	—
Swedish EPA[b]	KM	(mg/kg)	0.8	80	80	40	50	250	1	3.5	3	0.008
	Detection	(No)	0	0	4	1	2	13	13	9	0	7
		(%)	0	0	14	4	7	46	81	56	0	44
	MKM	(mg/kg)	12	150	200	120	180	500	10	20	15	0.2
	Detection	(No)	0	0	0	1	0	3	5	3	0	1
		(%)	0	0	0	4	0	11	31	19	0	6
NEPC 1999[c]	Residential A	(mg/kg)	20	100	6,000	400	300	7,400	—	—	—	—
	Detection	(No)	0	0	0	0	0	0	—	—	—	—
		(%)	0	0	0	0	0	0	—	—	—	—
UK CL:AIRE [d]	Residential	(mg/kg)	10	—	—	130	—	—	—	—	—	—
	Detection	(No)	0	—	—	0	—	—	—	—	—	—
		(%)	0	—	—	0	—	—	—	—	—	—
	Allotment	(mg/kg)	1.8	—	—	230	—	—	—	—	—	—
	Detection	(No)	0	—	—	0	—	—	—	—	—	—
		(%)	0	—	—	0	—	—	—	—	—	—
	Commercial	(mg/kg)	230	—	—	1,800	—	—	—	—	—	—
	Detection	(No)	0	—	—	0	—	—	—	—	—	—
		(%)	0	—	—	0	—	—	—	—	—	—
40CFR503[e]	Land use	(mg/kg)	85	3,000	4,300	420	840	7,500	—	—	—	—
	Detection	(No)	0	0	0	0	0	0	—	—	—	—
		(%)	0	0	0	0	0	0	—	—	—	—

Note: Further description of the guidelines in Supplemental Materials Section 3.
[a] USEPA (2023).
[b] Swedish EPA (2022, 2009).
[c] NEPC (1999).
[d] UK, CL:AIRE (Martin et al. 2009b, c).
[e] 40CFR503 (USEPA 1993).

concentrations in different studies. Despite the higher fraction of fine sediment in larger facilities, the sediments from the smaller forebay devices in this study had higher metals and OMP concentrations compared with previous studies.

Similarities and variations in concentrations in the forebay OMPs and metals concentrations occurred between and within pollutant groups (metals, phthalates, alkylphenols, PAHs, and PCBs). These may be related to different substance properties, e.g., mobility, solubility, attachment to particles, and, for OMPs, hydrophobicity.

The main conclusions of this study are as follows:

- Most examined substances showed high occurrence in the sediment samples collected from the bioretention forebays. All six analyzed metals were detected in all forebay samples, except Cd (detected in 27 of 28 samples), and 31 of 38 investigated OMP analytes were detected in at least one of 16 samples.
- High concentrations were generally detected in the forebay sediments. Zn and PAHs with high and median high molecular weight and PCBs were frequently detected at concentrations above soil quality guidelines (Swedish EPA 2022; USEPA 2023). Cu and Ni were also detected above soil quality guidelines (Swedish EPA 2022).
- Pollutant concentrations in sediments herein were generally similar or higher than those found in previous studies. However, only a few studies have considered forebay sediments; comparisons with previously published values are complex and should be treated with caution. More research is needed to enhance the scientific understanding of toxic pollutant accumulation in bioretention forebays.
- Since forebays regularly need to be excavated to maintain their function, it is important that sediments are handled safely during maintenance work and final disposal.

Data Availability Statement

Some or all data, models, or code generated or used during the study are available in the data repository found in Beryani et al. (2024) in accordance with funder data retention policies.

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Supplemental Materials

Figs. S1.1–S1.22 and Tables S1–S2 are available online in the ASCE Library (www.ascelibrary.org).

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Paper IV

Robert Furén, Maria Viklander, Godecke-Tobias Blecken

Influence of salt on total and dissolved metal treatment in bioretention: A Field study

Under review in

Water Air and Soil Pollution

INFLUENCE OF SALT ON TOTAL AND DISSOLVED METAL TREATMENT IN BIORETENTION: A FIELD STUDY

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Abstract

Urban areas are affected by anthropogenic activities that cause pollutant load on receiving water bodies. Stormwater bioretention are popular and effective in removing pollutants. The main treatment is filtration and adsorption in the top layer (0-10cm) of the filters. So far, few in-field studies have evaluated effects of cold climate and de-icing salt on bioretention for treating metals. Thus, a comprehensive study of total and dissolved metal (Cd, Cr, Cu, Ni, Pb and Zn) treatment in a bioretention system for management of road runoff from the European highway E4 was carried out. Three different filter configurations were examined: a sand filter (SF), a vegetated sand filter (BF) and a vegetated sand filter with chalk additive (BFC). The results show a general trend of significant metal treatment in all filters, BFC, BF and SF, both under impact of high (Cl^{-}>210 mg/l) and low (Cl^{-}≤98.2 mg/l) chloride concentrations. For total concentrations, the results show that treatment was most efficient in filter BFC, then BF and least efficient in filter SF. For metals such as Cu, Ni and Pb, this may indicate that better treatment could be achieved using vegetation and chalk additives that affect pH. For dissolved metals, there is a tendence of treatment of Cr, Cu, Ni, Pb and Zn in filter BFC when lower chloride impact. With higher of chlorides concentrations, there tended to be a release of metals from the filters. Only dissolved Ni show a tendence of treatment when there was a higher chloride concentration in filter BFC.

1 Introduction

Urban areas are affected by anthropogenic activities that create pollutant loads which are stored on surfaces and transported through surface runoff and/or snowmelt to receiving water bodies (Müller et al., 2020). Untreated stormwater is considered a major cause of environmental degradation in urban waters (Walsh et al., 2005). As awareness of stormwater pollution and its effects has increased (Makepeace et al., 1995; Müller et al., 2020), so has the interest in stormwater quality treatment (Fletcher et al., 2015). Of all pollutants, metals contribute to degradation of receiving water bodies (Göbel et al., 2007), with Cd, Cr, Cu, Ni, Pb, and Zn in stormwater considered as contaminants of concern for humans and aquatic life (Eriksson et al., 2007). Cu, Pb and Zn are considered toxic in road runoff by the Nationwide Urban Runoff Program (U.S. EPA, 1983).

Stormwater bioretention technologies are becoming increasingly popular and are widely used for urban stormwater treatment (Kratky et al., 2017; McGrane, 2016). The technology is considered effective in removing pollutants such as total suspended solids (Hsieh and Davis, 2005), particulate and, less effectively, dissolved metals (Blecken et al., 2009) and a wide range of organic micropollutants (Zhang et al., 2014). Studies of bioretention technology have reported total metal removal often exceeding 85% to 90%. (Søberg et al., 2017). Most metal treatment occurs by filtration and adsorption to the top layer (ca. 0–10cm) in the filter material (Furén et al., 2023; Davis et al., 2009; Hatt et al., 2008). Different configurations of filter materials are utilised, typically based on engineered sand with low organic matter content. Different additives are sometimes included, such as organic matter, biochar, and chalk, to support plant growth or metal treatment. Additives of chalk ($CaCO_3$) may increase pH in the filter media and improve metal adsorption (Hatt et al., 2011; Søberg et al., 2019). Filters can also be topped with a mulch layer and vegetation (Davis et al., 2009; Hunt et al., 2012). Although vegetation contributes to total metal removal, the filter material accounts for most metal removal and thus filter composition is crucial for effective removal of dissolved metals (Muthanna et al., 2007; Søberg et al., 2019). While total concentrations of metals such as Pb, Cu and Zn have been reported to be significantly reduced by bioretention systems, removal of dissolved metals has been reported as being comparably lower, with leaching of Cd, Cu (Lange et al., 2022b) and Pb (Søberg et al., 2017) being observed. Lange et al. (2022)

reported a high percentage of particulate Cu, Pb and Zn (86%, >99% and 72% respectively) in highway runoff, while the speciation of metals such as Cu and Zn shifted towards increased fractions of dissolved metals in the bioretention effluent (Lange et al., 2022b).

Relatively few studies have evaluated the effect of cold climate and de-icing salt on bioretention function for treating metals, as summarised in a review by Kratky et al. (2017). Marsalek (2003) reported an increased potential impact on the environment from road salting (1972–2000). The main concerns with chlorides in stormwater were described as contamination of groundwater, leaching of trace metals, direct and indirect toxic effects, benthic drift, and loss of biodiversity. Furthermore, Marsalek (2003) concluded that associated environmental risks need to be reduced through chloride source control, and prevention of chloride accumulation by appropriate design for, and operation of, stormwater facilities in winter months. Elevated salinity can negatively impact stormwater treatment by reducing the ability to capture pollutants through alteration of the stability of suspended particles. Sodium chloride (NaCl) is the most common road de-icing agent (Antonson et al., 2021; Fischel, 2001; Shi et al., 2013). Further, concentration of fine particles (< 10 μm) increases under the influence of salts due to attraction of ions to the particle surface, resulting in induced repulsive forces that could prevent coagulation (Behbahani et al., 2021). Higher salinity also results in increased desorption of exchangeable Cr, Cu, Zn and Pb, likely due to cation exchange and formation of aqueous metal complexes (Behbahani et al., 2021).

Paus et al. (2014) carried out a study of temperature and NaCl impact on metal retention in bioretention columns. The study reported an effective capture of Cd and Zn, reduced removal of particulate Cu at lower temperatures, and noted that NaCl caused already accumulated metals to leach (Cd>Zn>Cu). This observation was explained by the effect of salt on the distribution of metals towards the dissolved phase, thus increasing dissolved metal outflow and/or release of accumulated metals from the filter material (Paus et al., 2014). Also, in a laboratory study of temperature and salt influence on metal removal in bioretention, Søberg et al. (2014) detected significant removal of dissolved Zn and Cd (> 90%), while removal of dissolved Cu and Pb was less efficient (−1345% to 71%), particularly in the presence of salt which increased metal mobilization. Further, Søberg et al. (2017) reported that salt had a significant effect on increasing metal concentrations in stormwater, while only a significant decreasing effect on

Cd accumulation in the top layer filter material. Géhéniau et al. (2015) reported that, in a case study of rain gardens, there were significantly increased effluent chloride concentrations during the cold season due to use of de-icing salts. Further, Géhéniau et al. (2015) observed effective removal of Pb and Zn and no removal of Cu and Ni (for which concentrations were sometimes higher in the outlet than the inlet); however Zn removal was greater in the warm season. In a field study of metal treatment in a bioretention system, Lange et al. (2022b) observed that total metals were efficiently removed while there was less effective removal of dissolved metals. Lange et al. (2022b) recommended future research should focus on the bioretention treatment of dissolved and truly dissolved metals, and more field experiments including road salt application.

In previous research, bioretention has mainly been studied in temperate or warm climates and, thus, data relating to cold climates and/or under winter are still limited. There have been few studies, especially field studies, that have evaluated the effect that de-icing salt has on bioretention function for treating metals (Kratky et al., 2017). In a laboratory study assessing low temperature in bioretention cells, Søberg et al. (2017) addressed the need for further studies on the effects of road salt on stormwater runoff and metal treatment in bioretention cells. Also, Géhéniau et al. (2015) in a case study of rain gardens in cold climates, addressed the need for further investigation of the fate of metals (Cu, Ni, and Zn). Previous studies on the effect of vegetation have mainly focused on TSS, metal, and nutrient removal (Dagenais et al., 2018), while not including the impact of cold climate and influence from de-icing salt. Muerdter et al. (2018) identified the need for future research into the impact of bioretention vegetation on treating pollutants including metals, and the potential synergy between vegetation and various novel filter media. There have been very few studies on the effect of chalk additives in bioretention media and impact of vegetation.

Thus, we carried out a comprehensive study of total and dissolved metal (Cd, Cr, Cu, Ni, Pb and Zn) treatment in a bioretention system, used for management of road runoff from the European highway E4 in Sweden. The study includes three different filter configurations (a sand filter, a vegetated sand filter and a vegetated sand filter with chalk additive).

2 Method

2.1 Sampling site

The field study was carried out on a bioretention facility treating highway runoff from a bridge and associated traffic areas located along the European highway E4 in Sweden. The catchment area for the bioretention facility was 8.2 ha and consisted of 4.7 ha of hard surfaces (with the bridge accounting for 1.9 ha) and 3.5 ha of green areas. The E4 highway bridge had an average traffic load of 13,000 vehicles/day. The highway is located in an area with a continental subarctic climate (Köppen climate zone Dfb). The bioretention facility was designed according to the German guidelines for biofilters for treatment of stormwater from motorways (DWA, 2005). The site (bioretention and highway) was put into operation in the fall of 2018, and was between 2–4 years old at the time of sampling.

During precipitation or snowmelt, the stormwater (SW) is conveyed from the bridge through a 100 m long stormwater pipe (d=800 mm) to the plant. The system (Figure 1) consists of a Gross Pollutant Trap Tank (GPT) followed by three parallel filters, a biofilter (BF), a sand filter (SF) and biofilter with chalk additive (BFC). In the GPT, the water passes through a sand trap to separate out coarser particles (also including an oil separation filter) and a distribution tank, before being discharged to the three parallel filters. The approximate area of each filter section is 230 m^2. The water is spread over the filter surface using a spreader pipe. The sand-based filter material has a depth of 0.5 m. and is placed over an underdrain which discharges the treated water to a sampling manhole and then to the receiving water body. The filter material in BFC contains 10% (weight) $CaCO_3$ as a pH buffer (Lange et al., 2021), as recommended by DWA (2005). The BFC and BF filters have a vegetation layer planted in a 3–4 cm topsoil layer. The sand filter SF is not vegetated.

In previous research, the same treatment facility has been investigated for removal and intra-event variations of total, dissolved and truly dissolved metal concentrations (Lange et al., 2022b) as well as for the removal of microplastics (Lange et al., 2021 and Lange et al., 2022a) and organic micropollutants (Beryani et al., 2023).

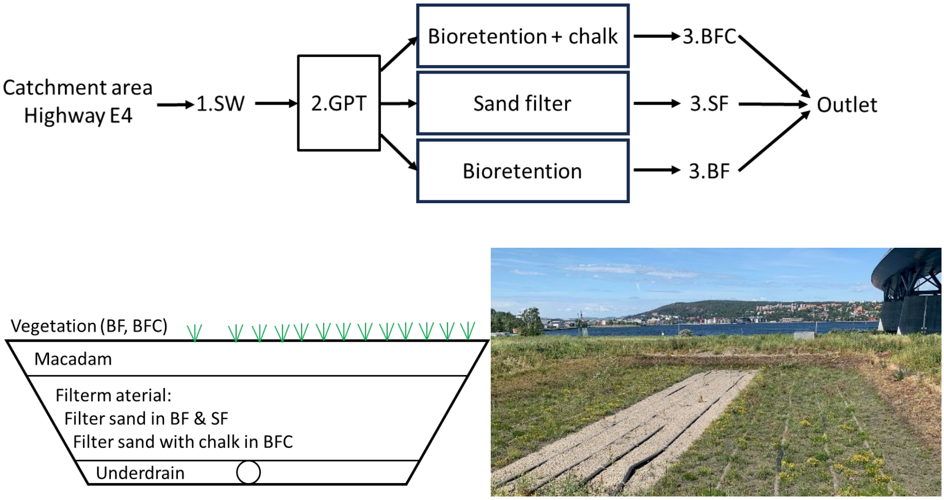

Figure 1. Schematic of studied bioretention facility and filter configuration from catchment area (Highway E4) to outlet (Baltic Sea). Numbers with name indicate sampling locations i.e. 1.SW incoming stormwater, 2.GPT sampled by outlet from GPT tank, 3.BFC, 3.SF and 3.BF is the location of sampling points after the three parallel filters. To the lower right there is a picture of the three filters, 3.BFC to the right, 3.SF in the middle, and 3.BF to the right.

2.2 Sampling

In total, water was sampled at the five different sampling points SW, GPT, BFC, BF and SF (locations in Figure. 1).

- 1.SW: Sampling location for incoming untreated stormwater (SW) from the catchment area.
- 2.GPT: Sampling location by outlets of GPT before entering the three parallel filters.
- 3.BFC: Sampling location after treatment in BFC, a vegetated bioretention filter with filter sand and chalk additives.
- 3.BF: Sampling location after treatment in BF, a vegetated bioretention filter with filter sand.
- 3.SF: Sampling after treatment in SF, a non-vegetated sand filter.

Sampling of 12 rain events with varying characteristics (Table 1) took place between autumn 2020 and spring/summer 2022. All water samples were collected volume proportionally using automatic samplers (ISCO6712). For the first six rain events (A–F), each sampler was equipped with 24 acid washed plastic bottles. Sub-samples were collected and analysed separately for these rain events (Lange et al., 2022b). Event mean concentrations were calculated based on that data. For rain events G–L, composite water samples were taken. The volume proportional sampling at SW and GPT was controlled by valves in the GPT opening when the water reached a maximum level. These pulses were also logged and used for calculations of inflow and outflow to/from the GPT. The samplers downstream of the filters (BFC, BF and SF) were controlled by in-pipe electromagnetic flowmeters installed in the outflow pipes of the bioretention systems (MAG 5100 Siemens AG, München, Germany). Rain characteristics (Table 1) were determined using a tipping bucket rain gauge (ISCO 674) installed next to the treatment facility. For rain event C, precipitation data from a local weather station (0.2 km away) were used, due to technical problems with the rain gauge on site.

Table 1. Precipitation data with stormwater chloride concentrations for 12 precipitation events (A–L), sampling date, event duration, event total precipitation, highest measured rain intensity, antecedent dry days (ADD) and precipitation day before sampling. *Indicates precipitation event with higher chloride concentration in Tables 2 and 3. **Warm weather season ***Days without rain i.e. without rainfall runoff, however period includes snowmelt of accumulated snow during the period.

Event	Date	Duration [hr]	Total precipitation [mm]	Max. intensity [mm/min]	ADD [days]	Precipitation day before [mm]	**Cl^-** in SW [mg/l]
A	2020-09-17	8	6.4	1.4	3	0	9.65
B	2020-09-29	11	31	6.3	8	0	3.18
C	2020-10-07	9	13	≥1.8	7	0	4.70
D	2020-10-26	7	3	0.6	0	17	37.4
E	2020-11-05	22	18	4.7	0	1	21.8
F*	2020-12-07	34	7.6	1.0	8	0	1380

G	2021-10-28	5	6	1.2	7	0	86.8
H	2021-11-04	12	5	12.1	2	0	33.9
I*	2021-12-13	33	15	26	17	0	2390
J*	2022-01-14	<48	<35	Snowmelt	22***	0	3330
K*	2022-06-01**	13	30	90	1	1	210
L	2022-06-20**	7	4	18	1	0	47.8

2.3 Chemical analyses

All samples were analysed for total and dissolved concentrations of Cd, Cr, Cu, Ni, Pb, and Zn. Also, for each sample concentration of chloride (Cl$^-$), total organic carbon (TOC), dissolved organic carbon (DOC), total suspended solids (TSS), and pH were determined.

Total metal analyses samples were pretreated with nitric acid and autoclaved according to Swedish standard SS 28150 (SS, 1993). Samples were analysed using inductively coupled plasma-sector field mass spectrometry ICP-SFMS according to Swedish standard SS-EN ISO 17294-2:2016 (SS-EN ISO, 2016) and U.S. EPA Method 200.8:1994 (US EPA, 1983). Limits of quantification (LOQ) for total metal analysis were, for Cd 0.05 µg/L, Pb 0.5 µg/L, Cu 1 µg/L and Zn 4 µg/L. For dissolved fractions, sub-samples were first filtered according to SS-EN ISO 5667-3:2018 (SS-EN ISO, 2018), before being acidified (1 ml HNO_3/100 ml). Analysis of dissolved metals was carried out using ICP-SFMS, following SS-EN ISO 17294-2:2016 (SS-EN ISO, 2016) and US EPA Method 200.8:1994 (US EPA, 1983). LOQs for analysis of dissolved metals were, for Cd 0.002 µg/L, Pb 0.01 µg/L, Cu 0.1 µg/L and Zn 0.2 µg/L. Chlorides were measured using ion chromatography according to method CSN EN ISO10304-1 (CSN-EN ISO, 2009) and CSN EN 16192 (CSN EN, 2012). TOC and DOC were determined with IR detection based on CSN EN 1484 (CSN EN, 1998), CSN EN 16192 (CSN EN, 2012) and SM 5310 (SM, 1998). TSS were determined by filtration with 1.6 µm filters using method SS-EN 872-2:2005 (SS-EN, 2005). pH was measured on site using the handheld WTW pH 330 (WTW GmbH, Weilheim, Germany).

For each sampling event, as a quality control, a blank sample was also analysed. Analyses of metal content was carried out by a laboratory accredited by the Swedish Board for Accreditation and

Conformity Assessment (SWEDAC). Further description of sampling procedures and sampling can be found in Lange et al. (2022b), section S2.

2.4 Statistical analysis

To interpret the data, Minitab® 20.4 software was mainly used. 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 non-parametric Kruskal-Wallis test was used for determination of whether there were any statistically significant differences (significance level for $\alpha=0.05$) between median concentrations in different stages of the treatment process (SW, GPT, BFC, BF and SF). The pairwise spearman correlation test was used for testing the statistical significance of correlation between chloride and metal concentrations. Concentrations of metals and chlorides were also examined using principal components analysis (PCA), using SIMCA 17 software for visualization of the main characteristics and correlations of the analysis results. The PCA included concentrations from the laboratory analysis with the parameters total organic carbon (TOC), dissolved organic carbon (DOC), total suspended solids (TSS), pH, total rain intensity (mm/rain) (Tot-i) and maximum rain intensity (mm/min). The model in Simca was UV-scaled.

3 Results and Discussion

3.1 Concentrations

All analysed metals were detected in all sampled rain events. Precipitation data are presented in Table 1, and data for chloride influence, total and dissolved metal concentrations for the different components (SW, GPT, BFC, BF and SF) of the stormwater treatment system are presented as descriptive statistics in Table 2, and as boxplots in Figures 3 and 4. Compared to a major literature study of road and highway runoff (Göbel et al., 2007), concentrations of Cd and Pb were generally lower, Ni was within the same range or lower, while Cr, Cu, and Zn had higher maximum and lower minimum concentrations. Compared to Davis and Birch (2010), our study had similar levels of Cu, generally lower concentrations of Pb and similar or higher concentrations of Zn. Thus, in general, the concentrations of Cd, Cr, Cu, Ni, Pb and Zn in this study were in comparable ranges as in previous studies of highway runoff. Consequently, the treated water represents a commonly occurring highway runoff.

During warmer weather (April–September), the Cl^- concentrations were low and did not vary much between four rain events (Table 1). During the winter runoff events (October–March), Cl^- concentrations increased considerably and varied a good deal between the eight different rain events (Fig. 2). For further investigation of the impact of road salt, the runoff events were grouped into “low-salt” events (Table 1) with Cl^- concentrations ≤ 98.2 mg/L (left panel in Fig 2) and “road-salt-impact” events (Table 1) with Cl^- concentrations increasing that value (right panel in Fig. 2). The 98.2 mg/L was the highest chloride concentration in the “low-salt” events group (ranging 9.65–98.2), and 210 mg/L was the lowest chloride concentration in the “road-salt-impact” group (210–3330 mg/L), (Figure 2 and Supplementary material Table S3.1).

Table 2. Descriptive statistics for all metals in all components of the studied stormwater treatment system. All mean metal concentrations are in µg/l, mean concentrations of Cl⁻, TOC, DOC, TSS are in mg/l and Removal is in %.

Substance		Cl⁻	1.SW	2.GPT		3.BFC		3.BF		3.SF	
			Mean	Mean	Removal	Mean	Removal	Mean	Removal	Mean	Removal
Cd	Tot	≤98.2	0.10 ± 0.08	0.11 ± 0.12	-5.56 ± 20.2	0.05 ± 0.00	30.9 ± 28.8	0.06 ± 0.03	23.6 ± 83.9	0.07 ± 0.04	13.9 ± 25.5
		>210	0.15 ± 0.04	0.11 ± 0.04	26.1 ± 19.1	0.10 ± 0.06	20.3 ± 63.3	0.11 ± 0.06	68.1 ± *	0.13 ± 0.05	-8.5 ± 59.8
	Diss.	≤98.2	0.02 ± 0.01	0.01 ± 0.01	15.3 ± 36.0	0.01 ± 0.00	25.7 ± 53.4	0.03 ± 0.04	-286 ± 90.5	0.02 ± 0.01	-25.8 ± 56.1
		>210	0.05 ± 0.03	0.05 ± 0.02	4.70 ± 25.5	0.09 ± 0.08	-53.9 ± 97.0	0.10 ± 0.07	-123 ± *	0.11 ± 0.05	-99.0 ± 26.5
Cr	Tot	≤98.2	25.4 ± 36.1	29.9 ± 48.7	-3.72 ± 17.9	1.59 ± 1.03	84.1 ± 17.1	1.37 ± 0.72	96.7 ± 1.54	11.9 ± 17.5	45.2 ± 9.8
		>210	31.5 ± 28.8	29.0 ± 15.8	-14.5 ± 33.6	1.31 ± 0.82	94.4 ± 3.03	1.13 ± 0.32	98.1 ± *	8.01 ± 4.79	58.2 ± 18.5
	Diss.	≤98.2	1.48 ± 1.20	1.35 ± 1.16	12.1 ± 10.7	0.79 ± 0.68	41.9 ± 36.2	0.75 ± 0.57	-13.8 ± 140	1.09 ± 0.90	26.7 ± 7.48
		>210	0.76 ± 0.73	0.65 ± 0.59	17.6 ± 20.2	0.43 ± 0.24	14.9 ± 52.6	0.55 ± 0.52	48.2 ± *	0.53 ± 0.41	16.5 ± 33.0
Cu	Tot	≤98.2	51.8 ± 54.3	56.3 ± 75.2	4.21 ± 18.3	7.63 ± 6.74	81.3 ± 11.8	13.0 ± 14.6	79.6 ± 1.34	27.0 ± 32.9	31.7 ± 11.3
		>210	63.1 ± 48.6	58.7 ± 29.3	-4.10 ± 22.6	13.0 ± 9.02	77.2 ± 10.0	20.6 ± 21.7	73.4 ± *	27.5 ± 18.5	43.5 ± 15.3
	Diss.	≤98.2	5.38 ± 1.11	4.93 ± 0.86	6.58 ± 14.5	5.45 ± 5.59	4.90 ± 78.8	11.1 ± 13.3	-207 ± 302	5.84 ± 2.19	-18.1 ± 23.8
		>210	9.73 ± 4.95	9.82 ± 6.82	4.26 ± 16.4	10.6 ± 7.61	-2.50 ± 20.6	19.8 ± 20.8	-105 ± *	10.3 ± 6.86	-3.5 ± 15.0
Ni	Tot	≤98.2	12.7 ± 16.6	14.9 ± 22.8	-6.52 ± 26.4	1.03 ± 0.58	78.2 ± 22.8	1.72 ± 0.96	86.3 ± 12.3	6.30 ± 8.29	31.6 ± 21.8
		>210	18.6 ± 14.2	16.4 ± 7.22	-3.00 ± 31.0	2.12 ± 0.89	84.3 ± 10.8	3.90 ± 1.28	92.4 ± *	7.73 ± 2.31	34.7 ± 34.2
	Diss.	≤98.2	1.16 ± 0.75	1.11 ± 0.69	3.17 ± 8.99	0.47 ± 0.33	56.4 ± 17.3	1.70 ± 0.87	-42.0 ± 96.8	1.20 ± 0.75	-4.91 ± 7.46
		>210	3.21 ± 1.11	3.00 ± 1.13	7.78 ± 9.19	1.58 ± 0.58	49.7 ± 13.2	4.17 ± 2.23	33.8 ± *	3.57 ± 0.35	-0.52 ± 17.2

Pb	Tot	≤98.2	9.04 ± 11.6	10.7 ± 17.0	-0.95 ± 21.9	6.41 ± 15.7	-66.0 ± 406	0.90 ± 0.72	93.1 ± 1.34	5.25 ± 7.05	23.7 ± 21.0
		>210	12.1 ± 11.6	11.4 ± 6.82	-19.8 ± 35.6	0.90 ± 0.80	90.9 ± 4.29	1.02 ± 0.7	94.7 ± *	4.51 ± 3.87	42.7 ± 20.2
	Diss.	≤98.2	0.09 ± 0.10	0.07 ± 0.07	21.7 ± 19.8	0.10 ± 0.17	-5.20 ± 66.9	0.30 ± 0.50	-258 ± 3.37	0.12 ± 0.22	-17.0 ± 67.4
		>210	0.07 ± 0.10	0.09 ± 0.15	-3.40 ± 28.8	0.16 ± 0.12	-476 ± 445	0.43 ± 0.48	-253 ± *	0.10 ± 0.17	-36.1 ± 47.1
Zn	Tot	≤98.2	429 ± 368	498 ± 570	-4.28 ± 17.2	24.0 ± 19.2	94.1 ± 2.07	106 ± 102	62.9 ± 39.4	272 ± 270	21.4 ± 19.8
		>210	671 ± 601	609 ± 352	-5.80 ± 25.4	150 ± 99.3	63.1 ± 35.2	202 ± 98.3	82.7 ± *	412 ± 155	-2.00 ± 61.0
	Diss.	≤98.2	80.2 ± 49.2	81.5 ± 56.5	4.86 ± 23.9	14.9 ± 10.1	68.2 ± 34.2	97.4 ± 104	-337 ± 90.6	78.0 ± 47.1	-40.4 ± 52.7
		>210	99.5 ± 38.6	106 ± 44.9	-5.90 ± 24.6	116 ± 87.0	-11.8 ± 76.8	174 ± 73.5	-111 ± *	205 ± 98.0	-96.1 ± 59.9
TOC		≤98.2	20.9 ± 48.6	25.6 ± 61.6	-4.23 ± 14.5	4.11 ± 5.31	40.0 ± 35.1	12.0 ± 14.2	74.1 ± 14.5	21.4 ± 33.5	23.2 ± 17.6
		>210	35.0 ± 38.2	28.7 ± 25.7	10.6 ± 24.7	9.24 ± 10.2	72.7 ± 5.01	21.7 ± *	76.3 ± *	14.7 ± 7.18	55.2 ± 17.9
DOC		≤98.2	4.78 ± 2.94	4.64 ± 2.81	3.07 ± 9.69	4.04 ± 4.85	28.7 ± 35.5	11.3 ± 13.4	-13.7 ± 112	6.63 ± 4.28	6.31 ± 15.7
		>210	9.91 ± 4.23	11.4 ± 9.02	-6.10 ± 36.4	9.03 ± 9.89	21.0 ± 52.0	0.73 ± *	95.4 ± *	9.29 ± 4.91	10.7 ± 6.81
TSS		≤98.2	215 ± 364	244 ± 470	-6.30 ± 30.0	12.3 ± 18.4	47.1 ± 128	11.0 ± *	99.0 ± *	199 ± 263	30.3 ± 39.8
		>210	359 ± 358	303 ± 189	-11.1 ± 38.2	4.42 ± 4.39	98.5 ± 0.70	4.00 ± *	99.5 ± *	79.3 ± 45.2	62.8 ± 19.4
pH		≤98.2	7.20 ± 0.27	7.20 ± 0.27	0.00 ± 0.00	7.97 ± 0.15	-10.7 ± 3.74	7.45 ± 0.07	-4.20 ± *	7.20 ± 0.20	-0.03 ± 1.35
		>210	7.63 ± 0.25	7.60 ± 0.20	0.43 ± 0.75	7.70 ± 0.46	-1.07 ± 9.25	7.60 ± *	-2.70 ± *	7.50 ± 0.10	1.67 ± 3.98

3.2 Influence of chlorides

Chlorides in the sampled stormwater varied between different rain events and over time (Figure 2 and supplementary material Figure S1.1), mainly due to use of road salts (e.g. NaCl) during winter road maintenance. Previous studies have found chloride concentrations to be less in warmer regions than in the colder (northern) regions during winter, and that chloride loads observed in urban areas were significantly larger than those of rural areas (Beom et al., 2021; Gavrić et al., 2021; Marsalek, 2003). In our study, we observed that both total and dissolved metal concentrations varied over time, similar to the variation in chloride concentrations. This pattern of variations in chloride and metal concentrations show a positive correlation (Figures 2, 3 and 4) for all total metal concentrations and dissolved Cd, Ni and Zn concentrations.

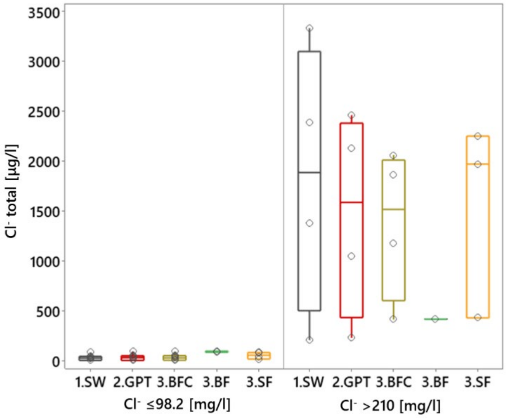

Figure 2. Chloride concentrations for all rain events in SW, GPT, BF and SF for low chloride concentrations ($Cl^- \leq 98.2$ mg/l) and high chloride concentrations ($Cl^- > 210$ mg/l).

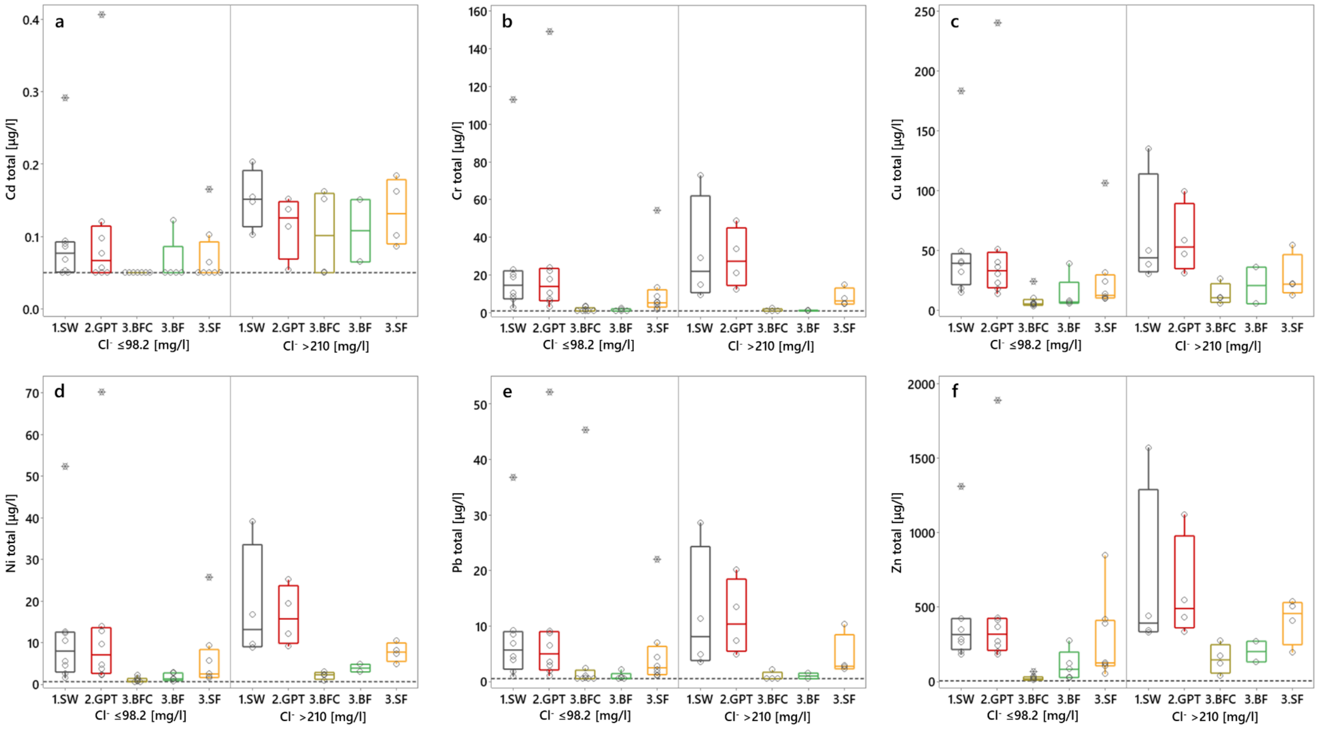

Figure 3. Total metal concentrations for low chloride concentrations ($Cl^{-}\leq 98.2$ mg/l) and high chloride concentrations ($Cl^{-}>210$ mg/l) for all stages in studied bioretention test site. The letters (a–f) in the graphs are for reference in the text.

The pairwise spearman correlation test was used to test the statistical significance of correlation between chloride concentration metal concentrations (Table 3). Statistical significance ($p<0.05$) was identified in BFC for total Zn and for total Cd ($p=0.053$ and $\rho = 0.57$) a correlation was observed. Statistical significance was also identified in BFC for dissolved Pb and Zn, and in SF for dissolved Cd, Ni and Zn. This was also confirmed with a PCA (Figure 5b, second component in the score plot). Previous studies using laboratory tests by Nelson et al. (2006) found an indication that road salts affect metal mobility (e.g. Cu and Cd) in soil with release of metals and organic matter when exposed to salt solutions. McManus and Davis (2020) noted removal of metals (Cu and Zn) in a bioretention mesocosm study of NaCl influence.

Table 3. Pairwise Spearman correlation between Cl^- and total and dissolved metals. The Spearman's rank correlation coefficient (ρ) assesses how well the correlation between metals and Cl^- is described by the monotonic function. *Indicates no data due to too few samples i.e. for BF. **Indicates significant negative correlation for dissolved Cr.

Variable vs Cl^-		Type	N	Correlation ρ	95% CI for ρ	P Value
Cd	Tot	SW	12	0.715	(0.163; 0.926)	0.009
		GPT	12	0.592	(-0.028; 0.883)	0.043
		BFC	12	0.57	(-0.057; 0.874)	0.053
		BF	3	0.5	(*; *)	0.667
		SF	7	0.607	(-0.347; 0.944)	0.148
	Diss	SW	12	0.734	(0.199; 0.932)	0.007
		GPT	12	0.874	(0.524; 0.972)	0
		BFC	12	0.93	(0.705; 0.985)	0
		BF	3	0.5	(*; *)	0.667
		SF	7	0.964	(0.674; 0.997)	0
Cr	Tot	SW	12	0.385	(-0.265; 0.794)	0.217
		GPT	12	0.483	(-0.163; 0.839)	0.112
		BFC	12	-0.398	(-0.800; 0.252)	0.2
		BF	3	-0.5	(*; *)	0.667

		SF	7	-0.071	(-0.783; 0.721)	0.879
	Diss	SW	12	-0.706	(-0.923; -0.148)	0.01**
		GPT	12	-0.664	(-0.909; -0.079)	0.018**
		BFC	12	-0.469	(-0.833; 0.178)	0.124
		BF	3	-0.5	(*; *)	0.667
		SF	7	-0.107	(-0.797; 0.704)	0.819
Cu	Tot	SW	12	0.301	(-0.343; 0.752)	0.342
		GPT	12	0.545	(-0.088; 0.865)	0.067
		BFC	12	0.399	(-0.251; 0.801)	0.199
		BF	3	-0.5	(*; *)	0.667
		SF	7	-0.071	(-0.783; 0.721)	0.879
	Diss	SW	12	0.469	(-0.178; 0.833)	0.124
		GPT	12	0.455	(-0.193; 0.826)	0.138
		BFC	12	0.573	(-0.052; 0.876)	0.051
		BF	3	-0.5	(*; *)	0.667
		SF	7	0	(-0.753; 0.753)	1
Ni	Tot	SW	12	0.497	(-0.147; 0.845)	0.101
		GPT	12	0.524	(-0.114; 0.856)	0.08
		BFC	12	0.368	(-0.281; 0.786)	0.24
		BF	3	1	(*; *)	*
		SF	7	0.107	(-0.704; 0.797)	0.819
	Diss	SW	12	0.874	(0.524; 0.972)	0
		GPT	12	0.804	(0.344; 0.953)	0.002
		BFC	12	0.867	(0.504; 0.970)	0
		BF	3	0.5	(*; *)	0.667
		SF	7	0.893	(0.270; 0.989)	0.007
Pb	Tot	SW	12	0.378	(-0.272; 0.791)	0.226
		GPT	12	0.524	(-0.114; 0.856)	0.08
		BFC	12	-0.405	(-0.804; 0.244)	0.191
		BF	3	-0.5	(*; *)	0.667
		SF	7	-0.071	(-0.783; 0.721)	0.879
	Diss	SW	12	-0.566	(-0.873; 0.061)	0.055
		GPT	12	-0.545	(-0.865; 0.088)	0.067

		BFC	12	0.846	(0.447; 0.964)	0.001
		BF	3	-0.5	(*; *)	0.667
		SF	7	-0.393	(-0.892; 0.538)	0.383
Zn	Tot	SW	12	0.566	(-0.061; 0.873)	0.055
		GPT	12	0.65	(0.057; 0.904)	0.022
		BFC	12	0.916	(0.656; 0.982)	0
		BF	3	0.5	(*; *)	0.667
		SF	7	0.321	(-0.586; 0.871)	0.482
	Diss	SW	12	-0.126	(-0.654; 0.485)	0.697
		GPT	12	-0.042	(-0.602; 0.545)	0.897
		BFC	12	0.972	(0.870; 0.994)	0
		BF	3	0.5	(*; *)	0.667
		SF	7	0.821	(0.028; 0.980)	0.023
TOC		SW	12	0.699	(0.136; 0.921)	0.011
		GPT	12	0.65	(0.057; 0.904)	0.022
		BFC	12	0.364	(-0.285; 0.784)	0.245
		BF	3	-0.5	(*; *)	0.667
		SF	7	0.286	(-0.608; 0.860)	0.535
DOC		SW	12	0.566	(-0.061; 0.873)	0.055
		GPT	12	0.552	(-0.079; 0.868)	0.063
		BFC	12	0.322	(-0.324; 0.763)	0.308
		BF	3	-1	(*; *)	*
		SF	7	0.214	(-0.649; 0.836)	0.645
TS		SW	12	0.643	(0.046; 0.902)	0.024
		GPT	12	0.678	(0.101; 0.914)	0.015
		BFC	12	-0.324	(-0.764; 0.322)	0.304
		BF	2	-1	(*; *)	*
		SF	7	-0.071	(-0.783; 0.721)	0.879
pH		SW	6	0.6	(-0.490; 0.958)	0.208
		GPT	6	0.6	(-0.490; 0.958)	0.208
		BFC	6	-0.429	(-0.928; 0.620)	0.397
		BF	3	1	(*; *)	*
		SF	6	0.493	(-0.577; 0.940)	0.321

For treatment by the filters, the total concentrations presented in the boxplots in Figure 3a–f show there are similar concentrations of Cr, Cu, Ni, Pb and Zn, while Cd shows a different behaviour. This trend indicates treatment of incoming stormwater through the filters (BFC, BF and SF) and that treatment is most efficient in the BFC, followed by BF and then SF. Also, there is a trend of concentrations being higher with higher concentrations of chlorides ($Cl^{-}>210$ mg/l). The GPT did not show any significant treatment of incoming stormwater. This is likely since the GPT mix and distribute the stormwater when higher flows, rather than treat through sedimentation. Sediments were observed at the bottom of the tank, however, there is a risk that these sediments can be moved around during further higher intensity rain events. If sediments were to be removed between rainfall events, there may be a treatment effect by the sedimentation processes in the GPT. The GPT is also further discussed in Lange et al. (2022b).

For total median Cd concentrations, there is a significant difference (Kruskal-Wallis test, $p<0.05$) between SW, GPT and the three filters (BFC, BF and SF). Total Cd concentrations shown in the boxplot in Figure 3a are higher with higher chloride concentrations. Further, there is an indication of Cd being treated by all three filters (BFC, BF and SF) with lower chloride concentrations ($Cl^{-}\leq 98.2$ mg/l), but only in BFC and BF when chloride concentrations are higher ($Cl^{-}>210$ mg/l). In general, Cd concentrations were already low in the stormwater, compared to values reported by Göbel et al. (2007) and Davis and Birch (2010). Some samples (two in incoming stormwater) were below the detection limit for Cd (DL=0.05). Total Cu concentrations were significantly lower (Kruskal-Wallis test, $p<0.05$) after all three filters than in incoming SE, both under higher chloride concentrations ($Cl^{-}>210$ mg/l) as well as lower ones ($Cl^{-}\leq 98.2$ mg/l). As illustrated by Figure 3c, this was again particularly clear for the BFC filter, followed by the BF filter, and, less efficiently in SF. There is also a pattern of higher median Cu concentration in all system parts (SW, GPT, BFC, BF and SF) when salt is present; however, this is not statistically significant. Total Pb concentrations show significant differences (Kruskal-Wallis test, $p<0.05$) between median concentrations and treatment of stormwater after the filters, again mainly for BFC and BF, while less so for SF. Also, for Pb, there is a trend of higher concentrations of Pb with increasing concentrations of chlorides. The median total concentrations of Zn show that there are significant differences (Kruskal-Wallis test, $p<0.05$) between different stages in the facility (SW, GPT and filters). Zn in stormwater is treated by all three filters when there are low concentrations of chlorides ($Cl^- \leq 98.2$ mg/l), and for BFC and BF for stormwater with high concentrations of chlorides ($Cl^- > 210$ mg/l). Also, the total median Ni concentrations (Figure 3c) show significant differences between different stages (SW, GPT and filters). Ni is treated by filters both with low chloride concentrations ($Cl^- \leq 98.2$ mg/l) and high chloride concentrations ($Cl^- > 210$ mg/l), less so for SF than BF and BFC (SF>BF>BFC). There is also a general trend that Ni concentrations are higher with higher chloride concentrations ($Cl^- > 210$ mg/l). The Cr concentrations (Figure 3a) in stormwater (SW and GPT) compared to after the filters (BFC, BF and SF) indicate treatment by all three filters, however less so in SF. The median Cr concentrations show a weak trend of being higher under higher chloride concentrations ($Cl^- > 210$ mg/l).

To determine whether differences between median concentrations in the different parts (SW, GPT, BFC, BF and SF) of the bioretention system were statistically significant and under what conditions (high or low chloride concentrations), the Kruskal-Wallis test was used to indicate how the average rank for each group compares to the average rank of all observations (Z values in Table 4). The general observed trend for Z values was that there was good treatment for total concentrations with lower chloride concentrations except for Cr and Pb in SF. Treatment was found to be most efficient in BFC, followed by BF while less efficient or none (Cr and Pb) in SF. For total metals with high chloride concentrations, there is treatment for all metals except Cd in BFC and BF while not in SF. Dissolved metals only show a weak trend for treatment in BFC for Zn with lower chloride concentrations and for Pb with higher chloride concentrations.

Table 4. H values, P values and Z values from Kruskal-Wallis test. Null hypothesis H_0: All medians are equal and Alternative hypothesis H_1: At least one median is different. Cl^- concentration (mg/l).

				Cd		Cr		Cu		Ni		Pb		Zn	
Parameter	Type	Cl⁻	N	Tot.	Diss.	Tot.	Diss.	Tot.	Diss.	Tot.	Diss.	Tot.	Diss.	Tot.	Diss.
H Values	Not adj. for ties		-	22.3	33.3	39.0	8.3	30.5	17.8	33.3	35.9	28.0	13.9	34.7	25.8
	Adj. For ties		-	24.1	33.3	39.3	-	30.6	17.8	33.3	36.0	28.2	13.9	-	25.8
P Values	Not adj. for ties		-	0.01	0.00	0.00	0.51	0.00	0.04	0.00	0.00	0.00	0.13	0.00	0.00
	Adj. For ties		-	0.00	0.00	0.00	-	0.00	0.04	0.00	0.00	0.00	0.13	-	0.00
Z Values	SW		8	0.24	-1.34	2.03	1.77	2.08	-0.72	1.42	-1.05	1.50	0.64	1.48	0.02
	GPT		8	0.05	-2.10	2.03	1.17	1.58	-1.48	1.46	-1.23	1.46	-0.31	1.41	-0.17
	BFC	≤98.2	8	-3.06	-2.91	-3.06	-0.41	-3.68	-2.72	-3.99	-3.93	-2.27	-0.29	-4.34	-4.13
	BF		5	-1.46	0.50	-2.63	-0.20	-1.82	0.40	-2.02	0.44	-2.31	1.35	-1.84	-0.35
	SF		8	-1.11	-1.10	0.29	0.62	-0.49	-0.25	-0.36	-0.81	0.24	-0.41	-0.36	-0.14
	SW		4	2.32	1.85	2.11	-0.49	1.91	1.65	2.20	2.43	1.85	-1.35	1.91	0.68
	GPT		4	1.39	1.72	2.33	-0.62	2.20	1.26	2.30	2.01	2.17	-1.51	2.30	0.96
	BFC	>210	4	0.66	1.99	-2.46	-1.46	-1.38	1.52	-1.39	0.52	-2.35	1.88	-1.10	0.94
	BF		2	0.81	1.80	-1.66	-0.67	-0.49	0.94	0.04	1.80	-1.42	1.75	-0.27	1.66
	SF		4	1.93	2.71	0.39	-1.00	0.32	1.46	1.09	2.79	0.65	-1.30	1.59	2.61

The general trend for removal of total metals is also reflected by the removal percentages which exceed 78% in BFC without salt (Cr, Cu, Ni and Zn) and 79% in BF (Cr, Cu, Ni and Pb), which being significantly lower for SF (Table 2). Also, for the high salt concentration events, removals are higher in BFC and BF, exceeding 77% (Cr, Cu, Ni and Pb), than in SF.

Dissolved metal concentrations (presented in boxplots in Figure 4a–f) differ compared to the total concentrations. While total metal concentrations show treatment by all filters (BFC, BF and SF), dissolved metal concentrations show no significant (Kruskal-Wallis test, $p<0.05$) treatment by the filters. However, the dissolved metal concentrations (Cd, Cu, Ni, Pb and Zn) also have higher concentrations when chloride concentrations are higher ($Cl^{-}>210$ mg/l) except for Cr concentrations that decrease with higher chloride concentrations. The increased concentrations through the filter material (BFC, BF and SF) under higher chloride concentrations could indicate that there is a release of metals previously accumulated by the filter material. Dissolved Cd concentration (Figure 4a) shows no significant treatment (Kruskal-Wallis test, $p<0.05$) of incoming stormwater under low chloride concentrations ($Cl^{-} \leq 98.2$ mg/l). However, there is a significant difference for Cd concentrations which are higher with higher chloride concentrations ($Cl^{-}>210$ mg/l). There is also a clear trend of increased Cd concentrations through all three filters (BFC, BF and SF) with higher chloride concentrations. For dissolved Cu, there is no observed treatment of stormwater by any of the filters (BFC, BF and SF) and an increased concentration through BF. Boxplots (Figure 4c) show a trend of higher concentrations under higher chloride concentrations ($Cl^{-}>210$ mg/l) than with lower ones ($Cl^{-}\leq 98.2$ mg/l), particularly in BFC which removed dissolved metals comparably well when no road salt was present, but not at all when there was. Median Cu concentration in BF is much higher with higher chloride concentrations than with low. However, due to there being only a few samples from BF with high chloride concentrations, it is difficult to draw any conclusions for the high median value other than it is an outlier. Dissolved Pb concentrations show no significant differences (Kruskal-Wallis test, $p<0.05$) in concentrations between incoming stormwater (SW) and after the filters (BFC, BF and SF). The concentrations where chloride concentrations were low ($Cl^{-}\leq 98.2$ mg/l) all had medians in a similar range (Table 2) in all stages of the treatment facility, which may indicate no treatment at all. The dissolved Pb concentrations were also relatively low (Table 2), close to DL=0.01 mg/l (two samples, one each in SW and in GPT were below the detection limit). For high chloride concentrations ($Cl^- > 210$ mg/l), there is a pattern of release of Pb from the filters, particularly from BFC and BF. These high Pb concentrations under higher chloride concentrations may indicate a release of previously accumulated Pb, as previously shown by Søberg et al. (2017). Boxplots of dissolved Zn concentrations in Figure 4f show higher concentrations with higher chloride concentrations ($Cl^- > 210$ mg/l), particularly after the filters. With lower chloride concentrations ($Cl^- \leq 98.2$ mg/l), BFC appears to treat the stormwater, whereas BF and SF do not. For higher chloride concentrations, the boxplots show that BFC does not treat stormwater, whilst they show a release of Zn from BF and SF The dissolved Ni concentrations indicate treatment of stormwater only by BFC, and not by SF, with an increase in Ni concentration after BF. The concentration of Ni is higher (Kruskal-Wallis test, $p < 0.05$) with higher chloride concentrations ($Cl^- > 210$ mg/l) in all parts of the system (SW, GPT, BFC and SF). Concentrations of dissolved Cr show a large spread in the incoming stormwater as well as the outflow from the filters, particularly under lower chloride concentrations. However, no significant difference between the median concentrations was identified (Kruskal-Wallis test, $p < 0.05$). There is also a tendency for higher median concentrations with lower chloride concentrations ($Cl^- \leq 98.2$ mg/l) in the stormwater, however, it is not statistically significant.

The Kruskal-Wallis test ($p < 0.05$ and Z values, Table 4) confirms observations shown in the boxplots in Figure 4. There is an indication of dissolved concentrations being significantly higher in the stormwater when there are lower chloride concentrations. For example, Z values for Zn in the filters (BFC, BF and SF) are all negative when $Cl^- \leq 98.2$ mg/l, whereas Z values in filters for $Cl^- > 210$ mg/l are all positive. This also indicates that the median concentrations of Zn are higher with higher chloride concentrations as also observed in the boxplots. Further, the test indicates that there is a reduction in Zn concentration, and a smaller reduction in Cr, Cu and Ni concentrations in BFC when there are low chloride concentrations. These effects are less pronounced for BF and SF. When there are high chloride concentrations, there is only a reduction in the concentration of Pb in BFC and BF.

The removal percentages for dissolved metals were mainly negative (Table 2), except for BFC when there were low chloride concentrations. Further, Cd (25.7%), Cu (4.9%) and Zn (68.2%) only showed to have been treated in BFC when there were low chloride concentrations while there was an increase in their concentrations after BF and SF. Further, Cr was removed by FBC (41.9%) and SF (26.7%), and Ni was removed by BFC, while Pb appear not to be removed at all. For high chloride concentrations, only Cr was removed by all three filters (14.9–48%), and Ni by BFC (49.7%) and BF (39.8%). All other concentrations increased after all three filters.

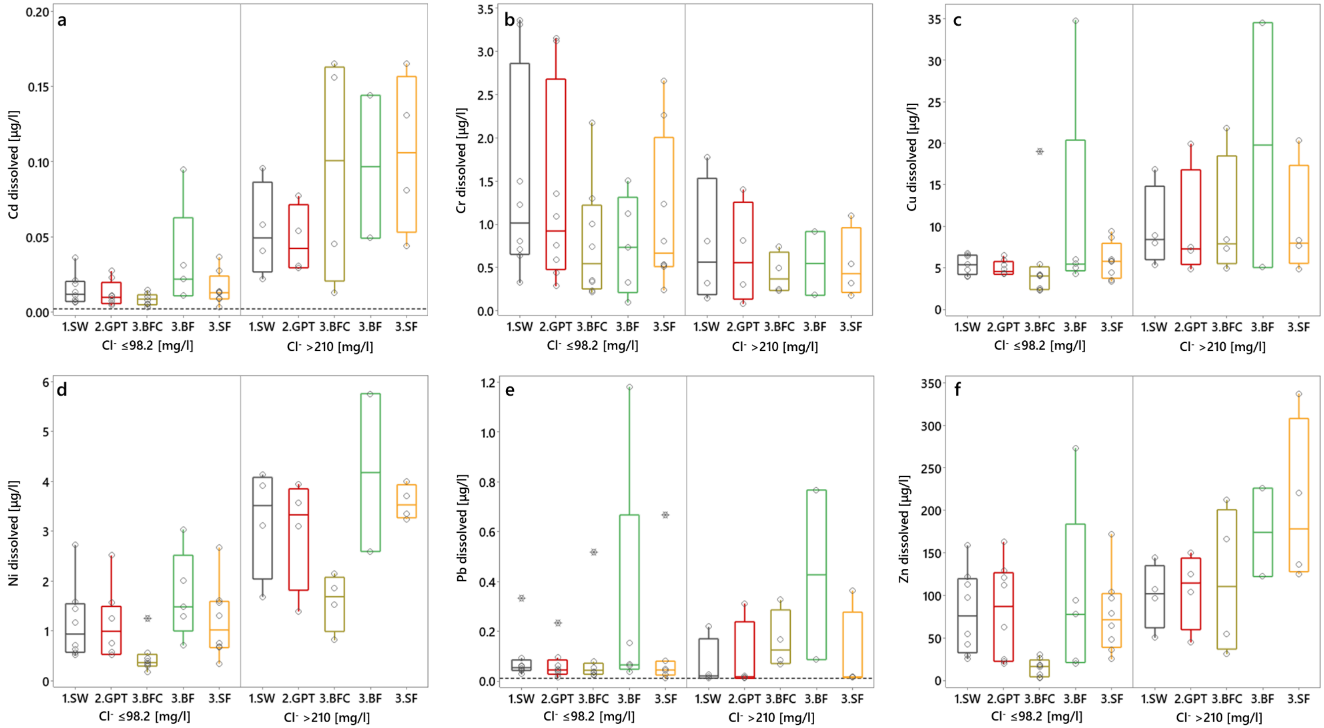

Figure 4. Dissolved metal concentrations for low chloride concentrations ($Cl^{-}\leq 98.2$ mg/l) and high chloride concentrations ($Cl^{-}>210$ mg/l) for all stages in the studied bioretention test site.

3.3 PCA

In the PCA score plot (Figure 5), there are no clear groupings as seen in the loading plot, however rain events K, J and L (Table 1) are partly outside the Hotelling's T2 95% ellipse, indicating outliers due to, for example, high concentrations (Supplementary material Table S3.1, All data table).

In the loading plot, total metal concentrations are grouped to the far right in the first component, while the dissolved metals are more spread out. For total metals, there is a correlation to rain event L in the loading plot. In component 1 (t[1] in Figure 5), the loading plot shows a strong correlation between total metal concentrations, TOC and TSS, indicating the high affinity for organic matter in the particle-bound metals with correlation to total metal concentrations (Alloway, 2013). The dissolved metals show correlation to DOC, which also could indicate affinity for OM (dissolved OM), especially for Cu, Ni and Pb. Cl^- is, in component 2, strongly correlated to dissolved Cd, Ni and Zn while we can see a negative correlation to Cr.

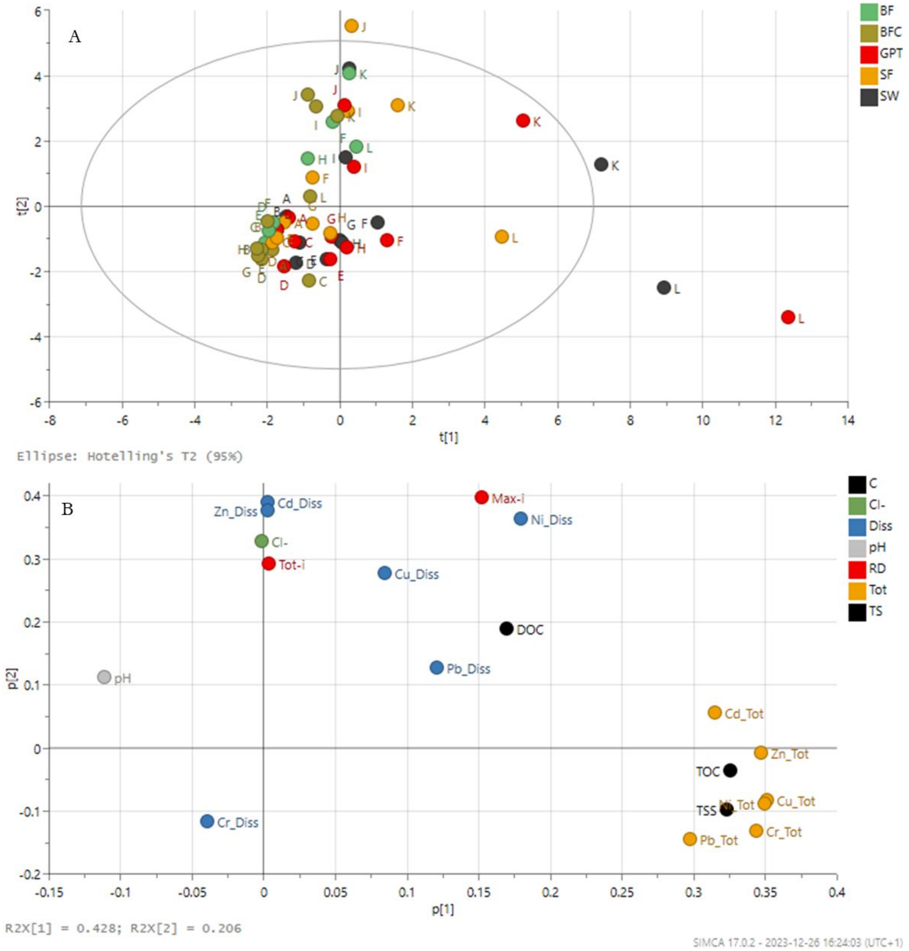

Figure 5. PCA for Total and dissolved concentrations for all sampled rain events in all sections of the treatment facility. Figure 5a shows the score plot with all sampled data coloured for location in the treatment facility. Figure 5b shows Cl^- and metal concentrations, DOC, TOC, TSS, and precipitation data.

4 Discussion

The general observed trend in the studied treatment facility is that all metal concentrations, except dissolved Cr, are higher in all parts of the system (WE, GPT, BFC, BF and SF) when experiencing higher chloride concentrations (Cl^{-}>210 mg/l). For total concentrations, there is significant treatment of all metals when there are low chloride concentrations (Table 2 and Figure 3). Under high chloride concentrations, total Cr, Cu, Ni, Pb and Zn are treated, while Cd only appears to be treated by BFC and BF, and not by SF. Treatment by filters is, generally, better by BFC than BF or SF (treatment: BFC>BF>SF), and best for all filters when there are lower chloride concentrations. Dissolved concentrations of Cd, Cu, Ni, Pb and Zn appear to be more greatly affected by salinity, increasing before and after the filters at higher chloride concentrations. Cr concentrations show a tendency to decrease when there are higher chloride concentrations. The concentrations in some cases increase after the filters to higher concentrations than in SW and GPT under higher chloride concentrations. For Cd, Cr, Cu, Ni and Zn, BFC seems to treat dissolved metals well in lower chloride concentrations, while Cd, Cu, Ni, Pb and Zn concentrations in BF are similar or higher than in SW and GPT. Under higher chloride concentrations, there is a release rather than an accumulation of dissolved Cd, Cu, Ni, Pb and Zn in BF. In BFC, under high chloride concentrations, there is a release of Cd and Pb while levels of Cu and Zn are similar to those in SW and GPT, and only Ni and, to some extent, Cr appear to be treated. SF has concentrations higher in its outlet than inlet for Cd, Ni and Zn, while Cr, Cu and Pb are at similar levels.

Previous studies of bioretention cells have reported mechanical filtration of suspended material as the main treatment process for removal of TSS and particulate metals (Blecken et al., 2009). Laboratory studies have also reported that bioretention cells efficiently remove metals with a mean removal in stormwater often exceeding 85%. Further leaching of dissolved Cu and Pb has been reported as mainly from deeper layers in filter material, and that salt had a statistically significant effect on metal treatment (Søberg et al., 2017). Studies have also shown that treatment of total metals is, in general, more efficient (Blecken et al., 2009; Hatt et al., 2007; Sun and Davis, 2007) than dissolved metal treatment (Hatt et al., 2007; Søberg et al., 2017) and truly dissolved metal treatment (Lange et al., 2020b, 2022b). Studies of chlorides have shown a negative effect on metal removal in bioretention systems. Paus et al. (2014) and

Søberg et al. (2017) found salt caused leaching of metals, while Lange et al. (2020a) found metal removal reduced when salt was added. Kratky et al. (2017) concluded in a review study that de-icing salts can increase salinity and metal solubility in spring runoff, explained by previously trapped metals that leach from the system and increase the dissolved fraction of metals.

An explanation for higher concentrations of Cr, Cu, Pb and Zn under higher chloride concentrations is that chlorides (NaCl, KCl, $MgCl_2$, and $CaCl_2$) can lead to increased desorption of exchangeable Cr, Cu, Pb and Zn, due to cation exchange and formation of aqueous metal complexes (Amrhein et al., 1992; Bäckström et al., 2004; Behbahani et al., 2021; Paus et al., 2014; Søberg et al., 2017). This could also explain the negative effect of salt on metal removal. Further, Lange (2021) studied bioretention and metal treatment and concluded that Cd and Zn (concentration and speciation), in general, are more affected by salt than, for example, Cu and Pb, since Cd and Zn are less strongly associated to minerals and organic matter. This is similar to that shown in the second component of the PCA (Figure 5), where dissolved Cd and Zn are closely associated with Cl^- while dissolved Cu and Pb seem more associated with DOC.

A factor that may explain the better performance of treating dissolved metals in BFC compared to BF and SF could be the chalk additive ($CaCO_3$) in BFC. Chalk could increase pH and decrease concentrations of soluble and extractable metals (Zn, Pb, Ni, Cd, and Cu) (Alloway, 2013; Gray et al., 2006). This would make the fate of metals and associated complexes more stable and rather particle-bound, thus more would accumulate in the filter material. Muthukrishnan and Oleske (2008) used limestone in a laboratory study to increase pH in soil and suggested the use of limestone to improve sorption of metals in bioretention media. Further, the weaker performance by SF compared to BF may be explained by the positive effect from vegetation increasing the treatment performance, as observed by Lange et al. (2020). The difference in outlet concentrations between the filters indicates a difference in treatment effect with different filter materials; however, such differences are not statistically significant. Several samples of stormwater after treatment in the filters were below the detection limit (DL=0.05) so one must be careful not to draw too many conclusions. However, concentrations below the detection limit do not conflict with the apparently reasonable treatment of metals by the filters.

4.1 Practical implications

The metal concentrations were compared to guideline values (Supplementary material Table S2.1) for protection of waters, lakes, and streams. Comparison was made with the Swedish Agency for Marine and Water Management (SwAM) Reports 2016:26 and 2019:25 (SwAM, 2019, 2016, which are the national implementation of the environmental quality criteria for status evaluation within the EU Water Framework Directive), the Swedish target value group 2009 (Jacobs et al., 2009), and target values from the environmental management department of Gothenburg (Landström et al., 2020). In general, the dissolved concentrations were lower than benchmark values for Cd, Cr, Ni and dissolved Pb.

Dissolved Cu concentrations was 10–40 times higher than SwAM threshold values (0.5 µg/l) for bioavailable Cu in SW, GPT and after all three filters (BFC, BF and SF). Dissolved Cd exceeded the threshold values (0.08 µg/l) after all three filters under high chloride concentrations while not in incoming stormwater. Ni exceeded the threshold value (4 µg/l) in BF when there were high chloride concentrations. These guideline values are intended to be applied to bioavailable concentrations (SwAM, 2019, 2016) which prevents a direct comparison. However, a median concentration below the bioavailability limit gives an indication that we are on the safe side of the limit e.g. for all measured Cr, Pb and Zn concentrations. Compared to the guideline threshold values recommended by the Swedish target value group 2009 (Jacobs et al., 2009), dissolved concentrations were all below, and total concentrations of Cr, Cu, Pb and Zn were higher in the stormwater while lower after the filters (BFC, BF and SF). Also, Ni had a higher total concentration than the target value in SW and lower after the filters. The threshold values from the environmental management department of Gothenburg (Landström et al., 2020) were exceeded by total Cu, total and dissolved Zn. However, they were below after treatment in BFC under lower chloride concentrations. Also, total Cr exceeded the threshold values in the SW, but this value was below after treatment by BFC and BF, but not by SF. Dissolved Cu was below the threshold value in stormwater with high chloride concentrations while above after all three filters. There is a general trend indicating treatment of stormwater from above threshold limits to below for total concentrations of all metals, particularly by filters BFC and BF.

The general conclusion from this study is that bioremediation is generally good for treating metals in stormwater, although treatment of dissolved metals is less effective. Biofilters generally have a positive effect over time. Different designs of biofilters provide great variation in their function for the treatment of metals, which is important to consider in the process of design and construction of bioretention facilities. A filter with vegetation (e.g. BF) has positive effects and is recommended compared to a sand filter (e.g. SF). In a filter with plants, there is less risk of clogging as the plants break up fine sediments accumulated on the surface thus maintaining infiltration capacity (Muerdter et al., 2018). A filter with chalk additives and vegetation (e.g. BFC) shows, in general, better treatment of metals in stormwater (Hamedani et al., 2019; Muthukrishnan and Oleske, 2008). The vegetated filter with chalk additives worked best for treating total metals, but was less efficient for dissolved metals and under high chloride concentrations. However, in this study, it was the most efficient mechanism compared to the filters without chalk and without vegetation.

5 Conclusions

There is significant treatment (Kruskal-Wallis test, $p<0.05$) of all metals in all three filters, BFC, BF and SF both under high ($Cl^{-}>210$ mg/l) and low ($Cl^{-}\leq 98.2$ mg/l) chloride concentrations. For total concentrations, the treatment was most efficient by filter BFC, then BF and least in filter SF. Particularly for Cu, Ni, and Pb, this may indicate better treatment of metals in a bioretention filter with vegetation and chalk additives.

For dissolved metals, filter BFC treated Cr, Cu, Ni, Pb and Zn under low chloride concentrations ($Cl^{-}\leq 98.2$ mg/l). With higher chloride concentrations ($Cl^{-}>210$ mg/l), there is a release of metals from the filters, particularly of Cd. Cu, Ni, Pb and Zn are mainly released from BF. Only dissolved Ni appears to be treated when there are high chloride concentrations ($Cl^{-}>210$ mg/l) in filter BFC. The strong effect of chloride concentration on the dissolved metals was also confirmed in the PCA where dissolved metals (Cd, Cu, Ni, Pb and Zn but not Cr) and DOC were strongly correlated to higher chloride concentrations.

6 Data Availability Statement

All data, models, or code generated or used during the study are available and included as electronic supplementary material.

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9. Competing interests

The authors declare that they have no conflict of interest.

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Paper V

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Metal treatment in stormwater bioretention systems with high hydraulic conductivity – designed for more efficient runoff volume capture in cold climates

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Metal treatment in stormwater bioretention systems with high hydraulic conductivity – designed for more efficient runoff volume capture and cold climates

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Abstract

Bioretention systems are used to treat stormwater. Using coarser filter media than commonly recommended with high saturated hydraulic conductivities may increase annual runoff volume capture, facilitate smaller filters, less overflow and adaptation to cold winters. However, this may affect water quality treatment negatively. Therefore, we investigated total and dissolved metal treatment at three full scale bioretention systems with a coarse filter material and saturated hydraulic conductivities >1500 mm/hr in Malmö/Sweden. One bioretention system was designed with a coarse sand-based filter medium, another with coarse sand-based filter medium and a submerged zone and the third with a 50:50 mixture of coarse sand and pumice as filter medium. The study included 19 rain events, partly during winter season when road salt was applied. The results suggest that also filter media with high hydraulic conductivity can be an effective option when metal treatment is targeted. The two systems with coarse sand filter media treated total metals effectively with median removals >80% for Cu, Pb and Zn and median removals > 35% for Ni and Cr. Dissolved metal treatment was variable reaching from effective treatment for dissolved Cu, Pb and Zn with median removals > 60% to overall leaching of dissolved Cd, Ni and Cr. Applying a submerged zone did not showed benefits for total or dissolved metal removal. Further, treatment of total and partly dissolved metals was significantly impaired due to pumice addition of the filter media, discouraging pumice as a filter media amendment.

Keywords

Stormwater biofilter, metals, filter material, pumice, submerged zone, road runoff, winter conditions

Highlights

- Biofilters with coarse filter media treat total metals
- Dissolved metal treatment variable in biofilter with coarse filter media
- Saturated hydraulic conductivities of bioretention filter media >1500 mm/hr
- Pumice addition impairs metal treatment
- Submerged zone did not affect metal treatment

1. Introduction

Stormwater usually contains metals from anthropogenic sources (1) that can be toxic to various biota (e.g., 2). Previous research has indicated that stormwater bioretention systems containing vegetation and engineered soil media can effectively treat water polluted with particulates including particle-associated metals (3; 4). Metals in the dissolved (< 0.45 µm) fraction have been shown to be less consistently retained and more prone to leaching than the total metal fraction (5; 6; 7). The underlying mechanisms for the removal of particulate metals are filtration and sedimentation, while the removal of dissolved metals depends on sorption (8; 4).

It is well established that bioretention media play an important role for metal treatment in bioretention systems (9; 10; 11). The optimal bioretention medium for metal removal is a compromise between different objectives (e.g. 12). It needs to be a fine medium that provides good capacity for effective filtration and sorption (8; 13). However, in addition to controlling pollution, bioretention systems should also support the effective infiltration of stormwater to meet requirements such as reducing the volume of runoff and mitigating peak flow during rain events such as those occurring up to once in every10 years according to the Average Return Intervals (14, 3, 8, 4). To conform to these opposing goals, hydraulic capacities of bioretention filter materials are recommended to range from around 10 to 400 mm/h (15).

Bioretention systems that incorporate filter material with high hydraulic conductivities might be a good choice to fulfill these goals, especially in regions that experience climatic conditions cold enough to induce concrete frost formation (16). This strongly impairs flow and hence the functionality of bioretention systems and involves relatively large facilities (often 2-5% of the catchment area) to manage the required amounts of water. This could be mitigated by ensuring faster drainage which can be maintained by choosing a suitable filter material (16). In this context, filter material with high saturated hydraulic conductivity (i.e. > 400 mm/hr) can contribute to a more efficient annual runoff volume capture and thus treat a higher fraction of stormwater than is commonly observed or allow an area-efficient facility when space is limited (17; 18; 19; 20). Coarse materials can further allow infiltration into frozen soils during winter operation (21). However, such a coarse filter media used to achieve higher hydraulic conductivities can reduce metal removal since the larger pore sizes and decreased specific surface area render filtration less effective and lowers sorption (22; 16; 13; 12). Furthermore, winter conditions can exacerbate the negative effects of coarse material on metal removal, e.g. through the formation of preferential flow paths and increased salt application to roads (23; 16; 24).

Laboratory studies have shown that bioretention systems with coarse sand-based filter material can remove total and dissolved metals in ranges previously observed in other studies with finer filter material (e.g., 25; 24; 26; 27). Some mesocosm and full-scale field-studies of how bioretention systems with coarse filter material performed found that, while total metal removal was generally effective, dissolved metal removal was variable (28; 29; 7). Only [29] described a field-scale bioretention system which included a submerged zone to remove ca. 50% of total Zn and total Pb; however, total Cu and total Ni were leached. The designs of the bioretention systems in those studies were very different. For example, some included organic layers (e.g. mulch) above the filter material, while others, even though they incorporated filter materials of a relatively coarse structure, still had hydraulic conductivities within the range commonly recommended (see above). This highlights the need for studies to investigate the efficacy of bioretention systems with filter materials that have high saturated hydraulic conductivities; this has also been highlighted by [16] especially regarding bioretention systems adapted to cold climates and/or when space is limited.

Because a bioretention filter material with high hydraulic capacity might reduce metal removal, the performance of different filter materials and any added amendment materials should be assessed ([12]). In the present study, pumice was chosen as the filter material amendment. Previous laboratory-scale stormwater bioretention studies have shown pumice to be effective in the removal of phosphorus, nitrogen and total suspended solids ([30]; [31]). Pumice also improves water storage within its pores thus making it available to plants and so supporting plant growth in fast drained filter media ([32]). Pumice has also been studied for use in wastewater treatment of vertical flow constructed wetlands; results indicate the efficient treatment of TSS, nutrients and coliforms ([33]). Other previous studies found that amending filter media with added pumice had positive effects on contaminant treatment capacity due to its large specific surface area and the presence of silanol groups, which can bind cations ([34]; [35]; [33]). It has therefore been hypothesized that pumice could also support the sorption of dissolved metals in bioretention systems with coarse-grained media.

The aim of the present study was to investigate if bioretention systems designed with coarse filter media and, consequently, a high saturated hydraulic conductivity can treat total and dissolved metals in stormwater. We therefore monitored total and dissolved metal concentrations in influent and effluent waters at field-scale bioretention cells in Malmö, Sweden during autumn, winter, and spring seasons. Designs included pumice being added to the filter material. Submerged zones are a common design feature of bioretention systems and are sometimes recommended to improve removal of nutrients (e.g., [36]). However, they can also impair their function in cold climates due to freezing ([16]). Thus, one bioretention cell was equipped with a submerged zone in this study. During the study, the bioretention cells were affected by road salt.

2. Material and method

The study was carried out at a bioretention system in Malmö, Sweden from spring 2019 (when the site was first taken into use) until autumn 2023.

2.1 Sampling site

The bioretention system was located along an urban road in the city centre of Malmö in Sweden. The system includes three sections, each consisting of six bioretention cells (BRC) with different filter configurations and catchment areas mainly including paved sidewalks and urban roads. Each BRC includes a forebay and a filter with a sand-based filter material (650 mm) and an underdrain connected to the outlet (Figure 1). The filters were vegetated with a mix of perennial forbs and grasses, which in previous studies have been reported to aid the retention of total metals (Read et al. 2008; Dagenais et al. 2018; Lange et al. 2020b). The outflow from the six filters of each section is discharged through a common pipe leading to a sampling well, i.e. the cells are connected in series (Figure 2). The catchment areas of each filter are approximately 350 m²; the area of filter and forebay are 15 m² and 1 m², respectively.

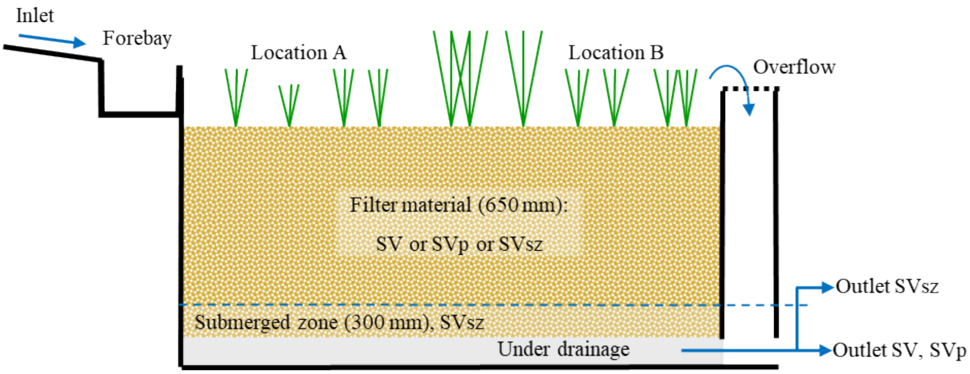

Figure 1 Cross section sketch of bioretention with (SVsz) and without a submerged zone. Location A and B are for infiltration tests.

Figure 1. Cross section sketch of bioretention with (SVsz) and without a submerged zone. Location A and B are for infiltration tests.

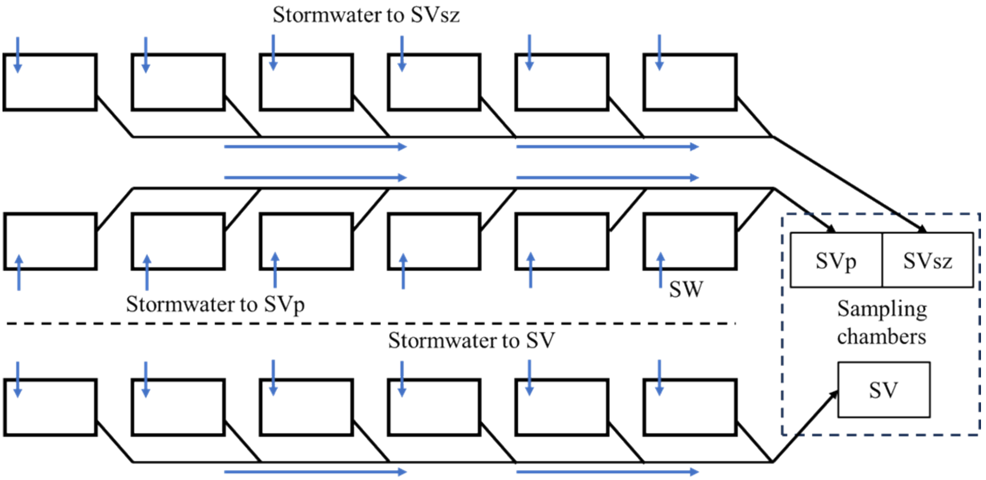

Figure 2 Malmö facilities and test site setup. Stormwater was sampled at inlet (SW), in the forebay (FB) and, the treated water was sampled in sampling chambers after the filters, SVp, SVsz and SV.

In all three filter sections the sand-based filter material used was one specially adapted to cold climates, i.e. a type with high hydraulic conductivity (Median K_{sat} ranging 1517–2834 mm/hr; particle size distribution: Table 1). Such a filter material allows infiltration into frozen soil ([21]) or to construct a significantly smaller filter compared to the commonly recommended materials with K_{sat} around 10-400 mm/hr ([15]). The first section's design is a conventional bioretention with a vegetated sand filter (SV), the second section is additionally equipped with a 300 mm submerged zone (SVsz) and the third section with 50% pumice amendment (labelled SVp).

Table 1 Particle size distribution for each of the three different filter configurations. For pumice 2mm -8 mm, no particle size distribution was available.

Material	Sieve	SV/SVsz	SVp
	[mm]	[%]	
Sand	0.063 – 0.15	4	2
	0.15 – 0.25	8	4
	0.25 – 0.5	28	14
	0.5 – 1.0	25	12.5
	1.0 – 2.0	25	12.5
	2.0 – 4.0	10	5
Pumice	2.0 – 8.0	-	50

Sampling

To investigate the treatment performance, event mean composite samples of 19 rainfall events (labelled as rain A–S, Table 2) were collected from the influent (i.e. stormwater) and from the effluent of each of the three-filter section (Figure 2, Figure 3). The rainfall events occurred at different seasons, temperatures and with different intensities (Table 2).

Figure 3 Photographs with examples from the Malmö bioretention facility with inlet, forebay and overflow device.

The stormwater inflow (SW) was sampled rain-proportionally (as reliable flow measurements at the inlets were not possible). The effluent was also sampled flow-proportionally to the outflow. Automatic samplers (ISCO6712) were used. The flow at the outlets was measured using a Isco Flow Metering Insert with the ISCO 730 bubbler module. The samples were analysed for total and dissolved metal concentrations (Cd, Cr, Cu, Ni, Pb, and Zn), chloride (Cl), total suspended solids (TSS), total organic carbon (TOC), dissolved organic carbon (DOC) by a commercial laboratory using accredited standard methods (Supplementary Section S1). For dissolved metal analyses samples were filtered with 0.45 µm filters by the laboratory within 24 to 48 hours. pH was measured with a handheld WTW pH 330 (WTW GmbH, Weilheim, Germany) on site after sampling.

Table 2 Precipitation data and rain characteristics. Asterisks (*) indicate data were provided by the Swedish Metrological and Hydrological Institute (37) from nearest weather and climate station Malmö 2 (SMHI 53370), located 300 m – 350 m from the bioretention cells.

		Temp		Precipitation			ADD		
Event	Date	Low	High	Total	Max intensity	Duration	>0	>0.2	>1
		[C°]		[mm]	[mm/hr]	[hr]		[d]	
A	2021-04-30	4.2*	13.1*	5.4*	2*	6.8*	7*	7*	17*
B	2021-09-16	11.1*	20.2*	14.2*	5.2*	11*	2*	17*	17*
C	2021-10-20	0.5	15.0	27.9	9.2	22	3	4	4
D	2021-11-06	3.2	11.6	3.3	3.2	5	1	1	8
E	2021-11-17	4.8	7.7	3.1	2.4	3	2	3	10
F	2021-11-25	4.8	9.3	5.1	1.6	8	4	4	5
G	2021-12-10	0.1	1.1	5.5	1.2	8	5	6	6
H	2022-01-20	-1.8	5.3	2	2.8*	2*	2	2	2
I	2022-01-27	-2.8	8.2	6.2	16.4	9	1	2	2
J	2022-01-29	1.3	8.3	6.3	2	7	0	0	0
K	2022-02-03	-2.4	6.0	14.3	2.4	15	1	1	1
L	2022-02-06	1.2	6.5	12.9	13.6	11	0	0	0
M	2022-02-16	2.8	9.0	20.3	4.8	12	2	4	4
N	2022-02-18	0.7	8.3	18.1	6	12	0	0	0
O	2022-02-22	1.0	3.0	21.9*	3.6*	19.3*	0	0	0
P	2022-05-13	9.6*	15.2*	4.8*	6*	2.5*	1*	1*	1*
Q	2022-05-20	12.5*	24.9*	0.4*	1.6*	0.3*	5*	5*	5*
R	2022-05-24	11.6*	18.7*	3.4*	4*	2.5*	1*	1*	3*
S	2022-05-30	8.4*	18.5*	40.1*	16.4*	16.3*	0*	0*	0*

The saturated hydraulic conductivity of the filters was measured six times during the period March 2019 to December 2022 (Supplementary Table S1), using a modified Phillip Dunne (MPD) infiltrometer from Upstream Technologies, Minneapolis US. Measurements were performed at two locations at each filter. Locations A and B were approx. 100 cm and 400 cm, respectively, from the inlet (Supplementary Figure 1 and 2). At each location (A and B) three replicate infiltration tests were performed on each occasion. The hydraulic conductivity was generally very high (Supplementary Table S1; Figure 4) in all three filter materials compared to what has previously been recommended (10–400 mm/hr, Le Coustumer et al., 2009). Median K_{sat} was highest in SVp with 2834 mm/hr and was significantly lower in SV and SVsz with 1885 mm/hr and 1517 mm/hr, respectively (Kruskal-Wallis test: SVsz vs. SVp: $Z = 2.628$, $p = 0.009$; SV vs. SVp: $Z = 1.919$, $p = 0.055$). The first infiltration measurement was conducted in spring 2019 only a few months after the installation of the filters; the last measurement was taken on 2022-12-09.

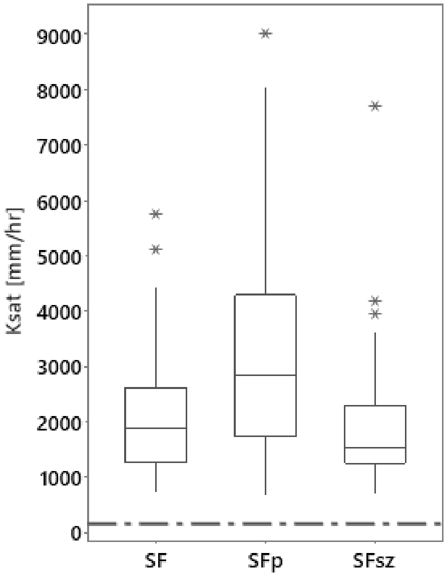

Figure 4 Hydraulic conductivity Ksat in three different filter materials. The reference line at 150 mm/hr indicates the highest recommended hydraulic conductivity according to [32]*.*

Data analysis

Boxplots were used to illustrate pollutant concentrations in stormwater before and after treatment in the various filter materials. Data were not normally distributed (Ryan-Joiner Normality test, data not presented). Differences between median concentrations determined at different steps of the treatment process (inflow (stormwater) vs. outflow (SV, SVp and SVsz)) were therefore investigated using the non-parametric Wilcoxon test. The non-parametric Kruskal-Wallis test was used to determine whether there were any statistically significant differences between different BRCs (SV, SVp and SVsz). To determine the statistical dependency between metal concentrations and TSS, DOC, TOC and pH Spearman correlation tests were carried out. For all statistical tests significance was accepted at $p = 0.05$. For non-detects half-detection limits were used. Minitab® 20.4 software and RStudio 2024.09.1 Build 394© 2009-2024 Posit Software, PBC were used to analyse the data.

3. Results

3.1 Characterisation of the stormwater

Total and dissolved metal concentrations in stormwater varied between the sampling events (Figure 5, Figure 7). The median concentrations of total Cd, Cr, Cu, Ni, Pb and Zn in the stormwater were 0.07, 5.85, 32.7, 4.96, 10.8 and 176 µg/L, respectively (

Table *3*). Stormwater median concentrations for dissolved Cd, Cr, Cu, Ni, Pb and Zn were 0.007, 0.443, 6.18, 1.01, 0.11 and 27.6 µg/L, respectively (

Table *3*). This corresponds to median percentages of dissolved fractions of Cr = 7.6 %, Cu = 17%, Ni = 17%, Pb = 1.4% and Zn = 16 %. Median dissolved fractions of Cd could not be estimated since 30% of the total Cd influent data were below the detection limit.

Correlation analyses revealed strong positive monotonic association of total metal concentrations and TSS (spearman correlation coefficient generally ≥ 0.935, $p = 0.000$, Supplementary table S5, Supplementary figure S5). Significant positive monotonic correlations were also found between dissolved Cu and DOC (spearman correlation coefficient 0.74, $p = 0.001$) and dissolved Ni (spearman correlation coefficient 0.78 $p = 0.000$). Dissolved Cd and dissolved Zn were moderately positively correlated to DOC (Supplementary Table S5).

Road salt is commonly applied at the sampling site during winter. Cl concentrations in the influent determined at the sampling events in this study ranged mostly between 2.28 and 73.2 mg/L and were clearly elevated on only three sampling days with 1850, 347, and 159 mg/L. However, increased bioretention effluent Cl concentrations indicate that bioretention systems were affected from mid November 2021 to mid of February 2022 by road salt application (Supplementary Table S2).

Table 3 Descriptive statistics for concentrations of all examined substances in stormwater (SW) and the effluent from all three bioretention cells (SV, SVp and SVsz).

Substance		Variable	Concentrations			
			SW	SV	SVp	SVsz
Total [µg/L]	Cd	N	16	19	16	18
		Min	0.025	0.025	0.025	0.025
		median	0.070	0.025	0.054	0.025
		max	0.350	0.133	0.344	0.210
	Cr	N	16	19	18	17
		Min	1.13	0.45	1.57	0.045
		median	5.85	2.52	7.20	3.08
		max	28.8	11.3	151	52.2
	Cu	N	16	19	16	18
		min	7.71	2.33	2.80	2.09
		median	32.7	4.19	8.99	4.16
		max	114	20.0	21.2	33.5
	Ni	N	16	19	16	18
		Min	0.30	0.30	2.77	0.30
		median	4.96	2.39	5.76	2.61
		max	25.8	21.3	21.1	18.1
	Pb	N	16	19	16	18
		Min	1.24	0.25	0.75	0.25
		median	10.8	0.25	2.40	0.44
		max	57.1	4.72	14.1	12.1
	Zn	N	16	19	16	18
		Min	37.3	2.00	9.56	2.00
		median	176	10.0	38.0	9.33

		max	792	84.7	94.6	195
Dissolved [µg/L]	Cd	N	16	18	16	17
		Min	0.001	0.001	0.002	0.002
		median	0.007	0.013	0.022	0.016
		max	0.063	0.121	0.279	0.126
	Cr	N	16	18	17	16
		Min	0.091	0.232	0.198	0.086
		median	0.443	0.502	0.781	0.398
		max	1.43	1.00	3.16	1.56
	Cu	N	16	18	16	17
		min	1.01	1.27	1.59	1.34
		median	6.18	2.55	3.36	2.09
		max	15.6	5.32	6.43	4.41
	Ni	N	16	18	16	17
		Min	0.497	0.229	0.633	0.289
		median	1.01	0.936	2.30	1.92
		max	2.63	20.4	14.0	16.0
	Pb	N	16	18	16	17
		Min	0.028	0.005	0.015	0.005
		median	0.110	0.026	0.053	0.035
		max	0.678	0.082	0.183	0.100
	Zn	N	16	18	16	17
		Min	10	0.409	1.52	0.362
		median	27.6	2.20	5.68	2.46
		max	78.5	17.0	23.5	11.5
[mg/l]	Cl-	N	16	18	16	18
		min	2.28	2.42	18.5	4.08
		median	19.9	130	141.5	93.0
		max	1850	5650	4540	6500
	TSS	N	16	18	15	16
		min	6.90	1.00	1.10	1.65
		median	86.0	6.15	16.0	6.30
		max	370	20.0	160	24.0
	TOC	N	16	18	15	17
		min	2.29	2.65	3.25	3.55
		median	15.65	5.54	6.08	6.04
		max	112	10.3	9.40	17.2
	DOC	N	16	18	15	17
		min	1.28	1.59	2.01	2.18
		median	5.08	4.45	4.17	5.69
		max	16.4	9.78	7.43	16.4
	pH	N	16	18	16	18
		min	6.80	7.80	7.90	7.70
		median	7.60	8.00	8.00	8.00
		max	8.10	8.30	8.20	8.10

3.2 Metal treatment in bioretention cells with high hydraulic conductivity

Total metals

Total Cu, Pb and Zn concentrations were reduced significantly at the three different BRCs in our present study (Table 4). The total Cu concentrations determined at the outflow of the vegetated sand filter cell (SV), the cell with added pumice ($\mathrm{SV_{P}}$) and the cell with a submerged zone ($\mathrm{SV_{SZ}}$) were significantly lower than the influent concentrations (median influent concentrations: 32.7 µg/L; median effluent concentrations: SV = 4.19 µg/L, $\mathrm{SV_{P}}$ =8.99 µg/L, $\mathrm{SV_{SZ}}$ =4.16 µg/L). Also, for total Pb and total Zn the effluent concentrations of the different bioretention cells were significantly reduced (median total Pb effluent concentrations: SV = 0.25 µg/L, $\mathrm{SV_{P}}$ =2.4 µg/L, $\mathrm{SV_{SZ}}$ =0.44 µg/L; median total Zn effluent concentrations: SV =10 µg/L, $\mathrm{SV_{P}}$ = 38 µg/L, $\mathrm{SV_{SZ}}$ = 9.33 µg/L) compared to the influent (median influent concentration Pb: 10.8 µg/L, median influent concentration Zn : 176 µg/L).

Total Cd concentration was only reduced significantly by the vegetated sand filter (SV) (median influent Cd concentration: 0.070 µg/L; median effluent Cd concentration: 0.025 µg/L). However, this result for total Cd should be interpreted with care since many values were below the LOQ, specifically in the effluent. Despite not being significant, the median reduction of Cd at the BRC $\mathrm{SV_{SZ}}$ was equal to that of the BRC SV (median effluent Cd concentration: 0.025 µg/L). For total Ni and total Cr significantly lower concentrations were observed at the vegetated sand filter (SV) and at the BRC with the submerged zone ($\mathrm{SV_{SZ}}$) compared to the influent (Ni: influent = 4.96 µg/L; SV = 2.39 µg/L, $\mathrm{SV_{SZ}}$ = 2.61 µg/L; Cr: influent = 5.85; SV = 2.52 µg/L, $\mathrm{SV_{SZ}}$ = 3.08 µg/L). No significant changes in total Ni and total Cr concentrations were determined for the bioretention system with pumice ($\mathrm{SF_{P}}$).

Table 4 p-values of paired Wilcoxon test for differences in influent and effluent contaminant concentrations of the specified bioretention cells. Differences were considered significant at p < 0.05 (marked bold). Asterisks (*) indicate that many values in the effluent (and influent for Cd) were below LOQ.

	Parameter	SV	$\mathrm{SV_{P}}$	$\mathrm{SV_{SZ}}$
Total	Cd	**0.007***	0.900*	0.224*
	Cr	**0.002**	0.698	**0.044**
	Cu	**0.000**	**0.000**	**0.000**
	Ni	**0.002**	0.980	**0.018**
	Pb	**0.000***	**0.004**	**0.000***
	Zn	**0.000**	**0.000**	**0.000**
Dissolved	Cd	0.222	**0.028**	**0.030**
	Cr	0.423	**0.011**	0.755
	Cu	**0.000**	**0.003**	**0.000**
	Ni	0.252	**0.001**	**0.035**
	Pb	**0.000**	**0.021**	**0.000**
	Zn	**0.000**	**0.000**	**0.000**
	TSS	**0.000**	**0.001**	**0.000**
	TOC	**0.001**	**0.002**	**0.018**
	DOC	0.159	0.169	0.762
	pH	**0.001**	**0.001**	**0.001**

The concentration reductions of total Cu, Pb and Zn correspond to high median removals for these elements (≥ 80% for SV and SV_{SZ}; > 60% for SV_P; Supplementary table S4). Inter-event variability was high, specifically for the filter with pumice where occasional leaching was also observed (Figure 5). Total Cr and Ni removal was generally lower. For the vegetated sand filter (SV) and the BRC with the added submerged zone (SV_{SZ}) total Cr and Ni median removals did not exceed 60% and occasional leaching of theses metals was also observed at some events (Figure 5). Further, at the BRC with added pumice (SV_P) total Cr and Ni median removals did not exceed 5% with considerable leaching of total metals during some events (Figure 5). For Total Cd, removals could not be calculated, since both influent and effluent data included too many values below the LOQ.

For total metals, Spearman correlations were strong, particularly for TSS and Cl concentrations. Total Cu, Pb and Zn concentrations in the effluent were significantly positively correlated to the TSS concentrations in all three BRCs (Spearman correlation: 0.588, $p = 0.01$ (SV); 0.761, $p = 0.001$ (SV_P); 0.712, $p = 0.002$ (SV_{SZ})). Total Cr and Ni in the BRC (SV) and the BRC with submerged zone (SV_{SZ}) were significantly positively correlated with Cl concentration (Spearman correlation: 0.553 (total Cr, SV); 0.641 (total Cr, SV_{SZ}); 0.676 (total Ni, SV); 0.686(total Ni, SV_{SZ}). In the BRC with pumice (SV_P) total Cu (Spearman correlation -0.709, $p = 0.002$) concentrations were negatively correlated to Cl^- concentrations. In some cases, further significant but moderate correlations between total metal concentrations in the effluent and TOC/DOC were found (Supplementary table S5). No significant correlations between pH and metal concentrations were observed (Supplementary table S5).

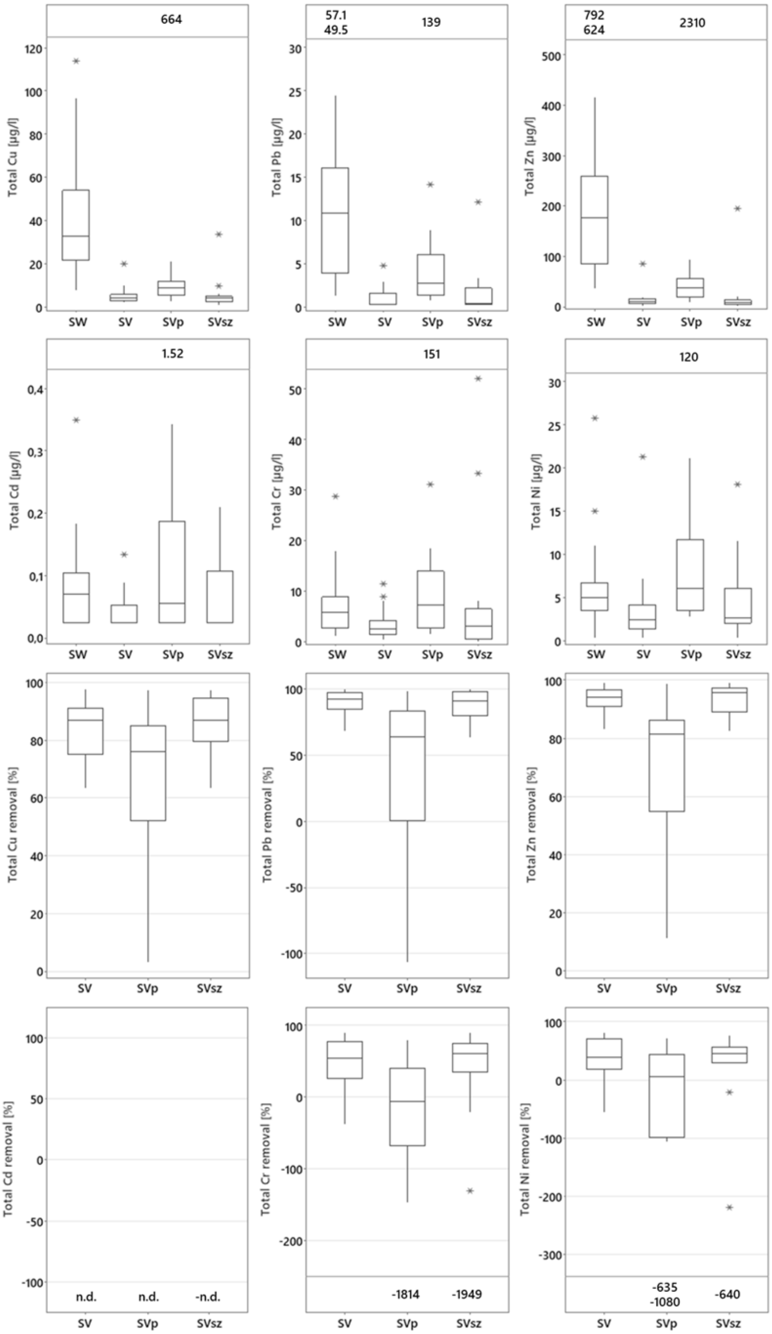

Figure 5 Boxplots of total metal concentrations for Cu, Pb, Zn, Cd, Cr and Ni and Zn in SW, in the three different bioretention configurations (SV, SVsz, SVp), and of removal by bioretention cells SV, SVp and SVsz .For clarity, the numbers above and below the boxplots represent outliers not plotted in the graph due to readability

Dissolved metals

Dissolved Cu, Pb, and Zn concentrations were reduced significantly in the effluent from all three BRCs (Table 4, Figure 7). Median dissolved Cu concentrations in the effluents were lower than in the influent (median concentration 6.18 µg/L) by 2.55 µg/L in BRC (SV), 3.36 µg/L in cell (SV_P) and by 2.09 µg/L in cell (SV_{SZ}). Median dissolved Pb concentrations were reduced from 0.110 µg/L in the influent to 0.026 µg/L (SV), 0.053 µg/L (SV_P) and 0.035 µg/L (SV_{SZ}) in the effluents of the BRCs. Median dissolved Zn concentrations were reduced from 27.6 µg/L at the inflow to 2.2 µg/L (SV), 5.68 µg/L (SV_P) and 2.46 µg/L (SV_{SZ}) at the outflow of the BRCs.

Dissolved Cd, Cr and Ni concentrations were not efficiently reduced by any of the three different BRCs (Table 4, Figure 7). In the effluent of cell SV no significant changes of the influent dissolved Cd, Cr and Ni concentration were observed. In the effluent of the cell with pumice (SV_P) and the cell with the submerged zone (SV_{SZ}) dissolved Cd and Ni concentrations were significantly higher than in the influent (median dissolved influent: Cd 0.007 µg/L, Ni 1.01 µg/L; median dissolved effluent Cd concentrations: 0.022 µg/L (SV_P), 0.016 µg/L (SV_{SZ}); median dissolved effluent Ni concentrations: 2.3 µg/L (SV_P), 1.92 µg/L (SV_{SZ})). Dissolved Cr concentrations were not significantly affected by the BRC with submerged zone (SV_{SZ}). Dissolved Cr concentrations (median 0.781 µg/L) at the outflow of the bioretention system with pumice (SV_P) were significantly higher than dissolved Cr concentrations at the inflow (median 0.443 µg/L).

In line with the significant concentration reductions of dissolved Cu, Pb and Zn, removal of dissolved Cu, Pb and Zn was generally effective. Dissolved Zn had the highest median removal (SV = 93 %, SVp = 80 % and, SVsz = 93 %) followed by Pb (SV >78 %, SVp = 54 % and, SVsz > 78 %) and then Cu (SV = 59 %, SVp = 49 % and, SVsz = 61 %). However, at some events leaching of dissolved Cu and Pb was observed at the effluent of the bioretention cells (Figure 7). This leaching was most pronounced at the BRC with pumice (Figure 7). For all studied BRCs overall leaching of dissolved Cd, Cr and Ni is indicated by negative median removal values in Figure 7.

Significant correlations between dissolved metal concentrations in the effluent of the BRCs were mainly with Cl, TOC/DOC and pH and depended on the metal and bioretention design (Supplementary table S5, Supplementary Figure S5-S8). Strongest correlations were found between Cl as well as DOC and metal concentrations. Positive correlations between Cl concentration and dissolved metal concentrations were found for dissolved Zn (0.560 SV, 0.532 SV_P) and dissolved Ni (0.802 SV, 0.664 SV_{SZ}). In the effluent of the BRC with added pumice (SV_P) dissolved Pb (spearman correlation -0.612) and dissolved Cu (spearman correlation -0.582) were negatively correlated to Cl concentrations. DOC concentrations were significantly positively correlated to dissolved Zn in the effluent of the three different BRCs (Spearman correlation: 0.560 (SV), 0.539 (SV_P) and 0.556 (SV_{SZ})). DOC concentrations were significantly positively correlated to dissolved Cd in the effluent of BRC SV (spearman corelation: 0.787) and SV_{SZ} (Spearman corelation: 0.581). Further DOC concentrations were significantly positively correlated to dissolved Cu in the effluent of BRC SV (Spearman corelation: 0.599). Dissolved Cr concentrations were negatively correlated to DOC at the BRC SV (Spearman correlation -0.671) and the BRC SV_{SZ} (Spearman correlation -0.590).

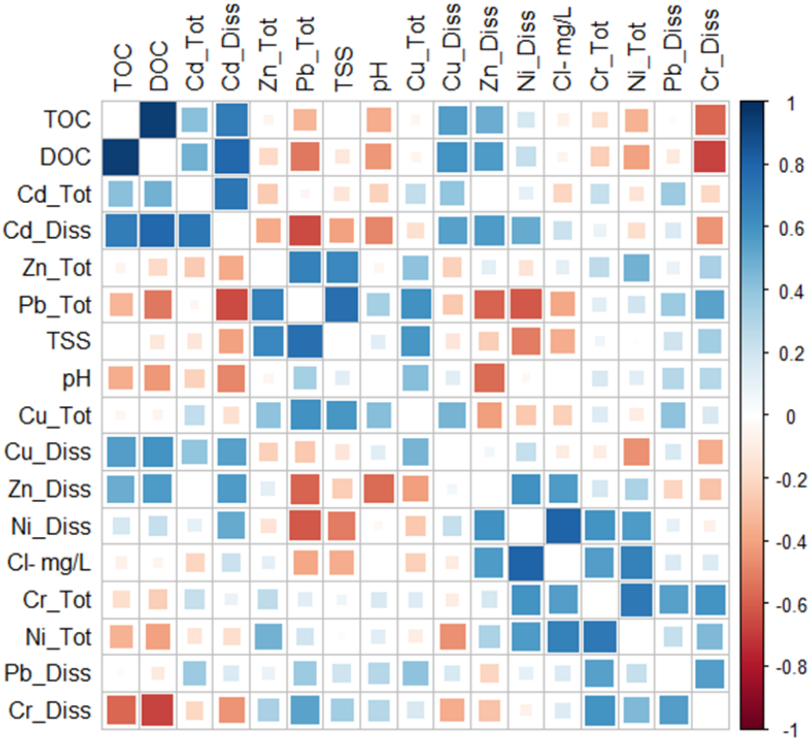

Figure 6 Correlation plot of investigated variables at the effluent of the sand and vegetation bioretention system (SV). The plot is clustered according to Ward's minimum variance method (Correlation plots from SW, SVP and SVSZ in supplementary material Figure S5-S8)

Speciation change

Mostly, a speciation change towards the dissolved fraction can be observed when comparing inflow and effluent metal speciation (Supplementary figure S4). In the influent a median 17% of the Cu was in the dissolved fraction while in the effluent, medians of 65% (SV), 37% (SV_P) and 63% (SV_{SZ}) of the Cu was dissolved. The median percentage of dissolved Zn in the influent was 16%. In the effluent of the BRCs SV and SV_{SZ} the median dissolved fractions were higher at 43% and 53%. The median percentage of the dissolved Zn fraction of the BRC with added pumice was with 19% which was in the same range as in the influent. Median percentage of the dissolved Cr fraction was 7.6% in the influent. In the effluent of the BRCs SV and SV_{SZ} 21% and 22% of the Cr was dissolved. In the effluent of the BRC with pumice, only 12% of the Cr was in dissolved form. In the influent 17% of the Ni was dissolved. In the effluent of the BRCs 68% (SV), 57% (SV_{SZ}) and 72% (SV_P) of the Ni was dissolved. Dissolved fractions have been calculated only for Cu, Zn, Cr and Ni, since Cd and Pb concentrations in the influents and effluents of the BRCs were often below the LOQ.

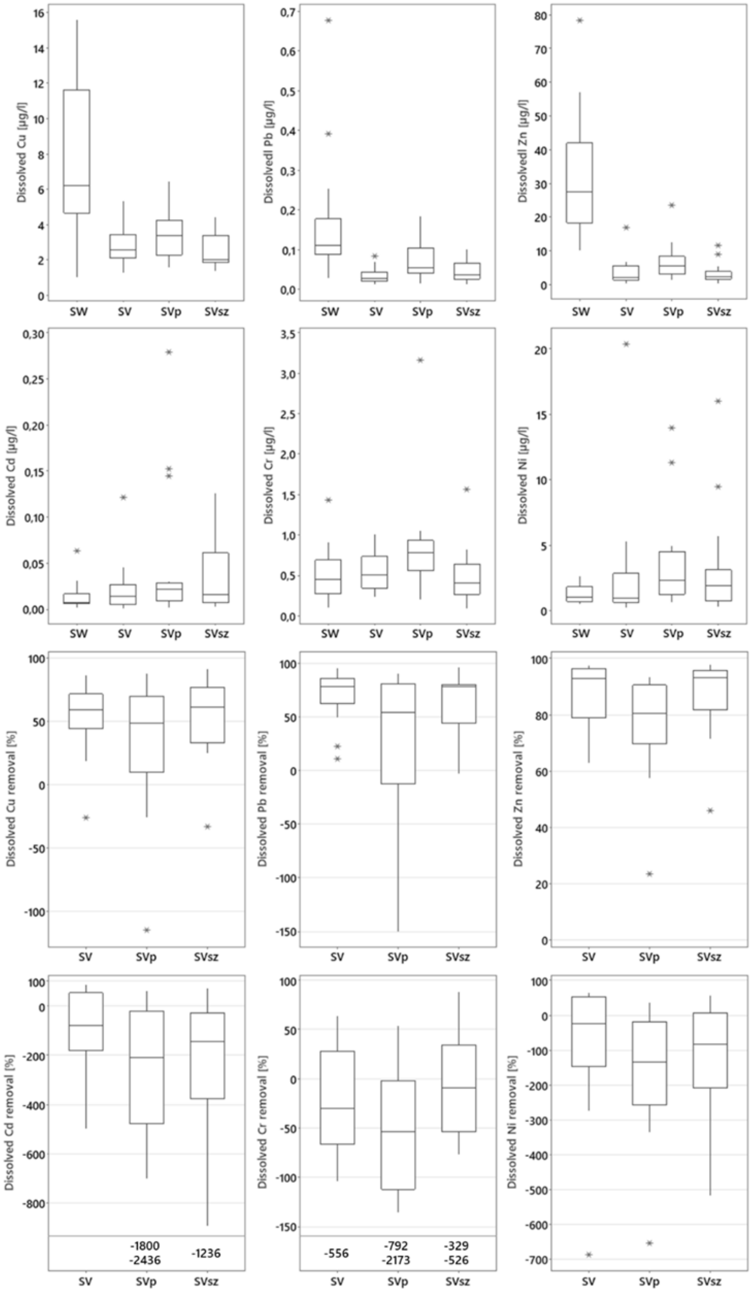

Figure 7 Boxplots of dissolved metal concentrations for Cu, Pb, Zn, Cd, Cr and Ni and Zn in SW, in the three different filter configurations (SV, SVsz, SVp) and of removal in filters SV, SVp and SVsz. Numbers below boxplots of removal represent outliers not plotted in the graph for more clear visualizations of boxplots.

Impact of added pumice

From the three studied BRCs the highest metal concentrations, both total and dissolved, in effluents were found at the BRC with added pumice ($\mathrm{SV_P}$) (Figure 5, Figure 7,

Table *3*). Total metal effluent concentrations were significantly higher in the BRC with added pumice ($\mathrm{SV_P}$) than in the SV BRC (Table 5). The significantly higher TSS concentrations in the effluent of the BRC with pumice ($\mathrm{SV_P}$) compared to the SV BRC, indicate that particulate contaminant retention is worse when pumice is added. For dissolved metals, only the effluent concentrations of Pb, Zn and Cr were significantly higher in the BRC with added pumice ($\mathrm{SV_P}$) than in the SV BRC.

Impact of submerged zone

No significant differences were found between the total and dissolved metal concentrations in the effluents of the BRCs SV and $\mathrm{SV_{SZ}}$ (Table 5). This indicates that the submerged zone had no effect on total and dissolved metal retention in this study.

Table 5 Results of the Kruskal-Wallis test for comparison of effluent element concentrations between the indicated bioretention cells (SV, $\mathrm{SV_P}$ and $\mathrm{SV_{SZ}}$). Significance was accepted when $Z \geq$ Bonferroni Z-value 1.834 and $p \leq 0.05$ (marked bold in table). Asterisks (*) indicates that many values are below LOQ.

Element		SV vs. SVP		SV vs. SVSZ	
		Z-value	p-value	Z-value	p-value
Total	Cd	**2.359***	**0.018***	1.381*	0.167*
	Cu	**3.127**	**0.002**	0.4340	0.664
	Pb	**3.615***	**0.000***	0.1849*	0.853*
	Zn	**3.709**	**0.000**	0.5338	0.593
	Cr	**2.393**	**0.017**	0.0903	0.928
	Ni	**3.204**	**0.001**	0.5451	0.586
Dissolved	Cd	1.314	0.189	0.5669	0.571
	Cu	1.564	0.118	0.7001	0.484
	Pb	**2.876**	**0.004**	0.9801	0.327
	Zn	**2.587**	**0.010**	0.0787	0.937
	Cr	**1.957**	**0.050**	0.9599	0.337
	Ni	1.789	0.074	0.9081	0.364
	TSS	**2.978**	**0.003**	0.0502	0.960
	TOC	0.3281	0.743	1.176	0.240
	DOC	0.6486	0.517	1.105	0.269
	pH	0.3552	0.722	0.6224	0.534

4. Discussion

Stormwater

In general, metal concentrations of stormwater in this study were within typical ranges expected for urban stormwater/road runoff, and are similar to other recently published data e.g. U.S. stormwater data ([38]), early published stormwater quality data ([39]) and the Stormtac Database for residential and downtown areas ([40]). TSS, TOC, DOC and Cl concentrations determined in this study are also within ranges previously published ([38] ; [39]; [40]; Supplementary Figure S3).

High proportions of the metals investigated in the stormwater in this study were associated with particulates as observed previously in other stormwater studies from traffic related catchments (e.g., [41], [42], [7]). In addition, the observations that total metal concentrations in stormwater correlate positively with TSS concentrations have also been reported previously (e.g., [7]). Positive correlations between dissolved metals and DOC (Supplementary figure S5 and table S5) were discovered in this study; and the dependency between organic matter and metal speciation has been explained by [43].

Altogether, these findings indicate that the stormwater inflow in this study is representative for 'typical' road runoff and/or urban stormwater and thus, our data, results and conclusions are not only specific for this site but are also more widely applicable.

Metal retention

The results of our study suggest that BRCs with coarse filter media and high hydraulic conductivity are capable of decreasing total metal concentrations in stormwater to a significant degree, in particular regarding the BRC SV. The SV_{SZ} filters showed a similar treatment performance, but the additional submerged zone did not enhance treatment further; thus, this additional feature is not necessary when metals and TSS are target pollutants. Comparing the effluent of BRC SV_P (with pumice), with the other two BRCs, we found significantly higher total metal concentrations (Table 5) as well as total Cr and Ni leaching (discussed in detail below under the heading "Effect of pumice amendment"). However, TSS, and total Pb, Cu and Zn were even retained efficiently in the BRC with pumice (Figure 5;

Table *3*; Table 4). Laboratory studies using vegetated bioretention columns (e.g., [25]; [24]; [44]; [10]) to investigate, among other things, removal of total Cd, Pb, Cu and Zn, have also suggested that this can be achieved in BRCs with relatively coarse filter material. In a mesocosm experiment, [28] found that two bioretention boxes with filter material consisting of 93% and 88% sand and a mulch layer on top efficiently retained total Cd, Pb, Cu, and Zn in snowmelt with concentration reductions ranging from 81% to 99%. Similarly, a field study by [7] using a bioretention system with coarse material and a dense substrate-vegetation layer, found that total Pb, Cu and Zn were reduced by >76%, 79% and 94%, respectively. However, due to differences in factors that can affect metal retention such as scale, placement of an organic substrate into or on top of the filter medium ([45]; [16]; [43]) and hydrological performance, the results of these studies are of only limited comparability with our present study. The efficiency of total metal retention has been documented in non-vegetated sand filters, which were also constructed with relatively coarse filter materials supplemented with different additional materials ([46]; [27]).

In the influent, most of the metals in the present study occurred in particulate form. Thus, the level of total metal removal achieved depends on particulate metals being filtered out or settling due to sedimentation - both processes primarily occurring in the top layer of the bioretention system (e.g.,[22]; [4]; [47]), even when applying relatively coarse filter materials (e.g. [48]). TSS concentrations, and total Cu, Pb and Zn concentrations were in the effluent of all three BRCs positively correlated; a source of the TSS in the effluent could be the runoff as well as fines washed out from the BRCs themselves ([41]). In the effluent, dissolved metal fractions were lower than expected (specifically for the bioretention system with pumice, discussed below), indicating a limited degree of particulate retention. In contrast to our study, [7] found, that 75% and 70% of the Cu and Zn, respectively were in the dissolved fraction in the effluent from their BRC with a dense vegetation-substrate cover, while in our present study only 65% (SV), 37% (SV_P) and 63% (SV_{SZ}) of dissolved Cu, and 43% (SV), 19% (SV_P) and 53% (SV_{SZ}) of the dissolved Zn were in the dissolved fraction in the effluents. These results may be explained by our BRCs having bigger pore size in the media and/or the formation of preferential flow paths ([49]; [22]). Impaired particulate metal retention could also have been triggered by smaller particle size of the TSS during winter conditions ([41]). The retention of dissolved metal contaminants in stormwater treatment cells is often very variable ([50]; [24]; [51]; [7]). Thus, it is not surprising that, depending on the metal, it also varied in our present study, in both the degree of retention in the filter media and regarding subsequent leaching from the cells. It is therefore difficult to attribute low retention or leaching to either the coarse filter material or the high hydraulic conductivity. Metal sorption is commonly considered to be a relatively fast process at less than 1 h ([13]; [52]); thus retention of dissolved metals did occur in the BRCs in our study, despite high hydraulic conductivities. Leaching of retained dissolved metals following sorption has been attributed in earlier studies to road salt application ([23]; [24]; [53]), the availability of DOC in stormwater or bioretention systems ([13]; [7]; [52]) or changes in filter material chemistry due to drying periods ([10, 54]). Depending on metal and bioretention design we observed in the present study in some cases positive or negative correlations between tested parameters - Cl, DOC, pH and dissolved metal concentrations This reflects the chemical, physical and operational complexity of bioretention systems when stormwater enters (depending on design and varying ambient conditions), which influences the removal of dissolved metals by different sorption mechanisms ([4] [13]; [52]).

Effect of pumice amendment

BRCs amended with pumice showed significantly higher concentrations of total metal in effluents compared to the SV BRC for all studied metals (Table 5). However, in the effluent of the BRC amended with pumice we observed no reductions in concentrations compared to the influent that were significant for total Cr and total Ni (Table 4); rather, we noted considerable leaching of total Cr and total Ni (Figure 5). The pore size of the filter media with added pumice (50% pumice content with grain size 2mm - 8mm) was bigger than in the filter media without pumice (grain size sand: 0.063mm –4 mm), and this probably led lead to the very high hydraulic conductivity (median 2834 mm/hr; Figure 4) and so to decreased retention of particulate metal ([22]). Moreover, with pumice in the filter medium dissolved fractions of Cu, Zn and Cr in the effluent were lower compared to the other two BRCs (Supplementary figure

S4). This also suggests that the particulate metals were probably less efficiently retained when pumice is added to the filter medium of a BRC. Ni behaved differently from the other metals in this respect. In the inflow, only 17% of the nickel was in its dissolved form, whereas in the effluent it was 72%. This suggests that the observed leaching of total Ni was probably due to a large proportion of it being in its mobile form.

The differences between the BRC with pumice and the other two BRCs were less pronounced regarding the retention of dissolved metals compared to total metals, with significantly higher concentrations being only found in the effluent of the BRC with pumice for Pb, Zn and Cr. This also suggests that pumice is not a good amendment to coarse filter material. Positive effects on dissolved metal treatment due to the large specific surface area and silanol groups which can bind for example cations were not observed ([34]; [35]; [33]). Pumice does, however, seem to reduce the adverse effect of road salt application on dissolved metal retention. While for the other two BRCs, metal concentrations in the effluent were positively correlated to Cl concentrations, dissolved Pb and dissolved Cu were negatively correlated to Cl concentrations in the effluent of the BRC with added pumice (SV_P). This observation, however, might be a statistical artefact due to a large degree of variation in the data; nevertheless, [53] also found that metal concentrations were significantly increased due to salt treatment in a bioretention column experiment.

Overall, these results suggest that pumice is not a good amendment in bioretention filter material when metal treatment is the design objective for the bioretention system. Further, it needs to be noted, that, as found by [55] that using pumice is bad from an environmental perspective too, due to the need of long distance transportation.

Effect of the submerged zone

A submerged zone is commonly integrated in a bioretention facility when nitrogen removal is targeted ([56]; [57]). Previous studies [58]; [54]; [24]) have shown that also metal removal can be enhanced in filters with a submerged zone and a solid carbon source (e.g. saw dust), although to lesser extent as nitrogen. In our present study we saw no significant differences between the BRC SV and the BRC with a submerged zone (SVsz). However, in contrast to the previous studies investigating submerged zone, no carbon source was added in the submerged zone filters and this, together with the very high hydraulic conductivity and the specific environmental conditions at the site, may explain why we found no significant effect of the submerged zone. This corroborates the explanation of [58] who suggests that rather the carbon source (solid organic matter) explains the better metal removal than the submerged zone itself.

Practical implications

For dissolved Cd, Cr, Ni and Pb median concentrations in influent and effluent did not exceed Swedish environmental threshold values for receiving waters ([59], [60], Supplementary table S3). Only at some rain events, dissolved Cd and Ni concentrations in the effluent were above those values. Dissolved Zn median concentrations exceeded Swedish environmental threshold values for receiving waters in the influent, and, only occasionally, also in the effluent. Dissolved Cu median concentrations exceeded threshold values in the influent and the effluent from the bioretention cells SV and SV_P. In the effluent of SV_{SZ}, Swedish environmental threshold values for receiving waters were occasional exceeded. It has been shown previously that influent and effluent values for dissolved Cu for a bioretention system with coarse filter material with a dense vegetation/substrate top layer can exceed environmental thresholds ([7]) and shows that other bioretention systems, which are differently designed, experience similar problems. This emphasises the need to further evaluate dissolved metal treatment (most studies only regard total metals) and further develop bioretention for better removal of dissolved metals ([7]).

Exceeding environmental threshold values is specifically problematic when, as with dissolved Cd and Ni, the influent water quality is better than the effluent water quality; in such cases the bioretention system poses a risk to the environment. However, in most cases the bioretention systems SV and SV_{SZ} in our present study (despite sometimes exceeding environmental threshold values) did improve the stormwater quality, also for most dissolved metals.

Even though the bioretention systems with high hydraulic conductivity did not retain metals as well as bioretention systems with lower hydraulic conductivity, the bioretention in the present study may be able to treat a larger amount of the annual total runoff ([17]; [18]; [19]; [20]), and thus may still protect receiving water bodies better. Another advantage of coarse filter media with high hydraulic conductivity is, that they are less likely to clog than those with finer filter material and thus recommended maintenance intervals could be extended ([61]; [62]; [16]; [63]). One important question remains: Are outflow rates of bioretention systems with filter material and saturated hydraulic conductivities between 1500 and 2800 mm/hr low enough to provide protection for geomorphology of downstream structures ([8]).

5. Conclusions

The results of this study suggest

- that bioretention systems with coarse filter material with high hydraulic conductivity treat stormwater effectively by retaining total metals
- that the retention of dissolved metals varies among bioretention systems with coarse filter material and high hydraulic conductivity, and depends on the metal and the environmental conditions, as has also been shown in previous studies in bioretention systems with finer filter materials and/or lower hydrologic conductivity
- that pumice is unsuitable as an amendment that aims to increase retention of total or dissolved metal in bioretention systems with coarse filter material and high hydraulic conductivity
- a submerged zone had no overall significant effect on metal retention

In summary, coarser filter materials could be implemented when space is restricted requiring specifically small facilities in relation to the catchment, when infiltration into frozen ground is expected. Further, in can in general reduce the risk for clogging and discharge of untreated overflows, at high rain intensity events. Thus, recommendations could include coarser materials than commonly done today.

Further studies should investigate the performance of bioretention systems with coarse filter material with high hydraulic conductivity in treating stormwater with regard to other contaminants - for example nutrients - and investigate the hydrological performance of such bioretention systems.

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