

Biofiltration Technologies for Stormwater Quality Treatment

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ABSTRACT

Due to high runoff volumes and peak flows, and significant contamination with (*inter alia*) sediment, metals, nutrients, polycyclic aromatic hydrocarbons and salt, urban stormwater is a major cause of degradation of urban water ways. Since current urban drainage systems, which heavily rely on piped sewer networks, may not be sustainable, attempts are being made to develop and refine sustainable urban drainage solutions, notably in Water Sensitive Urban Design (WSUD) and Low Impact Development (LID) concepts. Promising systems recommended for application in both WSUD and LID are stormwater biofilters (also known as bioretention systems or rain gardens) using vegetated filter media. Besides their capacity to attenuate flows and minimise runoff volumes, stormwater biofilters have proven efficacy for enhancing effluent water quality. Furthermore, they can be aesthetically pleasingly integrated even in dense urban environments. However, there are still gaps in our knowledge of the variability of biofilters' pollutant removal performance, and the factors that affect their performance.

In the studies this thesis is based upon, the effects of various ambient factors, stormwater characteristics and modifications of filter design on the removal of metals, nutrients and total suspended solids (TSS) in biofilters, and pollutant pathways through them, have been investigated. For these purposes, standard biofilters and variants equipped with a submerged zone, a carbon source and different filter materials were exposed to varying temperatures and dry periods, dosed with stormwater and snowmelt, and the inflow and outflow concentrations of the pollutants were measured.

Although removal percentages were consistently high (>70%), demonstrating that biofilters can reliably treat stormwater, the results show that metal outflow concentrations may vary widely depending on the biofilter design and the ambient conditions. Prolonged drying especially impaired their removal efficiency, but variations in temperature and filter media variations had little effect on metal removal rates. The adverse effects of drying could be mitigated by using a submerged zone, and thus providing a more constant moisture regime in the filters between storm events. Combined with embedded organic matter, the submerged zone especially significantly enhances Cu removal, helping to meet outflow target concentrations. Similarly, installing a mulch layer on top of the filter provides additional sorption capacity, hence metals do not ingress far into the filter and are mainly trapped on/in the top layer by sorption processes and/or mechanical trapping associated with TSS. This leads to significant metal accumulation, which facilitates biofilter maintenance since scraping off the top layer removes high proportions of previously accumulated metals, thus delaying the need to replace the whole filter media. However, removal of accumulated pollutants from the filter media is crucial for successful long-term performance of the filters to ensure that no pollutant breakthrough occurs.

Nitrogen removal was found to be more variable than metal removal, and to be adversely affected by temperature increases, leading to high nitrogen leaching in warm temperatures. Phosphorus removal rates were consistently high, since most phosphorus was particle-bound and thus trapped together with TSS. However, in initial stages phosphorus was washed out from the filter media, indicating that filter media that do not have high levels of labile phosphorus should be used to avoid high effluent concentrations.

Given that most outflow concentrations were far lower than those in the stormwater, biofilters are appropriate stormwater treatment systems. Dependent on the ambient conditions, the target pollutants and the sensitivity of the recipient, adaptation of the filter design is recommended. Further work is required to investigate the winter performance and improve the reliability of nitrogen removal, which is highly variable.

SAMMANFATTNING

Dagvatten är en viktig orsak till ekologiska försämringar av urbana vattendrag p.g.a. stora avrinningsvolymmer, och höga flöden samt en tillförsel av diverse föroreningar, t.ex. sediment, tungmetaller, näringsämnen, polycykliska aromatiska kolväten och salt. Dagvattenhanteringen har länge varit fokuserad enbart på att leda bort vattnet i rörledningar utan att hänsyn har tagits till retention av stora flöden eller till vattenkvaliteten. På grund av dessa problem har utvecklingen av uthålliga dagvattensystem blivit allt viktigare och koncept som *Lokalt Omhändertagande av Dagvatten* (LOD), *Water Sensitive Urban Design* (WSUD) och *Low Impact Development* (LID) har utvecklats. En uthållig lösning inom dessa koncept är dagvattenbiofiltrering.

Dagvattenbiofilter är infiltrationsbäddar med växter där dagvattnet infiltrerar och renas av växterna och filtermaterialet. De har en god förmåga att fördröja stora flöden samt att reducera föroreningar i dagvattnet innan det släpps ut till recipienten. Dessutom är det en estetisk och naturnära teknik som mycket väl kan integreras arkitektoniskt i både nya och befintliga stadsmiljöer. Dock saknas det fortfarande mycket kunskap om de processer som styr reningsförmågan samt hur de påverkas av varierande omgivningsförhållanden.

I denna avhandling har därför effekterna av olika omgivningsfaktorer, dagvattenegenskaper och design av biofilter på reningen av metaller, näringsämnen och sediment undersökts. För att undersöka detta har biofilter, som delvis försetts med olika filtermaterial eller en vattenmättad zon, till dels kombinerad med en kolkälla, och utsatts för olika temperaturer och torra perioder. Biofiltren har bevattnats med dagvatten eller smältvatten. Prover har tagits på ingående och utgående vatten och föroreningskoncentrationerna har analyserats.

Trots att reduktionsförmågan av metaller var hög (>70%), vilket bekräftar att biofiltren har förmågan att effektivt rena dagvattnet, visar resultaten att de utgående metallkoncentrationerna kan variera mycket beroende på utformningen av biofilter och varierande omgivningsfaktorer. Torra perioder som är längre än 3 till 4 veckor minskar metallavskiljningen i biofilter, medan växlande temperaturer och olika filtermaterial hade mindre betydelse för metallreningen. Dock kan en vattenmättad zon i filtermaterialet minimera (Cu och Zn) eller till och med avlägsna (Pb) den negativa effekten av torka med avseende på reningsförmågan. I kombination med en kolkälla kan en vattenmättad zon öka reningseffekten för framför allt Cu (som inte är lika bra i standardutförande av biofilter) på grund av en ökad komplexbildning och partikulärt organiskt material. Sediment, metaller och partikelbundna dagvattenföroreningar hålls tillbaka redan i det översta filterlagret vilket leder till en hög metallackumulation. Detta underlättar filterunderhållet: genom att skrapa och ersätta bara det översta jordlagret kan en hög andel ackumulerade föroreningar tas bort från filtret. Således kan utbyte av det hela filtermaterialet fördröjas.

Kvävereningen var inte lika effektiv som metallreningen. I varma temperaturer (20°C) har kväveutlakning i stället för reduktion observerats. Fosforreningen var dock hög eftersom fosfor var mestadels partikelbunden och blev därför filtrerat tillsammans med sedimentet i det översta filterlagret. I början av biofilterdriften har dock fosfurlakning från filtermaterialet observerats vilket tyder på att det inte ska innehålla höga halter av fosfor för att undvika utlakning från filtret.

Eftersom de flesta föroreningskoncentrationer i det utgående vattnet var betydligt lägre än i dagvattnet är biofilter en uthållig och tillförlitlig teknik för dagvattenrening. Beroende på olika omgivningsfaktorer samt de ekologiska förhållandena i recipienten rekommenderas dock anpassning av filterdesignen. Framtida forskning behövs för att undersöka biofiltrens reningsförmåga under vinterförhållanden och för att förbättra den varierande kvävereningen.

ZUSAMMENFASSUNG

Regenwasserabfluss von versiegelten Flächen ist aufgrund des im Vergleich zu ländlichen und naturnahen Einzugsgebieten hohen und schnellen Oberflächenabflusses und seiner Schadstoffbelastung Hauptgrund für die Verschlechterung der Gewässergüte urbaner Gewässer. Da die derzeitige Regenwasserbewirtschaftung (meist basierend auf Misch- oder Trennkanalisation) nicht nachhaltig ist, besteht ein dringender Bedarf an Neu- und Weiterentwicklungen alternativer nachhaltiger Systeme. Ein Beispiel hierfür sind Bodenfilter (eng. *stormwater biofilter*, *bioretention* oder *rain garden*) zur Speicherung, Behandlung und Versickerung von Regenwasser, die vor etwa 20 Jahren in den USA entwickelt worden sind. Forschungsergebnisse und praktische Erfahrungen damit sind viel versprechend und deuten auf ein hohes Potenzial hinsichtlich Regenwasserrückhalt und -behandlung hin. Außerdem können sie zu einer Aufwertung des Stadtbildes beitragen. Allerdings besteht nach wie vor Forschungsbedarf über das Reinigungsvermögen von Biofiltern und die Faktoren, die dieses beeinflussen.

Im Rahmen dieser Dissertation wurde anhand von Laborversuchen der Einfluss wechselnder äußerer Rahmenbedingungen, Regenwassereigenschaften und Anpassungen des Bodenfilteraufbaus auf die Reinigung des Regenwassers von Schwebstoffen, Schwermetallen und Nährstoffen untersucht. Für die Versuche wurden Bodenfilter mit einer wassergesättigten Zone (teilweise in Kombination mit organischem Material) und verschiedenen Filtermaterialien versehen, unterschiedlichen Regen-/Trockenphasen sowie unterschiedlichen Temperaturen ausgesetzt und mit Regen- oder Schneeschmelzwasser bewässert.

Obwohl die Metallkonzentrationen im behandelten Wasser deutlich unter denen des unbehandelten Regenwassers lagen, variierten die Konzentrationen im Ausflusswasser je nach Filtermaterial und Umgebungsbedingungen stark. Vor allem längere Trockenperioden verschlechterten die Reinigungsleistung bei nachfolgenden Regenereignissen deutlich. Die Regenwasserreinigung nach Trockenperioden ließ sich durch eine wassergesättigte Zone im Filter deutlich verbessern. Diese wassergesättigte Zone steigert außerdem maßgeblich die Kupferreinigung, wenn sie mit in den Filter eingebettetem organischem Material kombiniert wurde. Gleiches galt für eine Mulchschicht auf dem Filter, aufgrund der Bereitstellung zusätzlicher Sorptionskapazität. Temperaturunterschiede beeinflussten die Metallreinigung wenig.

Metalle drangen im Allgemeinen nicht tief in das Filtermaterial ein, sondern wurden in den oberen Filterschichten zurückgehalten. Hierdurch entstand eine erhebliche Ablagerung von Schwermetallen im obersten Filterbereich, welche in der Praxis regelmäßig entfernt werden muss, um Auswaschungen vorzubeugen. Im Vergleich zu Metallen war die Stickstoffreinigung weniger effektiv. Warme Temperaturen (bis 20°C) führten zu erhöhter Nitrifikation im Filter. Da keine anoxischen Bedingungen vorhanden waren, fand keine Denitrifikation statt und es wurden große Mengen Nitrat/Nitrit ausgespült, was zu einer Stickstoffnettoproduktion führte. Demgegenüber wurde eine effektive Phosphorreinigung erzielt, was durch den hohen Anteil partikulären Phosphors begünstigt wurde. Zu Beginn der Bodenfilteroperation wurde ein mit der Zeit abnehmendes Auswaschen von Feinsediment und Phosphor beobachtet. Dieses unterstreicht die Bedeutung des Filtermaterials für die Phosphorreinigung, da es (bei hohem Feinsediment- und Phosphorgehalt) zu Phosphorauswaschung aus dem Filter selbst kommen kann.

Biofilter haben das Potenzial, Regenwasser effektiv zu reinigen; in den meisten Fällen lagen die Schadstoffkonzentrationen im gereinigten Wasser deutlich unter denen des Regenwassers. Je nach den lokalen Rahmenbedingungen, den zu entfernenden Schadstoffen und der ökologischen Empfindlichkeit des Vorfluters werden Modifikationen des Bodenfilterdesigns empfohlen. Vor allem hinsichtlich der Stickstoffreinigung und der Anpassung an Winterverhältnisse besteht weiterer Forschungsbedarf.

ABBREVIATIONS

BMP	Best Management Practice
Cd	Cadmium
C	Carbon source (wood chips and pea straw embedded in biofilter media)
Cu	Copper
CV	Coefficient of Variance
EPA	Environmental Protection Agency
FAWB	Facility for Advancing Water Biofiltration
LID	Low Impact Development
LTU	Luleå University of Technology
N	Nitrogen
NH ₄	Ammonium
NO _x	Nitrate and nitrite
NTNU	Norwegian University of Science and Technology
P	Phosphorus
PAH	Polycyclic aromatic hydrocarbons
Pb	Lead
PE	Polyethylene
PVC	Polyvinyl chloride
RSZ	Retrofitted SZ
SZ	Water saturated zone / submerged zone
TN	Total Nitrogen
TP	Total Phosphorus
TSS	Total suspended solids
WSUD	Water Sensitive Urban Design
Zn	Zinc

APPENDED PAPERS

- Paper I.** Blecken, G.-T., Zinger, Y., Deletic, A., Fletcher, T.D., Viklander, M. (2009). Impact of a submerged zone and a carbon source on heavy metal removal in stormwater biofilters. *Ecol. Eng.* 35 (5), 769-778.
- Paper II.** Blecken, G.-T., Zinger, Y., Deletic, A., Fletcher, T.D., Viklander, M. (2010). Effect of retrofitting a saturated zone on the performance of biofiltration for heavy metal removal – preliminary results of a laboratory study. 7th International Conference on Sustainable Techniques and Strategies in Urban Water Management NOVATECH 2010, Lyon, France.
- Paper III.** Blecken, G.-T., Zinger, Y., Deletic, A., Fletcher, T.D., Viklander, M. (2009). Influence of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters. *Water Res.* 43 (18), 4590-4598.
- Paper IV.** Blecken, G.-T., Muthanna, T.M., Zinger, Y., Deletic, A., Fletcher, T.D., Viklander, M. (2007). The influence of temperature on nutrient treatment efficiency in stormwater biofilter systems. *Water Sci. Technol.* 56 (10), 83-91.
- Paper V.** Blecken, G.-T., Zinger, Y., Deletic, A., Fletcher, T.D., Hedström, A., Viklander, M. (submitted). Laboratory study on stormwater biofiltration: nutrient and sediment removal in cold temperatures. Re-submitted to *J. Hydrol.* after moderate revision, August 2010.
- Paper VI.** Blecken, G.-T., Marsalek, J., Viklander, M. (submitted). Laboratory study on stormwater biofiltration in cold temperatures: metal removal and fates. Submitted to *Water Air Soil Pollut.* September 2010
- Paper VII.** Muthanna, T.M., Viklander, M. Blecken, G.-T., Thorolfsson, S.T. (2007). Snowmelt pollutant removal in bioretention areas. *Water Res.* 41 (18), 4061-4072

Papers I, II and III are based on experiments conducted at Monash University in Melbourne, Australia. For those papers I was responsible for the data interpretation and writing. Furthermore, I participated in the experimental work described in paper III during my stay at Monash University. My co-authors commented on the data interpretation and the paper drafts.

Papers IV, V, and VI are based on experiments conducted at Luleå University of Technology. I significantly contributed to the ideas, the experimental design and work, the data collection and interpretation, and writing the papers, partly with supervision and guidance by Maria Viklander, Tim D. Fletcher, Ana Deletic and Yaron Zinger. Drafts of papers IV, V and VI were also commented upon by Tone M. Muthanna, Annelie Hedström and Jiri Marsalek, respectively. The practical laboratory work was supported by Monica Olofsson and Kerstin Nordqvist.

Paper IV presents and discusses preliminary results of the same study considered in Paper V. However, Paper V presents considerably more results, statistical analyses, kinetic parameters and discussion; thus the two papers do not significantly overlap.

The experiment reported in Paper VII was conducted in Trondheim, Norway, at the Norwegian University of Science and Technology. I participated in some of in the experimental work and planning and commented on a draft of the paper.

My contribution to the scientific papers was thus as outlined in the table below.

Paper	Idea	Experimental design	Experimental work	Data interpretation	Writing
I, II				responsible	responsible
III			participation	responsible	responsible
IV, V, VI	participation	participation	responsible	responsible	responsible
VII			minor participation		Commenting on paper draft

Luleå, September 2010

Godecke-Tobias Blecken

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CHAPTER 1

INTRODUCTION

Urbanisation results in increased stormwater volumes and peak flows as well as impaired water quality. Stormwater contamination is a major cause of ecological degradation of receiving water bodies. Consequently, in recent decades there has been increasing concern about pollutants in stormwater discharges into recipient waters (Ellis and Marsalek 1996). Hence, there is a need to develop, and implement, sustainable stormwater treatment technologies that reliably remove pollutants and are adapted to local ambient conditions.

Besides their capacity to attenuate flows and minimise runoff volumes, stormwater biofilter infiltration systems can improve effluent water quality using vegetated filter media (Davis et al. 2001b), thus contributing to a more sustainable urban environment. Furthermore, biofilters can be integrated into the urban environment, forming an important aesthetically pleasing part of the streetscape (Figure 1).



Figure 1: Stormwater biofilter installation as part of the urban streetscape, Sydney, Australia.
Photo courtesy of Professor Tony Wong, Monash University, Australia.

At the beginning of this PhD research project (2005), only a few studies about the pollutant removal efficiency of biofilters had been published (Lau et al. 2000; Mothersill et al. 2000; Davis et al. 2001b; Mazer et al. 2001; Davis et al. 2003; Kim et

al. 2003; Scholz 2004; Lloyd et al. 2001). The increasing popularity of this technology is reflected in the growing number of studies published since then globally, among others the papers appended to this thesis. While the first studies mainly investigated the overall pollutant removal performance of biofilters, subsequently the focus was increasingly on more detailed aspects of biofilter treatment, e.g. their efficiency under specific ambient conditions, the underlying processes and means to enhance their performance. This doctoral work should also be seen in this context; the effects of a range of factors possibly influencing removal efficiencies were investigated and the underlying processes discussed.

1.1 Thesis structure

This compilation thesis considers the research work presented in seven scientific papers, which are referred to as Papers I to VII (listed above). Four of these papers have been published in international, peer-reviewed scientific journals, two have been submitted to such journals and one presented at an international peer-reviewed conference.

The first chapter, the *Introduction*, briefly outlines the context of the research. It introduces the research field of urban hydrology and sustainable urban drainage, in which biofilters are used, thus outlining the significance of the research. Based on this, the research *objectives* are developed. The third chapter, *Stormwater biofilter processes and functions*, reviews the relevant literature focusing on water quality improvement by biofilters. The *Materials and Methods* chapter presents the experimental set-up and operation as well as the laboratory and data analyses. The *Results* of these studies are described in the fifth chapter. In the following *Discussion* those results are compared and discussed in relation to the objectives of the thesis and the relevant scientific literature, and practical implications of this research are summarised. Finally, the main *Conclusions* are presented. In the last chapter, recommendations for *Further Research* are developed.

1.2 Background

1.2.1 Stormwater quantity and quality

Urbanisation causes significant changes in the hydrological cycle compared to natural and rural catchments in terms of both hydrology and water chemistry and, thus, stormwater runoff has become a significant problem worldwide (Chocat et al. 2001).

Increased catchment imperviousness leads to reduced infiltration and evapotranspiration of precipitation water, and thus to increased surface runoff (Walsh et al. 2005). Compared to surface runoff hydrographs for natural or rural areas, urban runoff hydrographs (Figure 2) are characterised by a higher total runoff volume, a higher peak flows and a shorter time of concentration, hence they have steeper limbs (Rose and Peters 2001; Roy et al. 2009).

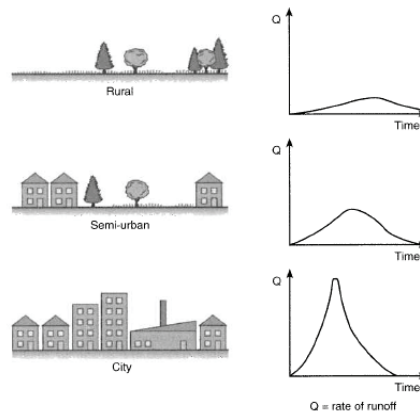


Figure 2: Effect of urbanisation on runoff hydrographs (Butler and Davies 2004).

Depending on the catchment characteristics, urban stormwater might be polluted with a wide range of substances (Ellis and Marsalek 1996). From about 1970 onwards, stormwater pollution has been identified as a significant environmental problem (Malmqvist 1983; Heaney and Huber 1984; Marsalek et al. 1999). *Inter alia*, significant loads of sediments, heavy metals, nutrients, oils, grease, bacteria and salt pollutants have been found, globally, in urban stormwater and snow (Söderlund and Lehtinen 1971; Browman et al. 1979; Lygren et al. 1984; Hewitt and Rashed 1990; Barret et al. 1998; Viklander 1999; Marsalek 2003; Lee and Bang 2000; Taylor et al. 2005). Stormwater contamination is heavily affected by the density, type and extent of urbanisation as well as the number and pattern of potential contamination sources (Carle et al. 2005).

Suspended solid sources include (*inter alia*) wet and dry atmospheric deposition, road and tyre wear, construction sites and erosion, and generally dense urban catchments generate higher TSS concentrations than more lightly urbanised areas (Duncan 1999). TSS are of varying sizes (Piro et al. 2010) and especially the fine fractions (<250 μm) of suspended solids are carriers of many other (particle-bound) pollutants such as metals, polycyclic aromatic hydrocarbons (PAHs) and phosphorus and are thus frequently used as an easily quantifiable indicator of stormwater pollution (Sansalone and Buchberger 1997a; Lau and Stenstrom 2005).

Phosphorus in stormwater can originate from sources such as construction sites, atmospheric deposition, fertilisers and plant debris (Carpenter et al. 1998; Duncan 1999) and is often bound to particles (Correll 1999) since it often exists as phosphate ions, which have strong affinity for sediment particles (Berge et al. 1997). *Nitrogen* is released from fertilisers, animal droppings, plant debris and other organic material, fossil fuel combustion, and wet deposition (Carpenter et al. 1998; Duncan 1999). In urban areas, residential or park catchments produce stormwater with especially high nutrient loads (Clark et al. 2007).

The most commonly reported *metals* in stormwater are Cd, Cu, Pb and Zn (Duncan 1999); however other metals have also been found (Makepeace 1995). Cd sources include combustion, tyre and brake wear, corrosion of galvanised metals, dumped batteries, fertilisers and pesticides (Makepeace 1995). Cu is released from tyres, engine and break wear, industrial emissions, fungicides and pesticides, leading to especially high concentrations in road runoff and runoff from non-residential urban catchments (Makepeace 1995). Nowadays, common Pb sources include tyre wear, deposition from industrial sources, paints and roof construction materials (Good 1993; Duncan 1999; Makepeace 1995). Before their use was banned, the most important source of Pb were petrol additives. Thus, using data presented in studies published from the 1970s to the early 1990s, Duncan (1999) found that Pb concentrations were highest in road runoff. However, Pb concentrations in road runoff have declined since source control measures were introduced, providing an example of the potential effects of such measures (Fuchs et al. 2002). The main Zn sources are tyre and brake wear, corrosion of galvanised roofs and other building materials (Duncan 1999; Makepeace 1995). Consequently, the highest Zn concentrations can be found in roof and road runoff (Duncan 1999).

The *pH* of stormwater ranges from 4.1 to 8.3, with a mean of ca. 7 according to Duncan (1999), and thus it is higher than rainfall pH. The cited author found no significant differences reported in stormwater pH among urban catchment types, except that direct roof runoff had a significantly lower pH than other types due to its generally short time of concentration. The pH of stormwater is particularly important for the solubility of a wide range of metals in it, hence the acute toxicity of a range of metals is influenced by pH (Makepeace 1995).

High amounts of *salt* are applied *inter alia* as a de-icing agent, especially during winter in areas with cold or temperate climates (Marsalek 2003). Besides its detrimental environmental effect (esp. plant damages; Caraco and Claytor 1997), salt affects the partitioning of metals (especially Cd and Zn) increasing the proportions present in the more environmentally hazardous dissolved phase (Marsalek 2003; Bäckström et al. 2004; Warren and Zimmermann 1994).

Stormwater contamination can vary extremely, both between different storm events and during single events, due to variations in a range of factors, e.g. catchment characteristics, the amount of precipitation, the duration of the preceding dry period,

stormwater flow and season (Duncan 1999; Westerlund et al. 2003; Browman et al. 1979). For instance, Duncan (1999) found total P, Cu and Zn concentrations in urban runoff ranging between 0.01–4.7, 0.005–7.0 and 0.01–43.7 mg L⁻¹ in a review of 306, 192 and 235 records, respectively, and similar variations for other contaminants. Due to factors such as combustion processes being less efficient at cold temperatures, increased heating and accumulations of contaminants in snow packs, pollutant concentrations have been shown to be higher during winter in areas with cold and temperate climates (Engelhard et al. 2007; Westerlund et al. 2003; Hallberg et al. 2007). Within a single runoff event, first flush phenomena may occur (i.e. pollutant concentrations may be highest in initial phases of the storm events; Bertrand-Krajewski et al. 1998).

1.2.2 Stormwater impact on recipient waters

The stormwater drainage system (e.g. proportion of directly connected impervious surfaces, combined or separated sewer system and stormwater treatment facilities) is a major determinant of the impact of stormwater contamination on recipient waters (Taylor et al. 2004; Lee and Bang 2000). Traditionally, stormwater has been managed for flood control, and direct connections between impervious surfaces and recipient waters via separate or combined sewers have been used to facilitate quick and efficient collection, conveyance and discharge of surface runoff water (Figure 3). However, these systems were usually installed without considering water quality aspects (Bedan and Clausen 2009; Walsh et al. 2005). Thus, while there has been substantial success in reducing point source discharges of pollutants (due to increasing implementation of effective waste water treatment) (Swedish EPA 2009), non-point source discharge remains a significant problem (U.S. EPA 2005).



Figure 3: Discharge of untreated stormwater from a stormwater sewer.

Urban stormwater is a major cause of ecological degradation of urban waterbodies, resulting in impairments of water quality, hydrology and habitats, often collectively referred to as 'urban stream syndrome' (Walsh et al. 2005). Common symptoms include increased hydrologic flashiness, higher stream velocities, enlarged stream profiles with modified morphology and eroded riverbanks, reduced base flows, water contamination, reduced biodiversity and higher proportions of tolerant species (U.S. EPA 2002; Walsh et al. 2005; Swedish EPA 2006; Roy et al. 2009; Taylor et al. 2004; Masterson and Bannerman 1994). Urban streams exhibit significantly elevated levels of TSS, heavy metals, nutrients, oil and grease, faecal coliform bacteria and biochemical oxygen demand compared to unimpaired reference streams (Carle et al. 2005; Masterson and Bannerman 1994).

Sediments might accumulate on the bottom of recipient waters, where they may change the aquatic habitat (Masterson and Bannerman 1994) and may be re-suspended in the future. Long-term accumulation might lead to markedly elevated metal concentrations in bottom sediments in urban recipients (Rentz 2008). Cu, Cd and Pb have been shown to bioaccumulate in urban water organisms (Masterson and Bannerman 1994), and stormwater can exhibit acute toxicity (Marsalek et al. 1999). Generally, dissolved metals are more bioavailable than particle-bound metals. Urban non-point sources contribute significantly to nitrogen and phosphorus contamination of surface waters (Carpenter et al. 1998). Even if P is mainly particle-bound it can be hazardous for the environment since it may be released from accumulated (stormwater) sediment (Correll 1999). This nutrient contamination might result in increased algal growth (possibly eutrophication) and oxygen deficiency (Taylor et al. 2004).

1.2.3 Sustainable urban drainage systems

Since urbanisation is increasing rapidly there is an urgent need to develop new, more sustainable solutions to mitigate the negative impacts of traditional urban drainage systems on the natural and urban environment (Chocat et al. 2007; Roy et al. 2009). Therefore, concepts like Water Sensitive Urban Design (WSUD) and Low Impact Development (LID) have been developed in efforts to re-establish near natural water cycles and restore the ecological condition of urban streams (Dietz 2007; Melbourne Water 2005; Walsh et al. 2005; Bedan and Clausen 2009; U.S. EPA 2000).



Figure 4: Urban streetscape before and after retrofitting a sustainable urban drainage systems. Photo courtesy of Kevin R. Perry, Nevue Ngan Assoc., Portland, OR, USA.

While public safety (flood prevention) remains a priority target in these concepts, water quality issues are also taken into account (water quality treatment and source control to improve ecological conditions of urban water bodies). The aim of LID or WSUD is to bring the urban hydrology more in line with pre-development conditions (Bedan and Clausen 2009; Dietz 2007). Furthermore, it is intended to enhance public amenities by integrating stormwater management technologies into the urban streetscape, (Figure 4; Lloyd et al. 2002). Thus, sustainable concepts for new installations, or improvements of existing urban drainage systems focus on:

- Stormwater quantity: increased runoff volumes and peak flows in urban areas have to be reduced.
- Stormwater quality: discharge of stormwater contaminants to recipient water bodies has to be reduced.
- Amenity: stormwater should be made visible to citizens and should be part of the urban streetscape.

In addition to non-structural options (e.g. source control, street sweeping, education), WSUD and LID incorporate a range of often combined retention and treatment technologies, commonly termed structural Best Management Practices (BMP). Examples of commonly implemented BMPs are listed below (based on Melbourne Water 2005; Barret 2005; Deletic and Fletcher 2006; Dietz 2007; Fletcher et al. 2003; Mikkelsen et al. 2001; Pitt et al. 1999; Stahre 2008; Villarreal et al. 2004):

- Buildings can be covered with a vegetated growing media over a waterproof layer to reduce stormwater runoff by disconnecting impervious surfaces from the stormwater pipe system. These *green roofs* can also provide a source control measure, if they replace metal roofing for instance. In addition, the 'heat island effect' is minimised when green roofs are installed.
- *Swales* convey stormwater relatively slowly (instead of or in combination with pipe systems) using overland flow and gentle slopes. Some sediment removal takes place and thus swales can provide pre-treatment in a stormwater treatment train.
- *Buffer strips* provide sediment removal by routing stormwater as a distributed sheet flow over a vegetated area.
- Stormwater *detention basins* are designed to manage downstream flows and thus provide flood protection by storing stormwater for a limited time.

- In addition, stormwater *retention/sediment basins* remove TSS by settling sediments. Design criteria are thus both stormwater volume and quality.
- Vertical flow *constructed wetlands* are artificial vegetated swamplands that remove pollutants by sedimentation, fine filtration and plant uptake.
- *Permeable pavements* reduce the proportion of impervious surfaces in urban areas, allowing stormwater to infiltrate the *in-situ* soil and thus recharge groundwater. Pollutants may be trapped or transported to the groundwater. Commonly used materials are concrete blocks or grids, or permeable pavements. Clogging of surfaces is a common problem and pollutant export to the groundwater may be of concern.
- Similarly, *infiltration measures* (e.g. soakaways, infiltration trenches or basins) capture stormwater and facilitate infiltration and groundwater recharge, thus reducing downstream peak flows and volumes. Since infiltration measures do not treat the water, they may have to be combined with pre-treatment systems.
- The aim of *stormwater biofilters* (Figure 6; also known as rain gardens or bioretention systems) is to retain stormwater flows and similarly improve water quality using filtration by soil media and vegetation incorporating a range of physical and biochemical processes, as described below.

Bedan et al. (2009) have compared two subdivisions of the same catchment in Connecticut, USA. One subdivision was a traditional and the other a low impact development (the latter incorporating swales, biofilters and permeable pavements). While storm flows and peak discharges from the traditional catchment increased dramatically after development, they were decreased from the LID development. Metal mass exports from the LID catchment were significantly lower than those from the traditional catchment. However, nitrogen and phosphorus concentrations were lower in the runoff from the traditional catchment, possibly due to homeowners' lawn care practices, fertiliser use on swales and leaching from organic litter. In addition, Rushton (2001) has shown that low impact design for a parking lot led to reductions in runoff volumes, peak flows and pollutant loads.

CHAPTER 2

OBJECTIVES

As with many other WSUD technologies (Marsalek et al. 2003), biofilters have been mostly developed without specific consideration for their operation under varying climate conditions. The biofilter treatment efficiency depends on a range of physical, biological and chemical processes, which to unknown extend might be influenced by variations of the ambient environmental conditions.

The overall aim of this thesis has been to provide a scientific basis for achieving reliable target pollutant removal from stormwater by biofilters under given varying conditions (Figure 5).

The effects of various ambient conditions, stormwater characteristics and modifications of filter design on the water quality treatment performance of biofilters has been investigated to: clarify the roles of features of biofilters, elucidate pollutant removal processes inside them, and facilitate the design of effective biofilters.

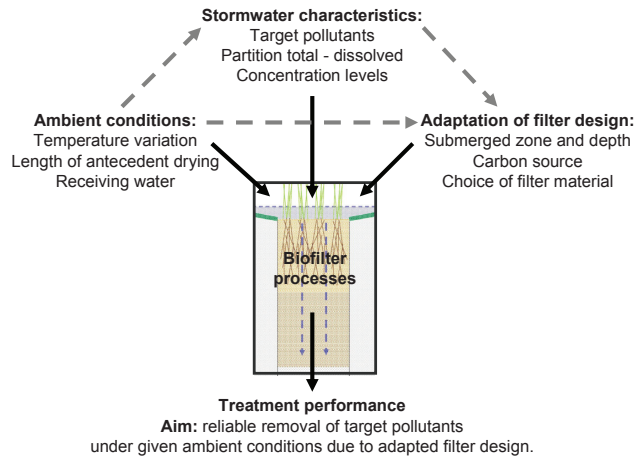


Figure 5: Examples of factors and their interactions (grey arrows) influencing biofilter processes and thus treatment performance.

- The ambient factors investigated were:
 - temperature,
 - length of time-interval between the storm events,
- The stormwater characteristics investigated were:
 - stormwater or snowmelt inflow.
 - the pollutant concentration.
- The filter design modifications investigated were:
 - coarse filter material,
 - a submerged zone, introduced to facilitate de-nitrification,
 - an embedded carbon source, introduced to facilitate de-nitrification.
- The pollutant pathways through biofilters were also investigated.

The main focus has been on the removal of metals and TSS. However, nutrient removal under varying temperatures has also been investigated.

CHAPTER 3

BIOFILTER FUNCTIONS AND PROCESSES

Vegetated vertical flow stormwater biofilters (also known as rain gardens or bioretention systems) are one promising system used in WSUD and LID for *in situ* water quality improvement and flow retention (Davis et al. 2009; Melbourne Water 2005). Biofilters were developed in the USA in the early 1990s (Prince George's County 1993). They are aesthetically pleasing, close-to-nature systems that can be widely applied (or retrofitted) even in dense urban areas (Figure 1 and Figure 6).



Figure 6: A stormwater biofilter as an example of a sustainable urban drainage technology. Photo courtesy of Kevin R. Perry, Nevue Ngan Assoc., Portland, OR, USA.

3.1 Function and design

There are several published guidelines describing the general function and design of stormwater biofilters (e.g. Prince George's County 2007; Melbourne Water 2005; U.S. EPA 2004), according to which they typically consist of a vegetated swale or basin, underlain by a filter medium (Figure 7). A detention storage on top allows temporary ponding of water if the inflow exceeds the infiltration flow (Figure 8). Stormwater is conveyed to the biofilter through an inlet with erosion protection (Figure 6). The area of a biofilter is commonly between 2 and 5% of the impervious catchment area.

The filter itself, which is usually ca. 700–900 mm thick, consists of either natural soil or engineered media (sandy loams commonly are used), in some cases topped by a 5–10 cm thick mulch layer (Melbourne Water 2005; Prince George's County 2007). Stormwater infiltrates and percolates through the filter and during its passage it is filtered by the filter media, plants and microbes via a combination of mechanical and biochemical processes (Davis et al. 2001b). Vegetation was furthermore shown to be critical in maintaining the infiltration capacity of biofiltration systems (Lewis et al. 2008). The treated water is either infiltrated into the surrounding soil or collected in a drainage pipe at the bottom of the filter and then discharged to a recipient or the existing sewer system. Biofilters can be conveniently retrofitted even in dense urban developments (Smith et al. 2007).

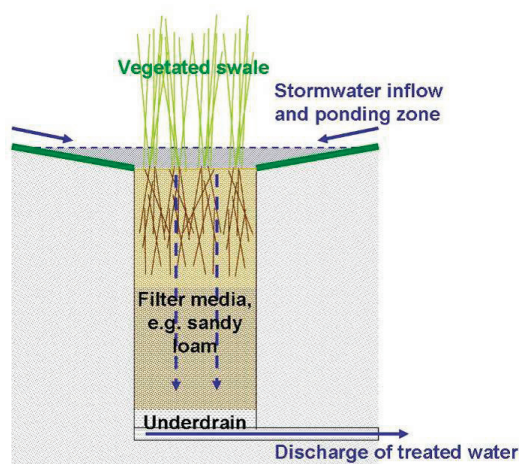


Figure 7: Cross-sectional drawing of a stormwater biofilter equipped with an underdrain



Figure 8: Biofilter during a storm event with stormwater ponding on top of the filter. Photo courtesy of Kevin R. Perry, Nevue Ngan Assoc., Portland, OR, USA.

3.2 Pollutant treatment and associated processes

From about 2000 onwards, a number of studies have been published on the pollutant removal performance of biofilters; a summary of metals and nutrient inflow and outflow concentrations observed in selected studies is given in Table 1 and Table 2. Removal of other pollutants such as oil/grease (Hong et al. 2006), PAHs (Dibiasi et al. 2009) and bacteria (Garbrecht et al. 2009; Hathaway et al. 2009; Rusciano and Obropta 2007) by biofilters have been investigated in a few studies, but are not discussed in detail here since they were not pollutants of concern in this thesis.

3.2.1 Metal and Total Suspended Solids removal

Total metal and TSS removal by stormwater biofilters often exceeds 80-90% (Bratieres et al. 2008; Davis et al. 2001b; Davis et al. 2003; Hatt et al. 2009; Hsieh and Davis 2005b; Lau et al. 2000; Muthanna et al. 2007; Read et al. 2008; Sun and Davis 2007). Since most metals entering biofilters are particle-bound, mechanical filtration of the incoming stormwater sediment also removes substantial loads of metals (and other particle-bound pollutants), thus the efficiency of TSS and particle-bound metal removal is correlated (Hatt et al. 2008).

In most biofilter studies only the total metal removal has been investigated (see Table 1), dissolved metal removal has been considered in fewer of the investigations (Chapman and Horner 2010; Lau et al. 2000; Muthanna et al. 2007; Read et al. 2008; Hatt et al. 2007; Sun and Davis 2007). Some findings indicate that dissolved metal removal is significantly lower than total metal removal, in particular Cu leaching being observed (Hatt et al. 2007; Chapman and Horner 2010; Muthanna et al. 2007). However, biofilters seem to have clear potential to provide adequate dissolved metal treatment (Sun and Davis 2007; Hsieh and Davis 2005a), while dissolved metals are not targeted at all e.g. in sedimentation ponds, although dissolved metal removal is of special concern since dissolved metals are far more bioavailable than particle-bound metals (Morrison 1989).

Dissolved metal removal is affected by diverse factors that influence soil and heavy metal interactions. Numerous studies in the field of soil sciences have investigated these interactions in soils. Dissolved metals may be removed by biofilters via sorption processes in the filter (cation exchange, specific adsorption, precipitation and organic complexation; Rieuwerts et al. 1998) and/or plant uptake (Fritioff and Greger 2003).

Table 1: Biofilter inflow and outflow concentrations of TSS (mg L⁻¹) and metals (µg L⁻¹) from selected studies. Data partly retrieved from Davis et al. (2009), (Lab., laboratory study; diss., dissolved concentrations; non-veg., non-vegetated; In., inflow concentrations; Out., outflow concentrations)

Filter type	Design attributes	Total/ diss.	TSS		Cd		Cu		Pb		Zn		Reference
			In	Out	In	Out	In	Out	In	Out	In	Out	
Lab.			150	(107)-<6									
Lab.	Non-veg.		42	21			22	7	41	3	285	122	Hsieh et al. (2005a)
Lab.	Non-veg.		206	6			237	6	146	<1	1800	10	Birch et al. (2005)
	Vegetated		206	5			237	5	146	<1	1800	20	Read et al. (2008)
Pilot							140	3.4	61	<2	600	<25	Davis et al. (2001b)
							64	4.9	<2	<2	590	<25	
Pilot							38-160	2.3-5.2	32-104	<2	260-1290	<25	Davis et al. (2003)
Pilot	Summer	Total					126	41.7	21.1	2.5	584	49	
	Summer	Diss.					<10	44	1.4	1.1			
	Winter	Total					26	15.2	4.4	0.8	412	22	Muthanna et al. (2007)
	Winter	Diss.					<10	10	0.05	0.026			
Field					5.6	1.9	56.8	1.9	41.4	10.2	98.3	20.6	Glass et al. (2005)
Field		34	13-18								107	44-48	Davis (2007)
Field		50	20								72	17	Hunt et al. (2008)
Field		39	3 to 5				10	4 to 6	6	2-3	100	13-30	Hatt et al. (2009)
		128	14	5	<1		60	5	110	7	330	13	
Field		66	6				19	16	6	3	71	12	Li et al. (2009)
		14	4				13	9	<2	<2	15	3	
Field	Total	120	30				16	6.3	17	4.5	120	47	Chapman et al. (2010)
	Diss.						3.6	2.9	<1	<1	49	26	

Table 2: Biofilter inflow and outflow concentrations of nutrients (mg L⁻¹) from selected studies. Data partly retrieved from Davis et al. (2009).

Filter type	Design attributes	Total/ diss.	P		N		Nitrite/nitrate-N		Ammonia-N		Reference
			In	Out	In	Out	In	Out	In	Out	
Lab.	Partly with saturated zone				2.1	0.1-3					Kim et al. (2003)
Lab.	Non-veg.		0.25	0.12	2.14	1.81	0.62	1.34			Birch et al. (2005)
Lab.		3	0.46-2.9								Hsieh et al. (2005a)
Lab.	Vegetated		0.48	0.03-0.07	5.44	1.23-2.04	0.69	0.05-0.24	0.48	0.02-0.03	Henderson et al. (2007)
Lab.	Non-veg.		0.48	0.05-0.33	5.44	4.06-6.09	0.69	1.75-2.69			
Lab.	Non-veg.	Total	0.260	0.106	1.02	2.18	0.393	0.370	0.113	0.474	Read et al. (2008)
Lab.	Non-veg.	Diss.	0.033	0.08	0.65	1.86					
Lab.	Vegetated	Total	0.260	0.082	1.02	1.69	0.393	0.083	0.113	0.456	
Lab.	Vegetated	Diss	0.033	0.027	0.65	1.40					
Pilot			0.44	0.13					1.2	0.48	Davis et al. (2001b)
Pilot			0.52	0.1			0.34	0.26	2.4	0.5	
Pilot		0.28-0.88	0.06-0.15		1.6-6	1.1-2.8					Davis et al. (2006)
Field		0.012-0.019	0.058-0.06								Dietz et al. (2006)
Field		0.11	0.56		1.35	4.38					Hunt et al. (2006)
Field		0.61	0.15-0.17								Davis (2007)
Field		0.19	0.13		1.68	1.14					Hunt et al. (2008)
Field		0.07	0.16-0.22		1.1	1.1-1.3	0.4	0.14-0.3	0.04	0.02-0.03	Hatt el at. (2009)
Field		0.4	0.07		2.7	2.2	1	1.6	0.5	0.02	
Field		0.1	0.35		1.6	2.5	0.36	1.0			Li et al. (2009)
Field		<0.1	<0.1		1	0.6	0.34	0.05			
Field		0.21	0.13		1.15	0.81					Chapman et al. (2010)

Of particular concern for the treatment efficiency of dissolved metals are the filter media and soil solution pH (since pH is the primary determinant of metal solubility and thus metal sorption processes, as is the stormwater pH for the distribution between particle-bound and dissolved metals in stormwater; Sansalone and Buchberger 1997b; Rieuwerts et al. 1998; Bradl 2004). However, in addition to pH, a range of other physical and (bio)chemical factors may influence metal solubility and soil surface chemistry (Bradl 2004; Warren and Haack 2001). Notably, the redox status also affects the partitioning of elements between solution and solid phases (Rieuwerts et al. 1998; Warren and Haack 2001).

As in stormwater, increasing salinity may raise the solubility of metals and thus reduce rates of metal sorption in the filter (Förstner et al. 1998; Warren and Zimmermann 1994). Temperature changes may influence biological and biochemical processes (e.g. nutrient treatment and plant metal uptake, see below), but not necessarily influence metal sorption by soils (Lucan Bouche et al. 1997; Rieuwerts et al. 1998).

Plants, especially their root activities, also strongly influence metal solubility in soils, and thus in filter media, via their effects on dissolved organic matter contents and/or pH (Zhao et al. 2007). Furthermore, plants have been shown to take up dissolved metals (Fritioff and Greger 2003), thereby accounting for up to ca. 10% of the total metal removal by biofilters (Davis et al. 2001b; Sun and Davis 2007). However, even non-vegetated soil filters remove metals quite effectively (Hatt et al. 2008; Read et al. 2008). Furthermore, dissolved metals may also be removed by sorption to bacteria and biofilms (Warren and Haack 2001).

Typically, metals do not ingress far into the filter, but are trapped on or near the top of the filter due to both mechanical removal and sorption processes (e.g. Davis et al. 2001b). However, the accumulation of fine stormwater sediment on top of the filter material and in the upper layers reduces the hydraulic conductivity relatively quickly, possibly leading to clogging (Le Coustumer et al. 2007; Li and Davis 2008). On the other hand, the high metal removal in the upper layer facilitates filter maintenance since merely scraping off the top layer may remove a high proportion of accumulated metals from the system, and thus postpone the need to replace the whole filter media (Hatt et al. 2008).

3.2.2 Nutrient removal

Nutrient removal is far more variable than metal and TSS removal in biofilters, thus nutrient treatment in biofilters might be problematic (Dietz 2007). Notably, both very efficient removal of N and P, and excessive leaching from them, have been observed. For example, Davis et al. (2006) reportedly observed 70–80 % TP removal in biofilter box experiments, but Li and Davis (2009) observed strong leaching (0.1 and 0.35 mg L⁻¹ TP in influent and effluent, respectively). Similarly, the efficacy of total nitrogen treatment is very variable, ranging from effective removal to significant leaching (Kim

et al. 2003). However, although the efficiency of biofilter treatment for both nutrients is similarly variable, the underlying mechanisms differ.

The removal of the mainly particle-bound incoming P is effective due to the mechanical filtration of particulate P (and hence correlated to TSS removal) and sorption of dissolved P by the filter media (Henderson et al. 2007; Hsieh and Davis 2005a; Hsieh et al. 2007a). However, in a number of studies, net P leaching from the filter media has been observed due to wash-out of fine materials with associated P (Hatt et al. 2009; Hunt et al. 2006; Li and Davis 2009; Read et al. 2008), especially from newly constructed filters often decreasing with time due to media stabilisation (e.g. repacking, settling) and/or depletion of the reserves (Hsieh et al. 2007a). Thus, to achieve low P concentrations in the effluent, it is essential to select appropriate filter media (Hunt et al. 2006), and filter media with high P concentrations should be avoided (Dietz 2007; FAWB 2008). In addition to stormwater runoff, eroded sediments are important non-point sources of P (Brady and Weil 2002), thus biofilters might indirectly reduce P discharge to recipients since they reduce surface runoff flows by reducing erosion losses in urban catchments.

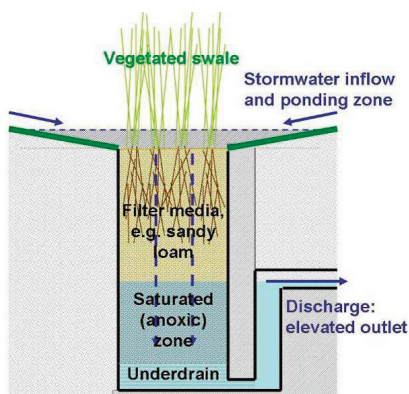


Figure 9: Sectional drawing of a stormwater biofilter equipped with submerged zone

Net N removal depends on the removal balance of the different N species. Effective NH_4 and total Kjeldahl N removal has commonly been shown (Bratieres et al. 2008; Davis et al. 2001a; Davis et al. 2006; Hsieh et al. 2007b; Henderson et al. 2007). However, NO_x removal is often inadequate and has been identified as the main reason for the N net leaching commonly observed (Birch et al. 2005; Bratieres et al. 2008; Davis et al. 2001b; Davis et al. 2006; Hatt et al. 2009; Hsieh et al. 2007b; Li and Davis 2009; Kim et al. 2003). To enhance total N removal a submerged zone (combined with a carbon source) has recently been introduced in the filter media to enable denitrification due to (partly) anoxic conditions and thus increase overall N treatment (Figure 9; Kim et al. 2003; Dietz and Clausen 2006).

Vegetated biofilters significantly enhance both P and N removal (Lucas and Greenway 2008; Read et al. 2008), but significant variations in nutrient removal between filters with different plant species have been reported (Read et al. 2008).

CHAPTER 4

MATERIALS AND METHODS

Papers I to VI present results of laboratory trials using *biofilter columns* (mesocosms) with essentially the same design. The studies described in Papers I, II, and III were conducted in the FAWB (Facility for Advancing Water Biofiltration) laboratories at Monash University, Clayton Campus, Melbourne, Australia and those described in Papers IV, V, and VI at Luleå University of Technology (LTU) in Luleå, Sweden. The design of the biofilters used in these studies was based on guidelines published by Melbourne Water (2005). To investigate the aspects considered in the papers, several design modifications of the columns were made, as described below.

The study presented in Paper VII was conducted at the Norwegian University of Science and Technology (NTNU), Trondheim. In this study a different biofilter design was implemented, a so-called *biofilter box*.

In the following sections the experimental set ups used in each of the studies are summarised. Full details can be found in the papers.

4.1 Biofilter column experiments

4.1.1 Column design

Biofilter columns (Figure 10 and Figure 13), 900 mm tall with an inner diameter of 377 mm (LTU) or 375 mm (FAWB) and an approximate cross-sectional area of 0.11 m² were made of PVC pipes. The inner walls were sandblasted to increase surface roughness in order to reduce the risk of preferential flow along the columns' walls. The columns had a 400 mm high transparent pipe on top, which allowed stormwater ponding without shading the plants and thus affecting their growth.

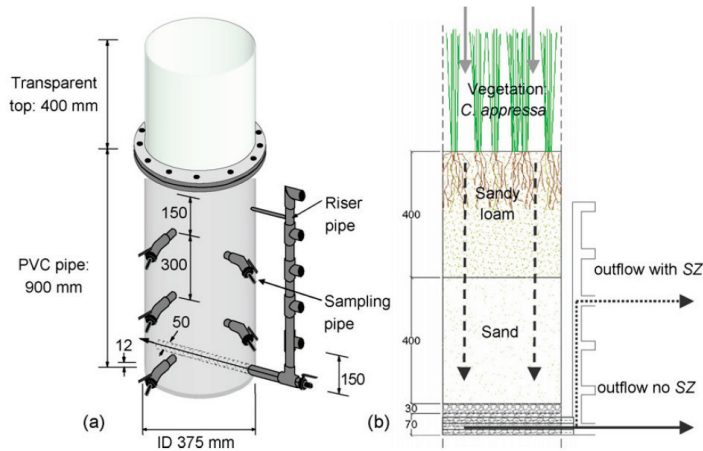


Figure 10: Biofilter column: (a) configuration with riser pipe, (b) general filter media set-up and vegetation. Figure source: Paper I.

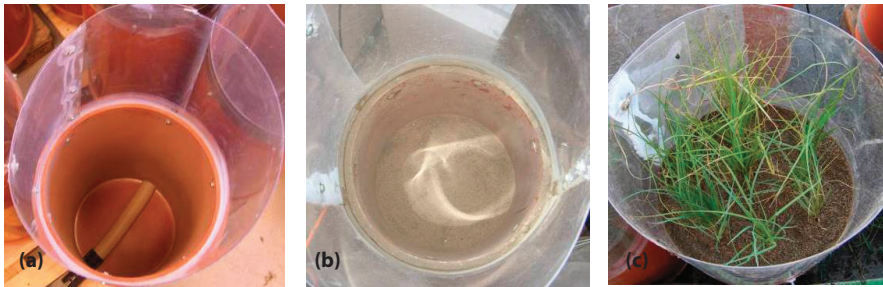


Figure 11: Biofilter columns at LTU under construction: (a) drainage pipe at the filter bottom, (b) bottom sand layer, (c) top layer with admixed top soil and plants.

The filter itself was 800 mm deep, divided into two 400 mm layers. The specifications of the filter media in those layers is summarised in Table 3, cf. Figure 11 and Figure 12. Since a coarse filter media is recommended for cold climate biofilters (Caraco and Claytor 1997) in order to facilitate sufficient infiltration even into frozen soils (Kane 1980), the filter media used in the experiments at LTU was coarser compared to the media used at FAWB. The filter itself was underlain by a 100 mm deep drainage layer consisting of a transition layer (30 mm) and the drain itself (70 mm). A slotted horizontal drainage pipe (50 mm diameter at FAWB, 58 mm at LTU, Figure 11a) was placed on the bottom of the filter to convey the water to a sampling port. The columns were planted with native *Carex* species: *C. appressa* R.Br. (tall sedge) at FAWB (Figure 13a and b) and *C. rostrata* Stokes (bottle sedge) at LTU (Figure 11c).

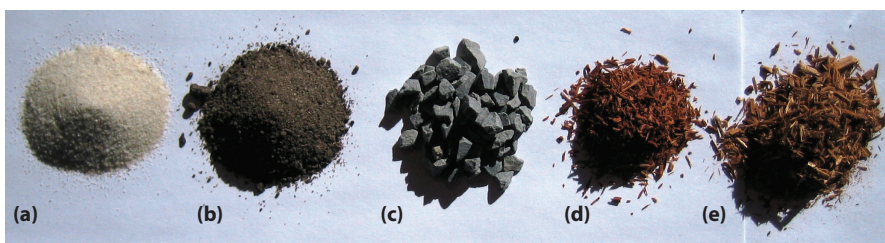


Figure 12: Filter media used in the FAWB columns: (a) fine sand, 0.25–0.50 mm, in the bottom filter layer; (b) sandy loam in the top filter layer; (c) fine gravel, 2–4mm, in the underdrain; (d) wood chips and (e) pea straw as carbon sources.

Table 3: Summary of experimental design specifications of the biofilter columns used in the studies at Luleå University of Technology (LTU) and Monash University (Facility for Advancing Water Biofiltration – FAWB) presented in Papers I to VI.

	LTU columns	FAWB columns
Column specifications		
Material	PVC	PVC
Height	900 mm + 400 mm transparent top	900 mm + 400 mm transparent top
Riser pipe to create SZ	no	yes
Sampling pipes in filter media	no	yes; enabling SZ heights of 150, 450, 600 mm
Vegetation		
Plant species	<i>C. rostrata</i> Stokes	<i>C. appressa</i> R.Br. (Paper II also <i>Dianella revoluta</i> , and <i>Microleana stipoides</i>)
Filter media		
Top filter layer (400 mm)	sand with 5% silt and 14% fine gravel, d ₅₀ = 620 µm UC = 2.4 mixed with top soil in the upper 100 mm	sandy loam d ₅₀ = 330 µm UC = 6.4
Bottom filter layer (400 mm)	fine sand	fine sand *; partly with embedded carbon source: pea straw/wood chips
Underdrain (30 + 70 mm)	coarse sand fine gravel with embedded drainage pipe	coarse sand gravel with embedded drainage pipe
Stormwater application		
Stormwater volume	15 L twice weekly	25 L twice weekly with design variations
Main design variations		
	Temperature : 5 replicates each in climate rooms at 2, 8 and 20°C	Impact of a (retrofitted) SZ, Impact of C, Drying and wetting

* The biofilters with the retrofitted SZ described in Paper II had only one filter layer of sandy loam

After constructing, filling and planting the biofilter columns, the biofilters were irrigated with tap water to allow plant establishment and then flushed with stormwater pond water (FAWB) or natural water from an enclosed urban bay in Luleå (LTU) three times during one day each to promote natural biofilm development.

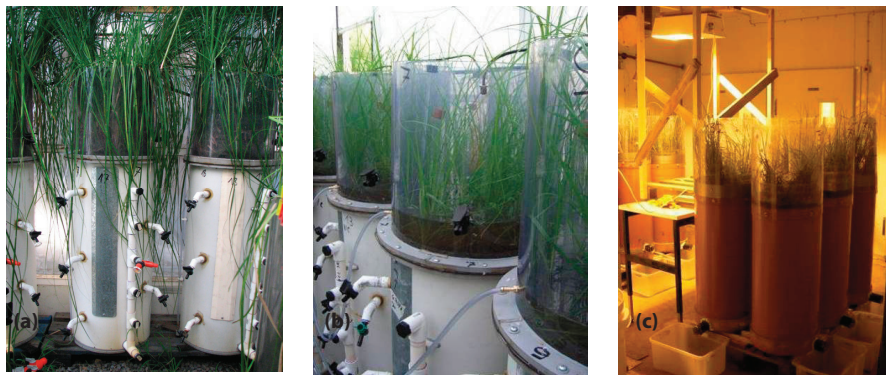


Figure 13: Biofilter columns in a greenhouse, FAWB (a and b) and a climate room, LTU (c).

The biofilter columns at FAWB were placed in a greenhouse (Figure 13a and b) with open mesh on its sides to ensure that local climatic conditions were maintained. At LTU, the columns were placed indoors in climate rooms (Figure 13c). To enable plant growth, they were illuminated with greenhouse lamps 12 h daily. Both arrangements ensured that the columns received inflow water solely by controlled dosing (i.e. non from precipitation).

4.1.2 Stormwater application

For stormwater dosing, artificial stormwater was utilised: natural stormwater sediment (from a stormwater gully pot for the experiments at LTU and from a stormwater pond for the experiments at FAWB) and laboratory-grade chemicals were added to tap water in amounts required to achieve target stormwater pollutant concentrations (Table 4).

In general, the biofilter columns were dosed twice weekly with 15 L (136 mm) and 25 L (227 mm) stormwater at LTU and FAWB, respectively. The calculation of the stormwater volume was based on typical percentage biofilter area of an impervious catchment with typical rainfall patterns and depths, as described in detail in the Papers I and IV. In between the storm the biofilter was exposed to gravity drainage.

Over the experimental run times, composite samples were taken to enable monitoring of the stormwater inflow quality.

Table 4: Stormwater inflow characteristics for each of the studies (Papers I to VII). Metal concentrations in $\mu\text{g L}^{-1}$, TSS, chloride and nutrient concentrations in mg L^{-1} .

Pollutant	I	II	III	IV	V, VI	VII	
TSS	150	179		143	131	2900 – 9600	
Total Cd	5.8		6.7		4.2	0.30	0.44 1.52
Dissolved Cd					3.4	0.02	0.02 0.01
Total Cu	54.7	67.5	95.1		153.0	123.4	200.4 543.3
Dissolved Cu					21.9	36.4	19.0 13.5
Total Pb	142.9	154.5	181.5		41.2	24.6	34.8 93.7
Dissolved Pb					0.3	0.3	0.18 0.19
Total Zn	576.9	450.3	587.3		267.0	386.4	537.6 1465.3
Dissolved Zn					211.0	7.2	6.1 2.6
Chloride						49.0	215.8 20.9
Total N	2.24		2.84	1.38	1.80		
Dissolved N				1.16	1.68		
Dissolved $\text{NO}_x\text{-N}$				0.24	0.4		
Dissolved $\text{NH}_4\text{-N}$				0.32	0.22		
Total P	0.47		0.44	0.29	0.31		
Dissolved P				0.03	0.03		
pH	7.1		6.9	6.9	6.7 – 7.0		

4.1.3 Design variations

The following text describes the design variations of the columns made to enable evaluation of the effects of the factors described in the Papers I to VI. For each design variation at least three (FAWB) or five (LTU) replicates were used to enable statistical analyses and validate the results. In all experiments, the columns were randomly allocated to the different design variation groups.

Percolating water sampling pipes (I). In the filter media, gravel filled PVC sampling pipes with 21 mm diameter were installed at different depth (Figure 10a). These pipes traversed the entire column diameter, they had open tops to enable sampling of the seepage and were surrounded by sand to prevent washout of the overlying soil. Unfortunately, some clogged, so samples were not available from all depths.

Submerged zone (I, II, III) and Carbon source (I, III). To test the effect of submerged zones with different heights, the sampling port was elevated using an external riser pipe with six outlet taps installed at different heights (Figure 10 and Figure 13). By opening one of these taps, the water level could be kept constant at the bottom of the column, thus creating submerged zones of different depths (according to the height of the open tap). For the studies presented in Papers I and III, the SZ was fitted to the biofilters from the beginning of the experimental run time, while for the columns investigated in described in Paper II the SZ was retrofitted after one year of biofilter operation as standard filters.

To promote denitrification a cellulose-based carbon source was embedded in the bottom filter layer. For the filters used in the studies presented in Papers I and III, a carbon source was embedded in the deeper filter layer (i.e. in the submerged zone) from the beginning. No additional carbon source was implemented if the submerged zone was retrofitted into standard biofilters (cf. Paper II). The carbon source consisted of 1/3 pea straw and 2/3 wood chips. Thus, in the studies presented in Papers I to III, different combinations of SZ and C were tested as outlined in Table 5.

Table 5: SZ and C combinations in the studies presented in Papers I to III. RSZ: Retrofitted SZ after ca. one year of operation. SZ height in mm, cf. Figure 10.

Paper I		Paper II		Paper III	
SZ	C	SZ	C	SZ	C
0	non	0	non	0	non
450	non	RSZ 450	non	450	with
0	with				
150	with				
450	with				
600	with				

Extended drying periods (III). To investigate the effects of extended drying on the filter performance (Paper III), the columns were divided into three groups of six columns each: one of biofilters equipped with a 450 mm SZ combined with C and one of standard biofilter columns. The three groups were dosed with stormwater according to three different drying and wetting schemes (Table 6).

Table 6: Drying and wetting scheme, cf. Paper III.

Group	Wet	Dry	Wet	Dry	Wet	Dry	Wet
A	1 week	7 weeks	4 weeks				
B	1 week	1 week	1 week	2 weeks	2 weeks	3 weeks	2 weeks
C	1 week	4 weeks	2 weeks	3 weeks	2 weeks		

During wet periods, the columns were dosed with 25 L stormwater twice weekly while they received no inflow at all during dry periods. As for the whole biofilter system, the submerged zone was also subject to drying, and thus allowed to draw down over time. In this manner, the experimental operation realistically reflected the behaviour of a real biofiltration system during long dry periods.

Temperature (IV, V, VI). To investigate the effect of varying temperatures on biofilter treatment efficiency under controlled laboratory conditions, the columns were tested in three thermostat-controlled climate rooms at nearly constant air temperatures (mean 1.8, 7.3 and 20.3 °C, hereafter referred to as 2, 7 and 20°C⁽¹⁾). Five columns were placed in every room. The air temperature in the rooms was logged at 15 minute intervals. All columns were illuminated with high pressure sodium greenhouse lamps (400 W, Figure 13c) for 12 hours daily. For these experiments, the stormwater

⁽¹⁾ In Papers IV and VI the intermediate temperature is referred to as 8°C since this was the primary target temperature.

had to be prepared separately in each room for temperature adjustment, however, no significant differences in stormwater quality between the three temperatures were detected (One-way ANOVA, $\alpha=0.05$).

4.1.4 Sampling

Effluent. During the periodic outflow sampling runs composite samples from all columns were taken. The sampling strategy differed partly between the experiments. In the C/SZ study (Paper I), two samples were taken and analysed in order to evaluate the first (i.e. resident pore water) and later flow (i.e. the newly treated water) from the filter separately. In the studies described in Papers II and III, for each column one 1 L composite inflow sample was collected, consisting of five 200 mL sub-samples. The first sub-sample was collected after 1 L of the treated water had flowed out, followed by four other sub-samples each after a further 5 L outflow of water. In the temperature studies (Papers IV to VI), the outflow water was collected until at least 14 L of treated water had been discharged. This collected water was stirred and then the samples were taken.

Percolating water. In the C/SZ study (Paper I), in addition to the outflow samples from the underdrain, samples were taken from the lateral outlets (one from each outlet at the start of the sampling event to track the waterfront progress).

Filter media. After the stormwater applications, filter media samples were taken from the FAWB columns described in Papers I and III and from the columns at LTU. At FAWB, 25 mm thick filter media slices were taken at depths of 0–25, 25–50, 60–80, 200–225, 470–495, and 600–625 mm from each of the columns with and without SZ. The samples were extracted from two vertical cores of 100 mm diameter per column. At LTU, filter media samples were taken at three filter depths: the top (0–50 mm) and at 250 and 600 mm. The top samples were taken manually as grab samples, while the two other samples were horizontal cores (35 mm) spanning the whole column diameter. In addition, for all columns prior to the experiments, a grab sample of the different filter material layers (only the top layer at FAWB) were taken to determine the initial metal concentrations.

Plants. In the experiments at LTU, before and after stormwater application plant root and shoot samples were collected. Prior to the experiments, a composite sample of randomly selected plants was taken to investigate the initial plant metal concentrations. After finished stormwater application, a composite root and shoot sample was collected separately from each column.

4.2 Biofilter box experiments

4.2.1 Biofilter box design

The biofilters were constructed using two PE boxes (height 800 mm, width 880 mm, length 109 mm) with a 150 mm freeboard to allow temporary ponding of water on the filter.

The filter media assembly was based on the bioretention recommendations of Prince George's County (1993). However, as in the studies conducted at LTU and recommended by Caraco and Claytor (1997) for cold climates, a coarse medium with <3% clay content was chosen rather than the usually implemented loamy sand (Prince George's County 1993). Each filter consisted of two layers: a 500 mm deep sand soil layer overlain by a 50–100 mm deep mulch layer. At the bottom a 100 mm deep gravel layer provided drainage of the filter. A mesh was placed on top of it to prevent washout of fine media into the underdrain to avoid clogging. In the underdrain a 20 mm slotted drainage pipe conveyed the water to the outlet.

The biofilter was planted with *Iris pseudacorus* L. (yellow iris), *Lythrum salicaria* L. (purple loosestrife), *Hippophaë rhamnoides* L. (sea buckthorn) and *Vinca minor* L. (lesser periwinkle).



Figure 14: (a) Biofilter box at NTNU and its (b) top mulch layer

4.2.2 Snow application

The snow was collected from three sites with differing catchment characteristics (a residential street, 1550 vehicles per day; a collector road, 5000 vehicles per day; and a highway, 47000 vehicles per day) in Trondheim, Norway. As intended, the quality of the snow collected from the three sites clearly differed, Table 4. The snow from each site was mixed and then 75 L of each was applied on both biofilters. This approach

was repeated for all three snow samples. The biofilters were covered by a tarpaulin to avoid precipitation inflow.

4.2.3 Sampling

Effluent. From the outflow, a total of eight samples were taken: three with 15 L outflow between them, then three after 10 L each and finally two samples after 15 to 20 L outflow each. Event mean concentrations were calculated as outflow volume-based mean concentration (equation 1, Paper VII).

Filter media and plants. Filter media and plant samples were taken before and after the snow applications, as described in detail in Paper VII.

4.3 Analytical methods

Sample analyses. The water samples were analysed for pH, TSS and total Cd, Cu, Pb and Zn. N, NO_x-N, NH₄-N, P and dissolved Cd, Cu, Pb and Zn were only analysed in the experiments at LTU. The dissolved samples were filtered using 0.45 µm pore size filters. The filter media and plant samples were analysed for metal concentrations (expressed per unit dry mass).

All chemical analyses were undertaken by accredited laboratories² using standard methods and quality assurance/quality control measures. The analytical methods and their detection limits are described in detail in the papers.

Data interpretation. The effects of the evaluated factors were investigated using standard statistical methods (for details, see the papers). The significance level was always $\alpha = 0.05$. All statistical analyses were conducted using the statistical software Minitab®, versions 15.1, © 2006 Minitab Inc. and 16.1.0, © 2010 Minitab Inc.

Based on the inflow and outflow concentrations, removal (%) was calculated as follows: $\text{removal} = (1 - \text{outflow concentration} / \text{inflow concentration}) \times 100\%$.

² The nutrient analyses were undertaken by the laboratory at LTU.

In this chapter, the main results of the experiments presented in Papers I to VII, in which vegetated biofilter mesocosms were subjected to various treatments in the laboratory, are presented and synthesized. To give a general overview, here the mean outflow concentrations of nutrients and metals from the biofilters recorded in the studies are summarised in Table 7 and Table 8, respectively. Then the impact of several design features and environmental variables (submerged zone, carbon source, temperature, simulated storm events and snowmelt) on outflow concentrations is described. Thirdly, the metal pathways in the filter are presented.

Table 7: Selected mean stormwater and biofilter outflow concentrations from the biofilter studies included in this thesis. All concentrations in mg L^{-1} . For detailed results and standard deviations it is referred to the papers.

Paper	Temp.	TSS	P		N		NO _x -N	NH ₄ -N	pH
			Total	Diss.	Total	Diss.	Diss.	Diss.	
STORMWATER CONCENTRATIONS									
IV		143	0.29	0.03	1.38	1.16	0.24	0.32	6.9
V		131	0.31	0.03	1.80	1.68	0.4	0.22	6.7-7.0
OUTFLOW CONCENTRATIONS									
IV	2 °C	3.6	0.055	0.007	1.38	1.33	0.72	0.11	7.3
V	2 °C	2	0.03		1.89	1.90	1.14	0.17	7.3 to 7.5
IV	7 °C	5.1	0.058	0.009	1.54	1.31	0.89	0.14	7.4
V	7 °C	3	0.03		2.24	2.28	1.57	0.11	7.4 to 7.7
IV	20 °C	4.6	0.056	0.010	4.23	3.94	3.79	0.15	7.5
V	20 °C	3	0.03		4.86	4.71	3.76	0.06	7.5 to 7.7

Table 8: Selected mean stormwater and effluent concentrations from the biofilter studies included in this thesis. Metals in $\mu\text{g L}^{-1}$, TSS in mg L^{-1} . For detailed results and standard deviations it is referred to the papers.

Paper	Design variation	TSS	Tot. Cd	Diss. Cd	Tot. Cu	Diss. Cu	Tot. Pb	Diss. Pb	Tot. Zn	Diss. Zn	pH
STORMWATER CONCENTRATIONS											
VI		131	4.2	3.4	153.0	21.9	41.2	0.3	267.0	211	6.7-7.0
VIII	Residential Road Highway	2900to 9600	0.30 0.44 1.52	0.02 0.02 0.01	123.4 200.4 543.3	36.4 19.0 13.5	24.6 34.8 93.7	0.3 0.18 0.19	386.4 537.6 1465.3	7.2 6.1 2.6	
I		150	5.8		54.7		142.9		576.9		7.1
II		179			67.5		154.5		450.3		
III			6.7		95.1		181.5		587.3		6.9
OUTFLOW CONCENTRATIONS											
VI	2 °C	2	0.05	0.02	10.1	6.9	1.9	0.1	4.8	1.9	7.3 to 7.5
	7 °C	3	0.05	0.02	11.7	8.1	1.9	0.1	4.8	1.9	7.4 to 7.7
	20 °C	3	0.05	0.02	16.0	13.4	1.7	0.1	4.7	2.1	7.5 to 7.7
VII	Snow Residential	<10	0.04	0.04	92.6	60.3	1.6	0.2	72.6	57.1	
	Snow Road	<10	0.06	0.06	75.4	55.1	1.1	0.18	85.8	63.0	
	Snow Highway	<10	0.09	0.05	52.0	42.6	0.6	0.15	36.4	27.1	
I	Non-C		<0.7		5.7		1.5		9.4		6.9
	Non-C		<0.7		10.5		0.5		6.7		6.8
	C		<0.7		6.3		2.4		10.5		6.8
	C		<0.7		1.4		1.5		5.7		6.7
II	Non-SZ		<0.7		4.1 5.1		2.7 3.1		8.4 5.7		
	Retrof.-SZ *		<0.7		1.5 5.7		2.7 3.3		1.1 6.6		
III	3 **	Non-SZ/non-C	<0.7		9.5		1.9		15.6		
	20 **	Non-SZ/non-C	<0.7		17.3		6.1		22.8		
	27 **	Non-SZ/non-C	<0.7		16.8		10.5		24.3		
	48 **	Non-SZ/non-C	<0.7		29.5		15.0		34.4		
	3 **	SZ / C	<0.7		1.5		2.1		12.8		
	20 **	SZ / C	<0.7		6.3		0.5		15.8		
	27 **	SZ / C	<0.7		8.1		1.4		27		
	48 **	SZ / C	<0.7		15.7		1.7		57.6		

* SZ depth 450 mm, ** Antecedent dry days

5.1 Effect of inflow on outflow metal concentrations

Correlations between inflow and outflow concentration were evaluated in Papers I and VII.

In the study described in Paper I the inflow concentrations of the measured pollutants were nearly uniform during single sampling runs, but they varied significantly between the four sampling rounds. Therefore, effects of these inflow variations on the outflow concentrations and removal rates of metals from standard columns were assessed by linear regression. The results showed that the outflow concentrations were positively correlated to the inflow concentrations (Figure 15). Hence, the variations in outflow concentrations were relatively high, e.g. Pb and Zn outflow concentrations varied between $>0.3 - 4.6 \mu\text{g L}^{-1}$ (Coefficient of variance $\text{CV} = 114.7$) and $1.8 - 26.1 \mu\text{g L}^{-1}$ ($\text{CV} = 74.7$) respectively. However, the correlations between inflow concentrations and removal percentages were much weaker, and only significant for Pb removal, which varied between 97.6 and 99.8% ($\text{CV} = 0.9$).

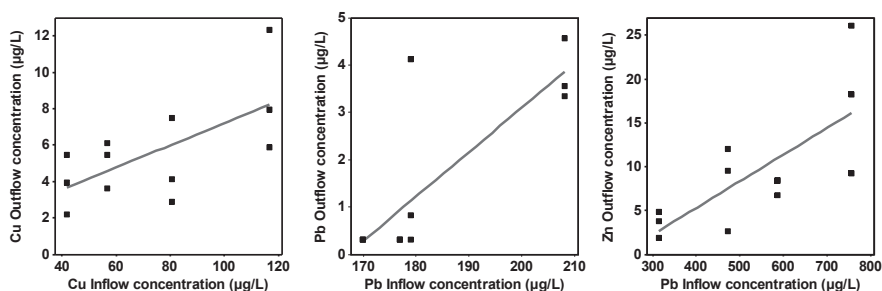


Figure 15: Linear regression: metal inflow vs. outflow concentrations, cf Paper I. The p-values and $R^2(\text{adj.})$ coefficients of the regressions were 0.022 and 36.5% for Cu, 0.01 and 62.5% for Pb, and 0.06 and 50.5% for Zn, respectively.

In contrast, in the snowmelt study (Paper VII) no significant correlations between variations in inflow concentrations (i.e. variations in metal concentrations in the snow from the three sampling sites) and outflow concentrations were detected.

5.2 Effluent concentrations at different temperatures over run-time

5.2.1 Total Suspended Solids

In this section the TSS results presented in Papers IV and V are summarised.

The TSS outflow concentrations recorded in trials at three temperatures (2, 7 and 20°C) are summarised in Table 7. The variations in TSS outflow concentrations associated with the temperature variations were minor (Table 9). Nevertheless, a General Linear Model showed that both temperature and experimental run-time had a significant effect on the TSS outflow concentrations. However, in Table 9 only the effect of run time is shown since the temperature accounted for very little of the variation. Collectively, the results presented in Paper IV (initial decrease) and Paper V (longer-term changes) show that TSS outflow concentrations decreased over the run-time following simulated storm events (Table 9).

Table 9: TSS outflow concentrations during sampling runs presented in Papers IV and V.

Run time (weeks)	Paper	TSS outflow conc. (mg L ⁻¹)
0.5	IV	5.4 ± 2.1
1	IV	5.1 ± 2.1
1.5	IV	4.5 ± 1.9
2	IV / V	4.8 ± 1.5
2.5	IV	4.1 ± 2.1
3	IV	4.8 ± 1.8
3.5	IV	3.4 ± 1.4
4	IV / V	3.3 ± 1.0
6	V	2.2 ± 1.0
8	V	2.3 ± 1.1
10	V	2.2 ± 0.8
12	V	1.4 ± 0.5

5.2.2 Metals

The effects of temperature on the removal of metals by the biofilter columns were studied in Paper VI.

Both total and dissolved metal outflow concentrations up to week 10 with two-weekly sampling resolution were analysed, and are summarised in Table 8. The total metal outflow concentrations recorded at each temperatures in each sampling run are presented in Figure 16.

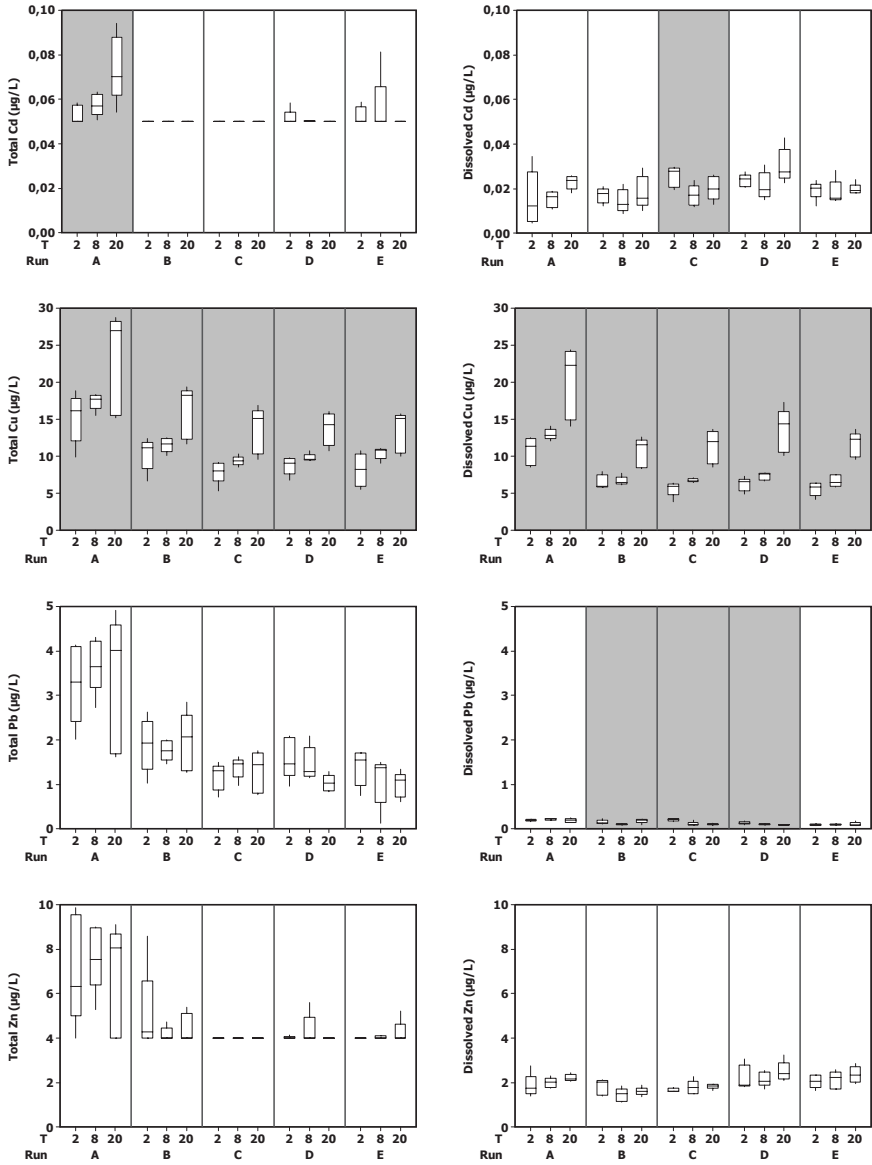


Figure 16: Total and dissolved metal outflow concentrations vs. temperature (2°C, 7/8°C and 20°C) in each, two-weekly sampling run (A to E, from two weeks onwards). Shaded background indicates sampling runs where there were statistically significant ($\alpha=0.05$) temperature effects (not for total Cd in sampling runs B to E, since most values in these runs were < detection limit, $0.05 \mu\text{g L}^{-1}$). Figure source: Paper VI.

Total Cu, Pb and Zn concentrations were significantly correlated to the TSS outflow concentrations (linear regression: $p < 0.001$, $R^2(\text{adj}) = 57\%$ for Cu, 64% for Pb and 46% for Zn). Both metal and TSS concentrations declined, at least at the beginning of the experiment, as the run-time progressed.

Both total and dissolved Cu effluent concentrations significantly increased with increases in temperature (Figure 16). The observed temperature-dependence of the Cu concentration in the outflow is mainly attributable to its effects on levels of dissolved Cu, since concentrations of particle-bound Cu in the outflow (which accounted for a relatively low proportion of the total, calculated as the difference between total and dissolved Cu) were not correlated to temperature. Cu removal was more efficient at colder temperatures: while only 24% of the incoming Cu was removed by the filter at 20°C, 64 and 66% was removed at 2 and 7°C, respectively.

The total and dissolved Zn outflow concentrations were not affected by temperature. No significant effects of temperature on total Pb concentrations in the outflow were observed either, but in three of the five sampling runs a significant effect of temperature on dissolved Pb effluent concentrations was detected (run B, C, D). However, since Pb in the outflow is >90% particle bound, this temperature effect on the dissolved metal concentrations is of minor importance for total Pb removal. For total Cd, no statistical analyses could be conducted since most total outflow concentrations were below the detection limit.

5.2.3 Nutrients

The nutrient results are described in detail in Papers IV and V.

Phosphorus. Total P outflow concentrations decreased with run time (Table 10, Figure 17). Especially in the first three to four weeks both the outflow concentrations and their standard deviations dropped markedly, from about 0.10 ± 0.04 to $>0.02 \pm 0.01 \text{ mg L}^{-1}$, and thereafter, the decrease continued at a lower rate. As for the decline in TSS concentrations, the drop in total P outflow concentrations can be clearly seen when the results presented in Papers IV and V are combined (Table 10). They show a logarithmic correlation with outflow concentrations, levelling out at an outflow concentration of approximately 0.01 mg L^{-1} (Figure 17).

For both datasets a possible effect of the different temperatures was tested using a One-Way ANOVA (mean outflow concentrations observed in all sampling runs vs. temperature, thus disregarding the time effect, Paper IV) and a General Linear Model (mean outflow concentration in each sampling run vs. run-time, temperature and TSS). For both datasets, no significant effect of temperature was detected. However, the General Linear Model showed significant correlations between total P outflow concentrations, run-time and TSS outflow concentrations.

Unfortunately, the partitioning between total and dissolved P was not determined for all samples, but only for the samples taken after a run-times of two and four weeks (i.e. data presented in Paper IV). These results showed that (similarly to the inflow) P was mainly particle-bound in the outflow ($84 \pm 9\%$).

Run time (weeks)	Paper	P outflow conc. (mg L ⁻¹)
0.5	IV	0.10 ± 0.04
1	IV	0.08 ± 0.02
1.5	IV	0.08 ± 0.02
2	IV / V	0.07 ± 0.02
2.5	IV	0.06 ± 0.02
3	IV	0.03 ± 0.01
3.5	IV	0.02 ± 0.01
4	IV / V	0.02 ± 0.01
6	V	0.03 ± 0.01
8	V	0.03 ± 0.01
10	V	0.01 ± 0.01
12	V	$0.01 \pm <0.01$

Table 10: Total P outflow concentrations in the sample runs presented in Papers IV and V.

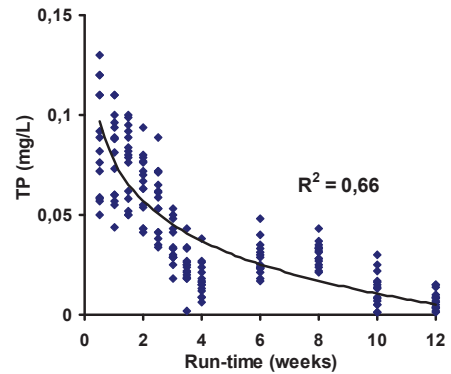


Figure 17: Logarithmic regression: total P outflow concentrations vs. run-time.

The dissolved P concentrations observed in samples from the two sampling runs, they were analysed, were slightly higher at higher temperatures (0.007 ± 0.002 mg L⁻¹ at 2°C; 0.009 ± 0.004 mg L⁻¹ at 7°C; 0.010 ± 0.005 mg L⁻¹ at 20°C), but this difference was not statistically significant (One-way ANOVA: $p = 0.285$).

Nitrogen. Similarly to the P results described above, the N outflow concentrations published in Papers IV and V were combined, and are jointly presented in Table 11. However, in contrast to P, data on dissolved N, NO_x-N and NH₄-N concentrations were only collected and analyzed for the first four sampling runs (i.e. the first two weeks, Paper IV). Since nitrogen was nearly completely dissolved in the outflow ($96 \pm 8\%$) during the whole run-time, and for NO_x-N and NH₄-N only the dissolved concentrations were available, in Table 11 the dissolved fractions are presented.

As shown in Table 9, and Paper IV, no significant effect of the run time on either total or dissolved N outflow concentrations was detected during the first samplings (regression analysis: $p > 0.05$). Total and dissolved outflow concentrations were, however, significantly affected by the ambient temperature; both outflow concentrations and their standard deviations increased with rising temperature (linear regression N outflow concentrations vs. run-time: $p > 0.001$, $R^2(\text{adjusted}) = 82\%$ for total N and 72% for dissolved N). At 20°C the nitrogen outflow concentrations exceeded the inflow concentrations two to three fold.

Table 11: Dissolved N, NO_x-N and NH₄-N outflow concentrations at the different sample runs presented in Papers IV and V.

Run time (weeks)	Paper	N			NO _x -N			NH ₄ -N		
		2	7	20	2	7	20	2	7	20
0.5	IV	1.3±0.4	1.4±0.2	5.4±0.7	0.9±0.3	0.9±0.1	4.5±0.5	0.1±0.1	0.1±<0.1	0.2±0.1
1	IV	1.4±0.2	1.4±0.1	3.8±0.6	0.6±0.2	0.7±<0.1	3.8±0.5	0.1±<0.1	0.1±<0.1	0.2±<0.1
1.5	IV	1.4±0.2	1.2±0.1	3.4±0.3	0.7±0.2	1.0±<0.1	3.6±0.2	0.1±0.1	0.2±<0.1	0.1±<0.1
2	IV/V	1.2±0.2	1.2±0.1	3.1±0.2	0.8±0.2	1.0±0.1	3.3±0.2	0.1±<0.1	0.2±<0.1	0.1±<0.1
4	IV/V	-	-	-	1.0±0.2	1.1±0.4	2.6±1.1	0.1±<0.1	0.1±<0.1	<0.1±<0.1
6	V	1.9±0.2	2.3±0.1	5.2±0.6	1.0±0.1	1.5±0.1	3.9±0.4	0.2±<0.1	0.1±<0.1	<0.1±<0.1
8	V	2.3±0.3	2.5±0.1	5.8±0.5	1.4±0.4	1.7±0.1	4.6±0.7	0.2±<0.1	0.1±<0.1	<0.1±<0.1
10	V	2.0±0.2	2.5±0.2	4.7±0.2	1.1±0.2	1.8±0.2	3.9±0.3	0.2±<0.1	0.1±<0.1	<0.1±<0.1
12	V	2.1±0.4	2.8±0.5	4.8±0.6	1.7±0.4	2.3±0.5	4.2±0.5	0.2±<0.1	0.1±<0.1	0.1±0.1

However, for data acquired from the subsequent sampling runs (weeks 4 to 12), a General Linear Model showed that both run time and temperature had significant, positive effect on N outflow concentrations. Temperature also positively affected the variation of the outflow concentrations of the five columns at each temperature. The NH₄-N concentrations in the outflow were significantly lower at warmer temperatures while NO_x outflow concentrations were positively correlated to temperature. The temperature effect on the NO_x-N production rate was well described by the Arrhenius relationship, the R² value for the regression was 0.9994, cf. Figure 18.

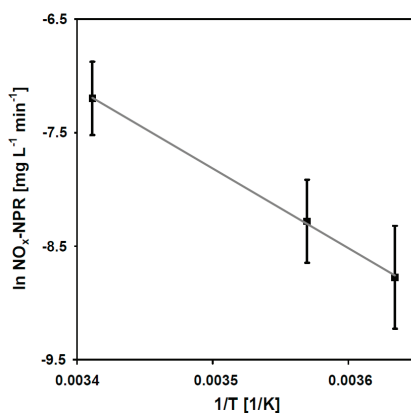


Figure 18: Arrhenius plot, NO_x-N production rate versus 1/T. Figure source: Paper V

5.3 Snowmelt pollutant removal

In the following section, the results presented in Paper VII are summarised.

For the snow and outflow concentrations see Table 8. The TSS concentrations in the outflow were always $<10 \text{ mg L}^{-1}$; far lower than the snow concentrations, which were clearly higher than those in the stormwater utilised in the other biofilter studies. Despite efficient mass removal of total metals ($>80\%$ for Cu and $>90\%$ for Zn) the Cu and Zn outflow concentrations remained clearly higher (especially for the event using snow from the highway) than those observed in the other biofilter studies. In contrast, both snow and effluent Cd and Pb concentrations were in the same ranges as those observed in the other studies.

In the snow small percentages of the total metals were dissolved (1 to 7% for Cd, 2 to 29% for Cu, $<2\%$ for Pb and Zn; despite the influence of road salts), but in the outflow high percentages were dissolved (56 or 100 % for Cd, 65 – 82% for Cu, 13 – 25% for Pb and 73 – 79% for Zn, Table 8). Thus, while particle-bound metals were trapped in the filter, dissolved metals were either not removed or even leached out from the filter material. Leaching was detected for dissolved Cd, Cu and Zn, leading sometimes to >10 -fold higher outflow concentrations than inflow concentrations.

The chloride concentrations in the snow, originating from road salt applied as a de-icing agent, were 49, 216 and 21 mg L^{-1} , depending on the sampling site (residential street, collector road, highway, respectively; cf. Paper VII). In the outflow the corresponding concentrations were 56, 85 and 136 mg L^{-1} , respectively. Thus, high leaching of chloride was observed in some sample runs, and high removal in others. No correlation between chloride and dissolved metal fractions was detected in either inflow or outflow.

5.4 Impact of a submerged zone and a carbon source on pollutant removal

In this section, the results of the studies presented in Papers I and II are summarised.

The comparison of advanced biofilter columns equipped with different heights of a submerged zone (SZ) and with or without a carbon source (C) with standard biofilters showed statistically significant differences in outflow concentrations between the different factor combinations.

Outflow concentrations in the biofilters equipped with a SZ tended to be lower than those of filters without one (Figure 19; Paper I, Table 2). However, although statistically significant for all metals, the effect of the SZ on Pb and Zn outflow concentrations was relatively minor given the large variations in the outflow concentrations. Embedding a solid organic matter as C into the biofilter media did not affect Pb and Zn outflow concentrations significantly.

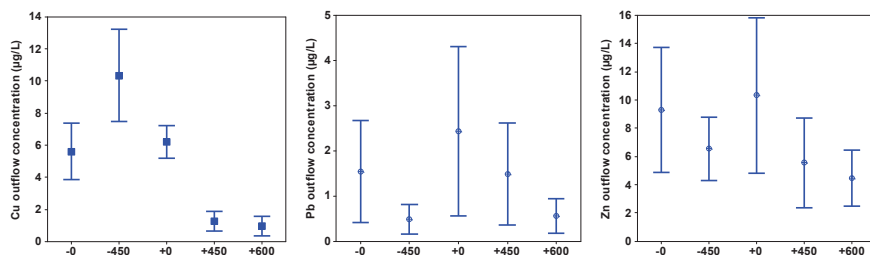


Figure 19: Cu, Pb and Zn outflow concentrations from columns with and without a carbon source (+ and - indicate columns with and without a carbon source, respectively) and submerged zone (numbers indicate the depth of the submerged zone in mm). Mean inflow concentrations were 54.7 , 142.9 and $576.9 \mu\text{g L}^{-1}$ for Cu, Pb and Zn, respectively. Interval plots (95 CI of the mean).

For Zn, the significant effect of a SZ was corroborated by the results of the study presented in Paper II: outflow concentrations were significantly lower after retrofitting a SZ ($4.0 \pm 3.3 \mu\text{g L}^{-1}$) compared those in the four sample runs before retrofitting ($8.0 \pm 5.3 \mu\text{g L}^{-1}$). However, for Pb no significant difference between the outflow concentrations before and after retrofitting the SZ were detected (2-sample t-test for Pb outflow vs. inflow concentration: $p=0.896$, Figure 20).

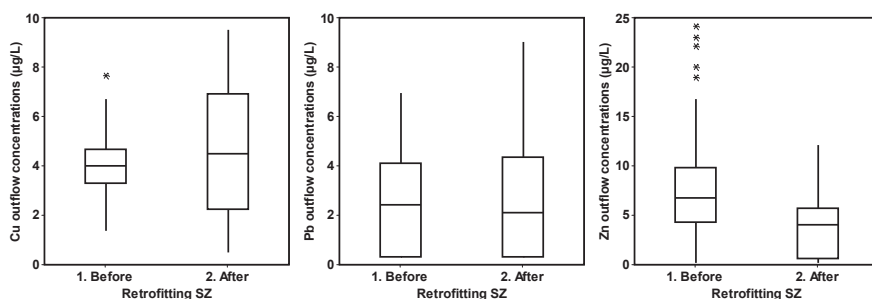


Figure 20: Effects of retrofitting a submerged zone (SZ) on outflow concentrations of the indicated metals.

Cu outflow concentrations were significantly affected by the implementation of both a SZ and C (Figure 19). The lowest Cu outflow concentrations ($1.4 \mu\text{g L}^{-1}$), and thus

the best treatment performance for Cu, were obtained using a combination of both the SZ (450 or 600 mm) and C. However, the SZ alone was not beneficial for Cu treatment since it induced higher Cu outflow concentrations ($10.5 \mu\text{g L}^{-1}$) compared to non-SZ filters ($5.7 \mu\text{g L}^{-1}$).

This was corroborated by the findings of the study presented in Paper II. Retrofitting a SZ alone (without C) into existing standard biofilters after about one year of operation did not have a statistically significant effect on Cu outflow concentrations (2-sample t-test: $p=0.291$, cf. Figure 20). In the first events after retrofitting, Cu outflow concentrations were rather increased. However, after some months of operation with the retrofitted SZ, the Cu outflow concentrations declined to the same levels as before.

5.5 Impact of drying on metal outflow concentrations

Paper I describes differences in metal concentrations observed between the first and later flows leaving the biofilters, while effects of varying lengths of drying period are described in detail in Paper III.

While the studies reported in the other papers appended to this thesis examined outflow event mean concentrations (like most other published biofilter studies), in the study presented in Paper I two sets of sub-samples of the outflow were analysed: one representing the first flow of resident pore water (designated A) and the other representing the subsequently discharged newly treated effluent (B).

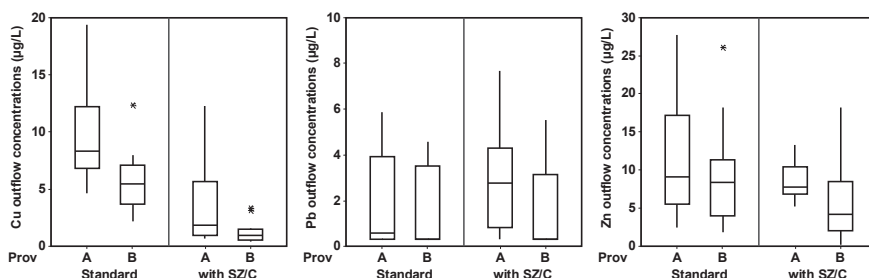


Figure 21: Outflow concentrations of total Cu, Pb and Zn in the first flow of resident pore water (A) and the newly treated water (later flow, B) from standard biofilters and biofilters equipped with a submerged zone and a carbon source (SZ/C).

The results showed that Cu and Zn outflow concentrations tended to be higher in the first flow (sub-samples A), which had remained in the biofilter columns since the last sampling (i.e. for two or three days), than in the B samples (Figure 21). However,

applying an α -level of 0.05, the difference between A and B outflow concentrations was only statistically significant for Cu outflow concentrations from standard columns (paired t-test; p-values and estimated differences are given in Table 12) due to relatively high standard variations and small sampling sizes (three replicate columns and four sampling runs: $n=12$). The event mean concentrations were close to those in the B samples (Table 8) since the volume of the later flow was 17 L, compared to just 0.5 L in the first flow.

Table 12: Results of the paired t-test comparing first flow (A) and later flow (B) outflow concentrations from columns with and without a submerged zone/carbon source.

	Cu		Pb		Zn	
	Standard	SZ / C	Standard	SZ / C	Standard	SZ / C
Concentration A	9.7 \pm 4.5	3.5 \pm 3.5	1.9 \pm 2.1	2.9 \pm 1.2	11.5 \pm 7.7	8.5 \pm 2.3
Concentration B	5.6 \pm 2.8	1.3 \pm 1.0	1.5 \pm 1.8	1.5 \pm 1.8	9.3 \pm 6.9	5.6 \pm 5.0
Estimated difference	4.1 \pm 5.0	2.2 \pm 3.9	0.4 \pm 3.5	1.4 \pm 2.6	2.2 \pm 6.9	3.0 \pm 4.9
p-value paired t-test	0.016	0.06	0.64	0.09	0.29	0.06
Event mean concentration	5.7 \pm 2.7	1.3 \pm 0.9	1.6 \pm 1.7	1.5 \pm 1.7	9.4 \pm 6.9	5.7 \pm 4.9

On the basis of the results presented in Paper I, in the following experiment (Paper III), the length of the dry period between the storm events was extended up to seven weeks. However, in that analysis, only event mean concentrations were considered, i.e. the samples were not divided into first and later flow samples.

Given a regular stormwater inflow (twice weekly), the metal effluent concentrations from standard biofilters lacking a submerged zone and/or carbon source were in the same range as those observed in the other studies (using columns with a similar design; cf. Papers I, II and VI; Table 8).

Increasing the length of the dry interval between consecutive storm events up to one or two weeks did not clearly affect the Cu and Zn outflow concentrations, while Pb outflow seemed to increase even after that short drying period (Paper III, Figure 3). However, since only one data point was available for these two drying lengths, time trends could not be statistically analysed.

Nevertheless, the effect of increasingly extended dry intervals on the outflow concentrations became clear when the drying length was extended: drying for more than 3–4 weeks caused significant increases in outflow Cu, Pb and Zn concentrations, which were well described by linear regressions (outflow concentration vs. antecedent dry days; $R^2=74.7\%$ for Cu, 94.5% for Pb and 60.8% for Zn; Figure 22). After seven dry weeks the outflow concentrations were increased 3-, 8- and 5-fold for Cu, Pb and Zn, respectively.

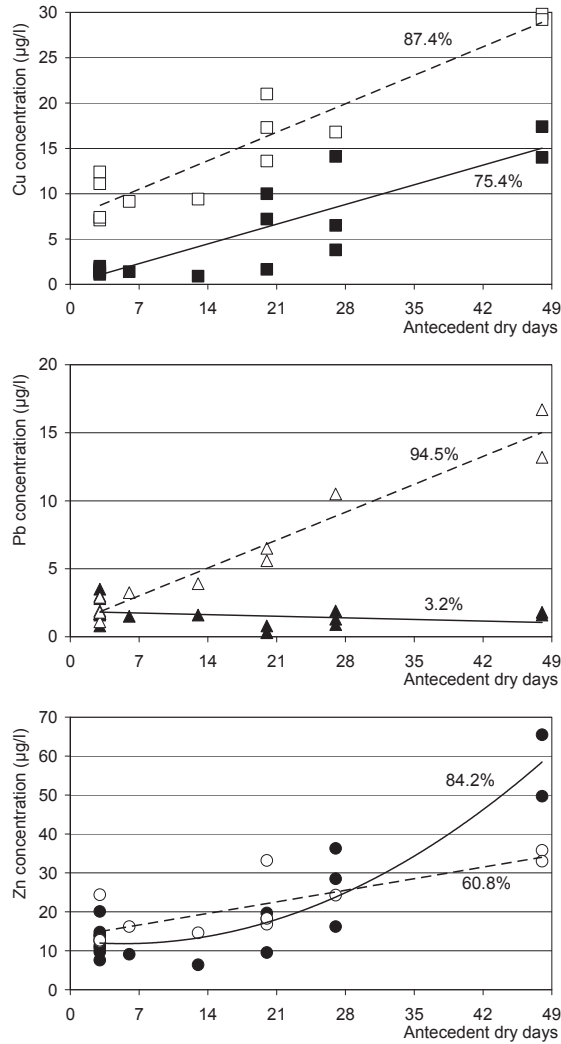


Figure 22: Indicated metal outflow concentrations and corresponding regression lines with correlation coefficients $R^2(\text{adjusted})$ (%) from columns with SZ and C (closed markers, solid lines) and without SZ and C (open markers, dashed lines) affected by length of drying (antecedent dry days). Figure source: Paper III.

Drying caused a non-linear drop of the filter media moisture content (measured 225 mm from top; Figure 23). Thus, metal outflow concentrations and metal removal were clearly correlated linearly to the length of antecedent drying and non-linearly to the filter media moisture content.

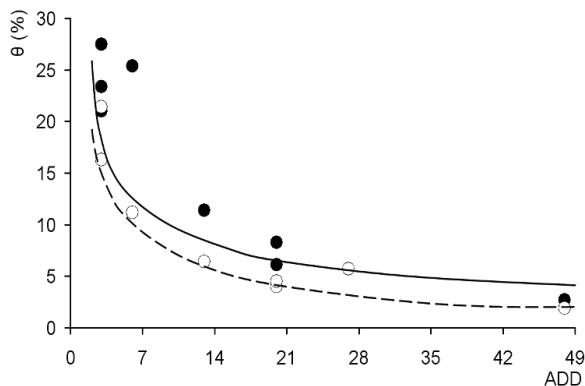


Figure 23: Moisture content θ (%; measured 225 mm from top) and regression lines for columns without SZ/C (open markers, dashed line) and with SZ/C (closed markers, solid line) affected by length of drying (Antecedent Dry Days: ADD). The regression equations are $\lg(\theta) = 1.649 - 0.7698 \lg(\text{ADD})$, for columns without SZ/C and $\lg(\theta) = 1.728 - 0.7028 \lg(\text{ADD})$ for columns with SZ/C. $R^2(\text{adjusted}) = 95\%$ and 94% , respectively.

By introducing a SZ (in the columns used in the experiments combined with C) into biofilters the negative effect of drying on the water quality improvement performance was mitigated for Cu; for instance, while Cu outflow concentrations in filters with a SZ were about $8 \mu\text{g L}^{-1}$ lower during wet periods (with just two to three days between simulated storm events) this difference increased to about $15 \mu\text{g L}^{-1}$ after seven weeks of antecedent drying. For Pb outflow concentrations, the SZ even eliminated the effect of drying: when those features were implemented, Pb outflow concentrations were always around 1.7 to $2.1 \mu\text{g L}^{-1}$, irrespective of the length of drying, in contrast to $15.0 \mu\text{g L}^{-1}$ Pb in the outflow after seven dry weeks. For Zn, the effect of the SZ is inconsistent (Paper III, Figure 2): in some cases no difference in the outflow concentrations from the two column types was detected (after three and four weeks drying, group B), while in one case a submerged zone was beneficial (after three weeks of drying, group A) and in others the standard filters yielded lower outflow concentrations (after seven weeks of drying, group C). Further, even for columns equipped with a submerged zone differences were observed in concentrations between the first flow of discharged resident pore water and the newly treated water (sub-samples A and B, resp.; Figure 21, Table 12).

Similarly to standard columns, the moisture content (measured 225 mm from the filter media top, i.e. above the SZ) in the columns equipped with a submerged zone dropped non-linearly during the storm events, but even near the column top it was always about 3 to 4% higher (Figure 23). Further, in contrast to standard columns without a SZ, better plant growth and no stress symptoms such as drought damage were observed in the columns with a SZ even after seven dry weeks, indicating that a continuous water supply was maintained in the latter. However, no measurements were taken of moisture contents in the deeper layers to validate this assumption.

5.6 Metal pathways in the biofilter

In this section, firstly the depth profiles of the metal concentrations in the percolating water are described, based on results presented in Paper I. Secondly, the fate of metals in the biofilter media and plants is described, summarising and comparing the results reported in Papers III and VI. Similar results presented in Paper VII are also briefly summarised.

Percolating water. It was shown for all design combinations (with/without SZ and C) that already after 150 mm of penetration into the filter media the metal concentrations in the water were far lower than the initial stormwater concentrations (Table 13, cf. Paper I). On the subsequent way down to the outlet (i.e. further 750 mm) the metal concentrations decreased even further. Thus, comparison the three values clearly shows that the main reduction in metal concentrations occurred immediately after the water entered the filter media, highlighting the importance of the top layer.

Table 13: Total metal concentrations in influent stormwater, the seepage after 150 mm penetration and at the outlet (i.e. after 900 mm penetration) in $\mu\text{g L}^{-1}$. The data are shown for standard biofilters in the fourth sampling run presented in Paper I (cf. Paper I, Figure 3).

Depth	Cd	Cu	Pb	Zn
Inflow	6.4	56	167	456
150 mm from top	<0.7	7	15	22
Outflow	<0.7	5	2	8

Filter media. Figure 24 shows the metal concentrations observed in the filter media in different filter depths before and after the stormwater application. Both results from the temperature study presented in Paper VI and the results from the studies presented in Papers I and III are juxtaposed. In the latter study, clearly higher metal concentrations were detected in the filters. However, due to the longer run time each of those filters received far higher stormwater inflow volumes (about 1700 L per column, corresponding to 15 420 mm) and thus higher pollutant loads than the other columns (360 L per column, 3265 mm).

Corresponding to the difference in stormwater loads, there was a clear difference in filter media metal concentrations between the two experiments. However, in both studies most of the metals were retained in the upper 100 to 200 mm of the filter. Independently of the incoming pollution load, the metal concentrations in the deeper layers of both filters were in approximately the same range.

However, even in the deeper layers some metals were retained since at 250 mm and 600 mm depths metal concentrations after stormwater application were higher than the initial values (at least in the temperature study; in the other study the

concentrations in the deeper layers were below the detection limit and thus comparisons were impossible).

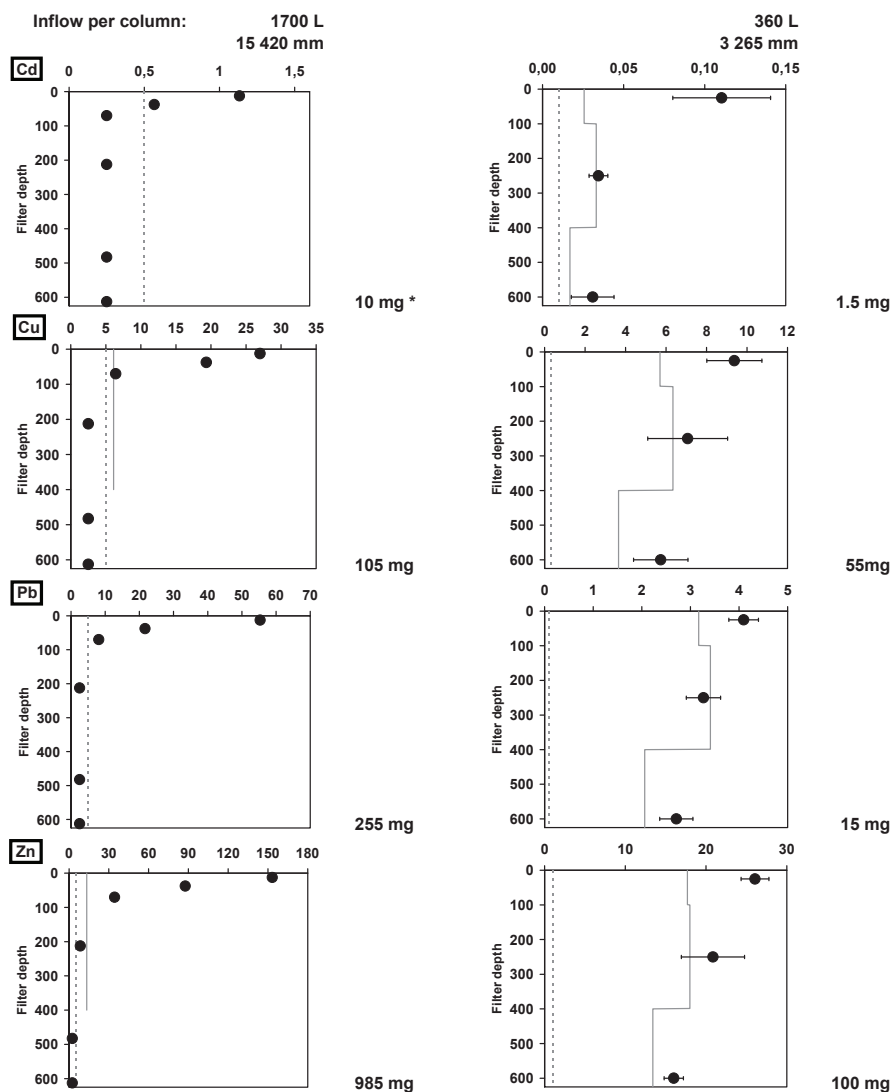


Figure 24: Metal concentrations (in mg kg^{-1} dry mass) in different filter media of standard biofilters (without SZ and C) after stormwater applications (closed markers) in comparison to the initial filter media metal concentrations in the different filter layers (grey solid line). Concentrations below the detection limit (grey dashed lines) are plotted at half the detection limit. The scale to the right of each graph indicates the approximate total metal inflow mass from stormwater before analysing the filter media (* inflow values in some cases below detection limit, see Paper III). Left column: filters used in the study presented in Paper I and III. Right column: filters used in the study presented in Papers VI.

Filter media after snowmelt. As in the other studies, mass balances showed that the majority of Cu and Zn was retained in the top mulch layer. In contrast, most Pb was retained in the soil filter media below the mulch. Plant metal uptake accounted for less than 10% of the total retention for all metals.

Even here, in the top layer, higher metal concentrations were detected than in the underlying filter layers (Paper VII, Figure 3a and b). However, in contrast to the other studies, in these biofilter systems the 5 cm top layer consisted of mulch, which accounted for most of the metal uptake.

Plants. In the studies presented in the Papers VI and VII, the plants were analysed for metal concentrations before and after stormwater application. The metal concentrations in both the roots and shoots were higher after than before stormwater application. Trends indicating temperature dependence were also observed; while in the shoots the metal concentrations declined with increasing temperature, in the roots temperature rises caused metal concentrations to increase.

Overall, the biofilters showed typical water quality treatment behaviour compared to those examined in other studies. The removal of total metals and TSS was relatively constant for the standard biofilters with regular, simulated stormwater inflows. TSS, Cd, Pb and Zn removal usually exceeded 90%, while Cu removal was somewhat more variable, but usually still efficient (>80 %). These findings corroborate the results of various authors, e.g. Lau et al. (2000), Davis et al. (2001b), Davis et al. (2003), Hsieh et al. (2005a), Muthanna et al. (2007) and Hatt et al. (2009), cf. the summary in Table 1. Dissolved metal removal efficiency was more variable, again in accordance with results of other studies (Hatt et al. 2007; Chapman and Horner 2010; Muthanna et al. 2007; Hsieh and Davis 2005a; Sun and Davis 2007). Often, highly variable nitrogen removal has also been shown (Davis et al. 2006; Dietz and Clausen 2006; Henderson et al. 2007; Hsieh et al. 2007b; Read et al. 2008). In the study presented in Papers IV and V, variability in N removal was shown to be correlated to temperature.

However, removal percentages might be misleading, since they are based on inflow concentrations, which varied greatly both between the studies and within the studies (those, for instance, reported in Paper I and VII). Thus, despite generally good removal, pollutant outflow concentrations vary depending on the ambient conditions, biofilter modifications and/or inflow characteristics, as described in the results section (cf. Table 7 and Table 8). The results provide indications of the processes influencing the outflow concentrations (and thus pollutant removal). These processes and their consequences for practical biofilter implementation and operation are discussed below.

6.1 Biofilter treatment processes

6.1.1 TSS treatment

The results show that the biofilters reliably removed TSS, yielding low outflow concentrations <10 mg L⁻¹ in all cases (Table 7 and Table 8; Papers III, IV, V and VII). Those low concentrations were consistently achieved despite the varying

ambient conditions (drying, Paper III; temperature, Paper V), biofilter design modifications (coarse filter media, Papers V and VII) and the inflow variations between stormwater events, in which concentrations ranged from ca. 130 to 180 mg L⁻¹ (Papers III, IV and V) and snowmelt, in which up to 9600 mg L⁻¹ TSS were present (Paper VII). However, while all outflow concentrations were low, they were statistically significantly influenced by some of the investigated factors (temperature and drying).

TSS entering a biofilter is mechanically trapped on top of the filter, as could be confirmed visually in all studies since a grey layer of fine sediments was clearly visible on all filters. This commonly reliable and efficient mechanical treatment process (Bratieres et al. 2008) is the main process determining the removal efficiency of particle-bound pollutants.

However, the removal of TSS on top will result in a layer of fine stormwater sediment with low permeability above the actual filter material (Siriwardene et al. 2007), which may clog of the filter quite rapidly after the start of operation (Le Coustumer et al. 2007). Thus, especially if high TSS inflow concentrations are expected, pre-treatment of the stormwater by incorporating buffer strips or swales has been suggested to minimise TSS loadings entering the filter and thus prolong the maintenance intervals; however, this combination requires more space (Davis et al. 2009).

Clogging due to formation of a fine sediment layer is particularly important for the winter operation of biofilters, for several reasons. Firstly in regions with cold winters sediment concentrations in winter runoff and snowmelt are often elevated due to the use of sand as an anti-slip agent (Engelhard et al. 2007; Westerlund and Viklander 2006). Secondly, water infiltration into frozen soils is correlated to the soil moisture content at the time of freezing, since freezing pore water will result in ice formation limiting or precluding water percolation (Kane 1980; Zhao and Gray 1999). Thus, in regions with cold winters a well-drained coarse filter medium with low clay and/or silt contents is recommended (Caraco and Claytor 1997), as implemented in the biofilters used in the temperature and snowmelt studies (Papers IV to VII). However, a fine stormwater sediment layer on top would cancel out the benefits of the coarse filter medium, since pore water would probably remain in the fine particle layer, causing ice to form in it during freezing, resulting in a barrier on the filter that would inhibit the entry of water into the biofilter, despite the presence of open pores in the underlying layers of the filter *per se* (Le Coustumer and Barraud 2007).

Storing snow on the filter (as suggested in Paper VII) might thus not be a suitable option since snow can contain extremely high TSS loads (Engelhard et al. 2007; and as shown for the natural snow samples utilised in the study reported in Paper VII), which all will end up on the filter. Given clogging problems in general, and the particular problems associated with freezing in winter, a better option seems to be storing snow next to the filter and conveying the snowmelt to the filter, possibly

combined with pre-treatment. This would result in operation conditions such as those addressed in Papers IV to VI (stormwater treatment in cold temperatures). To prevent clogging and maintain the infiltration capacity, the sediment layer on top should be removed regularly.

However, while TSS removal by mechanical filtration seems to be consistently efficient, sediment might be released from the filter leading to the appearance of TSS in the effluent (Bratieres et al. 2008; Hatt et al. 2007), having been observed especially for newly constructed facilities (Hsieh and Davis 2005a; Davis et al. 2009). Such sediment release is dependent on the filter material, its structure and composition, and possible changes over time or variations due to changes in ambient factors. Hence, internal filter processes might explain the effects of both drying and temperature on TSS outflow concentrations, and their changes over time (Papers III, IV and V).

After 4-7 weeks of drying, TSS outflow concentrations were elevated compared to those observed following shorter drying periods (Paper III). In some cases, full recovery of TSS removal was only observed after several subsequent storm events. This may be because drying of the filter media leads to small fissures, which might create preferential flow paths (Hatt et al. 2008). This hypothesis is supported by the outflow rates observed during the subsequent storm events; during the first storm event after drying, outflow started significantly later since the pores of the filter media had to be refilled with water. During subsequent events, high outflow rates quickly resumed. Those processes might have caused filter material disturbance, leading to sediment washout from the filter media. Some subsequent storm events after re-wetting, the filter media had resettled, and the pores allowing preferential flow were clogged, thus sediment washout no longer occurred.

Similarly, the importance of internal processes in filter media for the TSS concentrations in the effluent is shown by the TSS outflow concentration changes over time observed in the temperature study (Papers IV, V), as shown in (Table 9). A possible reason for the decreasing TSS outflow concentrations is reduction in sediment wash-out from the filter due to re-packing of the media and accompanying reductions in the pore size. Similar behaviour of newly constructed biofilters has been previously observed (Hsieh and Davis 2005a; Hsieh et al. 2007a), according to conclusions (that nearly all TSS entering the filter is trapped on/in the top layer, and that the sediment in the outflow originates from the filter itself) have been reached by Hatt et al. (2007). However, the effect of differences in filter media are not significant, and TSS outflow concentrations have been found to be in the same range for a number of filter materials (Hatt et al. 2007). Similarly, the TSS outflow concentrations from the columns considered in Paper III (incorporating a sandy loam) were not higher than those observed in the cold climate studies (Papers IV to VII) with a coarse filter media and thus a smaller supply of fines; in both cases TSS in the outflow was consistently low.

The variations in TSS outflow concentration, while significant in some cases, are considered to be of little practical importance given the constantly high removal. However, problems might occur, for instance if sediment wash-out from the filter causes leaching of other associated pollutants, as observed for P for example (Hsieh et al. 2007a).

6.1.2 Metal treatment

Theoretically, the removal of metals is dependent on their partitioning between the solid and solution phases in the stormwater, in the seepage in the filter and in the effluent. Incoming particle-bound metals are removed together with the TSS by mechanical filtration on top of the filter (Davis et al. 2009), as discussed above. However, possibly metals might be sorbed to sediment in suspension and thus (still) be present in the outflow (as also observed for P for example). The removal of dissolved metals is dependent on a range of biological and chemical processes in the biofilter, which might be influenced by a range of factors. Although pH is the dominating factor determining metal partitioning between the solid and solution phases, other factors, such as redox conditions and temperature can also affect it (Alloway 1995; Rieuwerts et al. 1998; Bradl 2004).

Metal sorption by soils. Sorption of metals by the filter media (and stormwater sediment) is mainly related to cation exchange, specific adsorption, precipitation and complexation (Rieuwerts et al. 1998; Bradl 2004). However, given the complex processes and interactions, it is difficult to identify the exact processes responsible for the overall metal extend of metal sorption in soils from the solution to the solid phase (Alloway 1995).

Metals have the highest affinity towards fine particles (ranking in terms of adsorption: sand < silt < clay; Rieuwerts et al. 1998), hence there are higher proportions of metals in solution in coarse sand soils than in sandy loams or clay soils (Bradl 2004). This is important since the filter media must provide sufficient sorption sites to enable effective treatment. Thus, it was hypothesised that a coarse medium recommended for cold climate biofilters (Caraco and Claytor 1997) might influence metal removal. In coarse filter media, the higher hydraulic capacity reduces the contact time of the pollutants in the stormwater with the filter media, and the lack of fine particles in filter media with marginal clay and silt fractions might reduce metal sorption capacity. However, installing coarse media in the biofilters investigated in the temperature study (Papers IV to VI) did not impair total and dissolved metal removal (Figure 16) despite relatively (visually) high flow rates. The importance of preferential flow through fissures has been shown by Hatt et al. (2008). Besides other factors, preferential flow through small cracks in the filter media might have been one reason for the less efficient treatment after drying (Paper III).

A coarse medium was also used in the biofilters investigated in the snowmelt study (Paper VII), but combined with a mulch layer on top. In this study too, the total metal removal was good, although some dissolved metal leaching was detected. However, since the top mulch layer should provide sufficient sorption capacity (Jang et al. 2005), it is not assumed that the leaching metals originated from the stormwater inflow. The metals in the outflow were probably washed out from the filter medium itself (as corroborated by leaching tests) or perhaps from decomposing OM in the mulch layer re-mobilising previously accumulated metals (see discussion regarding OM below).

The relatively high outflow concentrations of particle bound metals at the beginning of the run time (cf. Paper VI, Figure 16) might have been due to sorption of dissolved metal on the few fine clay or silt particles in the soil washed out from the filter before the filter media settled; after two to three weeks both TSS and metal (and P, see below) outflow concentrations declined. The elevated metal outflow concentrations during the early storm events were mainly attributable to particle-bound metals, dissolved metal outflow concentrations did not show similar behaviour at the beginning of the experiment.

pH. Both the inflows and the outflows in all studies showed a relatively constant pH (Table 7 and Table 8) within the optimal sorption range of the metals of concern (Bradl 2004). Only a SZ had a significant effect on pH (Paper I), indicating that a SZ will raise the pH, which might help to explain its beneficial impact in metal removal. However, due to the relatively small changes in outflow Pb and Zn concentrations associated with the presence of a SZ, and the finding that it caused only a slight increase in pH, the effect of pH should not be overestimated. Thus, since no practically significant effect of any of the tested factors on pH was detected, it is assumed that its impact on the variations in outflow concentrations was negligible compared to those of other factors. Thus, the metal treatment variations observed in the studies are likely to be controlled by a range of other physical, chemical and microbiological processes and parameters (Bradl 2004; Warren and Haack 2001), as discussed in the following text.

However, given the importance of pH for metal solubility, it is assumed that changing pH in stormwater will affect on metal behaviour in biofilters. Events such as an acidic shock in early spring runoff in a region with a cold climate (Goodison et al. 1986) might change the stormwater pH significantly and thus impair the removal performance and, further, possibly cause a release of previously sorbed metals from the filter media.

Cu-OM complexation. The most important process controlling (dissolved) Cu removal in biofilters may be Cu-OM complexation. Cu has the strongest affinity of all metals to OM (Ponizovsky et al. 2006; Yin et al. 2002), resulting in the formation of strong OM-Cu complexes (Matoura et al. 1978). The distribution of OM between its solid and dissolved forms does not influence the Cu complexation affinity (Yin et al. 2002).

However, importantly for Cu treatment in biofilters, dissolved OM mobilises Cu, by forming mobile dissolved OM–Cu complexes (Amery et al. 2007; Römken and Salomons 1998), while solid OM is the main Cu-adsorbing component in soil (Temminghoff et al. 1997). Consequently, as long as solid OM in the biofilter is not in suspension, it immobilises Cu, leading to better removal, while OM in solution or suspension will transport Cu out of the filter.

This behaviour of Cu probably influenced the Cu treatment in several of the studies presented in this thesis. Since Cu removal is highly dependent on OM behaviour it is likely to be affected by the same processes as OM. Thus, OM distribution in the filter media and the effect of (e.g. biological) ambient conditions on OM will be reflected in the Cu treatment performance. It is assumed that the beneficial effects of a SZ and C on Cu removal shown in Paper I (Figure 19) were mainly caused by the availability of C rather than by the SZ (although it had a significant influence on all metals too). C provided additional solid OM, which formed solid Cu-OM complexes, while the residual dissolved Cu in the water percolated in the deeper layers, thus improving Cu removal. Retrofitting only a SZ without added C did not enhance Cu removal in the same way (Figure 20; cf. Paper II). In contrast, flooding the filter media in order to retrofit the SZ may have re-suspended some OM (and other fine particles), and thus complexed Cu, leading to increased Cu outflow concentrations during the first storm events after retrofitting (Figure 20; cf. Paper II Figure 2). Similarly to C, the organic mulch layer incorporated in the snowmelt study (Paper VII) provides a solid OM sorption site for Cu, and for other metals (Davis et al. 2001b; Jang et al. 2005).

In the snowmelt study (Paper VII), however, leaching of Cu was detected, which might have been complexed with dissolved or suspended OM leaching from the filter media. Increased levels of dissolved OM in the outflow might have further caused the higher Cu outflow concentrations at 20°C compared to 2 and 7°C. At 20°C, rates of biological activities, and thus the turnover and decomposition of OM (e.g. plant debris, bacteria) are higher, leading to a subsequent flush of dissolved OM in the outflow. In cold temperatures, this biological process is less pronounced. Accordingly, higher concentrations of Cu (complexed to dissolved OM), in outflows from columns at warmer temperatures have been detected (cf. Martinez et al. 2003). A flush of dead, dissolved OM could also explain the clear increase of Cu outflow concentrations observed after drying (Paper III). Due (at least partly) to desiccation of the filter, biological activity decreases due to drought stress, which might eventually lead to the death of plant cells and bacteria (Baldwin and Mitchell 2000). Thus, dead organic material may have been present in the filters, causing a flush of dead OM during the subsequent storm event and increased Cu outflow concentrations due to Cu complexed with it. The introduction of a submerged zone delays the decrease in biological activity since drought stress is decreased which might partly explain the mitigation of drought effects on metal removal in the SZ columns.

The presence of solid OM in the filter media is beneficial for Cu removal, while the presence of dissolved (or suspended) OM in the outflow will decrease Cu removal by transporting it out of the filter. However, in the long term solid organic matter is subject to decomposition by bacteria and other microorganisms. Furthermore, root turnover will lead to release of OM into the solution phase and thus into the outflow. Since biological processes strongly influence the amount of OM in the outflow, the long-term changes in OM outflow concentrations are highly dependent on the ambient conditions, as illustrated by the effects of temperature and drying. Thus, filter media design should take the OM content in the filter media, and its long-term behaviour, into account to avoid OM and thus Cu leaching. Hence, an important maintenance aim is to remove debris and other organic litter from the filter to avoid additional supply of dissolved OM. Furthermore, if the beneficial solid OM is installed in form of a mulch layer on top, it can be readily replaced (thus also providing an opportunity to remove the Cu from the filter before leaching due to the decomposition of the mulch starts to be significant). In contrast, C (which was embedded in the deeper layer) can only be replaced by changing the whole filter media. However, since C was not primarily implemented to enhance Cu removal but to facilitate de-nitrification (as suggested by Dietz and Clausen 2006; Kim et al. 2003; Zinger et al. 2007b), before a biofilter is designed the target pollutants have to be defined and the filter media accordingly adapted. If Cu is of primary concern, use of a mulch layer rather than C is recommended.

Filter media aeration and oxidation between the storm events. The observed differences in metal concentrations between the first and later flows (Paper I) also clearly show that metals were transferred from the solid phase to the solution phase between the storm events. One process that may have strong influence on metal behaviour is aeration and thus oxidation of the filter media due to rapid reductions in soil moisture contents, enabling ingress of oxygen containing air in the filter media. The effects of drying, and associated changes in redox conditions, on soil-metal interaction processes have been examined in many soil science studies. Drying might have a significant effect on the metal partitioning between solid and dissolved phases in soil and soil pore waters (Bradl 2004; Rieuwerts et al. 1998; Sacki et al. 1993). In a literature review, Rieuwerts et al. (1998) found conflicting reports regarding the effects of redox potential on metal solubility. However, aeration and oxidation of sediment is likely to decrease metal sorption (Stephens et al. 2001; Förstner et al. 1998), leading to higher metal availability and thus higher concentrations in the pore water (De Carvalho et al. 1998). Drying and oxidation of initially anoxic sediments have been shown to mobilize previously sorbed metals into the water phase strongly (Förstner et al. 1998) with initially insoluble metals becoming soluble (Caille et al. 2003). Thus, higher soil solution metal concentrations have been detected in soil samples collected during wetting periods following drying periods than in samples collected during a continuously wet regime (Tack et al. 1998; Tack et al. 2006). Hence, the previous soil moisture content has a significant influence on metal solubility in soils (Tack et al. 2006).

The processes outlined above might explain the higher metal concentrations observed in the first flow of resident pore water leaving the columns in the study described in Paper I. During the two to three days of drying between the storm events the filter media moisture content rapidly decreased (Figure 23), and at least some parts of the filter media were subject to oxidation, thereby mobilizing previously sorbed metals into the remaining pore water. Those re-released metals would be flushed out at the beginning of the subsequent storm event. However, since the drying periods between the storm events were short and the newly entering stormwater (which accounted for most of the outflow volume) was treated well, the first flow had no strong influence on the event mean outflow concentrations.

The oxidation processes that release metals into solution will start after the filter media moisture content has fallen below a certain threshold level and then continue, leading to a cumulative increase of soluble metals with time. Thus, when the drying was prolonged (Paper III), the event mean metal outflow concentrations were clearly elevated after about 3-4 weeks of antecedent drying (Figure 22). Unfortunately, in that study no sub-samples of the first and later flows were taken; only the event mean concentrations of metals were analysed. However, assuming that metals are transferred during drying to the soluble phase and subsequently washed out during the following storm event, it can be assumed that after longer drying periods extremely high metal outflow concentrations may have been present in the first flow of resident pore water, which would have been revealed by analysing sub-samples taken at different times.

The assumption that oxidation of the filter media influences the elevated metal outflow concentrations is also supported by the finding that the introduction of a submerged zone in the filter minimises the negative effect of drying; oxidation of the filter media is at least delayed due to a more constant water supply and thus lower amounts of metals are in solution after drying. However, the SZ is also beneficial for other processes, such as plant growth and thus metal uptake and biofilm growth.

Metal pathways in the filter media. The mechanical retention of particle-bound metals associated with TSS is one reason for the importance of the top layer for metal treatment, which is underlined by the metal concentrations observed in the seepage (Paper I) and the filter media after completion of the experiment (Papers III, VI and VII). Metal concentrations in the seepage decreased quickly after infiltration (Table 13), consequently relatively high metal concentrations were observed in the top 5 to 10 cm of the filter media (Figure 24).

Besides filtration of particle-bound metals, high percentages of the dissolved metals are retained in the top layer: e.g. in the temperature study (Paper VI) where Zn was mainly present in the dissolved form, the results show that Zn retention was highest in the top layer (Figure 24). In this context, the correlation between inflow and outflow concentrations described in Paper I was somewhat surprising, since and it was hypothesized that the metal concentrations in water would quickly reach a background equilibrium concentration on its way through the biofilter. However,

dissolved metals are likely to ingress deeper into the filter than particle-bound metals as indicated by further results described in Paper I. Contrary to the initial hypothesis that SZ and C, which were both located in the deeper layers of the filter, would not influence metal removal, since metals do not ingress far enough to come into contact with them, both SZ and C had a significant influence on metal removal. Further, in Paper VI it was shown that the filter media metal concentrations were also increased in the deeper layers (although to a much lower degree than in the top layer, Figure 24), indicating that some metals were first retained in the deeper layers.

The observed metal accumulation in the top layers results corroborate the findings of previous biofilter research; high metal concentrations in the top layer are commonly found in biofilters (Davis et al. 2001b; Hatt et al. 2007) and other stormwater infiltration facilities (Dechesne et al. 2004). In some of these studies, mulch or soils with high organic matter content were installed in the top layer (e.g. Davis et al. 2001b; Paper VII), providing optimal conditions for metal sorption (Jang et al. 2005). Processes in deeper biofilter layers also influence metal removal (as shown for C, Paper I; SZ, Papers I and III; and plant uptake through roots, Papers VI and VII) but are less important.

Plant uptake. Plants affect metal removal in biofilters directly, by taking up metals through their roots (Fritioff and Greger 2003; Raskin et al. 1997) and indirectly, via their influence on soil pH and OM content (Zhao et al. 2007). For these biofilter studies (Papers I, II, IV, V and VI), changes in soil pH in the rizosphere are assumed to be of little importance, given the stable pH in the outflow, as discussed above. However, plant and root turnover might lead to debris in and on the filter, providing a supply of OM (which affects metal behaviour, as discussed above). Since plant metal uptake is affected by plants' activity, it is also likely to be influenced by variations in ambient conditions (salinity, temperature and drying).

As described in Papers VI and VII, plants contribute to metal removal by direct uptake since the metal concentrations in plant shoots and roots were clearly elevated after stormwater application. However, the role of plant uptake on the metal removal should not be overestimated. Davis et al. (2001b) and Sun et al. (2007), for instance estimated that plant uptake accounts for at most ca. 5% of the total metal mass removal. In the snowmelt study (Paper VII), plant metal uptake was in the same range, but it could not be quantified in the temperature study (Paper VI) since unfortunately it was not possible to estimate the total plant dry mass in the filters. In the study of Read et al. (2008), however, a significant impact of plant species in metal removal has been shown.



Figure 25: Plant development in an illustrative biofilter column in the 20°C climate room at LTU after three weeks of operation (left) and 12 weeks of operation (right column and top view). Study described in Papers IV–VI. Figure source: Paper V.



Figure 26: Plant development in illustrative biofilter columns used in the experiments at Monash University, described in Papers I to III.

Sun et al. (2007) found higher metal concentrations in the roots compared to the shoots of biofilter plants they examined, and higher plant uptake when inflow concentrations were high. Thus, in the snowmelt study (Paper VII) the plant uptake should have been especially high, given the very high inflow concentrations. This was not the case, probably because the experiments were conducted in late winter when there was little plant activity. Visually, no effect of the salinity in the snowmelt on plant growth was detected. However, further investigation of this aspect under more controlled conditions is recommended since plant metal uptake is generally influenced by salt in stormwater (Fritioff et al. 2004).

Both drying and temperature changes affected plant activity (Papers III and VI). Plant stress syndromes due to drought were clearly visible after seven weeks of drying (Figure 27). In biofilters equipped with a submerged zone in the filter media no stress syndromes were visible. This might have been one reason for the increased metal removal in biofilters with a SZ after drying (Paper III).



Figure 27: Plants showing stress due to drought in biofilter columns after seven weeks of drying (foreground) compared to unstressed plants in columns exposed shorter drying periods and/or with a SZ (background).

The variation in plant metal concentrations associated with variations in temperature did not significantly influence the total metal removal (Paper VI). However, unfortunately the plants did not develop well in the climate rooms at all temperatures (Figure 25), compared to those used (for instance) in the biofilter experiments conducted at Monash University (Papers I to III; Figure 26). Thus, plant metal removal is assumed to have been of little importance in the temperature study described in Papers VI.

6.1.3 Phosphorus treatment

In previous biofilter studies, the removal of P has been highly variable (Table 2). While extremely high leaching has been reported in some studies (Dietz and Clausen 2006; Hatt et al. 2009; Li and Davis 2009), for instance Davis et al. (2006), Hsieh et al. (2007a) and Bratieres et al. (2008) have found effective P removal, similar to the studies presented in Papers IV and V.

Since P usually occurs in the form of phosphate ions, which have a strong affinity to particles, in stormwater, P is mainly particle-bound (Viklander 1999; Berge et al. 1997), as was the case in the artificial stormwater utilised in the studies described in Papers IV and V (Table 4). Thus, the incoming P was probably removed efficiently together with the TSS by mechanical filtration.

Accordingly, in various studies the selection of biofilter media and P content have been identified as critical factors for P removal efficiency (Hunt et al. 2006; Hsieh and Davis 2005a). Leaching of P from the filter media is a common problem; however, concentrations of P washed out in the effluent may decrease over the run times due to filter media stabilisation (Dietz and Clausen 2005; Hsieh et al. 2007a). These findings correspond to those described in Papers IV and V in which a decline in P outflow concentrations with increasing run time were observed (Table 10 and Figure 17), that

were positively correlated to TSS outflow concentrations, indicating that the effluent P originated from the filter media rather than the stormwater. However, in this study (Paper IV and V) the P outflow concentrations were relatively low, even during the first events (which were described in Paper IV). Possibly the coarse filter media with a low clay or silt content, and thus small pools of fines (with associated P) that could be washed out, contributed to the consistently excellent P removal as also described by Hsieh and Davis (2005a). The abovementioned processes were relatively temperature-independent (Paper IV and V), although temperature might have some effect on P sorption in soils (Barrow and Shaw 1975; Gardner and Preston Jones 1973).

Furthermore, P plant uptake might vary depending on plant activity, which is correlated to temperature. However, the effect of the plants on P treatment in the studies presented in Papers IV and V was low, presumably due to two reasons. Firstly, the plants did not develop well (Figure 25), thus their P uptake ability was assumed to be negligible. Secondly, plants have been shown to be beneficial for dissolved P treatment, while no significant effect of plants on (non-bioavailable) particle-bound P has been shown (Read et al. 2008). Thus, since P was nearly entirely particle-bound, plant uptake would only have been responsible for a small percentage of the total P removal. Nevertheless, although particulate P is not readily bioavailable, its treatment is important since it might subsequently be released to the environment if it is discharged and thus accumulated in the receiving water (Correll 1999). Thus, at least if eutrophication in the recipient is P-limited (as is often the case for freshwater ecosystems, Berge et al., 1997), P removal is of special concern (Swedish EPA 2003).

6.1.4 Nitrogen treatment

Compared to removal of the other investigated pollutants, N treatment was considerably less efficient (with extremely high leaching) and far more affected by temperature changes (Paper IV and V). In general too, N removal is quite variable due to the complex chemical processes affecting N behaviour in soils (Brady and Weil 2002), thus its treatment by biofilters (Davis et al. 2009). Highly variable N removal and in some cases leaching, has often been found by other workers (as summarised in Table 2).

Net N removal is controlled by a range of processes influencing the behaviour of the different N species in soils. Organic N originating from stormwater and dead OM is converted to NH_4 by ammonification. Together with the ammonium entering the filter with the stormwater, it is effectively converted to NO_x by oxic nitrification processes or sorbed by (negatively charged) soil particles and soil organic matter (Brady and Weil 2002). The often inadequate net N removal is mainly caused by low NO_x removal, with NO_x leaching commonly being observed (Birch et al. 2005; Bratieres et al. 2008; Davis et al. 2001b; Davis et al. 2006; Hatt et al. 2009; Hsieh et al. 2007b; Li and Davis 2009) in combination with the abovementioned additional NO_x production. In contrast to NH_4 , negatively charged NO_x is very mobile and thus

poorly adsorbed by biofilter media (Brady and Weil 2002; Hsieh et al. 2007b). Hence, NO_x leaches during the next storm event (Cho et al. 2009; Davis et al. 2001b; Davis et al. 2006). This NO_x leaching has been identified as the main obstacle for effective N net removal (Kim et al. 2003). Thus, to enhance anaerobic denitrification in the filter media, the introduction of a submerged (at last partly anoxic) zone in the filter, combined with a carbon source, has been suggested and successfully tested. The denitrification these measures provide, combined with nitrification in the upper oxic layer, has been shown to increase overall N removal substantially (Kim et al. 2003; Dietz and Clausen 2006). In the columns investigated in the C/SZ study (Paper I), NO_x removal of up to 99% was observed (Zinger et al. 2007b).

Taking the processes described above into account, it is clear why such a high N leaching and temperature dependency were observed in the temperature study (Papers IV and V). Since many of the N cycle processes in biofilters are biological, they are strongly dependent on temperature, with a temperature optimum around 20 to 35°C (Zhang et al. 2009; Stark 1996; Brady and Weil 2002) and minimum nitrification temperatures of between 2 and 5.5°C (Anderson and Purvis 1955; Brady and Weil 2002). The increases in rates of these processes with rising temperature are often well described by the Arrhenius function (Dessureault-Rompere et al. 2010; Stark 1996) as was shown for the biofilters examined in the temperature study (Paper V). The Q_{10} temperature coefficients (Kadlec and Reddy 2001) derived from the Arrhenius relationship (Paper V, Table 3) are in the range of 2-3, which is typical for equations describing the effects of temperature on nitrification in soils (Russell et al. 2002) and wastewater treatment wetlands (Kadlec and Reddy 2001).

The high nitrogen outflow concentrations at the warmer temperatures (Papers IV and V) were mainly due to temperature-induced increases in the NO_x production rate, causing three-fold increases in NO_x outflow concentrations at 20°C compared to 2°C. At 20°C near-optimal nitrification occurred in the filters converting NH_4 (originating from the stormwater and via ammonification of organic N) to NO_x . Thus, a high consumption of NH_4 occurred, leading to efficient treatment with around 75% removal. However, the NO_x produced was not converted to nitrogen gas, which would have removed N from the filter system and thus the water, since the lack of anoxic conditions inhibits denitrification. Thus, while NH_4 was removed efficiently from the stormwater at the warmer temperature, the NO_x production led to net leaching of total N. Thus, the filter was not effective for N removal.

This temperature dependence of N treatment processes is not only important for biofilter implementation in cold climate regions. In warmer regions too, temperatures can drop and thus affect N treatment processes. Furthermore, since current research focuses on enhancing nitrogen removal by biofilters, by enabling denitrification in a submerged zone or anoxic pockets in finer filter media than those used in this specific study, the temperature dependence detected for nitrification is important since denitrification is likely to show a similar temperature-dependent reaction rate. Thus, a

logical next step would be to validate the results obtained in this study for biofilters equipped with a submerged zone and or other filter media.

The coarse filter media intensified the nitrification processes further; due to the high pore volume optimal oxic conditions for nitrification were provided, while the well-drained soil prohibited denitrification due to the lack of anoxic conditions. In the commonly used sandy loams more pore water will remain in the pores, thus possibly leading to partly anoxic conditions in deeper biofilter layers.

Furthermore, vegetation has been shown to improve the effectiveness of biofilters in removing nitrogen from stormwater (Bratieres et al. 2008; Lucas and Greenway 2008); however significant variation has been shown for different plant species (Read et al. 2008), and plant size is positively correlated with N removal (Read et al. 2008). Plant uptake will most likely be affected by temperature changes. However, this could not be validated in this study since the plants did not develop well, regardless of the temperature (Figure 25).

6.2 Biofilter design

The research presented and discussed in this thesis has a range of implications for biofilter design. Depending on the target pollutant, a number of features need to be implemented to optimize performance.

Although a submerged zone has been shown to improve metal removal significantly, this effect is of minor practical importance (Papers I and II). However, it helps to mitigate the negative effect of longer drying on metal removal (Paper III). Thus, if no extended drying is expected and nitrogen removal (cf. Zinger et al. 2007b) is not of concern, the implementation of a submerged zone is not recommended. In contrast, if one of these two assumptions is true, a submerged zone can be applied or retrofitted in a biofilter without jeopardising metal removal. Furthermore, a combination of a 450 mm deep SZ and C enabled to meet Swedish and Australian freshwater guideline values in regard to Cu (ANZECC 2000; Swedish EPA 2000, c.f. Paper I: Table 4), which was not the case for standard biofilters (Paper I).

The fact that the major proportions of the metals are trapped in the top layer (Papers I, III, VI and VII) is important for biofilter design; since TSS, metals and P do not ingress far into the filter a lower filter depth compared to the often recommended 800 to 900 mm (e.g. Melbourne Water 2005) is sufficient. However, enough space for root growth and (if required) a SZ has to be provided.

The behaviour of OM is critical for Cu removal in biofilters. Implementing a filter media with a high solid OM content enhances Cu treatment (Papers I and VII). However, the long-term behaviour of this OM, and the associated Cu outflow

concentrations, should be evaluated during operation in order to avoid Cu leaching after some time.

To avoid leaching, possible P wash-out from the filter media has to be taken into account for biofilter design; the filter media should be low in P content, e.g. <100 mg/kg as recommended by FAWB (2008). The coarser filter material used in the temperature experiments (Papers IV and V) has shown promising P removal characteristics. The results of the studies included in this thesis have further shown that the recommendation to use a coarser filter material for cold climate biofilters does not jeopardise TSS and metal treatment (Papers VI and VII). Even in the coarse media the metals do not ingress far into the filter (Figure 24). However, (relatively coarse) sand filters have been shown to be more prone to clogging compared to sandy loam filters (Le Coustumer et al. 2009). Thus, similar to the temperature study (Papers IV to VI), a relatively thin layer with added topsoil or mulch (providing sufficient sorption capacity; Jang et al. 2005), underlain by coarse filter media providing sufficient water percolation even at (air) temperatures below 0°C could be a reliable combination of features for biofilters adapted to cold climates. The aim of incorporating such components is to obtain a balance between a relatively high hydraulic capacity and sufficient removal of stormwater metals.

However, one reason of the high nitrogen leaching reported in Papers IV and V, is probably the lack of at least anoxic pockets in the filter media. Thus, if nitrogen removal is targeted, the addition of a submerged zone is recommended, as suggested by Dietz and Clausen (2006), Kim et al. (2003) and Zinger et al. (2007b). Furthermore, in coarse well-drained filter media the negative effects of drying and oxidation on metal and nutrient removal (Zinger et al. 2007a) will start earlier or at least be accelerated due to a more rapidly decreasing moisture content.

6.3 Biofilter maintenance

While it might be problematic for the stormwater infiltration capacity, due to clogging, the sediment layer originating from TSS filtration on top of the filter facilitates maintenance. Scraping off the upper layer will remove a large percentage of the trapped solids and associated particle-bound pollutants, thereby maintaining the infiltration capacity. This might delay the need to replace the whole filter media and thus minimise operation and maintenance costs. Replacement of the top sediment layer is especially important in situations where high TSS loads are expected in the stormwater inflow (if, for instance, it includes highway, winter or periodical constructions site runoff). Furthermore, to avoid clogging due to ice formation, in areas with cold winters the biofilters should be inspected before the frost period to detect potential fine sediment layers.

To remove accumulated pollutants from the filter media is crucial for successful long-term performance of the filters so that no pollutant breakthrough occurs (Hatt et al. 2010). Depending on the pollutant concentration, the material removed from the filter surface may require landfilling or remediation (Anderson et al. 1998).

The release of previously accumulated metals from the filter, e.g. due to drying or acidic shocks, might be problematic for the successful long-term performance of biofilters. Due to metal retention, the filter media itself and the sediment layer on top might become sources of metals, leading to increased outflow concentrations. Thus, routine biofilter maintenance should include regular replacement of the filter media (or the top layer) to avoid the development of a metal supply source. Davis et al. (2003) have calculated live spans exceeding 20, years during which the filter media metal concentrations should not exceed toxicity values. However, their approach does not consider the risk of possible re-release of previously accumulated metals from the filter.

It has been shown that maintenance of biofilters, similar to other infiltration devices, is often inadequate in the long term and excessive sediment and debris layers on such facilities have been observed by Lindsey et al. (1992). Thus, maintenance has to be considered (already in the planning process, as e.g. recommended by Melbourne Water 2005) and regularly monitored.

6.4 Treatment efficiency and target pollutants

The outflow concentrations varied considerably, due both to the biofilter design variations and variations in ambient conditions. Further, there were relatively high variations in the outflow concentrations observed in the different studies. Despite these variations, the treatment of Cd, Pb and Zn in terms of removal percentages was excellent, often exceeding 90%. Cu removal was more variable, but in most cases >80%.

The variations in metal outflow concentrations also show that solely evaluating removal percentages can be misleading, since they are correlated to the inflow concentrations. In the C/SZ study (Paper I), for instance, the Zn outflow concentrations varied between 1.8 and 26.1 $\mu\text{g L}^{-1}$ (CV = 74.7; Figure 15), while Zn removal was always >96.4% for standard columns (CV = 0.9). Furthermore, in the snowmelt study (Paper VII), total Cu and Zn mass removals >89% were detected. However, this high removal was due more to the extremely high inflow concentrations than to low outflow concentrations; despite good removal, Cu and Zn effluent concentrations were many times higher than those in the other studies. Thus, the inflow concentrations seem to influence the filter performance in regard to outflow concentrations. However, the different design and operation modes of the

biofilter box in the snowmelt study compared to the biofilter columns utilised in the other experiments precludes direct comparison of the results.

The effects of (*inter alia*) the factors evaluated in this thesis on the outflow concentrations might explain the sometimes worse treatment efficiency observed in field studies compared to laboratory results, as summarised in Table 1 and Table 2. While stormwater biofilters in the laboratory are operated under strictly defined and controlled ambient conditions, biofilters in the field are continuously exposed to variations in ambient conditions, which might affect outflow concentrations leading to a more variable treatment performance.

Compared to the other studies, the outflow concentrations observed in the snowmelt study (Paper VII) were relatively high, despite effective mass removal. This example shows that for evaluations of treatment performance removal percentages have only limited suitability, and the outflow concentrations also have to be evaluated in regard to target outflow concentrations (e.g. depending on the sensitivity and characteristics of the recipient), for instance by comparing them to applicable freshwater quality guidelines (ANZECC 2000; Swedish EPA 2000; cf. Papers I, III, VI). Clearly, the Cu and Zn outflow concentrations reported in Paper VII do not meet the guideline values despite high removal percentages. However, discharge of the biofilter effluent would clearly have been less environmentally harmful than discharge of untreated stormwater, despite variations in outflow concentrations. Further, dilution effects will occur in the recipient, thus the recipient as a whole might meet guideline values.

Another example emphasizing the importance of the ecological conditions in the recipient, when evaluating biofilter performance, is the N:P ratio, determining the limiting nutrient for primary production in aqueous ecosystems. The limitation changes between N and P at a N:P ratio of about 15 to 30 (Correll 1999). The efficient removal of P (Table 10) and leaching of N (Table 11) influenced the N:P ratio (Table 14); in the outflow it was clearly higher than in the stormwater and increased with increasing temperature. Due to the less efficient P removal in the beginning (Paper IV, Figure 17), the N:P ratio was less.

Table 14: Mean N:P ratios in stormwater and biofilter outflows recorded in the temperature study (experimental run time: 1–4 weeks, Paper IV; 2–12 weeks, Paper V).

Temp.	N:P ratio	
	Paper IV	Paper V
Stormwater	4.8	5.8
Outflow 2°C	25	63
Outflow 7°C	27	75
Outflow 20°C	76	162

Due to the high N:P ratio, P would have been limiting in the outflow, while the stormwater would have been N-limited for primary production. Since P is commonly

the limiting nutrient in freshwater ecosystems (Berge et al. 1997; Correll 1999), the biofilter treatment would have contributed to less eutrophication, despite elevated N concentrations in the effluent. However, if the stormwater would have been discharged untreated to a P-limited recipient, all P in the stormwater would have been consumed for biomass production. In contrast, if the recipient is N-limited, as is commonly the case for coastal waters and estuaries (Vitousek et al. 1997), the N production would have contributed to clearly elevated eutrophication in the recipient. Thus, if N is a target pollutant, beneficial conditions for denitrification should be provided, e.g. by implementing a submerged zone combined with a carbon source (Zinger et al. 2007b).

Dependent on the ambient conditions, the target pollutants and the sensitivity of the recipient, adaptation of the filter design can enhance the biofilter treatment performance.

Biofilter laboratory experiments were used to investigate the stormwater quality treatment efficiency of biofilters with particular regards to the effects of variations in ambient conditions. Depending on the experimental design, biofilters used in the experiments were adapted with a submerged zone, a carbon source and coarse filter material in order to enhance target pollutant removal.

Given that the total TSS, metal and phosphorus outflow concentrations were, in all cases, far lower than those in the stormwater, biofilters were shown to be appropriate treatment systems. However, metal outflow concentrations were significantly affected by extended drying and temperature changes, the factors representing the varying ambient conditions biofilters are exposed to.

Total metals and TSS were also shown to be effectively removed from *snowmelt*. However, due to the sometimes extremely high metal concentrations in the snow, outflow concentrations were comparably high despite high removal. Given possibly high sediment concentrations, snowmelt might require pre-treatment.

Concerns that use of *coarse filter media* with no significant clay and silt contents may impair metal removal were not confirmed. However, substantial sorption capacity in the top layer was provided by using admixed top soil in one and mulch in the other. This could enable a combination of sufficient hydraulic conductivity and sorption capacity for biofilters in colder climates.

It was confirmed that the *top layer* is of prime importance for pollutant removal. Metal concentrations were found to be highest in the top layer and sediment accumulation resulted from effective TSS trapping on top of the filter. The deeper filter layers and plants retain pollutants as well, but to a minor degree. Furthermore, inflow concentrations have been shown to be significantly correlated with outflow concentrations (not with removal percentages) indicating that parts of the dissolved metal ingress deep in the filter, partly even ending up in the effluent.

Embedding a *submerged zone* in the filter combined with a solid organic matter *carbon source* (wood chips, pea straw) significantly enhanced metal removal. However, this has to be judged in context; the comparatively poor Cu removal was considerably improved by a combination of SZ and C (outflow concentrations were reduced from 5.6 to 1.3 $\mu\text{g L}^{-1}$), which helped to meet water quality guideline target concentrations that were not met without these features. In contrast, whilst Pb and Zn removal were statistically significantly improved, the improvements were of little practical significance since there was only a slight improvement of their already high removal.

Adverse *temperatures* can lead (*inter alia*) to high nitrate production instead of removal (following a strong Arrhenius relationship), thus jeopardising total nitrogen removal. However, even though further temperature effects on Cu outflow concentrations were observed, biofilters were found to provide reliable TSS, metal and P removal over a wide range of temperatures (2–20°C).

Extended *drying* of filter between two storm events increased outflow concentrations at the subsequent event significantly. For instance, compared with periods with regular stormwater inflow (i.e. twice weekly), after seven dry weeks mean outflow concentrations were highly elevated from 9.5 to 29.5, 1.9 to 15.0 and 15.6 to 34.4 $\mu\text{g L}^{-1}$ for Cu, Pb and Zn, respectively. However, a SZ helped to mitigate (Cu) or even eliminate (Pb) the negative effects of extended drying on metal removal. Thus, in regard to metal treatment, a submerged zone is certainly beneficial if either Cu removal is of particular local ecological significance or extended drying is expected.

Although the number of published biofilter studies has grown substantially in the last 5 to 10 years, much of the internal and external processes influencing the treatment and hydraulic performance of biofilters is still unknown. Based on the reviewed literature and the research findings presented in this thesis, several gaps have been identified.

Like other WSUD technologies, biofilters have been developed without considering their possibly critical winter operation (Marsalek et al. 2003). Concerns inhibiting increased implementation include possible effects of road salts (release of previously retained metals from the filter and increase of metal solubility in the runoff itself), reductions in infiltration capacity due to (partly) frozen filter media and temperature effects (cold temperatures might *inter alia* reduce biological N removal e.g. in a submerged zone).

Furthermore, several factors influencing the performance of the submerged zone/carbon source are unknown (Zinger et al. 2007b; Dietz and Clausen 2006). For instance, increases in salinity and/or changes in temperature might cause problems for effective denitrification in the submerged zone, the reliability of which feature is often crucial for effective biofilter use. Inclusion of a submerged zone might also reduce P removal, due to anoxic conditions releasing sorbed P from the filter media.

In addition, the choice of the filter media should be further investigated. Although the addition of solid organic matter has been shown to be beneficial, e.g. for Cu treatment, its long-term behaviour might be critical. Thus, decomposition rates of OM and their influence on the treatment performance should be further investigated. In addition, the infiltration capacity in frozen biofilter media should be evaluated under field conditions.

Besides being beneficial for maintaining the hydraulic capacity of biofilters (Lewis et al. 2008), plants have been shown to be important, at least for nutrient treatment (Lucas and Greenway 2008). However, for a range of Australian plant species significant variations in capacity to improve biofilter effectiveness has been reported

(Read et al. 2008). Thus, the choice of plant species seems to be crucial if nutrient treatment is targeted, and further investigation is warranted to identify optimally adapted plant species that can tolerate alternating drying/wetting cycles, temporary submergence, salinity, pollutants and possibly low temperatures.

Other potentially critical factors influencing the long-term performance of biofilters are the operation and maintenance of these facilities (Lindsey et al. 1992; Dietz 2007). Thus, evaluating existing biofilters and their maintenance would facilitate efforts to develop and implement reliable operation and maintenance schemes. Further investigation regarding the pollutant accumulation and possibly re-release (e.g. due to drying) is recommended to adapt biofilter maintenance so that biofilters do not become metal sources rather than treatment facilities.

The increased TSS, metals and P outflow concentrations from newly established biofilters observed in the temperature study (Papers IV–VI) are important for designing future biofilter experiments. Biofilter laboratory studies should aim to investigate sufficiently matured and established biofilters (*inter alia* incorporating well established plants and biofilms, terminated wash-out of fines) to achieve reliable results.

Investigation of these issues would help to overcome still existing obstacles for biofilter implementation. A biofilter design further adapted to varying ambient conditions and target pollutants would enable the implementation of biofilters as a main components of future sustainable urban drainage systems.

REFERENCES

- Alloway, B. J. (1995). Heavy metals in soils. *Blackie Academic and Professional, London, UK*.
- Amery, F., Degryse, F., Degeling, W., Smolders, E., & Merckx, R. (2007). The copper-mobilizing-potential of dissolved organic matter in soils varies 10-fold depending on soil incubation and extraction procedures. *Environ. Sci. Technol.*, 41(7), 2277-2281.
- Anderson, B. C., Brown, A. T. F., Watt, W. E., & Marsalek, J. (1998). Biological leaching of trace metals from stormwater sediment. *Water Sci. Technol.*, 38(10), 73-81.
- Anderson, O. E., & Purvis, E. R. (1955). Effects of low temperatures on nitrification of ammonia in soils. *Soil Sci.*, 80, 313-318.
- ANZECC (2000). Australian and New Zealand guidelines for fresh and marine water quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra, ACT, Australia.
- Baldwin, D. S., & Mitchell, A. M. (2000). The effects of drying and re-flooding on the sediment and soil nutrient dynamics of lowland river-floodplain systems: A synthesis. *Regul. Rivers: Res. Manage.*, 16, 457-467.
- Barret, M. E. (2005). Performance comparison of structural stormwater best management practices. *Water Environ. Res.*, 77(1), 78.
- Barret, M. E., Irish, L. B., Malina, J. F., & Charbeneau, R. J. (1998). Characterization of highway runoff in Austin, Texas, area. *J. Environ. Eng. - ASCE*, 124, 131-137.
- Barrow, N. J., & Shaw, T. C. (1975). The slow reactions between soil and anions: 2. Effect of time and temperature on the decrease in phosphate concentration in the soil solution. *Soil Sci.*, 119(2), 167.
- Bedan, E. S., & Clausen, J. (2009). Stormwater runoff quality and quantity from traditional and low impact development watersheds. *J. Am. Water Resour. Assoc.*, 45(4), 998-1008.
- Berge, D., Fjeld, E., Hindar, A., & Kaste, O. (1997). Nitrogen retention in two Norwegian watercourses of different trophic status. *Ambio*, 26(5), 282-288.
- Bertrand-Krajewski, J.-L., Chebro, G., & Saget, A. (1998). Distribution of pollutant mass vs volume in stormwater discharges and the first flush phenomenon. *Water Res.*, 32(8), 2341-2356.
- Birch, G. F., Fazeli, M. S., & Matthai, C. (2005). Efficiency of an infiltration basin in removing contaminants from urban stormwater. *Environ. Monit. Assess.*, 101, 23-38.
- Bradl, H. B. (2004). Adsorption of heavy metal ions on soil and soil constituents. *J. Colloid Interface Sci.*, 277, 1-18.
- Brady, N. C., & Weil, R. R. (2002). The nature and properties of soils, 13th ed. *Pearson Education, Upper Saddle River, NJ, USA*.
- Bratieres, K., Fletcher, T. D., Deletic, A., & Zinger, Y. (2008). Nutrient and sediment removal by stormwater biofilters; a large-scale design optimisation study. *Water Res.*, 42(14), 3930-3940.
- Browman, M. G., Harris, R. F., Ryden, J. C., & Syers, J. K. (1979). Phosphorus loading from urban stormwater runoff as a factor in lake eutrophication - theoretical considerations and qualitative aspects. *J. Environ. Qual.*, 8(4), 561-566.
- Butler, D., & Davies, J. W. (2004). Urban drainage. 2nd edition. *Spon Press, London, UK*.

- Bäckström, M., Karlsson, S., Bäckman, L., Folkesson, L., & Lind, B. (2004). Mobilisation of heavy metals by deicing salts in a roadside environment. *Water Res.*, 38, 720-732.
- Caille, N., Tiffreau, C., Leyval, C., & Morel, J. L. (2003). Solubility of metals in an anoxic sediment during prolonged aeration. *Sci. Total Environ.*, 301, 239-250.
- Caraco, D., & Claytor, R. (1997). Stormwater BMP design supplement for cold climates. *Center for Watershed Protection, Ellicott City, MD, USA.*
- Carle, M. V., Halpin, P. N., & Stow, C. A. (2005). Patterns of watershed urbanization and impacts on water quality. *J. Am. Water Resour. Assoc.*, 41(2), 693-708.
- Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., & Smith, V. H. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecol. Appl.*, 8(3), 559-568.
- Chapman, C., & Horner, R. R. (2010). Performance assessment of a street-drainage bioretention system. *Water Environ. Res.*, 82(2), 109-119.
- Cho, K. W., Song, K. G., Cho, J. W., Kim, T. G., & Ahn, K. H. (2009). Removal of nitrogen by a layered soil infiltration system during intermittent storm events. *Chemosphere*, 76(5), 690-696.
- Chocat, B., Ashley, R., Marsalek, J., Matos, M. R., Rauch, W., Schilling, W., et al. (2007). Toward the sustainable management of urban storm-water. *Indoor Built Environ.*, 16(3), 273-285.
- Chocat, B., Krebs, P., Marsalek, J., Rauch, W., & Schilling, W. (2001). Urban drainage redefined: From stormwater removal to integrated management. *Water Sci. Technol.*, 43(5), 61-68.
- Clark, S. E., Burian, S., Pitt, R., & Field, R. (2007). Urban wet-weather flows. *Water Environ. Res.*, 79(10), 1166-1227.
- Correll, D. L. (1999). Phosphorus: A rate limiting nutrient in surface waters. *Poultry Sci.*, 78(5), 674-682.
- Davis, A. P. (2007). Field performance of bioretention: Water quality. *Environ. Eng. Sci.*, 24(8), 1048-1064.
- Davis, A. P., Hunt, W. F., Traver, R. G., & Clar, M. (2009). Bioretention technology: Overview of current practice and future needs. *J. Environ. Eng. - ASCE*, 135(3), 109-117.
- Davis, A. P., Shokouhian, M., & Ni, S. (2001a). Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere*, 44, 997-1009.
- Davis, A. P., Shokouhian, M., Sharma, H., & Minami, C. (2001b). Laboratory study of biological retention for urban stormwater management. *Water Environ. Res.*, 73(1), 5-14.
- Davis, A. P., Shokouhian, M., Sharma, H., & Minami, C. (2006). Water quality improvement through bioretention media: Nitrogen and phosphorus removal. *Water Environ. Res.*, 78(3), 284.
- Davis, A. P., Shokouhian, M., Sharma, H., Minami, C., & Winogradoff, D. (2003). Water quality improvement through bioretention: Lead, copper, and zinc removal. *Water Environ. Res.*, 75(1), 73.
- De Carvalho, P. S. M., Zanardi, E., Buratini, S. V., Lamparelli, M. C., & Martins, M. C. (1998). Oxidizing effect on metal remobilization and daphnia similis toxicity from a brazilian reservoir sediment suspension. *Water Res.*, 32(1), 193-199.
- Dechesne, M., Barraud, S., & Bardin, J.-P. (2004). Spatial distribution of pollution in an urban stormwater infiltration basin. *J. Contam. Hydrol.*, 72, 189-205.
- Deletic, A., & Fletcher, T. D. (2006). Performance of grass filters used for stormwater treatment--a field and modelling study. *J. Hydrol.*, 317(3-4), 261.

- Dessureault-Rompere, J., Zebbarth, B. J., Georgallas, A., Burton, D. L., Grant, C. A., & Drury, C. F. (2010). Temperature dependence of soil nitrogen mineralization rate: Comparison of mathematical models, reference temperatures and origin of the soils. *Geoderma*, 157(3-4), 97-108.
- Dibiasi, C. J., Li, H., Davis, A. P., & Ghosh, U. (2009). Removal and fate of polycyclic aromatic hydrocarbon pollutants in an urban stormwater bioretention facility. *Environ. Sci. Technol.*, 43(2), 494-502.
- Dietz, M. E. (2007). Low impact development practices: A review of current research and recommendations for future directions. *Water Air Soil Pollut.*, 186, 351-363.
- Dietz, M. E., & Clausen, J. C. (2005). A field evaluation of rain garden flow and pollutant treatment. *Water Air Soil Pollut.*, 167(1-4), 123-138.
- Dietz, M. E., & Clausen, J. C. (2006). Saturation to improve pollutant retention in a rain garden. *Environ. Sci. Technol.*, 40, 1335-1340.
- Duncan, H. P. (1999). Urban stormwater quality: A statistical overview. Report 99/3, Cooperative Research Centre for Catchment Hydrology, Melbourne, Australia.
- Ellis, J. B., & Marsalek, J. (1996). Overview of urban drainage: Environmental impacts and concerns, means of mitigation and implementation policies *J. Hydraul. Res.*, 34(6), 723 - 732
- Engelhard, C., De Toffol, S., Lek, I., Rauch, W., & Dallinger, R. (2007). Environmental impacts of urban snow management - the alpine case study of Innsbruck. *Sci. Total Environ.*, 382(2-3), 286-294.
- FAWB (2008). Advancing the design of stormwater biofiltration. *Report. Facility for Advancing Water Biofiltration (FAWB)*. Monash University, Melbourne, Australia.
- Fletcher, T. D., Wong, T. H. F., & Breen, P. F. (2003). Buffer strips, vegetated swales and bioretention systems. *Australian Runoff Quality - A guide to Water sensitive urban design*. Engineers Australia, Sydney, NSW, Australia.
- Fritioff, Å., & Greger, M. (2003). Aquatic and terrestrial plant species with potential to remove heavy metals from stormwater. *Int. J. Phytorem.*, 5(3), 211-224.
- Fritioff, Å., Kautsky, L., & Greger, M. (2004). Influence of temperature and salinity on heavy metal uptake by submersed plants. *Environ. Poll.*, 133, 265-274.
- Fuchs, S., Scherer, U., Hillenbrand, T., Marscheider-Weidemann, F., Behrendt, H., & Opitz, D. (2002). Emissions of heavy metals and lindane into river basins of Germany. *Research Report 200 22 233, Texte 55/02, Federal Environmental Agency (Umweltbundesamt), Berlin*.
- Förstner, U., Ahlf, W., & Calmano, W. (1998). Studies on the transfer of heavy metals between sedimentary phases with a multi-chamber device: Combined effects of salinity and redox variation. *Mar. Chem.*, 28, 145-158.
- Garbrecht, K., Fox, G. A., Guzman, J. A., & Alexander, D. (2009). E.Coli transport through soil columns: Implications for bioretention cell removal efficiency. [Article]. *Transactions of the Asabe*, 52(2), 481-486.
- Gardner, B. R., & Preston Jones, J. (1973). Effects of temperature on phosphate sorption isotherms and phosphate desorption. *Commun. Soil Sci. Plant Anal.*, 4(2), 83-93.
- Glass, C., & Bissouma, S. (2005). Evaluation of a parking lot bioretention cell for removal of stormwater pollutants. *Ecosystems and Sustainable Development V Book Series: WIT Transactions on Ecology and the Environment*, 81, 699-708
- Good, J. C. (1993). Roof runoff as a diffuse source of metals and aquatic toxicity in storm water. *Water Sci. Technol.*, 28(3-5), 317-321.
- Goodison, B. E., Louie, P. Y. T., & Metcalfe, J. R. (1986). Snowmelt acidic shock study in south central Ontario. *Water Air Soil Pollut.*, 31(1-2), 131-138.

- Hallberg, M., Renman, G., & Lundbom, T. (2007). Seasonal variations of ten metals in highway runoff and their partition between dissolved and particulate matter. *Water Air Soil Pollut.*, 181, 183-191.
- Hathaway, J. M., Hunt, W. F., & Jadlocki, S. (2009). Indicator bacteria removal in stormwater best management practices in Charlotte, North Carolina. *J. Environ. Eng. - ASCE*, 135(12), 1275-1285.
- Hatt, B. E., Deletic, A., & Fletcher, T. D. (2007). Stormwater reuse: Designing biofiltration systems for reliable treatment. *Water Sci. Technol.*, 55(4), 201-209.
- Hatt, B. E., Fletcher, T. D., & Deletic, A. (2008). Hydraulic and pollutant removal performance of fine media stormwater filtration systems. *Environ. Sci. Technol.*, 42(7), 2535-2541.
- Hatt, B. E., Fletcher, T. D., & Deletic, A. (2009). Hydrologic and pollutant removal performance of biofiltration systems at field scale. *J. Hydrol.*, 365(3-4), 310-321.
- Hatt, B. E., Steinel, A., Deletic, A., & Fletcher, T. D. (2010). Retention of heavy metals by stormwater filtration systems: Breakthrough analysis. *Proceedings of NOVATECH, Lyon, France, 2010*.
- Heaney, J. P., & Huber, C. W. (1984). Nationwide assessment of urban runoff impact on receiving water quality. *Water Resour. Bull.*, 20, 35-42.
- Henderson, C., Greenway, M., & Phillips, I. (2007). Removal of dissolved nitrogen, phosphorus and carbon from stormwater by biofiltration mesocosms. *Water Sci. Technol.*, 55(4), 183-191.
- Hewitt, C. N., & Rashed, M. B. (1990). An integrated budget for selected pollutants for a major rural highway. *Sci. Total Environ.*, 93 375-384.
- Hong, E. Y., Seagren, E. A., & Davis, A. P. (2006). Sustainable oil and grease removal from synthetic stormwater runoff using bench-scale bioretention studies. *Water Environ. Res.*, 78(2), 141-155.
- Hsieh, C. H., & Davis, A. P. (2005a). Evaluation and optimization of bioretention media for treatment of urban storm water runoff. *J. Environ. Eng. - ASCE*, 131(11), 1521-1531.
- Hsieh, C. H., & Davis, A. P. (2005b). Multiple-event study of bioretention for treatment of urban storm water runoff. *Water Sci. Technol.*, 51(3-4), 177-181.
- Hsieh, C. H., Davis, A. P., & Needelman, B. A. (2007a). Bioretention column studies of phosphorus removal from urban stormwater runoff. *Water Environ. Res.*, 79(2), 177-184.
- Hsieh, C. H., Davis, A. P., & Needelman, B. A. (2007b). Nitrogen removal from urban stormwater runoff through layered bioretention columns. *Water Environ. Res.*, 79(12), 2404-2411.
- Hunt, W. F., Jarrett, A. R., Smith, J. T., & Sharkey, L. J. (2006). Evaluating bioretention hydrology and nutrient removal at three field sites in North Carolina. *J. Irrig. Drain. Eng.*, 132(6), 600-608.
- Hunt, W. F., Smith, J. T., Jadlocki, S., Hathaway, J., & Eubanks, P. (2008). Pollutant removal and peak flow mitigation by a bioretention cell in urban Charlotte, NC. *J. Environ. Eng.*, 134(5), 403-408.
- Jang, A., Seo, Y., & Bishop, P. L. (2005). The removal of heavy metals in urban runoff by sorption on mulch. *Environ. Pollut.*, 133(1), 117-.
- Kadlec, R. H., & Reddy, K. R. (2001). Temperature effects in treatment wetlands. *Water Environ. Res.*, 73(5), 543-557.
- Kane, D. L. (1980). Snowmelt infiltration into seasonally frozen soils. *Cold Reg. Sci. Technol.*, 3, 153-161.
- Kim, H., Seagren, E. A., & Davis, A. P. (2003). Engineered bioretention for removal of nitrate from stormwater runoff. *Water Environ. Res.*, 75(4), 355-367.

- Lau, S.-L., & Stenstrom, M. K. (2005). Metals and PAHs adsorbed to street particles. *Water Res.*, 39(17), 4083.
- Lau, Y. L., Marsalek, J., & Rochfort, Q. (2000). Use of a biofilter for treatment of heavy metals in highway runoff. *Water Qual. Res. J. Can.*, 35(3), 563-580.
- Le Coustumer, S., & Barraud, S. (2007). Long-term hydraulic and pollution retention performance of infiltration systems. *Water Sci. Technol.*, 55(4), 235-243.
- Le Coustumer, S., Fletcher, T. D., Deletic, A., & Barraud, S. (2007). Hydraulic performance of biofilters for stormwater management: First lessons from both laboratory and field studies. *Water Sci. Technol.*, 56(10), 93-100.
- Le Coustumer, S., Fletcher, T. D., Deletic, A., & Barraud, S. (2009). Hydraulic performance of biofilter systems for stormwater management: Influence of design and operation. *J. Hydrol.*, 376(1-2), 16-23.
- Lee, J., & Bang, K. (2000). Characterization of urban stormwater runoff. *Water Res.*, 34(6), 1773-1780.
- Lewis, J. F., Hatt, B. E., Le Coustumer, S., Deletic, A., Fletcher, T. D., & (2008). The impact of vegetation on the hydraulic conductivity of stormwater biofiltration systems. *11th International Conference on Urban Drainage ICUD*. Edinburgh, UK.
- Li, H., & Davis, A. P. (2008). Urban particle capture in bioretention media. I: Laboratory and field studies. *J. Environ. Eng. - ASCE*, 134(6), 409-418.
- Li, H., & Davis, A. P. (2009). Water quality improvement through reductions of pollutant loads using bioretention. *J. Environ. Eng. - ASCE*, 135(8), 567-576.
- Lindsey, G., Roberts, L., & Page, W. (1992). Inspection and maintenance of infiltration facilities. *J. Soil Water Conserv.*, 47(6), 481.
- Lloyd, S. D., Fletcher, T. D., Wong, T. H. F., & Wootton, R. M. Assessment of pollutant removal performance in a bio-filtration system - preliminary results. In *Second South Pacific Stormwater Conference, New Zealand, 2001* (pp. 12): New Zealand Water and Wastewater Association
- Lloyd, S. D., Wong, T. H. F., & Porter, B. (2002). The planning and construction of an urban stormwater management scheme. *Water Sci. Technol.*, 45(7), 1-10.
- Lucan Bouche, M. L., Habets, F., Biagianti Risbourg, S., & Vernet, G. (1997). The simultaneous influence of pH and temperature on binding and mobilisation of metals in sand. 2. Lead. *Fresenius Environ. Bull.*, 6(11-12), 719-726.
- Lucas, W. C., & Greenway, M. (2008). Nutrient retention in vegetated and nonvegetated bioretention mesocosms. *J. Irrig. Drain. Eng.*, 134(5), 613-623.
- Lygren, E., Gjessing, E., & Berglind, L. (1984). Pollution transport from a highway. *Sci. Total Environ.*, 33, 147-161.
- Makepeace, D. (1995). Urban stormwater quality - summary of contaminant data. *Crit. Rev. Environ. Sci. Tech.*, 25(2), 93-139.
- Malmqvist, P.-A. (1983). Urban stormwater pollutant sources. An analysis of inflows and outflows of nitrogen, phosphorus, lead, zinc and copper in urban areas. *Dissertation Series, Dept. of Sanitary Eng. CTH Gothenburg, Sweden*.
- Marsalek, J. (2003). Road salts in urban stormwater: An emerging issue in stormwater management in cold climate. *Water Sci. Technol.*, 48(9), 61-70.
- Marsalek, J., Oberts, G. L., Exall, K., & Viklander, M. (2003). Review of operation of urban drainage systems in cold weather: Water quality considerations. *Water Sci. Technol.*, 48(9), 11-20.
- Marsalek, J., Rochfort, Q., Brownlee, B., Mayer, T., & Servos, M. (1999). An exploratory study of urban runoff toxicity. *Water Sci. Technol.*, 39(12), 33-39.

- Martinez, C. E., Jacobson, A. R., & McBride, M. B. (2003). Aging and temperature effects on DOC and elemental release from a metal contaminated soil. *Environ. Pollut.*, 122(1), 135-143.
- Masterson, J. P., & Bannerman, R. T. (1994). Impacts of stormwater on urban streams in Milwaukee county, Wisconsin. *Proceedings of the American Water Resources Association National Symposium*.
- Matoura, R. F. C., Dickson, A., & Riley, J. P. (1978). The complexation of metals with humic materials in natural waters. *Estuarine Coastal Mar. Sci.*, 6, 387-409.
- Mazer, G., Booth, D., & Ewing, K. (2001). Limitation to vegetation establishment and growth in biofiltration swales. *Ecol. Eng.*, 17, 429-443.
- Melbourne Water (2005). *WSUD engineering procedures: Stormwater*. CSIRO Publishing.
- Mikkelsen, P. S., Viklander, M., Linde, J. J., & Malmqvist, P.-A. BMPs in urban stormwater management in denmark and Sweden. In *EF conference in Snowmass, USA, August 2001*
- Morrison, G. M. P. (1989). Bioavailable metal uptake rate in urban stormwater determined by dialysis with receiving resins. *Hydrobiologia*, 176/177, 491-495.
- Mothersill, C. L., Anderson, B. C., Watt, W. E., & Marsalek, J. (2000). Biological filtration of stormwater: Field operations and maintenance experiences. *Water Qual. Res. J. Can.*, 35(3), 541-562.
- Muthanna, T. M., Viklander, M., Gjesdahl, N., & Thorolfsson, S. T. (2007). Heavy metal removal in cold climate bioretention. *Water Air Soil Pollut.*, 183, 391-402.
- Piro, P., Carbone, M., Garofalo, G., & Sansalone, J. J. (2010). Size distribution of wet weather and dry weather particulate matter entrained in combined flows from an urbanizing sewershed. *Water Air Soil Pollut.*, 206(1-4), 83-94
- Pitt, R., Clark, S., & Field, R. (1999). Groundwater contamination potential from stormwater infiltration practices. *Urban Water J.*, 1(3), 217.
- Ponizovsky, A. A., Thakali, S., Allen, H. E., Di Toro, D. M., & Ackerman, A. J. (2006). Effect of soil properties on copper release in soil solutions at low moisture content. *Environ. Toxicol. Chem.*, 25(3), 671-682.
- Prince George's County (1993). Design manual for the use of bioretention in stormwater management. *The Prince George's County, Maryland, USA*.
- Prince George's County (2007). Bioretention manual. *Environmental Services Division, Department of Environmental Resources, The Prince George's County, Maryland, USA*.
- Raskin, I., Smith, R. D., & Salt, D. E. (1997). Phytoremediation of metals: Using plants to remove pollutants from the environment. *Curr. Opin. Biotechnol.*, 8(2), 221-226.
- Read, J., Wevill, T., Fletcher, T. D., & Deletic, A. (2008). Variation among plant species in pollutant removal from stormwater in biofiltration systems. *Water Res.*, 42, 893-902.
- Rentz, R. (2008). Urban impact on water bodies in the Luleå area, northern Sweden. *Licentiate thesis, 2008:48. ISSN: 1402-1757, Luleå University of Technology, Luleå, Sweden*.
- Rieuwerts, J. S., Thornton, I., Farago, M. E., & Ashmore, M. R. (1998). Factors influencing metal bioavailability in soils: Preliminary investigations for the development of a critical loads approach for metals. *Chem. Speciation Bioavailability*, 10(2), 61-75.
- Rose, S., & Peters, N. E. (2001). Effects of urbanization on streamflow in the atlanta area (Georgia, USA): A comparative hydrological approach. *Hydrol. Processes*, 15, 1441-1457.
- Roy, A. H., Purcell, A. H., Walsh, C. J., & Wenger, S. J. (2009). Urbanization and stream ecology: Five years later. *J. N. Am. Benthol. Soc.*, 28(4), 908-910.
- Rusciano, G. M., & Obropta, C. C. (2007). Bioretention column study: Fecal coliform and total suspended solids reductions. *Transactions of the Asabe*, 50(4), 1261-1269.

- Rushton, B. T. (2001). Low-impact parking lot design reduces runoff and pollutant loads. *J. Water Res. Pl-ASCE*, 12(3), 172-179.
- Russell, C. A., Fillery, I. R. P., Bootsma, N., & McInnes, K. J. (2002). Effect of temperature and nitrogen source on nitrification in a sandy soil. *Commun. Soil Sci. Plant Anal.*, 33(11-12), 1975-1989.
- Römkens, P. F. A. M., & Salomons, W. (1998). Cd, Cu and Zn solubility in arable and forest soils: Consequences of land use changes for metal mobility and risk assessment. *Soil Sci.*, 163(11), 859-871.
- Saeki, K., Okazaki, M., & Matsumoto, S. (1993). The chemical phase changes in heavy metals with drying and oxidation of the lake sediments. *Water Res.*, 27(7), 1243-1251.
- Sansalone, J. J., & Buchberger, S. G. (1997a). Characterization of solid and metal element distribution in urban highway stormwater. *Water Sci. Technol.*, 36(8-9), 155-160.
- Sansalone, J. J., & Buchberger, S. G. (1997b). Partitioning and first flush of metals in urban roadway storm water. *J. Environ. Eng. - ASCE*, 123(2), 134-143.
- Scholz, M. (2004). Treatment of gully pot effluent containing nickel and copper with constructed wetlands in a cold climate. *J. Chem. Technol. Biotechnol.*, 79, 153-162.
- Siriwardene, N. R., Deletic, A., & Fletcher, T. D. (2007). Clogging of stormwater gravel infiltration systems and filters: Insights from a laboratory study. *Water Res.*, 41(7), 1433-1440.
- Smith, N., Allen, A., McKenzie-McHarg, A., Deletic, A., Fletcher, T. D., & Hatt, B. E. (2007). Retrofitting functioning stormwater gardens into existing urban landscapes. . *Cairns International Public Works Conference. Cairns, Australia.*
- Stahre, P. (2008). Blue-green fingerprints in the city of Malmö, Sweden - Malmö's way towards a sustainable urban drainage. *VA SYD, Malmö, Sweden.*
- Stark, J. M. (1996). Modeling the temperature response of nitrification. *Biogeochemistry*, 35(3), 433-445.
- Stephens, S. R., Alloway, B. J., Parker, A., Carter, J. E., & Hodson, M. E. (2001). Changes in leachability of metals from dredged canal sediments during drying and oxidation. *Environ. Poll.*, 114, 407-413.
- Sun, X., & Davis, A. P. (2007). Heavy metal fates in laboratory bioretention systems. *Chemosphere*, 66(9), 1601-1609.
- Swedish EPA (2000). Environmental quality criteria - lakes and watercourses. *Report 5050. Swedish Environmental Protection Agency (Naturvårdsverket), Stockholm, Sweden.*
- Swedish EPA (2003). Environmental quality guidelines for phosphorus in lakes (in swedish: Miljökvalitetsnormer för fosfor - redovisning av regeringsuppdrag). *Report 5288. Swedish Environmental Protection Agency (Naturvårdsverket), Stockholm, Sweden.*
- Swedish EPA (2006). Ecological restoration of water courses in a landscape perspective (in swedish: Restaurering av vattendrag i ett landskapsperspektiv). *Report 5565, Swedish Environmental Protection Agency (Naturvårdsverket), Stockholm, Sweden.*
- Swedish EPA (2009). Waste water treatment in Sweden. *Swedish Environmental Protection Agency (Naturvårdsverket), Stockholm, Sweden.*
- Söderlund, G., & Lehtinen, H. (1971). Pollutants in urban stormwater (in swedish: Föroreningar i dagvatten från stadsbebyggelse). *Vatten*, 4, 326-335.
- Tack, F. M. G., Singh, S. P., & Verloo, M. G. (1998). Heavy metal concentrations in consecutive saturation extracts of dredged sediment derived surface soils. *Environ. Poll.*, 103, 109-115.
- Tack, F. M. G., Van Ranst, E., Lievens, C., & Vanderberghe, R. E. (2006). Soil solution Cd, Cu and Zn concentrations as affected by short-time drying or wetting: The role of hydrous oxides of Fe and Mn. *Geoderma*, 137, 83-89.

- Taylor, G. D., Fletcher, T. D., Wong, T. H. F., Breen, P. F., & Duncan, H. P. (2005). Nitrogen composition in urban runoff--implications for stormwater management. *Water Res.*, 39(10), 1982.
- Taylor, S. L., Roberts, S. C., Walsh, C. J., & Hatt, B. E. (2004). Catchment urbanisation and increased benthic algal biomass in streams: Linking mechanisms to management. *Freshwater Biol.*, 49(6), 835-851.
- Temminghoff, E. J. M., Van Der Zee, S. E. A. T. M., & De Haan, F. A. M. (1997). Copper mobility in a copper-contaminated sandy soil as affected by pH and solid and dissolved organic matter. *Environ. Sci. Technol.*, 31, 1109-1115.
- U.S. EPA (2000). Low impact development - a literature review. *EPA-841-B-00-005. United States Environmental Protection Agency, Washington DC, USA.*
- U.S. EPA (2002). 2000 national water quality inventory. *EPA-841-F-02-003. United States Environmental Protection Agency, Washington DC, USA.*
- U.S. EPA (2004). Stormwater best management practice design guide. Volume 2. Vegetative biofilters. Cincinnati, OH, USA. *EPA/600/R-04/121A. Office of Research and Development. United States Environmental Protection Agency, Cincinnati, OH, USA.*
- U.S. EPA (2005). National management measures to control nonpoint source pollution from urban areas. *EPA-841-B-05-004. United States Environmental Protection Agency, Washington DC, USA.*
- Walsh, C. J., Roy, A. H., Feminella, J. W., Cottingham, P. D., Groffman, P. M., & Morgan, R. P. (2005). The urban stream syndrome: Current knowledge and the search for a cure. *J. N. Am. Benthol. Soc.*, 24(3), 706-723.
- Warren, L. A., & Haack, E. A. (2001). Biogeochemical controls on metal behaviour in freshwater environments. *Earth Sci. Rev.*, 54, 261-320.
- Warren, L. A., & Zimmermann, A. P. (1994). The influence of temperature and NaCl in cadmium, copper and zinc partitioning among suspended particulate and dissolved phases in an urban river. *Water Resour.*, 28(9), 1921-1931.
- Westerlund, C., & Viklander, M. (2006). Particles and associated metals in road runoff during snowmelt and rainfall. *Sci. Total Environ.*, 362, 143-156.
- Westerlund, C., Viklander, M., & Bäckström, M. (2003). Seasonal variations in road runoff quality in Luleå, Sweden. *Water Sci. Technol.*, 48(9), 93-101.
- Viklander, M. (1999). Dissolved and particle-bound substances in urban snow. *Water Sci. Technol.*, 39(12), 27-32.
- Villareal, E. L., Semadeni-Davies, A., & Bengtsson, L. (2004). Inner city stormwater control using a combination of best management practices. *Ecol. Eng.*, 22, 279-298.
- Vitousek, P. M., Aber, J. D., Howarth, R. W., Likens, G. E., Matson, P. A., Schindler, D. W., et al. (1997). Technical report: Human alteration of the global nitrogen cycle: Sources and consequences. *Ecol. Appl.*, 7(3), 737-750.
- Yin, Y., Impellitteri, C. A., You, S.-J., & Allen, H. E. (2002). The importance of soil organic matter distribution and extract soil: Solution ratio on the desorption of heavy metals from soils. *Sci. Total Environ.*, 287, 107-119.
- Zhang, L. Q., Wei, C. H., Zhang, K. F., Zhang, C. S., Fang, Q., & Li, S. G. (2009). Effects of temperature on simultaneous nitrification and denitrification via nitrite in a sequencing batch biofilm reactor. *Bioprocess and Biosystems Engineering*, 32(2), 175-182.
- Zhao, L. D., & Gray, D. M. (1999). Estimating snowmelt infiltration into frozen soils. *Hydrol. Processes*, 13(12-13), 1827-1842.
- Zhao, L. Y. L., Schulin, R., & Nowack, B. (2007). The effect of plants on the mobilisation of Cu and Zn in soil columns. *Environ. Sci. Technol.*, 41(8), 2770-2775.

- Zinger, Y., Deletic, A., & Fletcher, T. D. (2007a). The effect of various intermittent dry-wet cycles on nitrogen removal capacity in biofilter systems. *Proceedings of rainwater & urban design 2007, Sydney, Australia*.
- Zinger, Y., Fletcher, T. D., Deletic, A., Blecken, G. T., & Viklander, M. (2007b). Optimisation of the nitrogen retention capacity of stormwater biofiltration systems. *Proceedings of NOVATECH 2007, Lyon, France*.

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Impact of a submerged zone and a carbon source on heavy metal removal in stormwater biofilters

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ABSTRACT

Biofilters are an effective treatment option for the substantial heavy metal loads in urban stormwater. However, to increase their nitrogen treatment efficacy, the introduction of a submerged (anoxic) zone (SZ) and a cellulose based carbon source (C) has been recommended because it has been shown to enhance denitrification and thereby increase overall nitrogen removal. To examine the impact of this design modification on heavy metal treatment, a laboratory study using biofilter mesocosms with different levels of SZ and with or without added C was conducted. The results show that SZ and C have a significant impact on metal treatment. In particular, the removal of Cu was improved significantly. The presence of SZ and C allows outflow Cu concentrations to meet Swedish and Australian water quality guidelines, which are not met with a standard biofilter without SZ or C. Although Zn and Pb removal was enhanced slightly by the presence of a SZ, this improvement is of less practical importance, since Zn and Pb removal is already very high (>95%) in standard biofilters. The best metal treatment was achieved with 450 and 600 mm SZ. Based on these results, the incorporation of SZ with C in stormwater biofilters is recommended.

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1. Introduction

Urban stormwater is a major source of aquatic pollution, leading to widespread environmental degradation (Marsalek et al., 1999; US Environmental Protection Agency, 2000). To treat stormwater and to re-establish near natural urban water cycles, sustainable stormwater treatment techniques have been recently developed, e.g., constructed wetlands and infiltration basins (Mitsch, 1992; Villarreal et al., 2004). These engineered ecosystems can even be retrofitted into existing urban environments making water visible to the people (Mitsch, 1992; Prince George's County, 2002). Thus, they have the ability to contribute both to ecological and societal improvements (Endreny, 2004).

Vertical flow stormwater biofilters are one of these treatment technologies which can help to restore water quality (and morphology) of urban streams and rivers (Melbourne Water, 2005). A typical biofilter consists of vegetated soil media placed in a trench or basin (that may or may not be lined). It has a detention storage on the top and commonly a drainage layer at the bottom, below the filter media, for collection of the treated water. Stormwater is treated by physical, biological and chemical processes in the soil media and plant matrix (Prince George's County, 2002; Hsieh and Davis, 2005).

Several laboratory studies have demonstrated the ability of stormwater biofilters to reduce concentrations of heavy metals (including Zn, Cu, and Pb) by more than 90% (Lau et al., 2000; Davis et al., 2001, 2003; Hatt et al., 2007; Sun and Davis,

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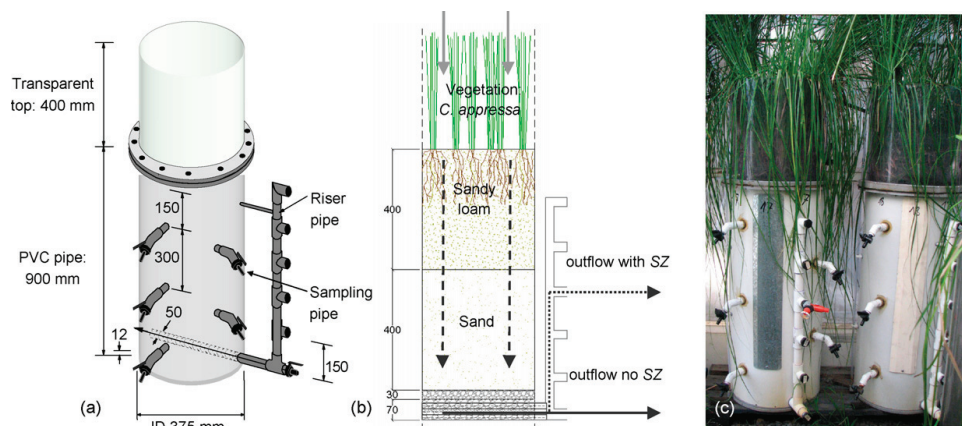


Fig. 1 – Biofilter column: (a) configuration, (b) filter media set-up and vegetation, (c) in greenhouse.

2007). Heavy metal removal has been shown to be high for a variety of different soil media, even in unvegetated soil filters (Hatt et al., 2007). The metals are not transported far in the filter media, but stay near the top of the soil profile (Davis et al., 2001; Hatt et al., 2007; Muthanna et al., 2007). It is thus clear that the soil, rather than vegetation, plays the dominant role in metal removal (Read et al., 2007; Sun and Davis, 2007).

It is difficult to achieve consistently high nitrogen removal in standard stormwater biofilters due to a lack of effective denitrification (Kim et al., 2003; Hsieh and Davis, 2005; Davis et al., 2006; Henderson et al., 2007). To support denitrification, a submerged (anoxic) zone (SZ) combined with a cellulose based carbon source (C) has recently been used to enhance nitrogen removal in biofilters (Kim et al., 2003; Zinger et al., 2007b). However, it is unclear whether this design modification will affect the behaviour of metals in biofilters—either positively or negatively. It is of particular interest to ascertain whether the introduction of SZ and C will diminish the high metal removal achieved in standard biofilter designs.

It is likely that redox potential and dissolved oxygen will decrease in the SZ, influencing the partitioning of metals between solution and the solid phase (Warren and Haack, 2001). The addition of organic matter in the form of C might provide an opportunity for enhanced metal uptake (Yin et al., 2002; Ponizovsky et al., 2006) since solid organic matter is the main component in soil to adsorb Cu (Temminghoff et al., 1997), thus immobilising the metal (Zhao et al., 2007). Furthermore, biofilms and bacteria in the submerged zone may have an impact on the metal behaviour (Warren and Haack, 2001). However, there is a lack of studies which reflect the special operating and environmental conditions which are typical of stormwater biofiltration systems. Thus, the effect of these factors and their interactions on metal treatment in a stormwater biofilter with a submerged zone cannot be readily estimated from the literature.

The aim of this research was to evaluate the influence of SZ and added C on metal removal by stormwater biofilters. The main hypothesis was that, due to trapping of the metals in the top layer of the soil filter (Hatt et al., 2007) the

presence of a submerged zone and a carbon source will not significantly influence metal removal, thus allowing the use of the design modification to improve nitrogen removal, without jeopardising metal treatment. Experiments were conducted on mesocosms (biofilter columns) representative of current typical design guidelines, with different levels of SZ with and without added C, to determine their influence on the efficiency of heavy metal removal (nutrient removal was also investigated and is reported in Zinger et al., 2007b).

2. Methods

2.1. Experimental set-up and procedure

2.1.1. Mesocosms and biofilter designs tested

Eighteen mesocosms, here named 'biofilter columns', were constructed from PVC stormwater pipes (375 mm in diameter, 900 mm in height; Fig. 1). A 400 mm high transparent plexiglas pipe was welded on the top, to allow stormwater ponding without affecting plant growth (shading). The inner wall of the PVC pipe was sandblasted to achieve a higher surface roughness in order to prevent preferential flow along the edge.

A slotted horizontal drainage pipe (50 mm in diameter) was placed at the bottom of the column and extended into a vertical riser pipe with 6 outlet taps installed at different heights (Fig. 1). By opening one of these taps, the water level could be kept constant at the bottom of the column, and thereby create SZ of different depths (according to the height of the open tap).

In the filter media sampling pipes were installed at 300, 600 and 750 mm from the bottom. These pipes were made of 21 mm PVC pipes traversing the entire column diameter to ensure samples were representative of the entire filter. The pipes had open tops (to collect water percolating through the filter), were filled with gravel and surrounded by sand above to prevent washout of the overlying soil.

The media in the columns consisted of four layers (listed from the top, Fig. 1):

- 400 mm of sandy loam (soil pH 8) supporting vegetation; its full specification can be viewed at <http://www.monash.edu.au/fawb/index.html>.
- 400 mm of fine sand in which SZ is created; in 12 out of 18 columns 800 g of a cellulose-based carbon source C was added into the sand, consisting of 1/3 pea straw and 2/3 Red River Gum (*Eucalyptus camaldulensis* Dehnh.) wood chips.
- 30 mm of coarse sand (mean diameter 0.62 mm) to prevent fine sand particles from being washed out.
- 70 mm of fine gravel (mean diameter 5 mm) to create a drainage layer at the bottom.

The columns were placed in an outdoor cage located in Melbourne, Australia, with transparent plastic roof and open mesh on the sides, to ensure that the only inflow water received was by controlled dosing (rather than rainfall).

The columns were planted with *Carex appressa* R.Br. (Tall Sedge) which is native to southeastern and eastern Australia (Botanic Gardens Trust, 2007). *Carex appressa* is a recommended species for biofiltration (Melbourne Water, 2005) and biofilters planted with *Carex appressa* show better nitrogen removal compared to other plant species (Bratieres et al., 2008). The plant density in the columns was 7 plants per column which is equivalent to approximately 64 plants m⁻².

The columns were irrigated with tap water for 15 weeks (starting in February 2006) to establish the plants. The hydraulic conductivity of the columns was then measured using standard constant head Darcy's method (without SZ formed in any of the columns). The average hydraulic conductivity \pm standard deviation was $1.59 \times 10^{-4} \pm 2.15 \times 10^{-4}$ m s⁻¹ ($=571 \pm 77$ mm h⁻¹) after an initial 4-week "settling period" for the media. There were no significant differences in the hydraulic conductivity of the columns with or without C. The columns were then flushed three times during 10 days with stormwater pond water, to promote natural biofilm development. For each flush 25 L of water were used; a 450 mm high SZ was formed overnight at the bottom of all 18 columns.

Six biofilter designs with three replicates of each design were then created. The height of the SZ is given in mm from the bottom of the filter (cf. Fig. 1b). The notation used for each design in Fig. 2 and Tables 2 and 4 is given in brackets.

1. No C and SZ=0 mm (–0)
2. No C and SZ=450 mm (–450)
3. With C and SZ=0 mm (+0)
4. With C and SZ=150 mm (+150)
5. With C and SZ=450 mm (+450)
6. With C and SZ=600 mm (+600)

2.1.2. Experimental procedure

The experiments were carried out over 22 weeks (starting June 6th, 2006, thus under winter and spring conditions). Each column was dosed with 25 L (226 mm) of stormwater twice per week. The calculation of the stormwater volume was based on Melbourne rainfall patterns (where it rains approx. twice weekly and the mean annual rainfall is 653 mm year⁻¹, thus 6.28 mm precipitation per event which is similar to a typical Mediterranean climate). Assuming a 90% impervious catchment and a biofilter with an area of 2.5% of the catchment

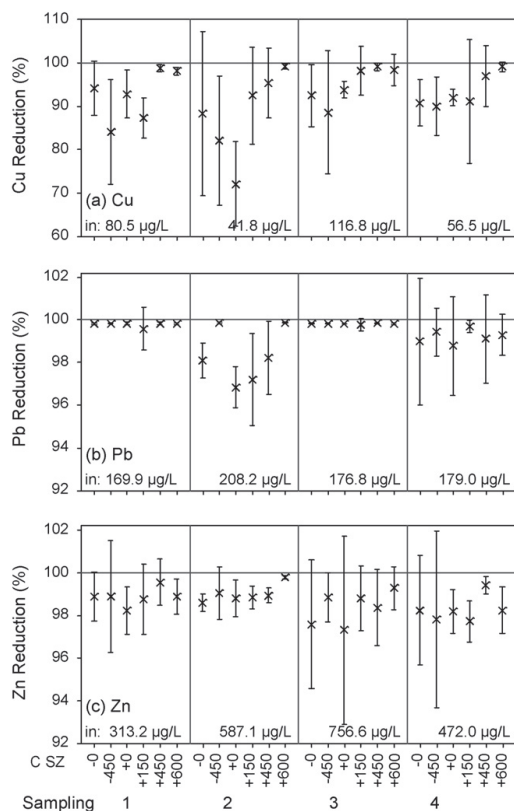


Fig. 2 – Mean and 95% confidence interval of Cu, Pb and Zn removal of the B samples for the different design combinations (+ and – indicates presence of C, and 0, 150, 450 and 600 indicates depth of SZ in mm) at all four sampling events. The mean inflow concentration at the respective sampling is given. Note: different scales on y-axis; metal reduction cannot exceed 100% in reality.

(i.e., one column for 4.42 m² catchment), which is typical of current practice, each biofilter was dosed with 25 L (226 mm) per event ($6.28 \text{ L/m}^2 \times 4.42 \text{ m}^2 \times 0.9 = 24.95 \text{ L} \approx 25 \text{ L}$) (Melbourne Water, 2005; Wong et al., 2006). The columns were left to gravity drainage between the applications.

As natural stormwater was not available in the required quantity (with the required consistency to ensure appropriate experimental control), semi-synthetic stormwater was used, made from stormwater sediment collected from a stormwater pond near its inlet (sieved through a 300 µm sieve), mixed with dechlorinated tap water (using sodium thiosulfate), and topped up by laboratory-grade chemicals as required to achieve concentrations representative of typical stormwater Event Mean Concentrations (Table 1), based on reviews of world wide stormwater data (Duncan, 1999; Taylor et al., 2005).

For every stormwater dosing, composite inflow samples (for all 18 columns) were taken to monitor the total inflows

Table 1 – Mean pollutant inflow target concentration (over all stormwater applications) and their sources in the synthetic stormwater.

Pollutant	Mean inflow pollutant concentration	Chemicals used for topping of sediment conc.
Total susp. solids (TSS)	150.0 mg/L	Stormwater pond sediment ($\leq 300 \mu\text{m}$)
pH	7.14	
Cadmium (Cd)	$<0.7 \mu\text{g/L}$	Cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$)
Copper (Cu)	$54.7 \mu\text{g/L}$	Copper sulphate (CuSO_4)
Lead (Pb)	$142.9 \mu\text{g/L}$	Lead nitrate (PbNO_3)
Zinc (Zn)	$576.9 \mu\text{g/L}$	Zinc chloride (ZnCl)
		Ammonium chloride (NH_4Cl)
Total nitrogen (N)	2.24 mg/L	Potassium nitrate (KNO_3)
		Nicotinic acid ($\text{C}_6\text{H}_5\text{O}_2\text{N}$)
Total phosphorus (P)	0.47 mg/L	Potassium phosphate (KH_2PO_4)

over the entire duration of the experiment. Both inflow and outflow samples for every column were taken at four events after 6, 9, 19 and 22 weeks from the start of dosing. From the outflow two 1 L samples were taken: *Sample A* after the first 0.5 L drained, representing the first flush of resident pore water in the media, and *Sample B* after 17 L drained, representing the newly treated water (later flush). Tracer tests were conducted on a pilot column (using NaCl) to refine this procedure. Additionally, samples were taken from the lateral outlets at 300, 600 and 750 mm from the bottom (one from each outlet at the very start of the sampling event to track the waterfront progress).

All samples were collected in polyethylene bottles and then digested with nitric acid according to Standard Methods (APHA/AWWA/WPCF, 1998). The samples were analysed for the following total concentrations of heavy metals using an ICP-OES (Varian 720-ES): Cu, Pb, Zn and Cd. The device detection limits were $0.7 \mu\text{g/L}$ for Cd, $0.3 \mu\text{g/L}$ for Cu, $0.6 \mu\text{g/L}$ for Pb and $0.5 \mu\text{g/L}$ for Zn. Furthermore, pH, dissolved oxygen and redox potential were measured immediately after each sampling using a Horiba W-22XD multi-probe device.

2.2. Data analyses

In this paper only the Cu, Pb and Zn data were analysed. These metals are regarded as the key stormwater pollutants, alongside Cd, which is not presented since outflow concentrations were always below the detection limit (and thus is very effectively removed in all cases).

2.2.1. Outflow concentrations and removal efficiencies

The outflow results were analysed for both concentrations and removal. The removal was calculated for both the first and later flush (i.e., *Samples A* and *B*) as a % of the inflow concentrations.

2.2.2. Difference between the first and later flushes (*Samples A* and *B*)

It was then determined whether the first flush from the biofilter (i.e., the resident pore water - *Sample A*) and the newly treated water (*Sample B*) showed different characteristics, by performing a paired t-test with $H_0: \mu_d = \mu_1 - \mu_2 = 0$ and $H_1: \mu_d \neq 0$. As with all following statistical analyses, the paired t-test was computed with MINITAB® 15.1, © 2006 Minitab Inc.

2.2.3. Impact of stormwater inflow concentration on outflow concentration and/or removal

The inflow concentrations were compared between the columns for each event and then between the events, to determine their variability. Linear regression was performed to investigate if there was a statistical relationship between the inflow concentration (predictor) and outflow concentration (and removal) of both *Samples A* and *B* (response). Because *Sample A* represents the residual pore water from the antecedent dosing and *Sample B* represents the newly treated water, the predictors were the inflow concentrations of the antecedent dosing for *Samples A*, and the inflow concentration of the current dosing for *Samples B*. The regression was performed using all data (for all designs together), and then separately for the different designs. Significance was accepted at $p \leq 0.05$.

2.2.4. Impact of SZ and C on metal removal

The mean and 95% confidence interval of removal were plotted for all designs and sampling events. To determine the influence of SZ and C, a General Linear Model (GLM) was applied to both concentration and removal of both *Samples A* and *B*. The inflow concentration was also included in the GLM since it also had an impact on the results (see below) along with the presence of SZ and C. The factors were accepted to significantly influence metal removal at $p \leq 0.05$. Finally, Analysis of Variance (ANOVA) was used to study the impact of SZ and C on pH, redox potential and dissolved oxygen in the outflow. Any change of these factors will influence metal solubility and thus might explain changes caused by SZ and/or C.

2.2.5. Depth profiles of metal removal

Depth profiles of metal removal in the water collected from the lateral sampling ports along the biofilter columns were compiled and plotted. While for the designs with 450 and 600 mm SZ the data was available for all sampling ports, for 0 mm SZ only inflow and outflow data were available (the other ports were clogged).

2.2.6. Comparison with water quality standards

The outflow concentrations were compared to Australian & New Zealand (ANZECC, 2000) and Swedish (Swedish EPA, 2000) guidelines. The ANZECC guidelines define ambient toxicant levels for aquatic ecosystems with a range of percentile trig-

ger values specified, based on the sensitivity of the receiving water. In the Swedish guidelines, metal concentrations in freshwater are allocated to five different classes (1: no or only very slight risk of biological effect, 2: slight risk, 3: effects may occur, 4 and 5: growing risk of effects).

3. Results and discussion

3.1. Inflow and outflow concentrations and removal efficiencies

The mean concentrations (\pm their standard deviations) of the inflows into 18 columns are listed below for the 1st to 4th sampling event, respectively:

- Cu: 81 $\mu\text{g/L}$ (± 6), 42 $\mu\text{g/L}$ (± 18), 117 $\mu\text{g/L}$ (± 3), and 57 $\mu\text{g/L}$ (± 1);
- Pb: 170 $\mu\text{g/L}$ (± 19), 208 $\mu\text{g/L}$ (± 14), 177 $\mu\text{g/L}$ (± 9), and 179 $\mu\text{g/L}$ (± 12);
- Zn: 313 $\mu\text{g/L}$ (± 20), 587 $\mu\text{g/L}$ (± 19), 756 $\mu\text{g/L}$ (± 21), and 472 $\mu\text{g/L}$ (± 17).

Since the inflow concentrations were nearly uniform for all columns during one event, it was possible to compare the performance of the different columns within one event. However, the inflow concentrations varied between the four sampling events due to variations in metal concentrations in the stormwater sediment used (as is the case in real stormwater events), precluding direct comparisons between columns over different events. Linear regression shows a positive relationship between inflow concentration and overall mean outflow concentrations (significant effect of inflow concentration on Cu: outflow conc. A, Pb: outflow conc. B, Zn: outflow conc. A and B). This result was somewhat surprising, since the main metal reduction commonly occurs in the top layer of a biofilter (Hatt et al., 2007) and it was hypothesised that the metal concentrations in water would quickly reach a background equilibrium concentration on its way through the biofilter. Testing the impact of the inflow concentration on the outflow concentration separately for the different designs, no interaction between the inflow concentration and the design combination can be seen: the significant impact of the inflow concentration was thus not affected by either C or SZ.

Outflow concentrations and removal is shown in Table 2. For Pb and Zn the overall removal was consistently high (between 96.6 and 99.7%). However, Cu treatment was far more variable with removal ranging between 67 and 99% and outflow concentrations between 1.0 and 17.4 $\mu\text{g/L}$.

A clear difference between Samples A and B was observed for most designs and all three metals (Table 2): the B samples have in all cases lower outflow concentrations than the samples representing the flush of antecedent water. The Cu outflow concentrations of Samples A were approximately two to three times higher than Samples B which is of practical significance. This shows that Cu removal at the start of storm events (or during very small events) may not be representative of its performance during larger events (once resident water, which has sat in the filter since the last storm event, has been flushed through). For Pb, around 50% of the outflow samples

were below the detection limit which was a problem for the t-test analysis. However, although significant for most designs, the difference in A and B has no practical implication since the overall removal for Pb was very high (around 99%), the outflow concentrations around the detection limit of 0.6 $\mu\text{g/L}$, and the removal difference between A and B less than 1.4%. However, it is interesting that introduction of a deep SZ increases the magnitude of this difference. The results for Zn are quite homogeneous even though outflow B is significantly less contaminated than A. However, for Sample A, the mean reduction was at least 97.6%, and therefore as for Pb, this makes the detected difference not of great practical significance.

A possible explanation for the detected difference in the first and later flush may be leaching of already accumulated metals into the pore water during dry weather, causing a 'first flush' of heavy metals at the start of each new storm event. Drying of the filter between storm events might cause oxidation of the upper layer (where most metals are retained, see below) and therewith mobilisation of metals. However, based on this data the reasons for the increased Sample A concentrations cannot be ascertained definitely and further research seems to be necessary to investigate the processes occurring in the filters between storm events.

3.2. Impact of submerged zone and carbon source on metal removal

A significant influence of the submerged zone (SZ) was found for all Samples B and all metals, as shown by the General Linear Model results (Table 3), and illustrated by the interval plots (Fig. 2a–c). It seems that the presence of a SZ enhances heavy metal removal and consequently the outflow concentrations are lower. The cellulose based carbon source (C) has the same effect on Cu while it has no significant effect on the other metals.

The presence of both SZ and C has the most consistent and practically important effect on Cu (Table 3), explaining the above-reported variations in the Cu removal. Designs without SZ had a removal of about 80% for A and 90% for B, while with 450 and 600 mm SZ and C removal was around 95% (for Sample A) and around 98% (for Sample B) (Table 2). Consequently, the introduction of SZ and C caused Cu outflow concentrations to drop substantially from 9.7 to 3.1 $\mu\text{g/L}$ (A) and from 5.6 $\mu\text{g/L}$ to only 1.0 $\mu\text{g/L}$ (B). The best treatment was achieved with 600 mm SZ, suggesting that Cu removal was enhanced with an increasing submerged zone in the pore water. For Pb and Zn the positive SZ effect, whilst statistically significant, is of little practical importance, since biofilters even without SZ perform very well. However, despite the small effect of SZ it still helps to meet guideline values (see below). For 150 mm SZ some samples show no enhanced metal treatment compared to filters without SZ. Thus, if introduced, SZ should be at least 450 mm deep which coincidentally corresponds with the findings of Zinger et al. (2007b) for nutrient removal (optimal SZ depth 450 mm).

A significant effect of SZ and C on dissolved oxygen (DO) and redox potential (ORP) in the outflow was detected for both samples A and B (data in Table 2). Both increasing SZ and addition of C decrease the DO from around 8.5 mg/L at SZ level of 0 mm and no C to around 6 mg/L for SZ levels of 600 mm with

Table 2 – Mean inflow and outflow concentrations, and removal of the four sampling events for Cu, Pb and Zn and each design. Results of the paired t-test to detect differences between metal concentrations/removal in Samples A and B if $p < 0.1$. Mean outflow redox potential (ORP), dissolved oxygen (DO) and pH for each designs.

Metal	Sample	Unit	Overall	Treatment					
				–0	–450	+0	+150	+450	+600
Cu	Inflow conc.	µg/L	73.9 (30)						
	Outflow conc. A	µg/L	10.3 (7.9)	9.7 (4.5)	17.3 (5.8)	10.9 (3.1)	17.4 (9.7)	3.5 (3.5)	3.1 (3.6)
	Outflow conc. B	µg/L	4.9 (4.1)	5.6 (2.8)	10.3 (4.5)	6.2 (1.6)	4.7 (3.5)	1.3 (1.0)	1 (0.9)
	Estimated difference	µg/L	5.5	4.1	6.9	4.7	12.7	2.2	2.1
	p-value		0.000	0.016	0.000	0.000	0.000	0.073	0.069
	Removal A	%	82.4 (17.3)	83.7 (13.3)	75.2 (13.7)	78.9 (15.7)	67.5 (24.8)	93.5 (6.9)	95.4 (4.6)
	Removal B	%	92.4 (7.0)	91.5 (4.4)	86.3 (5.4)	87.8 (9.7)	92.4 (5.2)	97.7 (2.4)	98.8 (0.8)
	Estimated difference	%	–10.0	–7.8	–11.1	–8.9	–24.9	–4.1	–3.4
Pb	p-value		0.000	0.075	0.002	0.002	0.003	0.055	0.027
	Inflow conc.	µg/L	183.5 (20)						
	Outflow conc. A	µg/L	2.3 (2.0)	1.9 (2.1)	1.8 (1.6)	1.7 (2.0)	2.2 (2.0)	2.9 (2.2)	3 (2.1)
	Outflow conc. B	µg/L	1.4 (2.0)	1.5 (1.8)	0.5 (0.5)	2.4 (2.9)	1.8 (2.5)	1.5 (1.8)	0.6 (0.6)
	Estimated difference	µg/L	0.9	0.4	1.4	0.7	0.4	1.4	2.4
	p-value		0.018	0.713	0.022	0.577	0.696	0.087	0.001
	Removal A	%	98.8 (1.1)	98.9 (1.2)	99 (0.9)	99 (1.2)	98.8 (1.0)	98.4 (1.2)	98.3 (1.2)
	Removal B	%	99.3 (0.9)	99.2 (0.9)	99.7 (0.3)	98.8 (1.4)	99.1 (1.2)	99.2 (0.8)	99.7 (0.3)
Zn	Estimated difference	%	–0.5	–0.3	–0.7	0.2	–0.2	–0.8	–1.4
	p-value		0.000		0.024			0.081	0.001
	Inflow conc.	µg/L	532.1 (164)						
	Outflow conc. A	µg/L	11.5 (7.0)	11.5 (7.7)	8.9 (4.8)	17.4 (8.4)	11.7 (3.7)	8.5 (2.3)	10.6 (9.3)
	Outflow conc. B	µg/L	7.3 (5.7)	9.3 (6.9)	6.6 (3.5)	10.3 (8.7)	7.4 (3.5)	5.6 (5.0)	4.5 (3.1)
	Estimated difference	µg/L	5.1	2.2	2.3	7.0	4.3	3.0	6.2
	p-value		0.000			0.048	0.004	0.062	0.016
	Removal A	%	97.7 (1.4)	97.9 (1.0)	98.3 (1.0)	96.6 (1.7)	97.6 (0.8)	98.3 (0.6)	97.9 (1.9)
ORP	Removal B	%	98.7 (0.8)	98.3 (0.9)	98.8 (0.7)	98.2 (1.0)	98.6 (0.7)	99.1 (0.6)	99.1 (0.7)
	Estimated difference	%	–1.1	–0.5	–0.5	–1.6	–0.9	–0.8	–1.2
	p-value		0.000			0.021	0.004	0.026	0.019
	Outflow conc. A	mV		252	194	290	255	97	138
	Outflow conc. B	mV		183	138	197	204	46	84
	Outflow conc. A	mg/L		8.5	8.2	7.9	6.9	6.3	7.3
	Outflow conc. B	mg/L		8.7	7.8	8.3	6.6	6.0	6.1
	pH	–		6.85	6.90	6.64	6.68	6.81	6.92
	Outflow A	–		6.94	6.79	6.79	6.70	6.74	6.91
	Outflow B								
Concentration, removal and difference: standard deviations in brackets.									
Outflows: mean values of 12 individual measurements (three replicates at four different sampling events), except for Zn outflow Sample A and design –450: 11 values (one outlier deleted, based on concerns about sample contamination).									
Inflow concentrations: means for all 18 columns and all sampling events (n = 72).									
t-test: significant difference at p ≤ 0.05.									

Concentration, removal and difference: standard deviations in brackets.
Outflows: mean values of 12 individual measurements (three replicates at four different sampling events), except for Zn outflow Sample A and design –450: 11 values (one outlier deleted, based on concerns about sample contamination).
Inflow concentrations: means for all 18 columns and all sampling events ($n = 72$).
t-test: significant difference at $p \leq 0.05$.

Table 3 – Results of the general linear model: p -values and R^2 (adjusted).

Metal	Sample	p -value of significant factors			R^2 (adjusted)
		C	SZ	Inflow concentration	
Cu	Outflow conc. A	0.001 ↓	0.000 ↓		35.2%
	Removal A	0.038 ↑	0.000 ↑	0.000	48.1%
	Outflow conc. B	0.000 ↓	0.041 ↓		34.3%
	Removal B	0.017 ↑	0.016 ↑	0.001	32.5%
Pb	Outflow conc. A				
	Removal A				
	Outflow conc. B		0.011 ↓	0.000	33.4%
	Removal B		0.011 ↑	0.000	29.4%
Zn	Outflow conc. A				
	Removal A		0.033 ↑	0.028	14.7%
	Outflow conc. B		0.005 ↓	0.000	32.5%
	Removal B		0.006 ↑		13.3%

↑ - indicates increase in removal and concentration related to standard design, and ↓ - indicates decrease in removal and concentration related to standard design.

added C. ORP decreased significantly and is lowest at 450 mm SZ while it increases again with increasing SZ to 600 mm (one-way ANOVA ORP vs. SZ: $p = 0.000$ for A and B). The ORP in the A samples is significantly higher than in the B samples (paired t -test: $p = 0.000$, mean difference = 66.0).

Given the very complex processes influencing metal behaviour in soils, it is comparatively difficult to define the exact mechanisms that influence the enhanced treatment in filters with SZ based on the existing data. Furthermore, for Pb and Zn only a relatively slight enhancement was detected.

Organic matter (OM) is an important factor in determining Cu behaviour in soils. The formation of Cu–organic matter complexes could explain the positive effect of C only on Cu treatment since of all metals Cu has the strongest affinity to OM (Yin et al., 2002; Ponizovsky et al., 2006) resulting in formation of strong OM–Cu complexes (Matoura et al., 1978). Whether OM is present in its solid or dissolved form does not influence the complexation affinity with Cu (Yin et al., 2002), but the Cu treatment in a stormwater biofilter filter is affected substantially by that distribution between solid and dissolved OM: while dissolved OM mobilises Cu, by forming mobile dissolved OM–Cu complexes (Römken and Salomons, 1998; Amery et al., 2007), solid OM is the main component in soil to adsorb Cu (Temminghoff et al., 1997). Because C is added to the biofilter columns in the form of wood chips and pea straw, Cu is adsorbed by this solid OM, thus immobilising the metal (Zhao et al., 2007). No significant effect of C on Pb and Zn was shown since these metals have less affinity to OM.

Anoxic conditions increase metal sorption of sediments compared to oxic conditions (Bradl, 2004) and soils tend to have slightly lower metal concentrations in the soil solution (Tack et al., 2006). Oxidation of (previously anoxic) sediment is estimated to be the most efficient way to mobilise metals into the environment (Förstner et al., 1989) since it is correlated with increased exchangeable and/or reducible metal fractions, induced by a decreasing pH and an increasing ORP (Saeki et al., 1993).

The conditions in the submerged zone are not strongly anoxic. However, analysing the same samples as used for this

experiment for nitrogen, Zinger et al. (2007b) showed that SZ with added C facilitated very efficient denitrification (achieving nitrate removal of typically greater than 99%). Such levels of denitrification would not occur in strongly oxic conditions. Thus we believe that the submerged zone contains adjacent microsites of both aerobic and anaerobic conditions, while the water front still is relatively oxidised. In general, the SZ can be characterised as a partly anoxic zone. Thus, it is assumed that the SZ enhances metal sorption by diminishing oxidising conditions.

It is assumed that this experiment reflects field conditions quite well even though the conditions in the SZ were not completely anoxic. It is unlikely that in reality, biofilters equipped with a submerged zone will achieve homogeneous anoxic conditions, since systems built according to current guidelines (Melbourne Water, 2005) typically have the same depth profiles as the mesocosms built for this experiment, and have a relatively large slotted under-drain which could facilitate the transfer of oxygen into the submerged zone.

Due to the large amount of root biomass observed in the SZ columns, it is likely that the high ORP and DO readings in SZ columns might be partly sourced from roots, as a study of *Carex* species showed high oxygen leakage from the roots in saturated soils (Moog, 1998). This might even explain the higher ORP in the A samples (which show worse treatment) since the resident water is exposed to that effect over a relatively longer period. Further research is needed to verify this hypothesis. The increase of ORP in columns with 600 mm SZ compared to 450 mm SZ however, might be caused by higher oxidation of the upper soil layers which might override the effect of the deeper SZ. This corresponds to the most effective metal treatment at 450 mm SZ (and nitrogen treatment as well (Zinger et al., 2007b)).

The introduction of a SZ led furthermore to a small but statistically significant increase in pH (data in Table 2; one-way ANOVA for pH vs. SZ: $p = 0.03$ and $p = 0.014$ for A and B, respectively) indicating that SZ will raise pH. In general, pH is the most important factor regarding metal solubility and soil

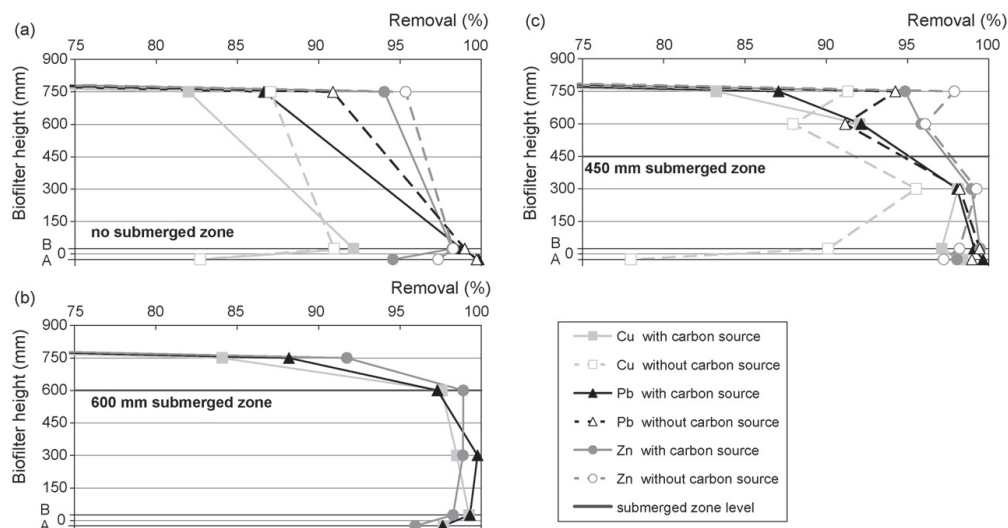


Fig. 3 – Depth profiles of Cu, Pb, Zn removal for the 4th sampling event (22 weeks run time). Samples A (resident water from the antecedent storm event) and B (newly treated water) were both taken at the bottom of the filter but plotted above and below 0 mm due to readability. (a) No submerged zone (SZ), (b) 450 mm SZ, (c) 600 mm SZ.

metal retention is greater at high pH (Bradl, 2004). Thus, the increasing pH in columns with SZ might help to explain why the positive effect of SZ on metal removal was seen and the slight increase of pH corresponds with the slightly enhanced Pb and Zn treatment. However, its effect should not be overstated, given that metal reactions are likely to be controlled by a range of other physical, chemical and microbiological processes and parameters (Warren and Haack, 2001; Bradl, 2004), as described above.

Indeed, the General Linear Model (with SZ, C and inflow concentration as variables) explains only around one third of the variance of the data (Table 3). Thus, factors other than those monitored in this study have an effect on the metal binding capacity of soils. Metal sorption within biofilms, for instance, has been shown to be highly effective (Warren and Haack, 2001).

3.3. Depth profiles of metal removal in the columns

Metal removal was already very high (>82%) after the water had passed only through the top section (150 mm) of the filter media (Fig. 3). For most samples, the removal continues up to the depth of 450 mm, and then levels out. These findings confirm the results found on unvegetated filters by Hatt et al. (2007) who showed a rapid metal decrease at the top of the filter. The implications are that standard biofilters do not have to be more than 500 mm deep to effectively remove metals. This finding is important for stormwater management practice, since current design practice advocates depths up to 900 mm (as used in this study (Melbourne Water, 2005)), and deep systems can often be difficult to construct, due to constraints in connecting to existing drainage infrastructure. However, it is necessary to allow enough depth for the planted soil media

above a saturated zone. This depth will vary, depending on the type of vegetation used.

3.4. Comparison with water quality standards

In Table 4, the outflow concentrations (Sample B) are shown, with respect to incorporation of C and SZ. It is clear that unfiltered stormwater would not meet Australian and New Zealand (ANZECC, 2000) and Swedish (Swedish EPA, 2000) water quality guidelines (Table 4).

However, it is very encouraging that Cu removal, especially, can be improved by the introduction of SZ and C. When outflow concentrations from the designs with 450 mm and 600 mm SZ in combination with C were compared with the ANZECC guidelines, it was found that Sample B from these filters met even the 95% (450 mm SZ) and 99% (600 mm SZ) protection limit, while even the lowest protection levels for Cu are not met at all without SZ and C. Regarding the Swedish EPA guidelines, the Cu concentration in outflow from biofilters with SZ and added C meets class 2, whilst other biofilters meet only classes 3 or 4 depending on the design. This clearly demonstrates that introduction of SZ and C is of critical importance in achieving the required removal of Cu.

For Pb, the designs without SZ meet the 95% level of protection stipulated by the Australian and New Zealand and class 3 protection of the Swedish water quality guidelines, while SZ increases this to the 99% (ANZECC) and class 2 (Swedish EPA). A similar trend is observed for Zn treatment, which is improved by SZ (SZ=600 mm) from the 90 to 95% limit (ANZECC) and from class 2 to class 1 (Swedish EPA).

It must also be taken into account that both guidelines refer to the receiving water quality as a whole, rather than spe-

Table 4 – Mean metal concentrations in outflow ($\mu\text{g/L}$, for respective standard deviations see Table 2 as compared to levels of protection/classes of Australian & New Zealand (ANZECC, 2000) and Swedish (Swedish EPA, 2000) water quality guidelines.

Metal	Mean outflow concentrations (B)				ANZECC				Swedish EPA			
	Carbon	SZ (mm)			Level of protection				Class			
		0	450	600	99%	95%	90%	80%	1	2	3	4
Cu	–	5.6	10.3	–	1	1.4	1.8	2.5	≤ 0.5	0.5–3	3–9	9–45
	+	6.2	1.3	1								
Pb	–	1.5	0.5	–	1	3.4	5.6	9.4	≤ 0.2	0.2–1	1–3	3–15
	+	2.4	1.5	0.6								
Zn	–	9.3	6.6	–	2.4	8	15	31	≤ 5	5–20	20–60	60–300
	+	10.3	5.6	4.5								
All metal concentrations in $\mu\text{g/L}$.												

cific discharge concentrations from the stormwater system. Regardless, it is more likely for the receiving waters to meet the stipulated guidelines if the discharged water has as low concentrations as possible; the cumulative effect of allowing above-required concentrations in stormwater discharge will ultimately lead to degradation of the receiving water quality.

4. Conclusions

In general, the removal of heavy metals from stormwater in the tested biofilters of all designs was very high. Substantial loads (mostly >95%) of metals are removed from the stormwater. Due to this high overall removal capacity, biofilters are a good management strategy to reduce concentrations of heavy metals in stormwater discharges.

Contrary to our initial hypotheses, the presence of a submerged zone SZ with added cellulose carbon C did significantly affect heavy metal removal, generally enhancing its uptake by the biofilter. Even though a significant improvement of metal removal and outflow concentrations by addition of C and SZ was shown, this effect has to be judged in context: the comparatively poor Cu treatment was considerably improved; a combination of SZ and C helps to meet target concentrations (ANZECC, 2000; Swedish EPA, 2000) which were not met without their incorporation. This enhancement is explained mostly by the introduction of C which supports Cu treatment by forming Cu-OM complexes. Whilst Pb and Zn treatment was statistically higher with the presence of SZ, the practical implications of these were small, since there is only slight enhancement of the already high removal of Pb and Zn (Davis et al., 2001).

The most efficient treatment was achieved for a SZ of 450 mm. Thus, in stormwater biofilters of 900 mm height the introduction of a 450 mm submerged zone (created by lining the whole system and raising the outlet to create a permanent pool at the base of the system.) and a cellulose based carbon source is strongly recommended. This combination helps to enhance Cu removal significantly, and SZ improves Pb and Zn treatment slightly, and does not measurably affect Cd. Furthermore, incorporation of a submerged zone with carbon has also been previously demonstrated to improve nutrient removal

(Zinger et al., 2007b) and to help vegetation survival during long dry weather spells (Zinger et al., 2007a).

However, even if the results of this study are promising, one has to be aware that this study was conducted with only 18 biofilters under laboratory conditions. Furthermore, the General Linear Model explains only about one third of the variance in the data, indicating that other factors also influence metal treatment. A logical next step would thus be to attempt to verify these observations in a field study of stormwater biofiltration systems under real operating conditions. Moreover, the influence of factors other than C and SZ (e.g., drying/wetting regime, temperature) on metal removal in stormwater biofilters should be investigated.

REFERENCES

- Amery, F., Degryse, F., Degeling, W., Smolders, E., Merckx, R., 2007. The copper-mobilizing-potential of dissolved organic matter in soils varies 10-fold depending on soil incubation and extraction procedures. *Environ. Sci. Technol.* 41 (7), 2277–2281.
- ANZECC, 2000. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra, ACT, Australia.
- APHA/AWWA/WPCF, 1998. Standard Methods for the Examination of Water and Wastewater, 20th edn. American Public Health Association/American Water Works Association/Water Pollution Control Federation, Washington, DC, USA.
- Botanic Gardens Trust, 2007. New South Wales Flora Online. PlantNET - The Plant Information Network System of Botanic Gardens Trust, Sydney, Australia. <http://plantnet.rbgsyd.nsw.gov.au>.
- Brad, H.B., 2004. Adsorption of heavy metal ions on soil and soil constituents. *J. Colloid Interf. Sci.* 277, 1–18.
- Bratieres, K., Fletcher, T.D., Deletic, A., Zinger, Y., 2008. Nutrient and sediment removal by stormwater biofilters; a large-scale design optimisation study. *Water Res.* 42 (14), 3930–3940.
- Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., 2001. Laboratory study of biological retention for urban stormwater management. *Water Environ. Res.* 73 (1), 5–14.
- Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., 2006. Water quality improvement through bioretention media: nitrogen and phosphorus removal. *Water Environ. Res.* 78 (3), 284.

- Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., Winogradoff, D., 2003. Water quality improvement through bioretention: lead, copper, and zinc removal. *Water Environ. Res.* 75 (1), 73.
- Duncan, H.P., 1999. Urban Stormwater Quality: A Statistical Overview. Report 99/3. Cooperative Research Centre for Catchment Hydrology, Melbourne, Australia.
- Endreny, T.A., 2004. Storm water management for society and nature via service learning, ecological engineering and ecohydrology. *Int. J. Water Res. Dev.* 20 (3), 445–462.
- Förstner, U., Ahlf, W., Calmano, W., 1989. Studies on the transfer of heavy metals between sedimentary phases with a multi-chamber device: combined effects of salinity and redox variation. *Marine Chem.* 28, 145–158.
- Hatt, B.E., Deletic, A., Fletcher, T.D., 2007. Stormwater reuse: designing biofiltration systems for reliable treatment. *Water Sci. Technol.* 55 (4), 201–209.
- Henderson, C., Greenway, M., Phillips, I., 2007. Removal of dissolved nitrogen, phosphorus and carbon from stormwater by biofiltration mesocosms. *Water Sci. Technol.* 55 (4), 183–191.
- Hsieh, C.-H., Davis, A.P., 2005. Multiple-event study of biofiltration for treatment of urban storm water runoff. *Water Sci. Technol.* 51 (3–4), 177–181.
- Kim, H., Seagren, E.A., Davis, A.P., 2003. Engineered bioretention for removal of nitrate from stormwater runoff. *Water Environ. Res.* 75 (4), 355–367.
- Lau, Y.L., Marsalek, J., Rochfort, Q., 2000. Use of a biofilter for treatment of heavy metals in highway runoff. *Water Qual. Res. J. Can.* 35 (3), 563–580.
- Marsalek, J., Rochfort, Q., Brownlee, B., Mayer, T., Servos, M., 1999. An exploratory study of urban runoff toxicity. *Water Sci. Technol.* 39 (12), 33–39.
- Matoura, R.F.C., Dickson, A., Riley, J.P., 1978. The complexation of metals with humic materials in natural waters. *Estuarine Coastal Marine Sci.* 6, 387–409.
- Melbourne Water, 2005. WSUD Engineering Procedures: Stormwater. CSIRO Publishing, Melbourne, Australia.
- Mitsch, W.J., 1992. Landscape design and the role of created, restored, and natural riparian wetlands in controlling nonpoint source pollution. *Ecol. Eng.* 1 (1–2), 27–47.
- Moog, P.R., 1998. Flooding tolerance of *Carex* species. I. Root structure. *Planta* 207 (2), 189–198.
- Muthanna, T.M., Viklander, M., Blecken, G.-T., Thorolfsson, S.T., 2007. Snowmelt pollutant removal in bioretention areas. *Water Res.* 41 (18), 4061–4072.
- Ponizovsky, A.A., Thakali, S., Allen, H.E., Di Toro, D.M., Ackerman, A.J., 2006. Effect of soil properties on copper release in soil solutions at low moisture content. *Environ. Toxicol. Chem.* 25 (3), 671–682.
- Prince George's County, 2002. Bioretention Manual. Department of Environmental Resources, Programs & Planning Division, Prince George's County, Maryland, USA.
- Read, J., Wevill, T., Fletcher, T.D., Deletic, A., 2007. Variation among plant species in pollutant removal from stormwater in biofiltration systems. *Water Res.* 42 (4–5), 893–902.
- Römkens, P.F.A.M., Salomons, W., 1998. Cd, Cu and Zn solubility in arable and forest soils: consequences of land use changes for metal mobility and risk assessment. *Soil Sci.* 163 (11), 859–871.
- Saeki, K., Okazaki, M., Matsumoto, S., 1993. The chemical phase changes in heavy metals with drying and oxidation of the lake sediments. *Water Res.* 27 (7), 1243–1251.
- Sun, X., Davis, A.P., 2007. Heavy metal fates in laboratory bioretention systems. *Chemosphere* 66 (9), 1601–1609.
- Swedish EPA, 2000. Environmental Quality Criteria - Lakes and Watercourses. Report 5050.
- Tack, F.M.G., Van Ranst, E., Lievens, C., Vanderberghe, R.E., 2006. Soil solution Cd, Cu and Zn concentrations as affected by short-time drying or wetting: the role of hydrous oxides of Fe and Mn. *Geoderma* 137, 83–89.
- Taylor, G.D., Fletcher, T.D., Wong, T.H.F., Breen, P.F., Duncan, H.P., 2005. Nitrogen composition in urban runoff—implications for stormwater management. *Water Res.* 39 (10), 1982.
- Temminghoff, E.J.M., Van Der Zee, S.E.A.T.M., De Haan, F.A.M., 1997. Copper Mobility in a copper-contaminated sandy soil as affected by pH and solid and dissolved organic matter. *Environ. Sci. Technol.* 31, 1109–1115.
- US Environmental Protection Agency, 2000. National Water Quality Inventory - 1998 Report to Congress. www.epa.gov/305b/398report. Washington, DC, USA.
- Villarreal, E.L., Semadeni-Davies, A., Bengtsson, L., 2004. Inner city stormwater control using a combination of best management practices. *Ecol. Eng.* 22, 279–298.
- Warren, L.A., Haack, E.A., 2001. Biogeochemical controls on metal behaviour in freshwater environments. *Earth Sci. Rev.* 54, 261–320.
- Wong, T.H.F., Fletcher, T.D., Duncan, H.P., Jenkins, G.A., 2006. Modelling urban stormwater treatment—a unified approach. *Ecol. Eng.* 27 (1), 58.
- Yin, Y., Impellitteri, C.A., You, S.-J., Allen, H.E., 2002. The importance of soil organic matter distribution and extract soil: solution ratio on the desorption of heavy metals from soils. *Sci. Total Environ.* 287, 107–119.
- Zhao, L.Y.L., Schulin, R., Weng, L., Nowack, B., 2007. Coupled mobilization of dissolved organic matter and metals (Cu and Zn) in soil columns. *Geochim. Cosmochim. Acta* 71, 3407–3418.
- Zinger, Y., Deletic, A., Fletcher, T.D., 2007a. The effect of various intermittent dry-wet cycles on nitrogen removal capacity in biofilter systems. *Rainwater & urban design 2007*, Sydney, Australia.
- Zinger, Y., Fletcher, T.D., Deletic, A., Blecken, G.-T., Viklander, M., 2007b. Optimisation of the nitrogen retention capacity of stormwater biofiltration systems. *NOVATECH 2007*, Lyon, France.

Paper II

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Effect of retrofitting a saturated zone on the performance of biofiltration
for heavy metal removal – preliminary results of a laboratory study

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Effect of retrofitting a saturated zone on the performance of biofiltration for heavy metal removal - preliminary results of a laboratory study

Traitement des eaux de ruissellement par biofiltration : influence d'une zone saturée sur l'absorption des métaux lourds - présentation des premiers résultats

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RÉSUMÉ

Le biofiltre végétalisé est un procédé biologique d'assainissement des eaux pluviales de plus en plus utilisé de nos jours pour ses qualités de traitement et son caractère écologique. Des études existantes ont permis de mettre en évidence une amélioration du rendement épuratoire de l'azote en termes d'efficacité et de fiabilité lorsque la base du biofiltre est saturée en eau. De plus, il a été montré qu'une telle zone saturée augmente la rétention des métaux lourds, notamment le cuivre. La plupart des biofiltres existants ne comportent pas de zone saturée mais peuvent facilement être réaménagés par un simple rehaussement de la sortie. Ce projet a pour but d'approfondir les conséquences d'une zone saturée en fond de biofiltre vis à vis du traitement des métaux lourds. L'étude, menée en laboratoire à l'aide de colonnes biofiltrantes, a permis de mettre en évidence une légère augmentation du rendement épuratoire des métaux lourds. La zone saturée augmente la rétention du zinc, mais son effet est variable pour le cuivre. Donc si le traitement des métaux lourds est le principal objectif, l'aménagement d'une zone saturée en fond de biofiltre n'est pas nécessaire. En revanche, celles-ci permettent de protéger le biofiltre contre de longues périodes sèches tout en augmentant la capacité de traitement de l'azote et sans compromettre celui des métaux lourds.

ABSTRACT

Stormwater biofilters are a stormwater treatment technology which has been becoming increasingly popular. Recently it has been shown that a submerged zone in the filter media improves the magnitude and consistency of nitrogen treatment. Furthermore, the submerged zone has even been shown to be beneficial for retention of heavy metals, particularly Cu. However, most existing biofilters do not include a saturated zone. Since it is relatively simple to retrofit a submerged zone by elevating the outflow, the effect of such a retrofitting on metal removal was investigated in this laboratory study using biofilter columns. It has been shown that a retrofitted submerged zone has a statistically significant but practically small effect on metal removal: Zn removal is slightly enhanced while the effect on Cu removal is inconsistent. Thus, retrofitting of a submerged zone is not recommended if metals are the main target pollutants. But if a submerged zone would have other benefits (e.g. for nitrogen removal or to protect the system from prolonged drying periods) it can be retrofitted without compromising metal removal.

KEYWORDS

Stormwater, biofilter, heavy metal removal, submerged zone, water sensitive urban design

1 INTRODUCTION

Stormwater has been identified as one major reason for degradation of urban waterways (Walsh et al., 2005) due to high peak flows and runoff volumes as well as a high contaminant loads. Key pollutants in stormwater are heavy metals (mainly Cd, Cu, Pb and Zn), nutrients and PAHs (Eriksson et al., 2007). In recent years, the focus in urban drainage has shifted increasingly from mainly considering runoff volumes and their rapid discharge to incorporating water quality issues (Dietz, 2007). Concepts including this more holistic view of urban drainage are given such names as. Water Sensitive Urban Design (WSUD) and Low Impact Development (LID).

Stormwater biofiltration (or bioretention) has been shown to be a promising technology within WSUD for both stormwater retention and water quality treatment (Davis et al., 2001; Muthanna et al., 2008). A biofilter consists of one or more vegetated filter media layers with a typical total depth of 700 to 900 mm. The filter is placed in a depression to provide stormwater storage above it. The filter media is often underlain by a drainage layer with an embedded drainage pipe which discharges the treated water to a receiving water or the conventional stormwater sewer system. Alternatively the treated water can be infiltrated into the surrounding soil (Melbourne Water, 2005). Due to their variable size, biofilters can even be retrofitted into an existing development.

Water quality treatment in stormwater biofilters is commonly effective and reliable. TSS, heavy metal and phosphorus removal is very efficient and the removal rates often exceed 90% (Blecken et al., 2007; Davis et al., 2006; Davis et al., 2003). However, nitrogen removal has commonly been less efficient. While aerobic nitrification (generating nitrate-N) occurs in the usually well drained filter media, anaerobic denitrification is often lacking. Thus, in several studies nitrate-N leaching has been shown which reduced the total nitrogen removal (Blecken et al., 2007; Bratieres et al., 2008; Davis et al., 2006; Hsieh et al., 2007; Passeport et al., 2009).

In order to enhance nitrogen removal, recently a submerged (partly anoxic) zone with an embedded carbon source has been introduced into the filter media in order to enhance nitrate-N removal due to enhanced denitrification. Using this feature, total nitrogen removal could be enhanced significantly (Dietz et al., 2006; Kim et al., 2003; Zinger et al., 2007). Since the primary aim of this submerged zone was to improve nitrogen treatment, studies about a submerged zone in biofilters have mainly been focusing only on nitrogen. However, one has to take care that elevating the nitrogen removal does not deteriorate effective metal removal. The limited research about the effect of a submerged zone on metal removal so far has however not indicated any conflicts between metal removal and a submerged zone with embedded carbon source (Blecken et al., 2009a). It has been shown, rather, that a submerged zone improves metal removal especially after prolonged drying periods, by providing a more stable moisture regime (Blecken et al., 2009b).

Due to its advantages, biofilters have been becoming increasingly popular in urban drainage during the last years. However, in most existing biofilters the submerged zone is not implemented since it has been developed only recently and has not been recommended in current technical design guidelines (e.g. (Melbourne Water, 2005; U.S. EPA, 2004). Despite this, if nitrogen treatment is primarily targeted and/or if prolonged dry periods are expected, one possible strategy is to retrofit a submerged zone into existing biofilters.

It has been shown that retrofitting a submerged zone into conventional biofilters without that feature could enhance nitrogen removal significantly (unpublished results of this study). However, no study so far has investigated the effect of a retrofitted submerged zone on metal removal. It is of particular interest to ascertain whether the introduction of a submerged zone (in this case without a carbon source) will diminish the high metal removal achieved in standard biofilter designs or if it will enhance metal removal as well, as has been shown in purpose-built systems previously (2009a).

The aim of this study is thus to investigate the effect of retrofitting a submerged zone on the metal removal in stormwater biofilters.

2 METHODS

2.1 Experimental set-up and procedure

In this study biofilter columns with the following configuration were used (Figure 1):

- Inner diameter 375 mm
- Height 1300 mm, made up of 900 mm PVC stormwater pipe and 400 mm transparent plexiglass (allowing ponding of water without shading the plants)
- Filter 700 mm sandy loam
- Drainage 100 mm transition and drainage layer with an embedded drainage pipe connected to the outflow port

Three groups of five replicate biofilter columns each were utilised which were planted with *Carex appressa* (Tall sedge), *Dianella revoluta* (Blueberry lily) and *Microleana stipoides* (Weeping Grass), resp.

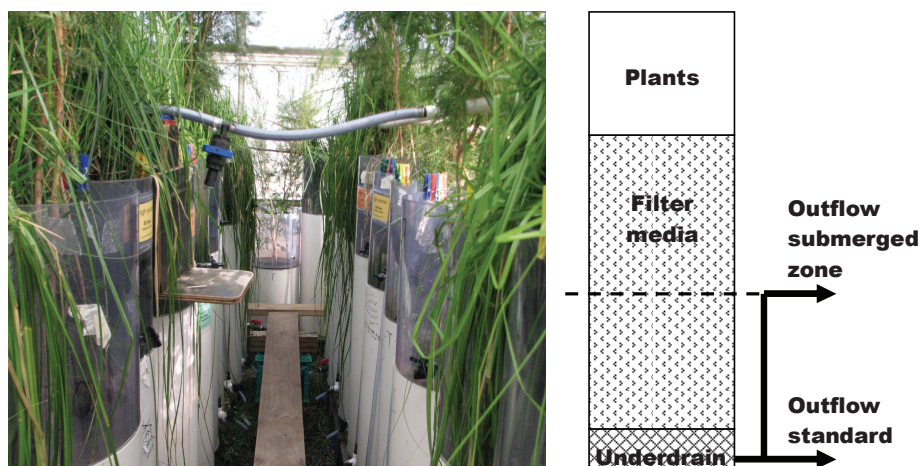


Figure 1: Biofilter columns in greenhouse.

The columns were dosed twice weekly with 50 L (*Carex* and *Microleana*) or 25 L (*Dianella*) stormwater per event. In order to assure constant stormwater quality over the run-time, semi artificial stormwater was used. It was prepared by adding stormwater pond sediment and chemicals to dechlorinated tap water (using sodium thiosulfate) in the required amount to achieve target pollutant concentrations (based on Duncan, 1999). The stormwater characteristics are presented in Table 1. Stormwater preparation and volume calculation are described in detail in Blecken et al. (2009a).

After about one year in operation a permanently water saturated submerged zone was retrofitted to all columns by elevating the outflow port by 450 mm. I.e. all 15 columns were tested as standard biofilters for one year and then the submerged zone was added to all of them. The saturated zone was subject to some drying in-between the storm events, i.e. no water was added to maintain a stable water table in the filter media.

The columns were placed in a greenhouse in Melbourne, Victoria, Australia, to ensure that they did not receive rainfall inflow. Open mesh on the sides maintained that the columns were exposed to local Melbourne climate conditions.

Pollutant	Mean stormwater concentration ± standard deviation	Chemicals used for topping up of existing sediment concentrations as required
Total susp. solids (TSS)	179 mg/L ± 71	stormwater pond sediment ($\leq 300\mu\text{m}$)
Copper (Cu)	67.5 $\mu\text{g/L}$ ± 32.8	copper sulphate (CuSO_4)
Lead (Pb)	154.5 $\mu\text{g/L}$ ± 50.5	lead nitrate (PbNO_3)
Zinc (Zn)	450.3 $\mu\text{g/L}$ ± 136.0	zinc chloride (ZnCl)

Table 1 Stormwater characteristics

2.2 Sampling procedure and analyses

Before retrofitting the submerged zone, six samplings (in the following labelled A to F) were conducted over the run time of nine month. Two months after retrofitting the submerged zone, three samples (labelled G to I) were taken over a period of three months. At each sampling, one 1 L composite outflow sample from each column was taken made of five sub- samples which were distributed evenly over the whole outflow event. Additionally, the inflow was controlled using two composite inflow samples per event. The samples were taken in one litre PE bottles and analysed for metals by a NATA-accredited laboratory using standard methods (APHA/AWWAWPCF, 1998). The instrument detection limits were 0.3 $\mu\text{g/L}$ for Cu, 0.6 $\mu\text{g/L}$ for Pb and 0.5 $\mu\text{g/L}$ for Zn.

2.3 Data analysis

Average metal outflow concentrations were compared to Swedish water quality guidelines (Swedish EPA, 2000). Detailed analyses were then conducted for the removal rate. Metal removal was calculated as follows: removal (%) = $(1 - \text{out} / \text{in}) \times 100$. To give an indication of the data variability over the run-time, the metal removal of the biofilter groups was plotted for each sampling event using box plots.

To detect a metal removal difference between the biofilter groups before retrofitting (samplings A to F) a one-way ANOVA was used (response: metal removal, factor: group).

To detect possible effects of the retrofitting of the submerged zone, for each group the outflow concentrations of the four events before and after retrofitting were compared using 2-sample t-tests. The first two events of the run-time were not regarded in order to eliminate the possibly misleading effect of the varying removal in the beginning of the experiment (see Figure 2, especially Cu removal). The mean difference was calculated as mean removal before retrofitting – mean removal after retrofitting. Thus, a positive value indicates worse removal after retrofitting while a negative difference indicates an enhanced removal after retrofitting.

For all statistical analyses, significance was accepted at an α -level of 0.05

3 RESULTS

The inflow Cu and Pb concentrations were relatively constant over the experimental run time while the Zn concentrations varied more. Outflow quality was enhanced significantly: Mean Cu outflow concentrations were 4.9 $\mu\text{g/L}$, Pb 2.6 $\mu\text{g/L}$ and Zn 5.4 $\mu\text{g/L}$. These outflow concentrations meet most often class 2 or 3 (2: **slight risk of biological effect, 3: effects may occur**) of Swedish water quality guidelines (Swedish EPA, 2000) while the stormwater inflow always lays far above the threshold for class 5 (very high concentration / growing risk of biological effects). Thus, all standard biofilters (i.e. before retrofitting the submerged zone) provided very high levels of heavy metal removal (Figure 2, samplings A to F). Pb and Zn stormwater concentrations were commonly reduced by more than 95 %. Cu removal was less effective at the first two samplings (around 70 to 80 %) but reached subsequently about the same excellent removal as Pb and Zn. There was no significant difference between the three biofilter groups at the events A to F (One-way ANOVA: Cu, Pb and Zn removal vs. Group, $\alpha = 0.05$, $R^2(\text{adj.}) = 0.000$).

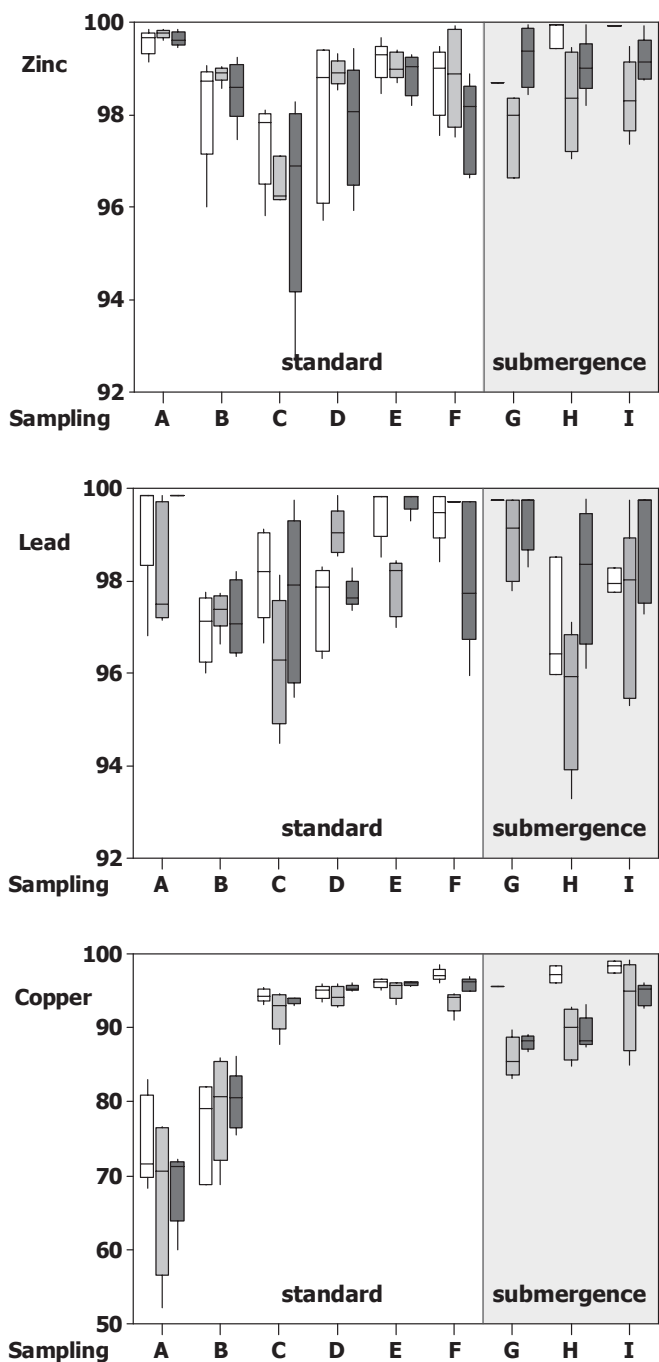


Figure 2: Box plot of Cu, Pb and Zn removal in % by biofilters with *Carex* (white boxes), *Dianella* (light grey boxes) and *Microleana* (dark grey boxes) at the samplings before (A to F, white background) and after retrofitting (G to I, shaded background) of the submerged zone.

Retrofitting of the submerged zone influenced Cu and Zn removal slightly while Pb removal remained unaffected at its high level in all groups. The effect of retrofitting the submerged zone on metal removal is presented in Table 2. Doing the same analyses for outflow concentrations gives about the same results.

Zn removal in the *Carex* and the *Microleana* groups was enhanced by around 1.5 %. For the *Dianella* groups no difference was detected. Cu removal was enhanced in the *Carex* group by 1.9 % while it was about 4 % worse in the other two groups.

Sample		Two sample t-test	
		p-value	estimate for difference (%)
Cu removal (%)	<i>Carex</i>	0.007	– 1.9 %
	<i>Dianella</i>	0.018	+ 4.2 %
	<i>Microleana</i>	0.000	+ 4.4 %
Pb removal (%)	<i>Carex</i>	0.170	
	<i>Dianella</i>	0.166	
	<i>Microleana</i>	0.281	
Zn removal (%)	<i>Carex</i>	0.000	– 1.4 %
	<i>Dianella</i>	0.352	
	<i>Microleana</i>	0.001	– 1.5 %

Table 2: Results of the two sample t-test comparing metal removal before and after retrofitting a submerged zone into the two biofilter groups. Negative difference indicates better removal after retrofitting and positive difference worse removal after retrofitting of the submerged zone.

4 DISCUSSION

The excellent metal removal in standard stormwater biofilters has commonly been shown in a number of both field and laboratory studies (e.g. (Davis et al., 2001; Dietz, 2007; Fletcher et al., 2007; Lau et al., 2000)).

Given the complex processes influencing metal removal in biofilters it is difficult to identify the mechanisms behind the effect of the submerged zone based on the existing data and given the very small detected difference compared to the total variation of the data (Figure 2).

A submerged zone in a stormwater biofilter reduces drying of the filter media by providing a constant pool of water which may be drawn up into the media via capillary and evaporative actions and thus provides a more stabile moisture regime. It has been shown that a submerged zone provides at least partially anoxic conditions (Zinger et al., 2007) under which metal sorption of sediments is higher than under oxic conditions (Bradl, 2004). Oxidation of (previously anoxic) sediment is estimated to be the most efficient way to mobilise metals into the environment (Förstner et al., 1989). By introducing a submerged zone into biofilters, oxidation between the storm events of the filter media is prevented (or at least minimised). Thus, less oxidation of the filter media might be one reason for the slight increase of some metal treatment after retrofitting. However, given the only small effect of the submerged zone and the regular dosing of the filters without prolonged drying (and thus oxidation), it is difficult to estimate the effect of drying and oxidation on the results. It has however been shown that drying exceeding three to four weeks has a negative effect on metal removal and that this effect can be minimised or eliminated by using a submerged zone (Blecken et al., 2009b).

Since only limited research has been done regarding the effect of a submerged zone on metal removal it is difficult to compare these results with other studies. It has been shown that a submerged zone with an embedded carbon source in stormwater biofilters improves metal removal significantly: especially Cu removal was enhanced while Pb and Zn removal was only effected slightly (Blecken et al., 2009a). Similarly, in the study at hand, Zn removal is enhanced slightly too, while Pb removal is not affected. The effect on Cu treatment was ambiguous since removal was enhanced for one group

and deteriorated for the other two.

In contrast to the retrofitted submerged zone in this study the submerged zone of Blecken et al. (2009a) contained an embedded carbon source (pea straw and wood chips). Since Cu has a clear affinity to organic matter the lack of an embedded carbon source (i.e. solid organic matter) might explain why Cu removal was not enhanced in this study: formation of (insoluble) Cu-organic matter complexes (which contribute to the enhanced Cu removal) was not enabled to the same degree as in the cited study where the carbon source was added. Thus, a comparison of the results at hand with Blecken et al. (2009a) indicates that it may not be the submerged zone itself, but rather the embedded carbon source, which is the main factor enhancing Cu removal. However, it is unclear what amount of organic matter is present in the columns with the retrofitted submerged zone; since nitrogen removal was enhanced in the columns at hand (yet unpublished) due to increased denitrification. For this to occur, some carbon (possibly from biomass turnover or stormwater input) must be available in the submerged zone. If this assumption that organic matter is provided by biomass turnover is true, this might explain the increasing Cu removal at the samplings A to C: little biomass detritus would have accumulated in the beginning, but given the availability of organic matter in the filter media, accumulation over time would be expected. Thus, the rate of Cu-organic matter complexation increased with time and enhanced removal after some months of establishment. Possibly by flooding the filter media by retrofitting the submerged zone, some organic matter and thus Cu was suspended and flushed out during subsequent sampling events (samplings G and H). Stabilising conditions after establishing of the submerged zone might explain the again increasing Cu removal over time after retrofitting. To validate these assumptions regarding Cu treatment, it would be necessary to investigate if organic matter from biomass turnover is present in the filter media, if it is in its dissolved or solid form and if it is flushed out after retrofitting of the submerged zone. Furthermore, if a carbon source is provided by plant detritus, the characteristics of this detritus could possibly explain the different Cu treatment in the groups with the different plant species (Figure 2). However, given only the existing data from this study, this impact remains to be hypothetical. Thus, given these differences in metal removal, the effect of different plant species on metal removal in general and on Cu-organic matter complexation in particular.

Given the very high removal rates both before and after retrofitting of the submerged zone and the unclear trends after retrofitting (both better and worse treatment for Cu, enhanced treatment in only two of the three groups), the detected (statistically) significant effect of the retrofitting has to be judged in context. Even if Zn treatment is enhanced significantly the practical implications of this are small since the mean removal was already above 98% before retrofitting the submerged zone. The same applies for Cu where even for the worst sampling after retrofitting the mean removal is still sufficient (89 %). Furthermore, after retrofitting Cu, removal increases with time and reaches at the last sampling, I, the same range as before retrofitting. Thus, possibly the detected effect would have been eliminated if the experimental run time had been extended.

Given the comparatively small effect on metal removal, retrofitting of a submerged zone is not recommended as being worthwhile if metals are the main target pollutants. However, if nitrogen removal is of concern, a submerged zone can be retrofitted to facilitate improved denitrification, without jeopardising the metal removal too much. Furthermore, if prolonged drying is expected, a retrofitted submerged zone might even enhance metal removal significantly (cf. Blecken et al., 2009b).

5 CONCLUSION

The heavy metal treatment in the tested biofilters was very efficient. Substantial loads (commonly exceeding 95%) of Cu, Pb and Zn were removed from the stormwater. This study confirms therefore that stormwater biofilters are a good management strategy to treat urban stormwater.

Retrofitting of a submerged zone into standard stormwater biofilters neither enhances nor degrades Cu, Pb and Zn removal by a practically significant amount. Thus, retrofitting is not recommended as being worthwhile if metals are the key pollutant group since no clear benefit can be obtained. However, since it has commonly been shown that nitrogen removal is significantly enhanced by introducing a submerged zone into stormwater biofilters, retrofitting can be recommended without compromising metal treatment.

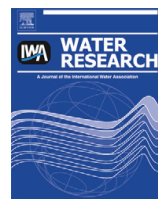
LIST OF REFERENCES

- APHA/AWWAWPCF. (1998). Standard Methods for the Examination of Water and Wastewater, 20th edn. American Public Health Association/American Water Works Association/Water Pollution Control Federation, Washington, DC, USA.
- Blecken, G.-T., Viklander, M., Muthanna, T. M., Zinger, Y., Deletic, A., & Fletcher, T. D. (2007). The influence of temperature on nutrient treatment efficiency in stormwater biofilter systems. *Water Science and Technology*, 56(10), 83-91.
- Blecken, G.-T., Zinger, Y., Deletic, A., Fletcher, T. D., & Viklander, M. (2009a). Impact of a submerged zone and a carbon source on heavy metal removal in stormwater biofilters. *Ecological Engineering*, 35(5), 769-778.
- Blecken, G.-T., Zinger, Y., Deletic, A., Fletcher, T. D., & Viklander, M. (2009b). Influence of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters. *Water Research*, 43(18), 4590-4598.
- Bradl, H. B. (2004). Adsorption of heavy metal ions on soil and soil constituents. *J. Colloid Interface Sci.*, 277, 1-18.
- Bratieres, K., Fletcher, T. D., Deletic, A., & Zinger, Y. (2008). Nutrient and sediment removal by stormwater biofilters; a large-scale design optimisation study. *Water Research*, 42(14), 3930-3940.
- Davis, A. P., Shokouhian, M., Sharma, H., & Minami, C. (2001). Laboratory Study of Biological Retention for Urban Stormwater Management. *Water Environment Research*, 73(1), 5-14.
- Davis, A. P., Shokouhian, M., Sharma, H., & Minami, C. (2006). Water Quality Improvement through Bioretention Media: Nitrogen and Phosphorus Removal. *Water Environment Research*, 78(3), 284.
- Davis, A. P., Shokouhian, M., Sharma, H., Minami, C., & Winogradoff, D. (2003). Water quality improvement through bioretention: Lead, copper, and zinc removal. *Water Environment Research*, 75(1), 73.
- Dietz, M. E. (2007). Low Impact Development Practices: A Review of Current Research and Recommendations for Future Directions. *Water Air and Soil Pollution*, 186, 351-363.
- Dietz, M. E., & Clausen, J. C. (2006). Saturation to improve pollutant retention in a rain garden. *Environ. Sci. Technol.*, 40, 1335-1340.
- Duncan, H. P. (1999). *Urban Stormwater Quality: A Statistical Overview*: Report 99/3, Cooperative Research Centre for Catchment Hydrology, Melbourne, Australia.
- Eriksson, E., Baun, A., Scholes, L., Ledin, A., Ahlman, S., Revitt, M., et al. (2007). Selected stormwater priority pollutants -- a European perspective. *Science of The Total Environment*, 383(1-3), 41-51.
- Fletcher, T. D., Zinger, Y., & Deletic, A. (2007). *Treatment efficiency of biofilters: results of a large-scale column study*. Paper presented at the rainwater & urban design 2007, Sydney, Australia.
- Förstner, U., Ahlf, W., & Calmano, W. (1989). Studies on the Transfer of Heavy Metals between Sedimentary Phases with a Multi-Chamber Device: Combined Effects of Salinity and Redox Variation. *Marine Chemistry*, 28, 145-158.
- Hsieh, C.-H., Davis, A. P., & Needelman, B. A. (2007). Nitrogen Removal from Urban Stormwater Runoff Through Layered Bioretention Columns. *Water Environment Research*, 79(12), 2404-2411.
- Kim, H., Seagren, E. A., & Davis, A. P. (2003). Engineered Bioretention for Removal of Nitrate from Stormwater Runoff. *Water Environment Research*, 75(4), 355-367.
- Lau, Y. L., Marsalek, J., & Rochfort, Q. (2000). Use of a Biofilter for Treatment of Heavy Metals in Highway Runoff. *Water Quality Research Journal of Canada*, 35(3), 563-580.
- Melbourne Water. (2005). *WSUD Engineering Procedures: Stormwater*. CSIRO Publishing.
- Muthanna, T. M., Viklander, M., & Thorolfsson, S. T. (2008). Seasonal climatic effects on the hydrology of a rain garden. *Hydrol. Process.*, 22, 1640-1649.
- Passepport, E., Hunt, W. F., Line, D. E., Smith, R. A., & Brown, R. A. (2009). Field Study of the Ability of Two Grassed Bioretention Cells to Reduce Storm-Water Runoff Pollution. *Journal of Irrigation and Drainage Engineering-Asce*, 135(4), 505-510.
- U.S. EPA. (2004). U.S. Environmental Protection Agency. Stormwater Best Management Practice Design Guide. Volume 2. Vegetative Biofilters. Cincinnati, OH, USA.
- Walsh, C. J., Roy, A. H., Feminella, J. W., Cottingham, P. D., Groffman, P. M., & Morgan, R. P. (2005). The urban stream syndrome: current knowledge and the search for a cure. *Journal of the North American Benthological Society*, 24(3), 706-723.
- Zinger, Y., Fletcher, T. D., Deletic, A., Blecken, G.-T., & Viklander, M. (2007). *Optimisation of the nitrogen retention capacity of stormwater biofiltration systems*. Paper presented at the NOVATECH 2007, Lyon, France.

Paper III

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Influence of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters

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ABSTRACT

Biofiltration is a technology to treat urban stormwater runoff, which conveys pollutants, including heavy metals. However, the variability of metals removal performance in biofiltration systems is as yet unknown.

A laboratory study has been conducted with vegetated biofilter mesocosms, partly fitted with a submerged zone at the bottom of the filter combined with a carbon source. The biofilters were dosed with stormwater according to three different dry/wet schemes, to investigate the effect of intermittent wetting and drying conditions on metal removal. Provided that the biofilters received regular stormwater input, metal removal exceeded 95%. The highest metal accumulation occurs in the top layer of the filter media.

However, after antecedent drying before a storm event exceeding 3–4 weeks the filters performed significantly worse, although metal removal still remained relatively high. Introducing a submerged zone into the filter improved the performance significantly after extended dry periods. In particular, copper removal in filters equipped with a submerged zone was increased by around 12% ($\alpha = 0.05$) both during wet and dry periods and for lead the negative effect of drying could completely be eliminated, with consistently low outflow concentrations even after long drying periods.

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1. Introduction

Infiltration of precipitation in urban areas is reduced by catchment imperviousness, causing high volumes of often contaminated stormwater runoff (Walsh, 2000). Urban stormwater is a major source of pollutants such as sediments, metals and nutrients and a key degrader of urban waterways in cities with a separate sewer system (Marsalek et al., 1999; Walsh, 2000). Source control, whilst important, is difficult due to the number and variety of sources and thus stormwater quality treatment is an essential component in urban drainage to protect receiving waters (Walsh, 2000).

Stormwater biofiltration (also called bioretention) using vegetated filter media is a promising technology to treat stormwater (Davis et al., 2001; Melbourne Water, 2005). Bio-filters increase the infiltration rate of precipitation water, thus helping to restore predevelopment hydrology, and can be used for pre-treatment for stormwater harvesting (Hatt et al., 2007a). Commonly, the treated water is collected in a drainage pipe and discharged to a recipient (Melbourne Water, 2005).

In several laboratory studies effective heavy metal removal from stormwater has been shown with Cu, Pb and Zn removal in excess of 90% (Blecken et al., 2009; Davis et al., 2001, 2003; Hatt et al., 2007a; Lau et al., 2000; Hsieh and Davis, 2005; Sun

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and Davis, 2007). The majority of metals do not ingress very far into the filter media, instead being trapped in the top layer (Davis et al., 2001; Muthanna et al., 2007; Hatt et al., 2008) and even in unvegetated filters metal removal has been shown to be very high (Hatt et al., 2007a,b). Thus, the filter media is the most important biofilter component regarding metal removal (Sun and Davis, 2007). Furthermore, plants and their roots affect the metal solubility and mobilisation in soils, e.g. due to changes of dissolved organic matter content and/or soil pH due to root activity (Zhao et al., 2007), and direct metal uptake by plants (Fritioff and Greger, 2003). The metal uptake by plants in biofilters was shown to be up to 10% of the total metal removal (Davis et al., 2001; Muthanna et al., 2007). Heavy metal sorption was shown to be highly effective within biofilms or microbial mats (Warren and Haack, 2001). Dissolved metals are retained by soil sorption processes (e.g. metal-sulphide and Cu-organic matter complexation). Recent research demonstrated that the introduction of a water saturated submerged zone combined with an organic carbon source helps to enhance nutrient removal to a sufficient level (Kim et al., 2003; Zinger et al., 2007a) and even supports metal removal (especially Cu) (Blecken et al., 2009).

However, stormwater events are very variable in frequency, quantity and duration, exposing biofilters to intermittent wetting and drying conditions of varying length. This variability has been ignored by most laboratory studies, which have been based on regular or constant dosing. In some studies the treatment performance of single events is evaluated without regarding the time factor (Davis et al., 2001, 2003) while other studies use constant intervals between 2 and 10 days (Blecken et al., 2009; Hatt et al., 2007a; Hsieh and Davis, 2005; Sun and Davis, 2007).

There are various studies about effects of drying/oxidation and (re-)wetting of soils and (dredged) sediments. Drying processes have a significant effect on the chemical phase distribution of metals in soils or sediments (Saeki et al., 1993) and therewith associated oxidation of initially anoxic sediments is estimated to be the most efficient way to mobilise metals into the environment (Förstner et al., 1989). Drying and oxidation of anoxic sediment is correlated with increased exchangeable and/or reducible fractions of Cd, Cu, Pb and Zn, induced by a decreasing pH and an increasing redox potential (Saeki et al., 1993) and initially insoluble metals become more soluble/available (Caille et al., 2003; Stephens et al., 2001). It was shown that (compared to continuously wet moisture regimes) the soil solution metal concentration was often much higher in rewetted soil samples after antecedent drying (Tack et al., 1998, 2006). Tack et al. (2006) concluded that previous soil moisture conditions might have a significant effect on metal concentration in the soil solution. Drying might also affect the soil structure (e.g. increased porosity, occurrence of fissures) and plant activity (decreased plant activity, possibly drought-induced damage) in biofilters and thus the retention time and the plant effect on metals might change.

However, despite the significant effect of drying on metal behaviour in soils, until now only Hatt et al. (2007b) and Lau et al. (2000) have investigated the effect of drying and wetting on metal removal by unvegetated stormwater biofilter systems. Hatt et al. (2007b) observed no significant influence of the drying and wetting regime on metal removal by unvegetated

filters. Likewise, after 6 weeks of drying Lau et al. (2000) found that the metal removal was slightly affected but remained above 96% for Cu and Zn. However, in that experiment only one single biofilter column was utilised which was not drained by gravity during drying. Increased knowledge of the behaviour of biofilters under natural conditions (e.g. variable runoff volumes, extended periods of drying) is thus required.

This paper presents the results of a laboratory study of vegetated biofilters with and without a submerged zone (combined with an embedded carbon source) under three different controlled drying and wetting regimes. Thus, the potentially significant factor drying, which is typical of 'real-world' conditions, was incorporated in this laboratory study.

The aim was to determine if there is an effect of drying up to 7 weeks on Cu, Pb and Zn removal during subsequent storm events and if this effect would be of practical concern compared to the removal during wet periods. It was also aimed to investigate if a submerged zone (constructed simply by raising the outlet pipe in the fully lined biofiltration system) could help mitigate any negative effects of drying on metal removal, and to ascertain in which filter depth the metals are retained.

2. Methods

2.1. Experimental set-up

Eighteen biofilters were constructed from PVC pipes (375 mm in diameter, 900 mm in height; Fig. 1) with a ponding zone provided by a transparent plexiglas pipe welded on top (400 mm in height), which allowed normal day light for plant growth. The inner wall of the PVC pipe was sandblasted to prevent preferential flow along the column edge. A previous pilot study showed that this was effective in stopping any such preferential flow paths.

The filter media consisted of four layers (Fig. 1a):

- Top filter layer (400 mm): sandy loam supporting vegetation (full specification: <http://www.monash.edu.au/fawb/index.html>).
- Bottom filter layer (400 mm): fine sand.
- Transition layer (30 mm): coarse sand (mean diameter 0.62 mm) to prevent washing out of fine sand particles.
- Drainage layer (70 mm): fine gravel (mean diameter 5 mm).

In 12 out of 18 columns, a submerged zone (SZ) of 450 mm was established by elevating the outflow port with a riser pipe (Fig. 1a). In the SZ, a cellulose based carbon source (C) was added into the sand (800 g consisting of 2/3 redgum wood chips and 1/3 pea straw); primarily to supply optimal conditions for denitrification, as part of a parallel study on nitrogen removal by biofilters (Zinger et al., 2007a). As per the whole biofilter system, the submerged zone was subject to drying and thus allowed to draw down over time. In this way, the experimental operation realistically reflected the behaviour of a real biofiltration system during long dry periods. This design reflects an emerging trend in biofiltration design, where the systems are built as fully lined, with the elevated outlet, to create a pool of moisture to resist drought, and to maximise denitrification potential (Zinger et al., 2007a).

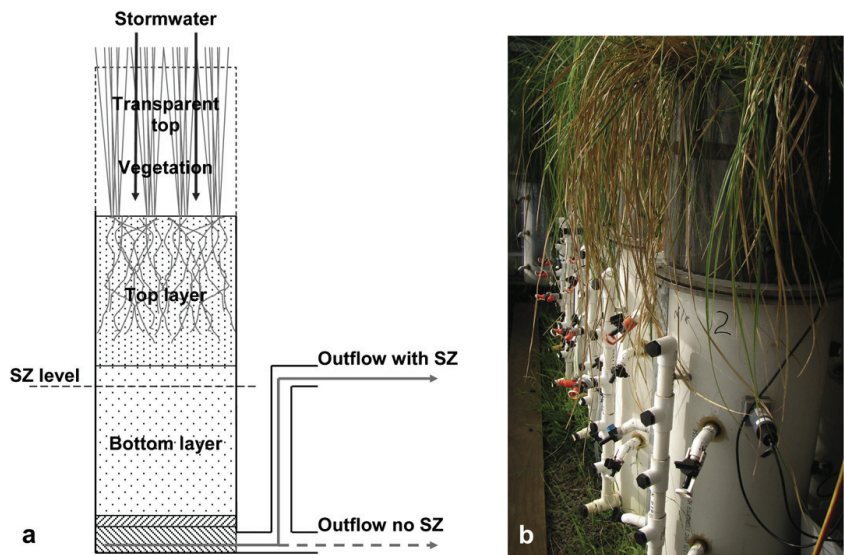


Fig. 1 – Biofilter columns: (a) configuration and filter media, and (b) columns in greenhouse.

To ensure that the columns did not receive inflow by precipitation water but only by controlled dosing, they were randomly arranged in a greenhouse located in Melbourne, Australia. It had open mesh on the sides to ensure that local climatic conditions were maintained.

Each biofilter column was planted with seven plants (64 plants m⁻²) of *Carex appressa* R.Br. (Tall Sedge) which is commonly used in biofilters and shows good nitrogen, phosphorus and metal removal (Read et al., 2007).

After 15 weeks of plant establishment, each column was dosed with 25 L stormwater twice weekly over 7 months and thus a total volume of around 1400 L stormwater per column prior to the recorded drying and wetting experiments (Blecken et al., 2009). As a result, appropriate system maturity was achieved.

2.2. Experimental procedure

The 18 columns were randomly allocated to three groups, each consisting of two standard columns (without SZ and C) and four columns with both SZ and C. Each group was dosed according to the following drying and wetting schemes, starting on January 15th, 2007:

- Group A: 1 week wet/7 weeks dry/4 weeks wet.
- Group B: 1 week wet/1 week dry/1 week wet/2 weeks dry/2 weeks wet/3 weeks dry/2 weeks wet.
- Group C: 1 week wet/4 weeks dry/2 weeks wet/3 weeks dry/2 weeks wet.

During wet periods the columns were dosed with 25 L stormwater each twice weekly, as per the approach previously published by Bratieres et al. (2008) and Blecken et al. (2009).

They received no inflow during dry periods. The lengths of the drying periods are intended to replicate the typical range of periods without effective rainfall, which occur in Australian cities. For dosing, semi-natural stormwater was used which was mixed from natural stormwater pond sediment and laboratory-grade chemicals to consistently achieve the target concentrations (Table 1) and matched to typical worldwide stormwater quality characteristics, as published by Hatt et al. (2008). The stormwater inflow concentrations were relatively consistent throughout the whole run-time for Cd, Pb and Zn (resulting in low standard deviations, Table 1). For Zn, the stormwater concentrations were far more variable ranging between 419 and 858 µg/L.

Table 1 – Total mean inflow concentration over the entire run-time and pollutant sources in the utilised stormwater.		
Pollutant	Concentration ± SD	Source
Cadmium (µg/L)	6.7 ± 0.6	Cadmium nitrate (Cd(NO ₃) ₂)
Copper (µg/L)	95.1 ± 11.3	Copper sulphate (CuSO ₄)
Lead (µg/L)	181.5 ± 12.8	Lead nitrate (Pb(NO ₃) ₂)
Zinc (µg/L)	587.3 ± 121.0	Zinc chloride (ZnCl ₂)
Susp. solids (mg/L)	154.2 ± 31.8	Stormwater pond sediment (≤300 µm)
pH	6.90 ± 0.25	Non
Nitrogen (mg/L)	2.84 ± 0.77	Ammonium chloride (NH ₄ Cl)
		Potassium nitrate (KNO ₃)
		Nicotinic acid (C ₆ H ₅ O ₂ N)
Phosphorus (mg/L)	0.44 ± 0.06	Potassium phosphate (KH ₂ PO ₄)

2.3. Data collection

2.3.1. Water quality

For every stormwater dosing, two replicate composite inflow samples were collected. For each column one 1 L composite outflow sample was taken, consisting of five 200 mL sub-samples. The first sub-sample was collected after 1 L of the treated water had flowed out, followed by four other sub-samples after 5 L outflow water each.

All samples were taken analysed for total suspended solids (TSS) and total Cd, Cu, Pb and Zn concentrations. The chemical analyses were undertaken by the NATA-accredited (<http://www.nata.asn.au>) Water Studies Centre analytical laboratory using standard methods and quality assurance/control procedures (APHA/AWWA/WPCF, 1998). Samples were collected into acid-washed polyethylene bottles and acidified prior to laboratory analysis (nitric acid digestion followed by spectroscopic analysis using a Varian ICP-OES). Instrument detection limits were: Cd 0.7 µg/L, Cu 0.3 µg/L, Pb 0.6 µg/L, Zn 0.5 µg/L. Unfortunately, resources were not available for metal partitioning. It is also acknowledged that the use of laboratory chemicals to supplement concentrations in the stormwater may lead to some artefacts in adsorption (or not) of metals to the sediment. However it is assumed that the metals are largely particulate-bound (Muthukumaran et al., 2002). pH was measured immediately after each sampling (W-22XD multi probe device, Horiba Ltd., Japan). The moisture content (q) in the biofilter top layer (at 225 mm below the soil surface) was continuously measured (ML2 ThetaProbes, Delta-T Devices Ltd., UK). Moisture content was measured for each drying and wetting scheme (i.e. groups A, B and C) in one column with and without SZ, respectively.

2.3.2. Metal accumulation in filter media

After the last stormwater application filter media samples of 25 mm slice thickness were taken at depths of 0–25, 25–50, 60–80, 200–225, 470–495, and 600–625 mm from three columns each with and without SZ. The samples were extracted from two vertical cores of 100 mm diameter each per column. Additionally, prior to the experiments, a grab sample of the top layer material was taken to identify the initial metal concentration. The samples were analysed for metals, pH and total organic carbon (TOC) by the same accredited laboratory according to standard methods (APHA/AWWA/WPCF, 1998; U.S. EPA, 1996). Detection limits are 5.0 mg/kg soil for Cu, Pb and Zn and 0.5 mg/kg for Cd.

2.4. Data analysis

2.4.1. Outflow concentrations and removal

The outflow heavy metal results were analysed for both concentration and removal. Removal was calculated as follows: $\text{removal} = (1 - \text{outflow concentration} / \text{inflow concentration}) \times 100\%$ with concentrations in µg/L.

2.4.2. Performance during wet periods

To compare the filter performance with similar studies (with regular stormwater applications), outflow concentration and removal of metals were analysed separately for all events during wet periods (i.e. with 2–3 antecedent dry days (ADD)).

A two-sample t-test was performed to investigate the difference between columns with and without SZ. All statistical tests were computed with MINITAB® 15.1, © 2006 Minitab Inc. and the significance level was $\alpha = 0.05$.

2.4.3. Effect of drying

The event mean outflow concentrations and the soil moisture content (q) were plotted vs. time separately for each of the three groups (i.e. dry/wet patterns) over the whole run-time to provide an overview of the performance of each group of biofilters. Furthermore, a regression analysis was performed separately for columns with and without SZ to detect correlation between outflow concentration and removal and (a) ADD, and (b) θ immediately before the stormwater dosing.

2.4.4. Effect of SZ on metal removal after drying

The difference in outflow concentration and removal between columns with and without SZ and C after drying extending 3 weeks was statistically tested using a two-sample t-test.

2.4.5. Water quality standards

The outflow concentrations were compared to Australian & New Zealand (ANZECC, 2000) and Swedish (Swedish EPA, 2000) freshwater quality guidelines. The Australian guidelines define ambient toxicant levels for aquatic ecosystems with a range of percentile trigger values specified, based on the sensitivity of the receiving water. In the Swedish guidelines, metal concentrations in freshwater are allocated to five classes (Supplementary Table 5).

3. Results and discussion

3.1. Performance during wet periods

Pb and Zn removal in the biofilters was excellent throughout wet periods (Table 2) with no significant difference between columns with and without SZ and C ($p = 0.31$ for Pb and 0.63 for Zn). Cu was also treated well, although with significantly better performance in columns with SZ and C ($p = 0.000$). Cd was always well removed with outflow concentrations being below the detection limit. This excellent metal removal in biofilters has been shown before (Davis et al., 2001, 2003; Lau et al., 2000). The significant influence of C and SZ on Cu removal confirms in general the results of a previous study

Table 2 – Overall mean pollutant outflow concentrations and removal during wet periods; significance of C and SZ.

Pollutant	SZ and C	Concentration (µg/L) ± SD	Removal (%) ± SD
Cu	With	4.46 ± 5.56	95.2 ± 5.7
	Without	11.05 ± 2.43	88.0 ± 3.0
Pb	With and without	1.56 ± 1.72	99.2 ± 0.9
Zn	With and without	15.43 ± 10.37	97.4 ± 1.7
Cd	With and without	<0.7	>89.6
TSS	With	3.7 ± 2.8	97.5 ± 2.0
	Without	2.5 ± 1.3	98.3 ± 1.3

undertaken with the same columns used for these experiments (Blecken et al., 2009). The positive effect of SZ with embedded C on Cu removal might be explained by an enhanced Cu-organic matter (OM) complexation, while other metals have less affinity to OM (Yin et al., 2002). The SZ has already been shown to create (partly) anoxic conditions (Zinger et al., 2007a) in which metal sorption of sediments is higher than under oxic conditions (Bradl, 2004). In particular, metal-sulphite complexation might be stimulated, as indicated by a decreasing sulphate concentration in the media during the experiment from 30.25 to <10 mg/kg.

TSS was removed well (Table 2) and thus sorbed metals will be efficiently trapped in the filter. The removal in columns with SZ and C was significantly worse (1.25 mg/L or 0.84%; $p = 0.001$ and $p = 0.003$, respectively). However, this is of no practical implication given the high removal in excess of 97%.

3.2. Effect of drying

Fig. 2 shows elevated outflow metal concentrations after antecedent drying extending 3 weeks and no effect after shorter dry periods (data in Supplementary Table 3). After drying the biofilters recover quickly.

Regression analysis between metal removal (concentrations and removal) and length of antecedent drying (ADD) shows mostly strong significant relationships. Using the log(10) transformed q immediately before the dosing as the predictor, similar results are achieved, however, with lower correlation coefficients. Furthermore, most regressions were not linear (as for ADD) but logarithmic (Fig. 3) due to the non-linear moisture content decrease during drying (Fig. 2).

The introduction of SZ and C maintains optimal Cu and Pb removal even after extended drying (Figs. 2 and 3): Cu outflow concentrations from columns with SZ and C are consistently around 12 µg/L lower ($p = 0.006$) and removal is around 12% higher ($p = 0.002$). In contrast, Pb removal in biofilters with SZ and C was not correlated to antecedent drying: a consistently high removal in excess of 98% and concentrations lower than 3.5 µg/L were always achieved, while Pb outflow concentrations from standard columns are elevated already as a result of shorter drying (effect of SZ and C: $p = 0.11$). The SZ with embedded C helps to buffer against any degradation in Cu and Pb removal during drying.

No effect of drying up to 4 weeks on TSS outflow concentrations from columns with C and SZ was detected, while after 7 dry weeks concentrations were highly increased at $10.4 \text{ mg/L} \pm 4.8$ and full recovery of TSS removal was reached not until the fifth dosing after drying. In columns without C and SZ, TSS concentrations were elevated already after 3 dry weeks ($10.4 \text{ mg/L} \pm 1.2$), while they were near the initial level (around 4 mg/L) after 7 dry weeks.

The outflow of the treated water from the biofilter at the first event after drying started significantly later compared to wet periods, while it was faster in the subsequent event. No difference could be seen between columns with and without SZ and C.

The decreased metal removal after drying is likely to be a consequence of a combination of factors: worse metal removal during the actual storm event combined with

leaching of already accumulated metals from former events and mobilisation of fine sediments.

It is likely that long dry periods with θ dropping in a decreasing exponential manner towards an asymptote result in small fissures appearing in the media, thus creating preferential flow paths (Hatt et al., 2007b). This was confirmed by hydraulic conductivity tests and corroborated by the outflow rate results after drying: directly after drying the filter media pores and fissures are filled before outflow occurs, thus explaining the delayed flow. At the subsequent event, a very fast outflow rate is achieved due to preferential flow paths. This results as well in the higher TSS outflow concentrations after drying and consequently higher metal concentrations. This effect might be minimised or at least delayed in columns with SZ due to a more even moisture regime since there is a significantly higher θ in these columns (paired t -test: $p = 0.000$, mean difference = 5.5%).

Plant metal uptake might have been reduced or eliminated due to drought. SZ extends plant activity during drying by extending the water availability since only plants in standard columns without SZ showed stress symptoms. However, the plant uptake itself should not be overestimated since it accounts only for 5–10% of the total metal removal (Davis et al., 2001; Muthanna et al., 2007). Even biofilms, which sorb metals effectively (Warren and Haack, 2001), might have been affected negatively by drought stress. Dead organic material (e.g. dead root cells and micro organisms due to drought stress) might lead to a flush of metal-OM complexes after drying which might particularly explain elevated Cu outflow (Yin et al., 2002). While processes such as oxidation of the filter media might stop immediately with the first re-wetting event, it will take some time until the plants have recovered their initial capacity, depending of the intensity of drought damage.

The increased outflow metal concentrations might also be affected directly by the decreasing moisture content: accumulated metals in the filter are likely to be oxidised and, thus, washed out in the next stormwater event. Oxidation of sediments is estimated to be the most efficient way to mobilise metals into the environment (Förstner et al., 1989). Again SZ might delay this effect.

The two prior drying and wetting biofilter studies (Lau et al., 2000; Hatt et al., 2007b) differed from this one since both utilised unvegetated filters, thus ignoring the role of plants. Furthermore, Lau et al. (2000) did not allow gravity drainage of the filter during drying: the filter material was only dried to a minor degree, causing less fissuring and oxidation of the material. The study at hand better represents 'real-world' conditions, particularly given the critical role of vegetation in nutrient removal and maintenance of hydraulic conductivity in biofilters (Zinger et al., 2007a,b; Read et al., 2007).

These processes will start after θ has fallen below a critical threshold percentage and continue thereafter, regardless of the further characteristics of the decreasing θ .

No repeated measurements for all drying periods could be conducted due to time and financial limitations. Despite this, the results are very clear and thus unlikely to be random artefacts. Furthermore, at least two replicate columns were always used, with results consistent between replicates in each case.

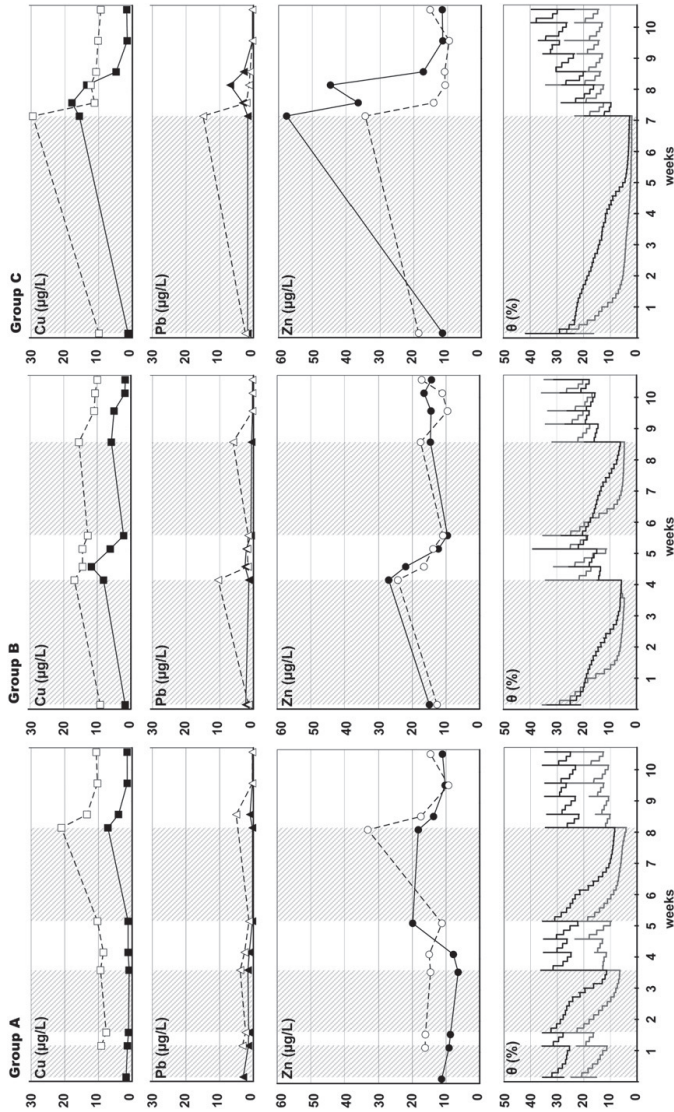


Fig. 2 – Mean metal outflow concentrations (μg/L) from columns with SZ and C (closed markers, solid line) and without SZ and C (open markers, dashed line) and soil moisture content θ in columns with SZ and C (black line) and without SZ and C (grey line) over the entire run-time for all three dry/wet patterns. Grey shading of the plot area indicates dry periods, no shading indicates wet periods.

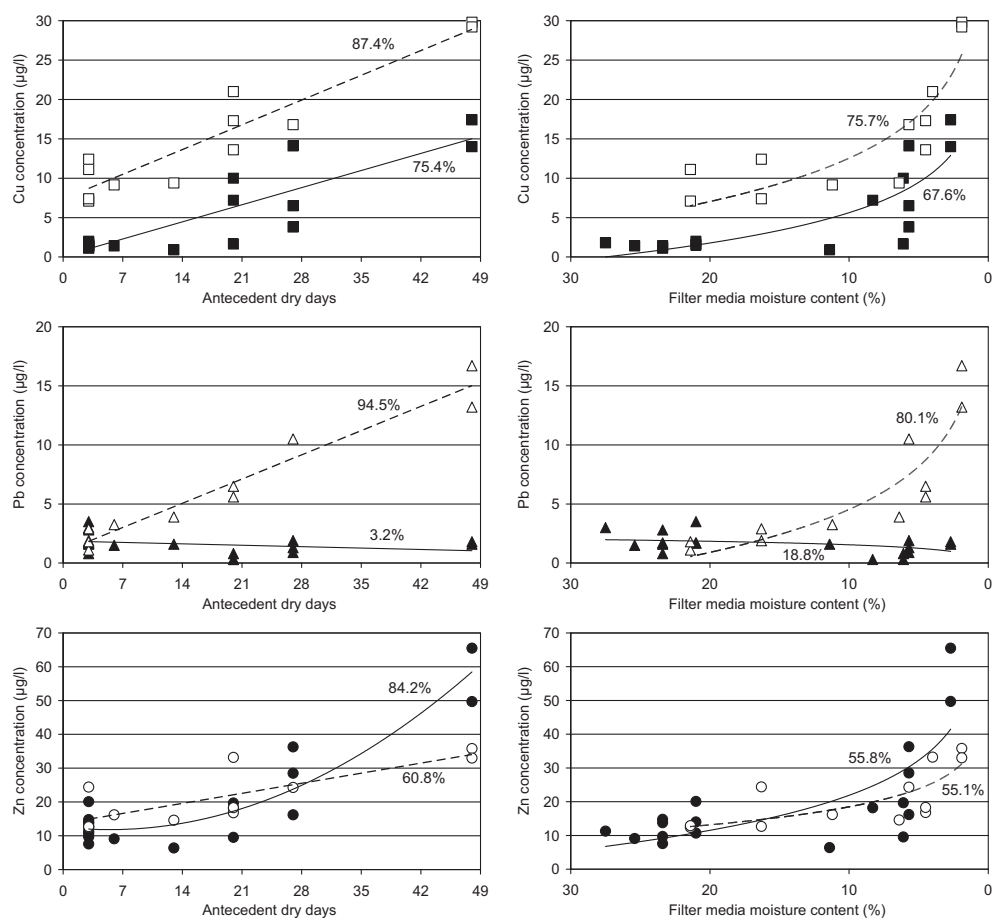


Fig. 3 – Metal outflow concentrations and regression lines with correlation coefficients R^2 (adjusted) (%) from columns with SZ and C (closed markers, solid line) and without SZ and C (open markers, dashed line) affected by length of drying (antecedent dry days) or filter media moisture content (%). N.B. different scale of y-axes.

3.3. Metal accumulation in filter media

Most metals are retained at the top of the filter. Concentrations below 200 mm are generally below detection limits (Fig. 4, data in Supplementary Table 4). A similar accumulation of metals in the top (mulch) layer of stormwater biofilters has previously been shown (Davis et al., 2001; Muthanna et al., 2007; Hatt et al., 2008). This is mainly caused by mechanical filtration of particle-bound metals (Muthukumaran et al., 2002), as well as metal adsorption onto soils and organic matter. The metal concentrations in the top sample were clearly elevated after stormwater application compared to the initial ones, thus, overall no metal leaching from the filter material into the water occurred (initial Cd concentration below detection limit). Only at 200–225 mm depth were the mean Cu and Zn concentrations lower than in the initial

sample. A possible reason might be metal leaching from the media during stormwater dosing (Muthanna et al., 2007), possibly due to oxidation of the media due to drying.

There is a slightly higher metal concentration in the top layer of biofilters with SZ, even if SZ does not affect the top layer directly. No effect of SZ on pH was shown. TOC was significantly increased in SZ columns in the upper 50 mm (Fig. 4), as was θ (Fig. 2) measured at 225 mm from the top (and in all probability above as well). It is assumed that less oxidation of the soil between stormwater applications (with θ maintained at a higher level by capillary action) causes the higher soil metal concentrations in SZ columns, as discussed above.

The high metal accumulation in the top layer facilitates filter maintenance as scraping the top layer would remove most of the already accumulated metals from the system.

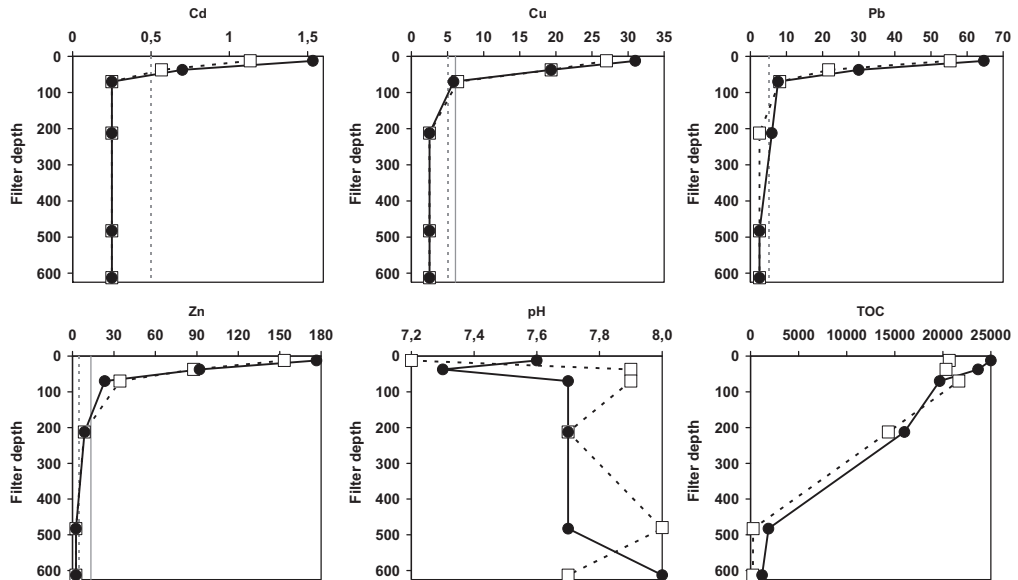


Fig. 4 – Metal and TOC soil concentrations and soil pH in biofilters with SZ and C (closed markers, solid line) and without SZ and C (open markers, dashed line) in comparison to the initial metal concentration (grey solid line). Concentrations below detection limit (grey dashed line) are plotted at half detection limit. N.B. different x-axis scales.

Thus, replacing of the whole filter media can be delayed (Hatt et al., 2008).

3.4. Comparison of metal outflow concentrations with water quality guidelines

Stormwater inflow concentrations in all cases exceed the guidelines (ANZECC, 2000; Swedish EPA, 2000) (Table 1 and Supplementary Table 5). However, most outflow concentrations meet the guidelines at least after shorter drying and with supporting SZ. After extended drying some target values are not met, particularly for systems without SZ. However, it must be taken into account that these guidelines refer to the receiving water quality as a whole, rather than specific discharge concentrations from the stormwater system.

3.5. Practical implications for biofilter design and application

The clear effect of drying shown in this study must be placed in perspective. Even in the worst case (long drying, no SZ and C) biofilters still remove 70% of Cu and approximately 90% of Pb and Zn from the stormwater, which is still better than a number of other stormwater treatment measures.

A submerged zone in stormwater biofilters seems to be very beneficial for removal of metals (Blecken et al., 2009) (and nitrogen as well (Zinger et al., 2007a)), particularly for systems that will be subjected to long drying periods. The results of this study suggest that design of biofiltration systems for metals

removal should consider the criticality of variations in outflow concentrations: where small variations in performance are permissible, 'standard' biofilters perform acceptably well. However, where consistent reductions of at least 95% are required and nitrogen removal is targeted as well (Zinger et al., 2007a), the presence of a submerged zone (by lining the filter and elevating the outflow) at the base of the filter is strongly recommended.

4. Conclusions

Given a regular stormwater inflow, vegetated biofilters are shown to remove substantial loads of heavy metals from stormwater, with Pb and Zn removal in excess of 95%. Similar Cu removal is achieved provided that the filter is equipped with a submerged zone, which increases Cu removal by around 12%. The main metal reduction occurs in the top layer of the filter.

Extended dry periods in excess of 3 weeks worsen the biofilter metal removal performance significantly and metal outflow concentrations were highly increased compared to events during wet periods. A significant regression between metal outflow concentration and length of antecedent drying was thus shown. However, by introducing a submerged zone the negative effect of drying could be minimised significantly for Cu removal and even eliminated for Pb removal. The submerged zone helps to meet guideline values even after extended drying.

Appendix. Supplementary information

Supplementary information related to this article can be found at [doi:10.1016/j.watres.2009.07.008](https://doi.org/10.1016/j.watres.2009.07.008).

REFERENCES

- ANZECC, 2000. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra, ACT, Australia.
- APHA/AWWA/WPCF, 1998. Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association/American Water Works Association/Water Pollution Control Federation, Washington, DC, USA.
- Blecken, G.-T., Zinger, Y., Deletic, A., Fletcher, T.D., Viklander, M., 2009. Impact of a submerged zone and a carbon source on heavy metal removal in stormwater biofilters. *Ecol. Eng.* doi: 10.1016/j.ecoleng.2008.12.009.
- Bradd, H.B., 2004. Adsorption of heavy metal ions on soil and soil constituents. *J. Colloid Interf. Sci.* 277, 1–18.
- Bratieres, K., Fletcher, T.D., Deletic, A., Zinger, Y., 2008. Nutrient and sediment removal by stormwater biofilters; a large-scale design optimisation study. *Water Res.* 42 (14), 3930–3940.
- Caille, N., Tiffreau, C., Leyval, C., Morel, J.L., 2003. Solubility of metals in an anoxic sediment during prolonged aeration. *Sci. Total Environ.* 301, 239–250.
- Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., 2001. Laboratory study of biological retention for urban stormwater management. *Water Environ. Res.* 73 (1), 5–14.
- Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., Winogradoff, D., 2003. Water quality improvement through bioretention: lead, copper, and zinc removal. *Water Environ. Res.* 75 (1), 73.
- Förstner, U., Ahlf, W., Calmano, W., 1989. Studies on the transfer of heavy metals between sedimentary phases with a multi-chamber device: combined effects of salinity and redox variation. *Mar. Chem.* 28, 145–158.
- Fritioff, Å., Greger, M., 2003. Aquatic and terrestrial plant species with potential to remove heavy metals from stormwater. *Int. J. Phytoremediat.* 5 (3), 211–224.
- Hatt, B.E., Deletic, A., Fletcher, T.D., 2007a. Stormwater reuse: designing biofiltration systems for reliable treatment. *Water Sci. Technol.* 55 (4), 201–209.
- Hatt, B.E., Fletcher, T.D., Deletic, A., 2007b. Hydraulic and pollutant removal performance of stormwater filters under variable wetting and drying regimes. *Water Sci. Technol.* 56 (12), 11–19.
- Hatt, B.E., Fletcher, T.D., Deletic, A., 2008. Hydraulic and pollutant removal performance of fine media stormwater filtration systems. *Environ. Sci. Technol.* 42, 2535–2541.
- Hsieh, C.-H., Davis, A.P., 2005. Multiple-event study of bioretention for treatment of urban storm water runoff. *Water Sci. Technol.* 51 (3–4), 177–181.
- Kim, H., Seagren, E.A., Davis, A.P., 2003. Engineered bioretention for removal of nitrate from stormwater runoff. *Water Environ. Res.* 75 (4), 355–367.
- Lau, Y.L., Marsalek, J., Rochfort, Q., 2000. Use of a biofilter for treatment of heavy metals in highway runoff. *Water Qual. Res. J. Can.* 35 (3), 563–580.
- Marsalek, J., Rochfort, Q., Brownlee, B., Mayer, T., Servos, M., 1999. An exploratory study of urban runoff toxicity. *Water Sci. Technol.* 39 (12), 33–39.
- Melbourne Water, 2005. WSUD Engineering Procedures: Stormwater. CSIRO Publishing, Melbourne, VIC, Australia.
- Muthanna, T.M., Viklander, M., Blecken, G.-T., Thorolfsson, S.T., 2007. Snowmelt pollutant removal in bioretention areas. *Water Res.* 41 (18), 4061–4072.
- Muthukumaran, M., Chiew, F.H.S., Wong, T.H.F., 2002. Size Distribution and Partitioning of Urban Pollutants. 9th International Conference on Urban Drainage, Portland, Oregon, USA.
- Read, J., Wevill, T., Fletcher, T.D., Deletic, A., 2007. Variation among plant species in pollutant removal from stormwater in biofiltration systems. *Water Res.* 42 (4–5), 893–902.
- Saeki, K., Okazaki, M., Matsumoto, S., 1993. The chemical phase changes in heavy metals with drying and oxidation of the lake sediments. *Water Res.* 27 (7), 1243–1251.
- Stephens, S.R., Alloway, B.J., Parker, A., Carter, J.E., Hodson, M.E., 2001. Changes in leachability of metals from dredged canal sediments during drying and oxidation. *Environ. Pollut.* 114, 407–413.
- Sun, X., Davis, A.P., 2007. Heavy metal fates in laboratory bioretention systems. *Chemosphere* 66 (9), 1601–1609.
- Swedish EPA, 2000. Environmental Quality Criteria – Lakes and Watercourses. Report 5050.
- Tack, F.M.G., Singh, S.P., Verloo, M.G., 1998. Heavy metal concentrations in consecutive saturation extracts of dredged sediment derived surface soils. *Environ. Pollut.* 103, 109–115.
- Tack, F.M.G., Van Ranst, E., Lievens, C., Vanderberghe, R.E., 2006. Soil solution Cd, Cu and Zn concentrations as affected by short-time drying or wetting: the role of hydrous oxides of Fe and Mn. *Geoderma* 137, 83–89.
- U.S. EPA, 1996. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. Method 6010B, EPA-publication SW-846. U. S. Environmental Protection Agency, Washington, DC, USA.
- Walsh, C.J., 2000. Urban impacts on the ecology of receiving waters: a framework for assessment, conservation and restoration. *Hydrobiologia* 431 (2–3), 107–114.
- Warren, L.A., Haack, E.A., 2001. Biogeochemical controls on metal behaviour in freshwater environments. *Earth Sci. Rev.* 54, 261–320.
- Yin, Y., Impellitteri, C.A., You, S.-J., Allen, H.E., 2002. The importance of soil organic matter distribution and extract soil: solution ratio on the desorption of heavy metals from soils. *Sci. Total Environ.* 287, 107–119.
- Zhao, L.Y.L., Schulin, R., Nowack, B., 2007. The effect of plants on the mobilisation of Cu and Zn in soil columns. *Environ. Sci. Technol.* 41 (8), 2770–2775.
- Zinger, Y., Fletcher, T.D., Deletic, A., Blecken, G.-T., Viklander, M., 2007a. Optimisation of the Nitrogen Retention Capacity of Stormwater Biofiltration Systems. 6th International Conference on Sustainable Techniques and Strategies in Urban Water Management NOVATECH 2007, Lyon, France.
- Zinger, Y., Deletic, A., Fletcher, T.D., 2007b. The Effect of Various Intermittent Dry-wet Cycles on Nitrogen Removal Capacity in Biofilter Systems. Rainwater & Urban Design, Sydney, NSW, Australia.

Appendix.

Supplementary information

Mean metal outflow concentration ± Standard deviation							
Metal	Parameter	SZ and C	after drying				
			wet ⁽¹⁾	1-2 weeks	3 weeks	4 weeks	7 weeks
Cu	concentration	with	1.5 ± 0.3	1.2 ± 0.4	6.3 ± 4.2	8.1 ± 5.3	15.7 ± 2.4
		without	9.5 ± 2.7	9.3 ± 0.2	17.3 ± 3.7	16.8 ± 0.0	29.5 ± 0.4
Pb	concentration	with	2.1 ± 0.9	1.6 ± 0.1	0.5 ± 0.3	1.4 ± 0.5	1.7 ± 0.1
		without	1.9 ± 0.7	3.6 ± 0.5	6.1 ± 0.6	10.5 ± 0.0	15.0 ± 2.5
Zn	concentration	with	12.8 ± 3.8	7.8 ± 1.9	15.8 ± 5.5	27.0 ± 10.1	57.6 ± 11.2
		without	15.6 ± 5.9	15.4 ± 1.1	22.8 ± 9.1	24.3 ± 0.0	34.4 ± 2.0

⁽¹⁾ only results of the first two stormwater applications (first week of the run-time)

Table 3. Mean metal outflow concentrations.

Pollutant	SZ and C	Depth						initial top layer conc.
		0 - 25	25 - 50	60 - 80	200 - 225	470 - 495	600-625	
Cd	with	1.5	1.1 ⁽²⁾	<0.5	<0.5	<0.5	<0.5	<0.5
	without	1.1	0.7 ⁽²⁾	<0.5	<0.5	<0.5	<0.5	
Cu	with	31.0	19.3	6.3 ⁽¹⁾	<5	<5	<5	5.4 ⁽²⁾
	without	27.0	19.3	6.4	<5	<5	<5	
Pb	with	64.7	30.0	7.6	5.9	<5	<5	5.0 ⁽²⁾
	without	55.3	21.7	8.1	<5	<5	<5	
Zn	with	176.7	92.0	23.3	8.7	<5	<5	13.3
	without	153.3	87.7	34.3	8.5	<5	<5	
TOC	with	25000	23667	19667	16000	1867	1200	40667
	without	20667	20333	21667	14333	263	230	
pH	with	7.6	7.3	7.7	7.7	7.7	8.0	8.0
	without	7.2	7.9	7.9	7.7	8.0	7.7	

⁽¹⁾ 1 of three samples below detection limit

⁽²⁾ 2 of 3 samples below detection limit

Table 4. Metals, TOC and pH in the filter media (average concentration of three samples, mg/kg) at different filter depths (mm).

Metal	ANZECC				Swedish EPA			
	Level of protection				Class ⁽¹⁾			
	99%	95%	90%	80%	1	2	3	4
Cu	1.0	1.4	1.8	2.5	≤ 0.5	0.5-3.0	3-9	9-45
Pb	1.0	3.4	5.6	9.4	≤ 0.2	0.2-1.0	1-3	3-15
Zn	2.4	8.0	15.0	31.0	≤ 5.0	5-20	20-60	60-300

⁽¹⁾ class 1: no or only very slight risk of biological effect, 2: slight risk,
3: effects may occur, 4 and 5: growing risk of effects

Table 5. Australian / New Zealand and Swedish freshwater quality guidelines (ANZECC, (2000, Swedish EPA, 2000) for selected heavy metals (total concentrations in µg/L).

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The influence of temperature on nutrient treatment efficiency
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The influence of temperature on nutrient treatment efficiency in stormwater biofilter systems

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Abstract Nutrients can cause eutrophication of natural water bodies. Thus, urban stormwater which is an important nutrient source in urbanised areas has to be treated in order to reduce its nutrient loads. Biofilters which use soil filter media, biofilms and plants, are a good treatment option for nutrients. This paper presents the results of a biofilter column study in cold temperatures (+2 °C, +8 °C, control at +20 °C) which may cause special problems regarding biofilter performance. It was shown that particle-bound pollutants as TSS and a high fraction of phosphorus were reduced well without being negatively influenced by cold temperatures. Nitrogen, however, was not reduced; especially NO_x was produced in the columns. This behaviour can be explained with both insufficient denitrification and high leaching from the columns.

Keywords Biofilter; cold climate; nutrients; stormwater treatment

Introduction

Nutrients can cause eutrophication in receiving natural water bodies (Browman *et al.*, 1979; Pitt *et al.*, 1999; Kim *et al.*, 2003). Stormwater runoff is an important source of nutrients in urbanised areas (Larm, 2000; Graves *et al.*, 2004; Taylor *et al.*, 2005), and it should therefore be treated.

Stormwater biofiltration, also known as bioretention, is a novel option that might be able to treat nutrients in stormwater in order to prevent eutrophication of recipients. A biofilter consists of filter media placed in a trench or basin that is planted on the top. It has a detention storage on the top (by placement in a depression) and a drainage pipe at the bottom to collect the treated water. Stormwater is treated by mechanical, biological and chemical processes in the filter media, but also by the plants and biofilms, that develops in the media and on the plant roots (Prince George's County, 2002; Hsieh and Davis, 2005).

Several studies conducted so far have shown a significant removal of phosphorus, phosphate and ammonium, but with low (and sometimes negative) removal of nitrate (Davis *et al.*, 2001; Lloyd *et al.*, 2001; Henderson *et al.*, 2007). However, biofilters are still a relatively new technology and hence, only limited data of the performance of these systems are available. Particular problems could arise when implementing biofilters in regions with constant or temporary cold temperatures, due to reduced biological activity, shorter growing seasons and a smaller number of adapted plant species. However, these systems may still perform well in these instances, since adequate nutrient removal has been achieved in constructed wetlands in cold subalpine climates (Heyvaert *et al.*, 2006). Biofilter performance in cold temperatures is the deciding factor to their successful implementation in regions with rainfall on non-frozen ground during cold periods

(autumn, winter and spring in temperate climate; autumn, later spring and summer in cold climate).

This paper presents preliminary results of a study of the performance of biofilters in relation to temperature. The aim was to determine the nutrient treatment performance of stormwater biofilters in low temperatures in order to enable an analysis of whether there is a correlation between temperature and treatment rate.

Material and methods

Experimental set-up

Laboratory tests were conducted on 15 biofilter mesocosms ('biofilter columns') made of PVC stormwater pipe (inner diameter: 377 mm, area: 0.11 m^2 , height: 900 mm). A transparent top (height: 400 mm) allowed water to pond without affecting light availability for plant growth. The inside wall was sandblasted to prevent preferential flow along the wall. A drainage pipe (diameter: 58 mm) at the bottom discharged to a sampling outlet (Figures 1 and 2).

The filter media in the columns included four layers (listed from top, Figure 2):

- (1) sandy loam layer, 400 mm, medium to coarse sand with 20% topsoil in the upper 100 mm,
- (2) sand layer, 400 mm, fine to medium sand,
- (3) transition layer, 30 mm, coarse sand and
- (4) underdrain, 70 mm, fine gravel with embedded drainage pipe.

The columns were planted with *Carex rostrata* Stokes (Bottle sedge) which is widespread in the northern hemisphere (Anderberg and Anderberg, 2006). The plant density in the columns was 8 plants per column, which corresponds to a density of approximately 73 plants/m^2 . Before they were planted in the columns, the plants were grown for 5 weeks outside to develop a substantial root system. Afterwards they were grown in the columns for two month and irrigated with tap water.



Figure 1 Biofilter columns in climate room

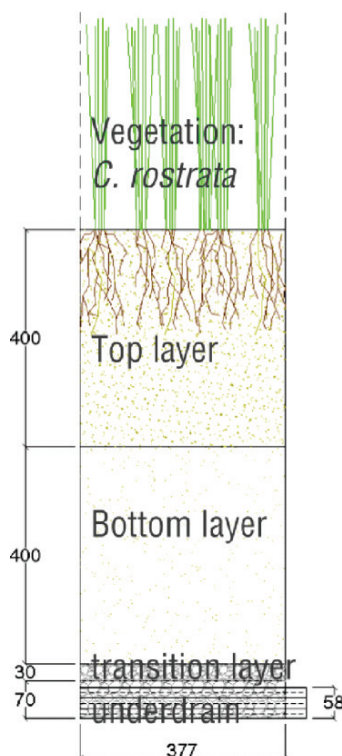


Figure 2 Biofilter column configuration

In order to investigate the temperature effect on the biofilter performance, the tests were carried out in three thermostat controlled climate rooms at constant target temperatures of $+2^{\circ}\text{C}$, $+8^{\circ}\text{C}$, and $+20^{\circ}\text{C}$ ($+35.6^{\circ}\text{F}$, $+46.4^{\circ}\text{F}$, and $+68^{\circ}\text{F}$, resp.). Five columns each were placed in every climate room (Figure 1). The air temperature in the climate rooms was logged at a 15 minute interval using one EBI 20-T (8°C) and two EBI 2T-112 (2°C and 20°C) temperature loggers (ebro Electronic, Ingolstadt, Germany). All columns were illuminated with high pressure sodium greenhouse lamps (G-Power Agro, 400 W, 55,000 Lm) 12 hours daily.

Experimental procedure

Stormwater. Since natural stormwater was not available in the required quantity and with constant water quality over the time of the experiment, nor could be stored without significant changes to its quality, semi-synthetic stormwater was used. It was made by mixing tap water with gully pot sediment to achieve the required TSS concentration, topped with certain pollutants to achieve the targeted pollutant concentrations, as outlined in Table 1 (only for nutrients; heavy metals were added as well, but are not reported in this paper). A new mixture was made for every stormwater application. The water was stored at the respective temperature (2°C , 8°C , 20°C , resp.) for at least 24 hours before dosing the columns in order to have similar water and air temperatures.

In Luleå (Sweden) it rains approximately two times per week in September and October (the month with the most rain events in cold temperatures) with a total precipitation amount of around 110 mm (SMHI, 2005). This corresponds to an average of 5.4 L/m^2 stormwater runoff per rain event from a catchment with 85% impervious surface. It

Table 1 Semi-synthetic stormwater pollutants and their sources

Pollutant	Targeted	Source
pH	6.9	H ₂ SO ₄
TSS	140 mg/L	Stormwater gully pot sediment ($\leq 400 \mu\text{m}$)
Phosphorus (total)	0.3 mg/L	KH ₂ PO ₄ (potassium dihydrogen phosphate) 0.32 mg/L nitrate: KNO ₃ (potassium nitrate)
Nitrogen (total)	1.4 mg/L	0.24 mg/L ammonium: NH ₄ Cl (ammonium chloride) organic nitrate: C ₆ H ₄ NO ₂ (nicotinic acid)

was assumed that the biofilter area represents appr. 4% of the catchment area (one column with 0.11 m^2 for 2.75 m^2 catchment) (Wong *et al.*, 2006). Therefore every column was dosed with 15 L ($5.4 \text{ L/m}^2 \cdot 2.75 \text{ m}^2 = 14.85 \text{ L} \approx 15 \text{ L}$) of stormwater twice weekly.

Sampling. From the stormwater a sample was taken in three replicates before every stormwater application. All outflow water was collected in PE-tanks until the next dosing event, it was stored at $+2^\circ\text{C}$, and a composite sample was taken from each PE-tank, i.e. 15 samples per each dosing. This paper reports on results of the first four weeks of stormwater dosing (i.e. eight events).

Analyses. All samples were analysed for total and dissolved N, ammonium (NH₄⁺), nitrate/nitrite (NO_x), TSS, and pH. The dissolved samples were filtered, using Whatman ME25 membrane $0.45 \mu\text{m}$ pore size filters. Before analysing P and N, the samples were digested with peroxy-disulphate (according to the Swedish standard method SS 028127) and oxidised with peroxisulphate (SS 028131), resp. The analyses were conducted with a continuous micro flow analyser (QuAAtro, Bran + Luebbe, Hamburg, Germany) according to the device-specific methods no. Q-031-04 for P, no. Q-003-04 for N and NO_x and no. Q-001-04 for NH₄⁺.

TSS was determined by filtration through Whatman GF/A $1.6 \mu\text{m}$ pore size glass microfibre filters (SS-EN 872) in one replicate. pH was measured with a field pH-meter (pH330, WTW GmbH, Weilheim, Germany).

Data analyses

Pollutant reduction was calculated as $\text{reduction} = (1 - (\text{out/in})) \cdot 100\%$. Thus, production of pollutants results in a negative reduction rate. Analysis of variance (ANOVA) was used to test the influence of temperature on outflow concentrations. Furthermore, box plots were created for nitrogen species and phosphorus to compare in- and outflow concentrations and their evolution over time. All statistical calculations and plots were computed with the software MINITAB[®] 15.1.

Results and discussion

The mean temperature in the three different rooms were 1.8°C (SD: 1.01°C), 7.4°C (SD: 0.35°C) and 20.3°C (SD: 1.02°C) respectively. Thus, the real temperatures were very near the target temperatures. The mean inflow and outflow pollutant concentrations (mg/L) as well as reduction rates (%) at the three different temperatures are shown in Table 2.

pH. The average pH-value of the stormwater was 6.9. The pH increased in the columns and the outflow pH at all temperatures was around 7.4.

Table 2 Pollutant concentrations and removal

		Stormwater ⁽²⁾ all temp.	Outflow ⁽³⁾		
			2 °C	8 °C	20 °C
pH		6.90 (0.20)	7.32 (0.13)	7.40 (0.10)	7.46 (0.18)
TSS	concentration	142.7 (13.9)	3.6 (1.4)	5.1 (1.7)	4.6 (2.1)
	mean reduction		97.5%	96.4%	96.8%
N _{total}	concentration	1.38 (0.16)	1.38 (0.29)	1.54 (0.25)	4.23 (0.68)
	mean reduction		− 0.5%	− 11.6%	− 207.8%
N _{dissolved}	concentration	1.16 (0.08)	1.33 (0.26)	1.31 (0.15)	3.94 (1.02)
	mean reduction		− 14.9%	− 13.2%	− 240%
NO _x ⁽¹⁾	concentration	0.24 (0.01)	0.72 (0.26)	0.89 (0.13)	3.79 (0.57)
	mean reduction		− 198%	− 265%	− 1461%
NH ₄ ⁽¹⁾	concentration	0.32 (0.05)	0.11 (0.05)	0.14 (0.06)	0.15 (0.05)
	mean reduction		64.5%	56.2%	51.7%
P _{total}	concentration	0.292 (0.018)	0.055 (0.036)	0.058 (0.032)	0.056 (0.030)
	mean reduction		81.2%	80.3%	80.7%
P _{dissolved}	concentration	0.031 (0.017)	0.007 (0.002)	0.009 (0.004)	0.010 (0.005)
	mean reduction		77.5%	71.5%	69.3%

⁽¹⁾ only the first 4 events have been analysed ⁽²⁾ three replicates per event analysed ⁽³⁾ mean value of five replicate columns and all events.

TSS. Reduction of TSS was around 97%, and whilst the effect of temperature on this removal was statistically significant ($p = 0.001$), it accounted for very little of the observed variation, and was of no practical significance (Table 3, Figure 3). Other factors are clearly influencing TSS removal, although it was high in all cases. The low difference between the columns at different temperatures is not surprising since the TSS removal is mainly a matter of mechanical filtration which itself is not influenced by temperature (unless the soil media soil freezes forming channels). Because of the high TSS removal, a high (and largely temperature independent) removal of particle bound pollutants could be expected.

Phosphorus. In the stormwater inflow 85% of the total phosphorus was particle bound. The fraction was slightly different in the outflow at the different temperatures (2 °C: 87% particle bound, 8 °C: 84% particle bound and 20 °C: 82% particle bound).

A temperature independent removal of about 80% was detected for total phosphorus ($p = 0.933$, Table 3). There is a very clear decrease in the outflow concentrations and their variances over time (Figure 4). Dissolved phosphorus was also well removed by the biofilter, with no significant temperature dependence ($p = 0.285$, Table 3). However, its reduction rate was slightly higher at cold temperatures. The results make sense, if we assume that physical filtration is the main mechanism for P removal, while biological activity within the soil may cause some leaching of P from media (the higher biological activity occurs at higher temperatures). This leaching is getting smaller with time as the

Table 3 One-way ANOVA: p-value of temperature influence on outflow concentrations and R^2 (adjusted) of the model

	p-value	R^2 (adj.)
TSS	0.001	9.0%
N _{total}	0.000	89.4%
N _{dissolved}	0.000	80.4%
NO _x ⁽²⁾	0.000	93.7%
NH ₄ ⁽²⁾	0.065	6.0%
P _{total}	0.933	0.0%
P _{diss.} ⁽²⁾	0.285	2.1%

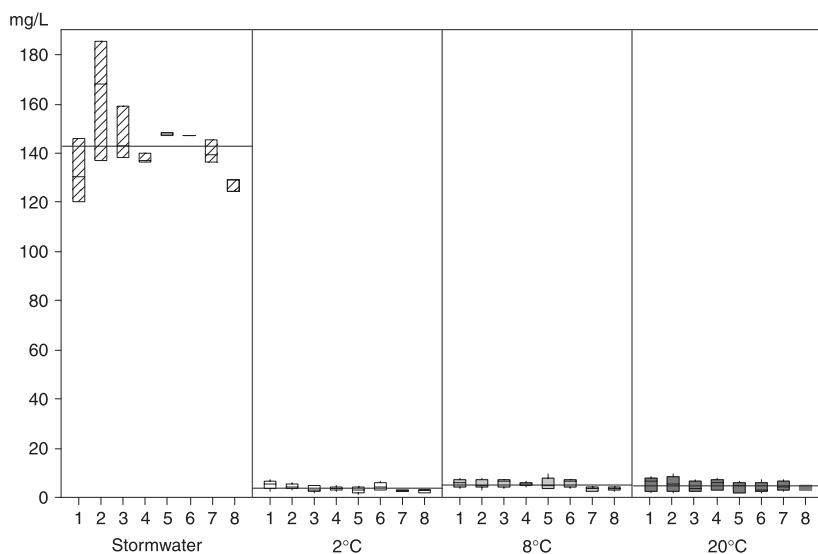


Figure 3 Box plot of in- and outflow TSS concentrations at the 3 different temperatures and 8 samplings

source is depleted, which explains the decreasing outflow concentrations with time in Figure 4. Overall however, mechanical removal of phosphorus is the most important factor and therefore overall P removal is high.

Nitrogen. While the biofilters at 2°C and 8°C showed little or no leaching of total nitrogen, a high production (on average –208% removal) was observed at 20°C (Figure 5, Table 2). No trend over time was observed.

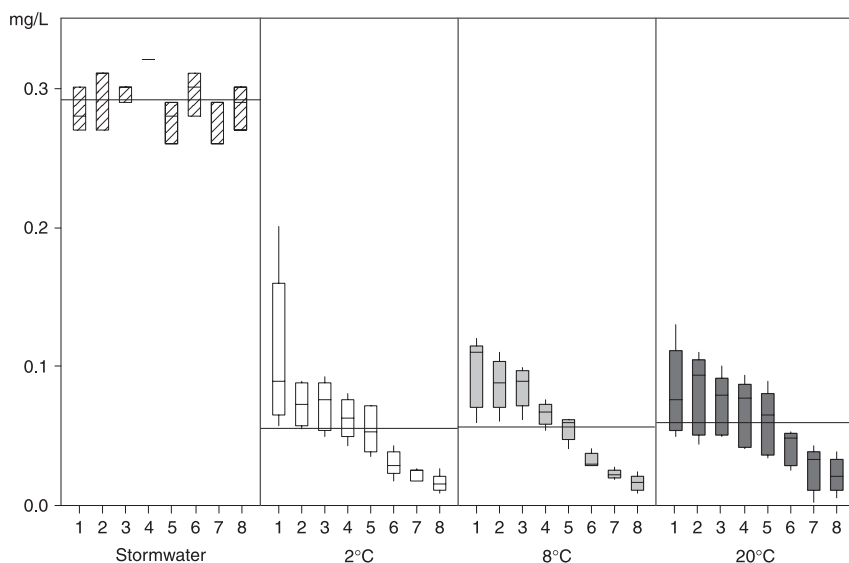


Figure 4 Box plots of in- and outflow total phosphorus concentrations at the 3 different temperatures and 8 samplings

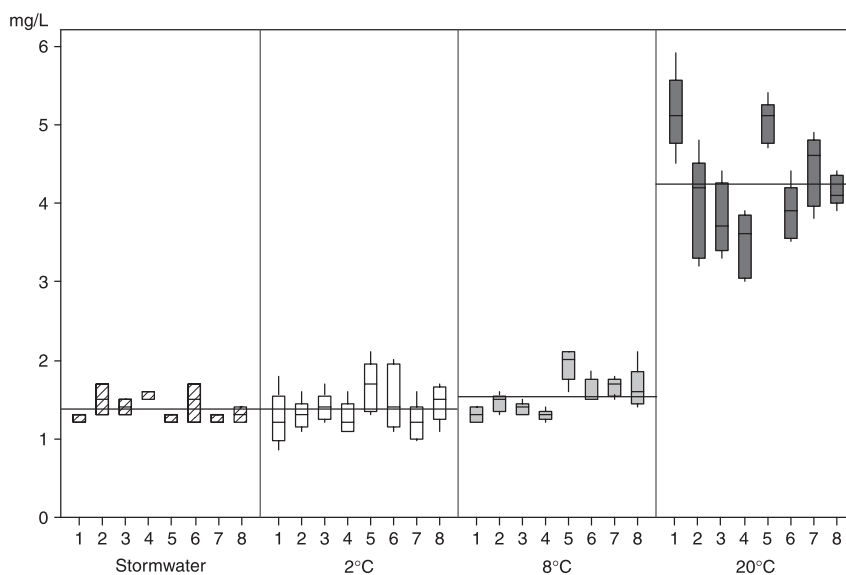


Figure 5 Box plots of in- and outflow total nitrogen concentrations at the 3 different temperatures and 8 samplings

The total nitrogen in the synthetic stormwater influent was 84% dissolved, whilst in the treated outflow water 96%, 85% and 93% was at 2 °C, 8 °C and 20 °C, respectively. The proportion of the nitrogen compounds changed during the treatment in the biofilter. NH_4^+ was reduced at all temperatures, whilst NO_x was produced (Table 2, Figure 6). This means that nitrification in the unsaturated zone of the biofilter was occurring and therefore NH_4^+ levels were decreased and NO_x levels were increased. Since no denitrification was taking place due to the lack of an anoxic zone and/or a carbon source, levels of NO_x at the outflow were highly elevated (Kim *et al.*, 2003; Zinger *et al.*, 2007).

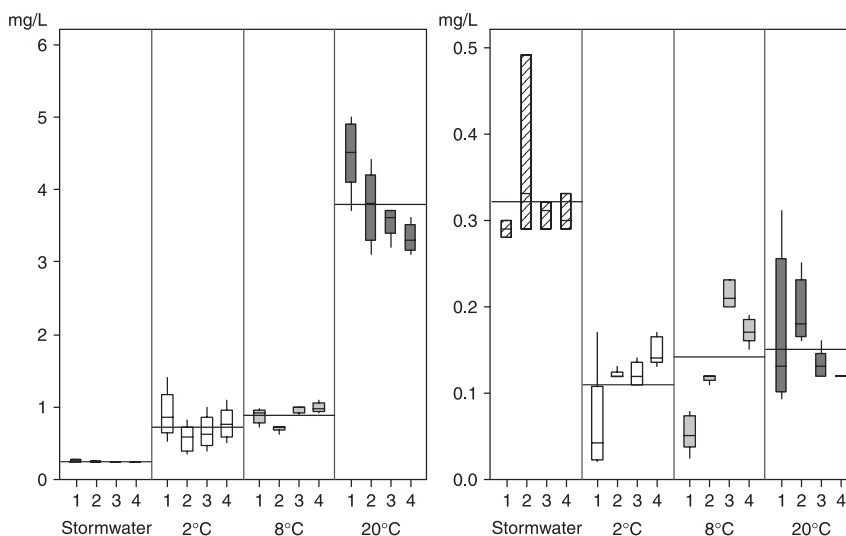


Figure 6 Box plots of in- and outflow: (a) dissolved NO_x , (b) and dissolved NH_4^+ concentrations at the 3 different temperatures and 8 samplings

However, a significant temperature effect was demonstrated for dissolved nitrogen behaviour ($p = 0.000$ dissolved N and NO_x , Table 3): the higher the temperature the higher the NO_3 production due to increasing nitrification with increasing temperatures. More importantly, more nitrogen from the soil leached to the outflow water at higher temperatures. Unfortunately, it is not clear yet whether the leaching will stop over time as plants mature, as has been observed in similar biofilter studies (Zinger *et al.*, 2007). The plants had only 2–3 months of establishment, while in Zinger *et al.*'s experiments they had 5 months to establish. It is known that plants (and in particular their roots) play a major role in N removal, since unvegetated biofilters are always demonstrated to leach nitrogen (Hatt *et al.*, 2006; Lee and Scholz, 2007), whilst vegetated biofilters do not (Henderson *et al.*, 2007).

Conclusion

Even in cold climates, it is clear that effective removal of particle-bound pollutants (TSS and particulate phosphorus) can be achieved. This verifies the findings of other cold climate studies (Bäckström, 2002; Muthanna *et al.*, 2007). However, the results showed poor overall removal of nitrogen from the stormwater. In particular, there was a very high production of NO_x , which was probably caused by nitrification, and limited denitrification. Such large net production of nitrogen was not expected as other studies have shown a reduction or at least only minor production of nitrogen even in biofilters without an anoxic zone (Kim *et al.*, 2003; Scholz, 2004; Zinger *et al.*, 2007). However, it is possible that the short establishment time of the plants in the presented experiments is the main cause of this. Further research should be conducted to investigate if the removal of N will begin to improve over time.

The biofilters showed the best performance for nitrogen (i.e. the lowest production) at the coldest temperatures. A key area of subsequent research is therefore to determine if the addition of an anoxic zone with added carbon source, which has been shown to improve denitrification in biofilters (Kim *et al.*, 2003; Zinger *et al.*, 2007), would remain effective, even in cold temperatures.

References

- Anderberg, A.-L. and Anderberg, A. (2006). Den virtuella floran: Naturhistoriska Riksmuseet. <http://linnaeus.nrm.se/flora/> (accessed 08 October 2007).
- Browman, M.G., Harris, R.F., Ryden, J.C. and Syers, J.K. (1979). Phosphorus loading from urban stormwater runoff as a factor in lake eutrophication - Theoretical considerations and qualitative aspects. *J. Environ. Qual.*, **8**(4), 561–566.
- Bäckström, M. (2002). *Grassed Swales for Urban Drainage*. Doctoral Thesis 2002:06, Division of Sanitary Engineering, Luleå University of Technology, Luleå, Sweden.
- Davis, A.P., Shokouhian, M., Sharma, H. and Minami, C. (2001). Laboratory study of biological retention for urban stormwater management. *Water Environ. Res.*, **73**(1), 5–14.
- Graves, G.A., Wan, Y. and Fike, D.L. (2004). Water quality characteristics of storm water from major land uses in south Florida. *J. Am. Water Resour. Assoc.*, **40**(6), 1405–1418.
- Hatt, B.E., Siriwardene, N., Deletic, A. and Fletcher, T.D. (2006). Filter media for stormwater treatment and recycling: the influence of hydraulic properties of flow on pollutant removal. *Water Sci. Technol.*, **54**(6–7), 263–271.
- Henderson, C., Greenway, M. and Phillips, I. (2007). Removal of dissolved nitrogen, phosphorus and carbon from stormwater by biofiltration mesocosms. *Water Sci. Technol.*, **55**(4), 183–191.
- Heyvaert, A.C., Reuter, J.E. and Goldman, C.R. (2006). Subalpine, cold climate, stormwater treatment with a constructed surface flow wetland. *J. Am. Water Resour. Assoc.*, **42**(1), 45–54.
- Hsieh, C.-H. and Davis, A.P. (2005). Multiple-event study of bioretention for treatment of urban storm water runoff. *Water Sci. Technol.*, **51**(3–4), 177–181.

- Kim, H., Seagren, E.A. and Davis, A.P. (2003). Engineered bioretention for removal of nitrate from stormwater runoff. *Water Environ. Res.*, **75**(4), 355–367.
- Larm, T. (2000). Stormwater quantity and quality in a multiple pond-wetland system: Flemingsbergsviken case study. *Ecol. Eng.*, **15**(1–2), 57.
- Lee, B.-H. and Scholz, M. (2007). What is the role of *Phragmites australis* in experimental constructed wetland filters treating urban runoff? *Ecol. Eng.*, **29**(1), 87–95.
- Lloyd, S., Fletcher, T.D., Wong, T.H.F. and Wootton, R.M. (2001). *Assessment of pollutant removal performance in a bio-filtration system - preliminary results*. Paper presented at the Second South Pacific Stormwater Conference, New Zealand.
- Muthanna, T.M., Viklander, M., Blecken, G.-T. and Thorolfsson, S.T. (2007). Snowmelt pollutant removal in bioretention areas. *Water Res.*, **41**(18), 4061–4072.
- Pitt, R., Clark, S. and Field, R. (1999). Groundwater contamination potential from stormwater infiltration practices. *Urban Water*, **1**(3), 217.
- Prince George's County (2002). *Bioretention Manual*. Lead Author: D.A. Winogradoff. Department of Environmental Resources, Programs & Planning Division, Prince George's County, Maryland, USA.
- Scholz, M. (2004). Treatment of gully pot effluent containing nickel and copper with constructed wetlands in a cold climate. *J. Chem. Technol. Biotechnol.*, **79**, 153–162.
- SMHI. Swedish Meteorological and Hydrological Institute (2005). Klimatkarta Uppmätt nederbörd 1961–1990, månadsvis. (In Swedish).
- Taylor, G.D., Fletcher, T.D., Wong, T.H.F., Breen, P.F. and Duncan, H.P. (2005). Nitrogen composition in urban runoff—implications for stormwater management. *Water Res.*, **39**(10), 1982.
- Wong, T.H.F., Fletcher, T.D., Duncan, H.P. and Jenkins, G.A. (2006). Modelling urban stormwater treatment—A unified approach. *Ecol. Eng.*, **27**(1), 58.
- Zinger, Y., Fletcher, T.D., Deletic, A., Blecken, G.-T. and Viklander, M. (2007). *Optimisation of the Nitrogen Retention Capacity of Stormwater Biofiltration Systems*. Paper presented at the NOVATECH 2007, Lyon, France.

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Laboratory study on stormwater biofiltration:
nutrient and sediment removal in cold temperatures

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1 Laboratory study on stormwater biofiltration: nutrient and
2 sediment removal in cold temperatures

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Abstract. Stormwater biofilters have the ability to remove nutrients from stormwater. Reliable pollutant removal during the cold season is particularly important due to the comparably high contamination levels. However, the removal performance might be negatively affected by low temperatures. A biofilter column study was conducted in thermostat-controlled climate rooms (at 2, 7 and 20 °C) to investigate the effect of low temperatures on nutrient removal. Phosphorus and suspended solids removal were significantly correlated and consistently very high (typically in excess of 90 and 95%, respectively, at all temperatures). This is important for the successful implementation of biofilters in cold climates since phosphorus is commonly of principal concern, often being the limiting factor for eutrophication in freshwater ecosystems. Unfortunately, nitrogen removal was poor and leaching was shown, which increased with temperature. The increasing nitrate-nitrogen production rates with temperature were well described by the Arrhenius relationship with temperature coefficients Q_{10} in the range which is typically used to describe temperature effects on nitrification. Thus, temperature effects have to be considered when nitrogen removal is targeted and the biofilter might be exposed to cold temperatures.

1 INTRODUCTION

Catchment imperviousness in cities with conventional drainage systems causes urban stormwater pollution as well as increased runoff volumes and peak flows (Burns et al., 2005; Walsh et al., 2005). Heavy metals, nutrients, polycyclic aromatic hydrocarbons and salt have been identified as key pollutants in stormwater (Eriksson et al., 2007). Worldwide significant nitrogen and phosphorus pollution has been reported in stormwater (Swedish EPA, 2003; Dillon and Chanton, 2005; Taylor et al., 2005; Eriksson et al., 2007). Snow or snow melt runoff might in particular be contaminated with (often particle bound) phosphorus, probably due to sand and salt application (Oberts, 1986; Viklander, 1999; Marsalek et al., 2003). Urban runoff is thus a major reason for ecological degradation of urban waterways resulting in water contamination, diminished biodiversity, altered morphology and changed hydrograph characteristics (Walsh et al., 2005). Nutrient contamination might result in eutrophication including excessive plant and algae growth and possibly oxygen depletion (Taylor et al., 2004). In freshwater ecosystems commonly the N:P ratios exceed 15 to 30 and thus phosphorus is the limiting nutrient for eutrophication (e.g. Berge et al., 1997). In large eutrophic systems with long turnover times, however, nitrogen may be limiting (Murray and Parslow, 1999; Taylor et al., 2005).

In recent years the dominant paradigms within urban drainage have changed and concepts like water sensitive urban design (WSUD) or low impact development have been implemented in an attempt to restore stormwater quality and flow regimes (Dietz, 2007; Roy et al., 2008). When implementing such concepts, the Swedish EPA (2003) requires nutrient removal from the stormwater in order to minimise in particular the release of phosphorus to freshwater ecosystems and nitrogen to marine ecosystems. One promising option is the use of stormwater biofiltration (also known as rain garden or bioretention) for in situ water quality improvement

and flow retention (e.g. Dietz, 2007). In these biofilters, stormwater percolates through vegetated filter media where water quality is improved by filtration, extended detention and plant uptake (Melbourne Water, 2005). The treated water is sometimes collected in an underdrain and discharged to the conventional sewer or receiving water (Melbourne Water, 2005), whilst in other cases it is allowed to infiltrate into surrounding soils.

Several laboratory studies have shown the ability of biofilters to remove significant nutrient loads from stormwater. Efficient total Kjeldahl nitrogen and ammonium (NH_4) removal has commonly been shown (Davis et al., 2001, 2006; Hsieh et al., 2007b; Bratieres et al., 2008). However, less nitrate and nitrite (NO_x) removal was observed, with net leaching even being observed in some cases (Davis et al., 2001, 2006; Hatt et al., 2009; Hsieh et al., 2007b; Bratieres et al., 2008; Passeport et al., 2009). Phosphorus removal in biofilters is typically good (Davis et al., 2001, 2006; Hatt et al., 2009; Hsieh et al., 2007a; Bratieres et al., 2008). However, the filter media selection is crucial for effective phosphorus removal since leaching from the media has to be avoided. Total suspended solids (TSS) removal has been shown to be very high, often exceeding 95% (e.g. Muthanna et al., 2007a; Bratieres et al., 2008; Blecken et al., 2009). Besides water quality improvement, biofilters were shown to effectively reduce runoff peak flow rates and runoff volumes (Gilroy and McCuena, 2009; Hatt et al., 2009).

However, as with many other WSUD technologies, biofilters have been mostly developed without specific consideration for their operation in cold weather, which may be critical (Marsalek et al., 2003; Roseen et al., 2009). Indeed, the effect of cold conditions on the biofilter processes is largely unknown. A number of factors controlling stormwater infiltration and nutrient removal in biofilters might be affected by different seasonal conditions: low

temperatures might influence nitrogen removal (or eventual leaching) since (de-)nitrification is highly affected by soil temperature. This temperature effect is best described by the Arrhenius equation up to a nitrification optimum between 20 and 35 °C (e.g. Anderson and Purvis, 1955; Stark, 1996; Russell et al., 2002). Furthermore, NH₄ fixation and microbial nitrogen uptake are also influenced by temperature (Reay et al., 1999; Juang et al., 2001). Phosphorus sorption in soils increases with rising temperature along a temperature gradient (Barrow and Shaw, 1975). Plant growth and thus plant nutrient uptake varies seasonally.

However, despite the evidence that biofilters may perform differently in low temperatures than they do in temperate zones, few studies have investigated the pollutant removal capability of stormwater biofilters in cold temperatures (Muthanna et al., 2007a; Muthanna et al., 2007b), with none of them dealing with nutrient removal. Only Scholz (2004) reports high nutrient removal in vertical flow constructed wetlands in a cold climate. Findings from a study in Trondheim, Norway, indicate that hydraulic detention in biofilters is significantly lower during winter (Muthanna et al., 2008). However, even at cold temperatures a significant peak runoff reduction has been shown; even though to a lesser degree than in summer (Muthanna et al., 2007b).

The development of reliable stormwater treatment technologies for cold weather regions is particularly important due to often high contamination levels in winter runoff e.g. due to extended storage and accumulation of pollutants in snowpacks, increased pollutant fallout from heating and increased vehicle engine wear and the application of de-icing salts and anti-skid agents (Viklander, 1999; Marsalek et al., 2003). Thus, further research is needed regarding biofilter pollutant removal efficiency in low temperatures. The aim of this study was thus to investigate the nutrient removal by biofilters and its degree of temperature

dependence. This study represents the first thorough assessment of this question, with only earlier *preliminary* data previously reported (Blecken et al., 2007).

2 METHODS

2.1 Experimental set-up

Biofilter mesocosms (“columns”) were tested in three thermostat-controlled climate rooms at nearly constant air temperatures (1.8 ± 1.0 , 7.3 ± 0.4 and 20.3 ± 1.0 °C; temperature logger ebro Electronic EBI 20-T at 7.3 °C and EBI 2T-112 at 1.8 and 20.3 °C). Five replicate columns were placed in each room (Supplementary Figure 3)

The columns (height 900 mm, inner diameter 377 mm, area 0.11 m^2) were made of PVC pipes with sandblasted inner walls to reduce the risk of preferential flow along the columns wall. On top, the column extended into a transparent pipe (height 400 mm) which allowed stormwater ponding during dosing without affecting plant growth by shade. The filter depth and ponding height of the columns is similar to current design recommendations (e.g. Melbourne Water, 2005).

The filter media consisted of two 400 mm deep layers: a top sand layer with 5% silt and 14% fine gravel (2–4 mm) ($d_{50} = 620 \text{ }\mu\text{m}$; uniformity coefficient (UC) = $d_{60}/d_{10} = 6.4$), mixed with top soil in the upper 100 mm and a bottom layer with medium to fine sand ($d_{50} = 280 \text{ }\mu\text{m}$, UC = 2.5) (Supplementary Figure 3). Infiltration into frozen soils is inversely related to the soil moisture content: in unsaturated frozen soils ice reduces the pore size which limits water infiltration, while solid ice formation near the soil surface of saturated soils restricts any infiltration (Zhao and Gray, 1999). Thus, a well drained soil medium is recommended in cold weather regions to prevent ice formation and thus to facilitate sufficient water infiltration even

for runoff events occurring subsequent to freezing (Caraco and Claytor, 1997; Muthanna et al., 2008). Consequently, a relatively coarse filter media with higher sand content than is typical in current practice in temperate climates was chosen for these experiments compared to otherwise recommended sandy loam soils (Melbourne Water, 2005). Below the filter a transition layer (30 mm) with coarse sand prevented clogging of the underlying drain (70 mm) consisting of fine gravel, with an embedded 54 mm diameter slotted drainage pipe draining to the sampling port.

Each column was planted with 8 plants *Carex rostrata* Stokes (Bottle sedge). Even if the plants had already developed a substantial root system, they were allowed to establish for two months after planting, before starting the experiment. The climate rooms were lit with greenhouse lamps (G-power Agro, 400 W, 55 000 Lm) for 12 h daily. Despite this, the plants did not appear to develop well in the climate rooms, independent of temperature (Supplementary Figure 4). After completion of the experiments, the approximate plant height was between 10 and 30 cm which is low compared to e.g. the results of Bratieres, et al (2008) and Blecken, et al. (2009) who used a similar column setup and observed plant heights of > 100 cm (*Carex appressa*). However, no measurement of plant biomass changes was carried out.

Before starting of the experiments, the columns were saturated three times with stormwater pond water over one day each in order to flush any fines from the media and to enable faster establishment of biofilms and bioactivity in the filter media.

For dosing, semi-artificial stormwater was used: immediately before dosing natural sediment from a stormwater gully pot and laboratory-grade chemicals were added to tap water in the

amount needed to achieve typical stormwater pollutant concentrations. After mixing the sediment with the tap water, the concentration of target pollutants was measured and laboratory grade chemicals were then added to make up any deficit between the target concentration (Table 1) and that of the tap water-sediment mix. Most nitrogen (N) was in its dissolved form while phosphorus (P) was 90% particle bound (Table 1). Total nitrogen (TN), dissolved nitrogen (DN) and nitrate-nitrogen ($\text{NO}_x\text{-N}$) inflow concentrations varied between the different events (TN and DN between 1.3 and 2.1 mg L^{-1} ; $\text{NO}_x\text{-N}$ 0.24 and 0.61 mg L^{-1}) resulting in a relatively high standard deviation (Table 1). $\text{NH}_4\text{-N}$, total phosphorus (TP) and TSS inflow concentrations were nearly constant over the entire experiment. Metals were added to the stormwater as well but are not reported in this paper. No de-icing agents (e.g. salts) were added.

Each column was dosed with 15 L of stormwater twice weekly over 12 weeks, based on the assumptions of 55 mm monthly rainfall (typical for northern Sweden autumn conditions) and a biofilter area of 4% of an 85% impervious catchment. Thus, each column received in total 360 L stormwater during the entire 12 week experiment distributed to 24 events. Between the dosings the columns were subject to gravity drainage for 2 or 3 days, respectively. Before dosing, the tap water was stored in open polyethylene containers for at least 24 h in the respective climate room to ensure temperature adjustment to the air temperature. Thus, the stormwater was prepared in each climate room separately (however with no significant differences between the inflow concentrations in the different climate rooms, $\alpha = 0.05$).

2.2 Water sampling

Before each dosing, the stormwater was sampled to monitor its quality. One 0.5 L composite sample was taken from the stormwater in each climate room made up of 5 sub-samples which were randomly taken from the stormwater.

Every second week (i.e. after every fourth ‘storm event’), outflow samples were taken separately for each column (i.e. 5 samples for each temperature). The outflow water from the columns was collected until at least 14 L treated water had been discharged. This collected water was stirred and then the samples were taken using a 0.5 L PE bottle. The results provide data on net removal within the biofilter. It is of course possible that removal may vary through the depth profile; it would for example be expected that ammonia removal would be greatest in the upper oxygenated layers, whilst nitrate removal will be greatest in the deeper, low-oxygen region. However, this experiment allows us to see, as is the case for most biofilter studies, to quantify the net effect of the biofiltration system on concentration of target pollutants.

All equipment which was in contact with storm- and treated water was acid washed before each use.

2.3 Water analyses

The samples were analysed for TN and DN, dissolved $\text{NH}_4\text{-N}$, dissolved $\text{NO}_x\text{-N}$, total P and TSS. The dissolved samples were filtered using Whatman ME25 membrane 0.45 μm pore size filters. Before analysing for P and N, the samples were digested and oxidised according to Swedish Standard Methods SS 028127 and SS 028131, respectively. The analyses were conducted with a continuous micro flow analyser (QuAAtro, Bran+Luebbe) according to the device-specific methods no. Q-031-04 for P, no. Q-003-04 for N and $\text{NO}_x\text{-N}$ and no. Q-001-

04 for $\text{NH}_4\text{-N}$. TSS was determined by filtration through Whatman GF/A 1.6 μm pore size glass micro fibre filters (SS-EN 872) in one replicate.

2.4 Data analysis

The outflow results were analysed for both concentration and removal. Removal was calculated as follows: $\text{removal} = (1 - \text{outflow concentration} / \text{inflow concentration}) \times 100\%$ with concentrations in mg/L .

For each sampling at each temperature the inflow and outflow mean concentrations and their 95% confidence intervals were plotted to give an overview over the effect of temperature and run-time. A general linear model (GLM) was used to statistically test the effect of temperature and run time on nutrient outflow concentration. Besides the temperature (2, 7, and 20 $^{\circ}\text{C}$), the sampling week (2, 4, 6, 8, 10, and 12) was added as a fixed factor and TSS concentration as covariates since it was hypothesised that these factors might influence the removal efficiency.

The $\text{NO}_x\text{-N}$ net production rate ($\text{NO}_x\text{-NPR}$) for each temperature was calculated as the difference between mean $\text{NO}_x\text{-N}$ outflow and inflow concentration (mg L^{-1}) divided by the time between two samplings (min). The data were plotted in an Arrhenius plot ($\ln \text{NO}_x\text{-NPR}$ versus $1/T$). Using the relationship derived from the Arrhenius plot, the temperature

coefficient Q_{10} was calculated $Q_{10} = \frac{\text{NO}_x \text{ NPR at } (T+10)}{\text{NO}_x \text{ NPR at } (T)} = \theta^{10}$ (Kadlec and Reddy, 2001).

The mean N:P mass ratio was calculated for the stormwater and the outflow at each temperature to determine the limiting nutrient for plant growth in the water.

The nutrient concentrations were compared to Swedish environmental quality criteria (Swedish EPA, 2000) to assess their potential impact on eutrophication of natural water bodies.

3 RESULTS AND DISCUSSION

3.1 Phosphorus and Total Suspended Solids

TP mean removal was $91.4 \pm 6.6\%$. Outflow concentrations were around 0.03 mg L^{-1} at all temperatures (Figure 1, Table 2). Thus, phosphorus removal was not significantly influenced by temperature. In contrast, phosphorus removal improved significantly with continuing run-time and was correlated significantly with TSS outflow concentrations (GLM: TP outflow concentrations vs. temperature, sampling event, TSS: $p = 0.719$ (temperature), $p = 0.000$ (sampling, TSS), $R^2(\text{adjusted}) = 88.5\%$). Even linear regression indicated some correlation between phosphorus and TSS outflow concentrations, as expected ($p = 0.000$ and $R^2(\text{adj.}) = 39.9\%$).

Whilst phosphorus in the stormwater was mainly particle-bound (Table 1), the percentage of dissolved phosphorus in the outflow was slightly higher and increased with increasing temperature (mean dissolved phosphorus at the first two sampling events: 12.7, 15.5 and 17.8% at 2, 7 and 20 °C, respectively).

Total suspended solids (TSS) were removed effectively in the biofilters with removal always exceeding 94% (Figure 1, Table 2). The TSS outflow concentrations were significantly influenced by both temperature and sampling event (GLM: TSS outflow concentrations vs. temperature, sampling event: $p = 0.000$ (temperature, sampling), $R^2(\text{adjusted}) = 57.0\%$). The outflow concentrations decreased significantly and constantly over the experimental run time

(from $4.9 \pm 1.8 \text{ mg L}^{-1}$ at the first sampling to $1.4 \pm 0.5 \text{ mg L}^{-1}$ after 12 weeks; linear regression:
 $p = 0.000$, $R^2(\text{adj.}) = 49.3\%$).

Although phosphorus in the stormwater was mainly particle-bound, it has to be regarded as potentially environmental hazardous since particulate P might cause eutrophication in the long term due to release from sediments under low-oxygen conditions (Correll, 1999). This might be of special concern during winter due to oxygen decrease under ice covers. Thus, even if particulate P is not directly bio-available its removal is of importance.

A high percentage of particle bound phosphorus is common in stormwater since phosphorus most often exists in the form of phosphate ions which have a strong affinity to particles (Berge et al., 1997; Viklander, 1999). Thus, phosphorus removal in biofilters is not as dependent on biological processes as is nitrogen removal, but rather on passive sedimentation and hence not influenced to the same degree by temperature (Kadlec and Reddy, 2001).

However, even phosphorus behaviour in soils can to some extent be influenced by temperature: with increasing temperature phosphorus concentration have been shown to decrease in soil solution, corresponding to increased sorption (Gardner and Preston Jones, 1973; Barrow and Shaw, 1975), suggesting higher plant available phosphorus in soils at low temperatures (Kadlec and Reddy, 2001). However, plant phosphorus uptake might be lower at low temperatures due to decreased plant activity (Gardner and Preston Jones, 1973). Further field studies are required to verify the lack of temperature influence on phosphorus removal observed in this study.

Similar to the results of this study, Hsieh et al. (2007a) found decreasing phosphorus and TSS outflow concentrations over time in newly established biofilters which is explained by media stabilisation, resulting in a decreasing wash out of sediments and its attached phosphorus. Even in this study phosphorus and TSS outflow concentration decrease over time, indicating a diminishing sediment wash out. Similar to these findings of Hsieh et al. (2007a), it is likely that repacking and settling of the filter media within the column might reduce pore sizes at depth which improves particulate retention. Furthermore, the potential washout of fines from newly established biofilters will most likely decrease during operation. This will consequently lead to less TSS and thus (often particle bound) TP outflow concentrations over time.

However, the statistically significant differences in TSS removal are not estimated to be of practical importance since the overall outflow concentrations are low at all temperatures (Figure 2, Table 2), with a mean reduction of $97.8 \pm 1.2\%$. The TSS outflow variations within different temperatures and events are thus negligible in practice.

No significant clogging due to TSS capture of the filter was observed. The columns were dimensioned according to current design guidelines, the stormwater volumes did not exceed those assumed in the guideline and also the TSS concentrations used were in a typical range. Given these similar surrounding conditions and the fact that biofilters commonly are designed for a lifespan of upwards of 15 years, which exceeds the experimental run time by far, it is relatively unlikely that TSS accumulation would cause significant clogging already after 12 weeks of operation, even if the hydraulic conductivity has been observed to drop relatively quickly after operation commencement (Le Coustumer, et al., 2007). However, clogging is a typical problem for biofilters and might be a major difficulty if snow melt runoff is applied which often contains relatively high TSS loads (due to sand applied as an anti-skid agent).

Thus, maintenance of cold region biofilters is of particular concern due to possible clogging problems.

Besides stormwater runoff, eroded sediments are an important non-point P source (Brady and Weil, 2002). Since biofilters reduce runoff rates (Hatt et al., 2009) they might indirectly reduce erosion lossess in urban catchments and thus further reduce P loads to waterways.

3.2 Nitrogen

Most of the TN both in the in- and outflow was in the dissolved form (93.3 ± 9.7 and $95.9 \pm 7.6\%$, respectively). Overall, the net removal of TN, DN and $\text{NO}_x\text{-N}$ in the biofilters was not effective; only $\text{NH}_4\text{-N}$ net removal was high especially at higher temperatures (Figure 1, $74 \pm 18\%$ removal at 20°C). Increasing temperature caused significantly increased TN, DN and $\text{NO}_x\text{-N}$ outflow concentrations and decreased $\text{NH}_4\text{-N}$ outflow concentrations (GLM: TN, DN, NO_x , and NH_4 outflow concentrations each vs. temperature, sampling event, TSS: $p < 0.000$ (temperature, sampling), $p > 0.050$ (TSS), $R^2(\text{adjusted}) = 91.1\%$ (TN, DN), 87.0% (NO_x), 59.5% (NH_4)). Significant TN, DN and $\text{NO}_x\text{-N}$ leaching was observed, particularly at 20°C (Table 2). However, even at 2°C $\text{NO}_x\text{-N}$ production with simultaneous $\text{NH}_4\text{-N}$ consumption was shown which indicates nitrification (Table 2).

The Arrhenius equation had a significant fit to the temperature effect on the mean $\text{NO}_x\text{-NPR}$ (Figure 2). The R^2 value for regression was 0.9994. The Q_{10} values were between 2.45 and 2.33 (Table 3).

TN leaching in biofilters due to NO_x production has been observed in other studies in which the temperature effect has not been considered (Davis et al., 2001, 2006; Hsieh et al., 2007b;

Bratieres et al., 2008; Passeport et al., 2009). In this case NO_x leaching at 20 °C is relatively high compared to the cited studies.

Key processes for nitrogen removal in biofilters are organic N-mineralization, NH_4 -fixation, microbial N-uptake, nitrification (and denitrification under anoxic conditions). The high NH_4 removal might be caused by NH_4 fixation by (negatively charged) soil particles and soil organic matter (Brady and Weil, 2002). During drying between storm events, absorbed NH_4 might be subject to (aerobic) nitrification. Furthermore, organic N ammonification and the decomposing organic matter might be additional sources increasing nitrification. Contrary to NH_4 , NO_x is very mobile in soils and thus possibly not sorbed to a great extent by biofilter media (Brady and Weil, 2002; Hsieh et al., 2007b). Thus the produced NO_x leaches during the subsequent storm event (Davis et al., 2001, 2006; Cho et al., 2009). The latter could also explain the increasing NO_x leaching over the timeframe of the experiment: the retained NH_4 in the filter media increased with every storm event and thus more nitrification source material was available over time, leading to increasing nitrification rates.

The temperature effect on nitrogen behaviour in soils has been investigated in numerous previous studies. Juang et al. (2001) showed increasing NH_4 fixation by soils with rising temperature; however, temperatures below 25 °C were not analyzed in that study. Nitrification and denitrification are biological processes whose rate is influenced by temperature, with an optimum at 20 to 35 °C, depending on the environment (Stark, 1996; Brady and Weil, 2002) and minimum nitrification temperatures of between 2 and 5.5 °C (Anderson and Purvis, 1955; Brady and Weil, 2002; Russell et al., 2002).

In this study, the lower temperatures substantially reduced nitrification rates. Little change between N inflow and outflow concentrations could be seen at 2 °C: at this temperature only parts of the NH_4 present in the filter media and the inflow are nitrified, resulting in the (comparably small) 2-fold increase of NO_x and only 18% removal of NH_4 concentrations in the outflow (Table 2). Conversely, at 20 °C enhanced nitrification occurs under nearly optimal temperature conditions; NH_4 concentrations were about 75% lower and NO_x concentrations were nearly 10-fold increased in the outflow (Table 2). Higher NH_4 outflow concentrations at cold temperatures might furthermore be caused by decreased NH_4 fixation at cold temperatures (Juang et al., 2001). Even microbial ammonium and nitrate uptake are influenced negatively by cold temperatures; however it is unclear to what extent these processes are distinct (and thus how they might nitrogen uptake in biofilters; Reay et al, 1999).

The temperature effect on nitrification in the temperature range used in this study is best described by the Arrhenius relationship (Stark, 1996) which was confirmed for stormwater biofilters by the results of this study (Figure 2). Even the temperature coefficients Q_{10} derived from the Arrhenius relationship (Table 3) are typical: Q_{10} between 2 and 3 (with decreasing Q_{10} at increasing temperature) has commonly been used to describe the temperature effect on nitrification in soils and waste water treatment wetlands (Kadlec and Reddy, 2001; Russell et al., 2002).

Due to the excellent fit of the Arrhenius relationship and the typical temperature coefficients it is assumed that the results of this study are reliable, though one has to be aware that it was conducted with only 15 biofilter columns under laboratory conditions. Given the high variation of nitrogen removal in other stormwater biofilter studies (Davis et al., 2001, , 2006;

Hsieh et al., 2007b; Bratieres et al., 2008; Passeport et al., 2009) and the significant temperature effect observed in this study, a reasonable next step would thus be to attempt to validate these results for other biofilters under field and laboratory conditions.

Bratieres et al. (2008) and Lucas and Greenway (2008) observed that vegetated stormwater biofilters remove significantly more nitrogen compared to unvegetated filters, (with NO_x removal between 96 and -630% depending on the plant species). _The rate of plant uptake and biological nitrogen fixation in the biofilters might be negatively influenced by low temperatures (Gardner and Preston Jones, 1973); Roseen et al. (2003) observed a decline in dissolved inorganic nitrogen removal in biofilters during winter which might be explained by less biological uptake. However, since in this particular study the plants did not grow well in the biofilters, it is assumed that they did not develop an extensive root system and, thus, the plants effect on nitrogen removal is probably small. Possibly, well growing plants might have had enhanced nitrogen removal.

Even if the nitrification in the filter media would consume oxygen which could cause partly anoxic conditions in deeper parts of the filter media (Hsieh and Davis, 2005), obviously denitrification in the well drained filter media used in this study would be (if at all) negligible due to the lack of such anoxic conditions. A finer filter media promoting a higher soil moisture content during the stormwater applications (Lucas and Greenway, 2008) might possibly have provided some denitrification due to partly anoxic conditions, leading to less NO_x leaching. Recently a submerged (anoxic) zone at the bottom of the filter with an embedded carbon source was tested in biofilters, and found to improve NO_x removal due to enhanced denitrification (Zinger et al., 2007; Kim et al., 2003), however without consideration of possible cold temperature effects. Given the results of this study, even the

denitrification may be precluded or eliminated, due to low temperatures. Freezing of the submerged zone might clog the filter. Further investigation of this aspect is required.

3.3 N:P ratio

The mean N:P ratio in the stormwater was 5.8. Due to the effective phosphorus removal (and partly simultaneous nitrogen leaching) the N:P ratios in the outflow were higher (63 at 2 °C, 74.7 at 7 °C, and 162.0 at 20 °C, Table 2).

The N:P ratio at which primary production limitation changes between nitrogen and phosphorus is around 15 to 30 (Correll, 1999; Swedish EPA, 2000). Thus in the stormwater inflows, nitrogen would be the limiting nutrient, since a phosphorus surplus exists. However, this changes towards phosphorus limitation in the treated outflow from the biofilters (Swedish EPA, 2000). This is important for stormwater treatment since phosphorus is commonly the limiting nutrient for eutrophication of freshwater ecosystems (Berge et al., 1997; Correll, 1999; Swedish EPA, 2000). We thus hypothesise that the high P removal will prevent eutrophication of receiving waters, despite the poor nitrogen removal.

3.4 Critical nutrient concentrations in receiving waters

It is difficult to define general acceptable nutrient concentrations in natural ecosystems or for treated stormwater. Total phosphorus concentration and the N:P ratio are more important values than the nitrogen concentration due to the common nitrogen deficiency in freshwaters (Swedish EPA, 2000). Correll (1999) considers 0.1 mg L⁻¹ total phosphorus in natural freshwaters as unacceptably high and suggests that even 0.02 mg L⁻¹ causes often problems. Brady and Weil (2002) assume that 0.1 mg L⁻¹ total phosphorus is an approximate trigger value for eutrophication. The Swedish EPA (2000) defines concentrations of below 0.0125

mg L⁻¹ TP as *low* and up to 0.025 mg L⁻¹ as *moderately high*. The stormwater phosphorus concentration in this study is clearly above these critical values and classified as *extremely high* (>0.1 mg L⁻¹) by (Swedish EPA, 2000). Due to the effective phosphorus removal the concentrations in the outflow are below the critical values (Figure 1). However, stormwater discharges will be diluted in natural ecosystems which will most often reduce the concentrations in the receiving water itself.

4 CONCLUSIONS

There is a clear need for reliable and effective stormwater treatment technologies in cold weather areas, to deal with both stormwater and snowmelt. Whilst biofilters are a promising technology, they remain to be relatively untested for their winter operation. This study thus tested the nutrient and sediment removal effectiveness of biofilters in low temperatures. Phosphorus and TSS removal was significantly correlated and not influenced by low temperature. This is important for biofilter implementation in cold weather regions since phosphorus is often the limiting nutrient in freshwater ecosystems and effective phosphorus removal from stormwater could thus prevent eutrophication. This observation is supported by the N:P ratio in the treated outflow water which suggests P-limited conditions. Unfortunately, nitrogen removal was poor, with strong leaching shown, which increased with temperature. This is most likely caused by high nitrification at warm temperatures. At low temperatures, N-related biological processes were reduced significantly, resulting in no net nitrogen leaching (although not achieving removal either). This temperature effect on the NO_x-N production was described by an Arrhenius relationship. Furthermore, the poor removal indicates that the type and / or growth of vegetation were inadequate. In cases where N removal is important, specific design modifications such as incorporation of a saturated zone with carbon source may be essential. Similarly, attention to vegetation selection may be

required, to achieve effective nitrogen removal in cold weather biofilters. The performance of such design modifications should be specifically investigated, given that biochemical processes affecting nitrogen (including denitrification) will likely be altered by temperature. This work provides the basis for a range of future studies to refine and optimise stormwater biofiltration technologies for cold weather regions.

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REFERENCES

- Anderson, O.E., Purvis, E.R., 1955. Effects of low temperatures on nitrification of ammonia in soils. *Soil Sci.* 80, 313-318.
- Barrow, N.J., Shaw, T.C., 1975. The slow reactions between soil and anions: 2. effect of time and temperature on the decrease in phosphate concentration in the soil solution. *Soil Sci.* 119, 167.
- Berge, D., Fjeld, E., Hindar, A., Kaste, O., 1997. Nitrogen retention in two Norwegian watercourses of different trophic status. *Ambio* 26, 282-288.
- Blecken, G.-T., Viklander, M., Muthanna, T.M., Zinger, Y., Deletic, A., Fletcher, T.D., 2007. The influence of temperature on nutrient treatment efficiency in stormwater biofilter systems. *Water Sci. Technol.* 56(10), 83-91.
- Blecken, G.-T., Zinger, Y., Deletic, A., Fletcher, T.D., Viklander, M., 2009. Influence of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters. *Water Res.* 43, 4590-4598.
- Brady, N.C., Weil, R.R., 2002. *The Nature and Properties of Soils*, 13th ed. Pearson Education, Upper Saddle River, NJ, USA.
- Bratieres, K., Fletcher, T.D., Deletic, A., Zinger, Y., 2008. Nutrient and sediment removal by stormwater biofilters; A large-scale design optimisation study. *Water Res.* 42, 3930-3940.
- Burns, D., Vitvar, T., McDonnell, J., Hassett, J., Duncan, J., Kendall, C., 2005. Effects of suburban development on runoff generation in the Croton River basin, New York, USA. *J. Hydrol.* 311, 266-281.
- Caraco, D., Claytor, R., 1997. *Stormwater BMP Design Supplement for Cold Climates*. Center for Watershed Protection. Ellicott City, MD, USA.
- Cho, K.W., Song, K.G., Cho, J.W., Kim, T.G., Ahn, K.H., 2009. Removal of nitrogen by a layered soil infiltration system during intermittent storm events. *Chemosphere* 76, 690-696.

482 Correll, D.L., 1999. Phosphorus: A rate limiting nutrient in surface waters. *Poultry Sci.* 78,
 483 674-682.

484 Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., 2001. Laboratory study of biological
 485 retention for urban stormwater management. *Water Environ. Res.* 73, 5-14.

486 Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., 2006. Water quality improvment
 487 through bioretention media: nitrogen and phosphorus removal. *Water Environ. Res.* 78, 284.

488 Dietz, M.E., 2007. Low impact development practices: A review of current research and
 489 recommendations for future directions. *Water Air Soil Pollut.* 186, 351-363.

490 Dillon, K.S., Chanton, J.P., 2005. Nutrient transformations between rainfall and stormwater
 491 runoff in an urbanized coastal environment: Sarasota Bay, Florida. *Limnol. Oceanogr.* 50, 62-
 492 69.

493 Eriksson, E., Baun, A., Scholes, L., Ledin, A., Ahlman, S., Revitt, M., Noutsopoulos, C.,
 494 Mikkelsen, P.S., 2007. Selected stormwater priority pollutants - A European perspective. *Sci.*
 495 *Total Environ.* 383, 41-51.

496 Gardner, B.R., Preston Jones, J., 1973. Effects of temperature on phosphate sorption
 497 isotherms and phosphate desorption. *Commun. Soil Sci. Plant Anal.* 4(2), 83-93.

498 Gilroy, K.L., McCuen, R.H., 2009. Spatio-temporal effects of low impact development
 499 practices. *J Hydrol.* 367, 228-236.

500 Hatt, B.E., Fletcher, T.D., Deletic, A., 2009. Hydrologic and pollutant removal performance
 501 of biofiltration systems at field scale. *J. Hydrol.* 365, 310-321.

502 Hsieh, C.H., Davis, A.P., 2005. Multiple-event study of bioretention for treatment of urban
 503 storm water runoff. *Water Sci. Technol.* 51(3-4), 177-181.

504 Hsieh, C.H., Davis, A.P., Needelman, B.A., 2007a. Bioretention column studies of
 505 phosphorus removal from urban stormwater runoff. *Water Environ. Res.* 79, 177-184.

506 Hsieh, C.H., Davis, A.P., Needelman, B.A., 2007b. Nitrogen removal from urban stormwater
 507 runoff through layered bioretention columns. *Water Environ. Res.* 79, 2404-2411.
 508 Juang, T.C., Wang, M.K., Chen, H.J., Tan, C.C., 2001. Ammonium fixation by surface soils
 509 and clays. *Soil Sci.* 166, 345-352.
 510 Kadlec, R.H., Reddy, K.R., 2001. Temperature effects in treatment wetlands. *Water Environ.*
 511 *Res.* 73, 543-557.
 512 Kim, H., Seagren, E.A., Davis, A.P., 2003. Engineered bioretention for removal of nitrate
 513 from stormwater runoff. *Water Environ. Res.* 75, 355-367.
 514 Marsalek, J., Oberts, G., Exall, K., Viklander, M., 2003. Review of operation of urban
 515 drainage systems in cold weather: Water quality considerations. *Water Sci. Technol.* 48(9),
 516 11-20.
 517 Melbourne Water, 2005. *WSUD Engineering Procedures: Stormwater*. CSIRO Publishing,
 518 Collingwood, VIC, Australia.
 519 Murray, A.G., Parslow, J.S., 1999. Modelling of nutrient impacts in Port Phillip Bay - A
 520 semi-enclosed marine Australia ecosystem. *Mar. Freshwater Res.* 50, 597-611.
 521 Muthanna, T.M., Viklander, M., Blecken, G.-T., Thorolfsson, S.T., 2007a. Snowmelt
 522 pollutant removal in bioretention areas. *Water Res.* 41, 4061-4072.
 523 Muthanna, T.M., Viklander, M., Gjesdahl, N., Thorolfsson, S.T., 2007b. Heavy metal
 524 removal in cold climate bioretention. *Water Air Soil Pollut.* 183, 391-402.
 525 Muthanna, T.M., Viklander, M., Thorolfsson, S.T., 2008. Seasonal climatic effects on the
 526 hydrology of a rain garden. *Hydrol. Process.* 22, 1640-1649.
 527 Oberts, G.L., 1986. Pollutants associated with sand and salt applied to roads in Minnesota.
 528 *Water Resour. Bull.* 22, 476-483.

529 Passeport, E., Hunt, W.F., Line, D.E., Smith, R.A., Brown, R.A., 2009. Field study of the
 530 ability of two grassed bioretention cells to reduce storm-water runoff pollution. *J. Irrig. Drain.*
 531 *E.-ASCE* 135, 505-510.

532 Reay, D.S., Nedwell, D.B., Priddle, J., Ellis-Evans, J.C., 1999. Temperature dependence of
 533 inorganic nitrogen uptake: reduced affinity for nitrate at suboptimal temperatures in both
 534 algae and bacteria. *Appl. Environ. Microbiol.*, 65, 2577-2584

535 Roseen, R.M., Ballesterio, T.P., Houle, J.J., Avellaneda, P., Briggs, J., Fowler, G., Wildey, R.,
 536 2009. Seasonal performance variations for storm-water management systems in cold climate
 537 conditions. *J. Environ. Eng. ASCE* 135, 128-137.

538 Roy, A. H., Wenger, S. J., Fletcher, T. D., Walsh, C. J., Ladson, A. R., Shuster, W. D.,
 539 Thurston, H.W., Brown, R.R., 2008. Impediments and solutions to sustainable, watershed-
 540 scale urban stormwater management: Lessons from Australia and the United States. *Environ.*
 541 *Manage.* 42(2), 344-359.

542 Russell, C.A., Fillery, I.R.P., Bootsma, N., McInnes, K.J., 2002. Effect of temperature and
 543 nitrogen source on nitrification in a sandy soil. *Commun. Soil Sci. Plant Anal.* 33, 1975-1989.

544 Scholz, M., 2004. Treatment of gully pot effluent containing nickel and copper with
 545 constructed wetlands in a cold climate. *J. Chem. Technol. Biot.* 79, 153-162.

546 Stark, J.M., 1996. Modeling the temperature response of nitrification. *Biogeochemistry* 35,
 547 433-445.

548 Swedish EPA, 2000. Environmental Quality Criteria - Lakes and Watercourses. Report 5050.
 549 Stockholm, Sweden.

550 Swedish EPA, 2003. Environmental Quality Guidelines for Phosphorus in lakes (in Swedish:
 551 *Miljökvalitetsnormer för fosfor - redovisning av regeringsuppdrag*). Report 5288. Stockholm,
 552 Sweden.

553 Taylor, G.D., Fletcher, T.D., Wong, T.H.F., Breen, P.F., Duncan, H.P., 2005. Nitrogen
 554 composition in urban runoff - Implications for stormwater management. *Water Res.* 39, 1982.
 555 Taylor, S.L., Roberts, S.C., Walsh, C.J., Hatt, B.E., 2004. Catchment urbanisation and
 556 increased benthic algal biomass in streams: Linking mechanisms to management. *Freshwater*
 557 *Biol.* 49, 835-851.
 558 Walsh, C.J., Roy, A.H., Feminella, J.W., Cottingham, P.D., Groffman, P.M., Morgan, R.P.,
 559 2005. The urban stream syndrome: Current knowledge and the search for a cure. *J. N. Am.*
 560 *Benthol. Soc.* 24, 706-723.
 561 Viklander, M., 1999. Dissolved and particle-bound substances in urban snow. *Water Sci.*
 562 *Technol.* 39(12), 27-32.
 563 Zhao, L.T., Gray, D.M., 1999. Estimating snowmelt infiltration into frozen soils. *Hydrol.*
 564 *Process.* 13, 1827-1842.
 565 Zinger, Y., Blecken, G.-T., Fletcher, T.D., Deletic, A., Viklander, M. (2007). Optimisation of
 566 the nitrogen retention capacity of stormwater biofiltration systems. *Proceedings of the 6th*
 567 *International Conference on Sustainable Techniques and Strategies in Urban Water*
 568 *Management NOVATECH 2007, Lyon, France.*

571 **Table 1.** Stormwater characterisation and pollutant sources

Pollutant	Mean concentration \pm SD	Source
TN	$1.80 \pm 0.29 \text{ mg L}^{-1}$	
thereof dissolved ⁽¹⁾	$93.3 \pm 9.7 \%$	
Dissolved NO _x -N	$0.40 \pm 0.16 \text{ mg L}^{-1}$	Potassium nitrate (KNO ₃)
Dissolved NH ₄ -N	$0.22 \pm 0.05 \text{ mg L}^{-1}$	Ammonium chloride (NH ₄ Cl)
Organic N	not analysed	Nicotinic acid (C ₆ H ₅ O ₂ N)
TP	$0.31 \pm 0.01 \text{ mg L}^{-1}$	Potassium dihydrogen phosphate (KH ₂ PO ₄)
thereof dissolved ⁽²⁾	$10.5 \pm 5.6 \%$	
TSS	$131 \pm 5 \text{ mg L}^{-1}$	stormwater pond sediment ($\leq 400\mu\text{m}$)
Cd	$4.2 \pm 3.3 \mu\text{g L}^{-1}$	CdCl ₂
Cu	$154.0 \pm 29.0 \mu\text{g L}^{-1}$	CuCl ₂
Pb	$41.8 \pm 4.2 \mu\text{g L}^{-1}$	PbCl ₂
Zn	$280.2 \pm 31.5 \mu\text{g L}^{-1}$	ZnCl ₂
pH (range)	6.7 to 7.0	H ₂ SO ₄
Temp	$3.2 \pm 1.0 \text{ }^\circ\text{C}$	
	$8.6 \pm 0.6 \text{ }^\circ\text{C}$	
	$18.6 \pm 1.0 \text{ }^\circ\text{C}$	

⁽¹⁾ second event not analysed

⁽²⁾ only the first two events analysed

573 **Table 2.** Mean inflow and outflow concentrations (mg/L) and metal removal (%) at the
574 different temperatures \pm standard deviation

			Outflow ⁽²⁾		
stormwater ⁽¹⁾			2°C	7°C	20°C
TN	concentration	1.80 \pm 0.29	1.89 \pm 1.51	2.24 \pm 0.64	4.86 \pm 0.98
	removal		-5 \pm 22	-23 \pm 27	-172 \pm 41
DN	concentration	1.79 \pm 0.34	1.90 \pm 0.46	2.28 \pm 0.60	4.71 \pm 0.99
	removal		-4 \pm 18	-24 \pm 25	-159 \pm 37
NO_x-N	concentration	0.40 \pm 0.16	1.14 \pm 0.40	1.57 \pm 0.52	3.76 \pm 0.87
	removal		-208 \pm 101	-320 \pm 127	-944 \pm 359
NH₄-N	concentration	0.22 \pm 0.05	0.17 \pm 0.04	0.11 \pm 0.04	0.06 \pm 0.05
	removal		18 \pm 26	51 \pm 15	74 \pm 18
TP	concentration	0.31 \pm 0.01	0.03 \pm 0.02	0.03 \pm 0.02	0.03 \pm 0.02
	removal		92 \pm 6	91 \pm 6	91 \pm 7
TN:TP ratio		5.8	63.0	74.7	162.0
TSS	concentration	131 \pm 5	2 \pm 1	3 \pm 2	3 \pm 2
	removal		98 \pm 1	98 \pm 1	98 \pm 1
pH	(range)	6.7 to 7.0	7.3 to 7.5	7.4 to 7.7	7.5 to 7.7

⁽¹⁾ three replicates per event analysed

⁽²⁾ mean value of five replicate columns and all events

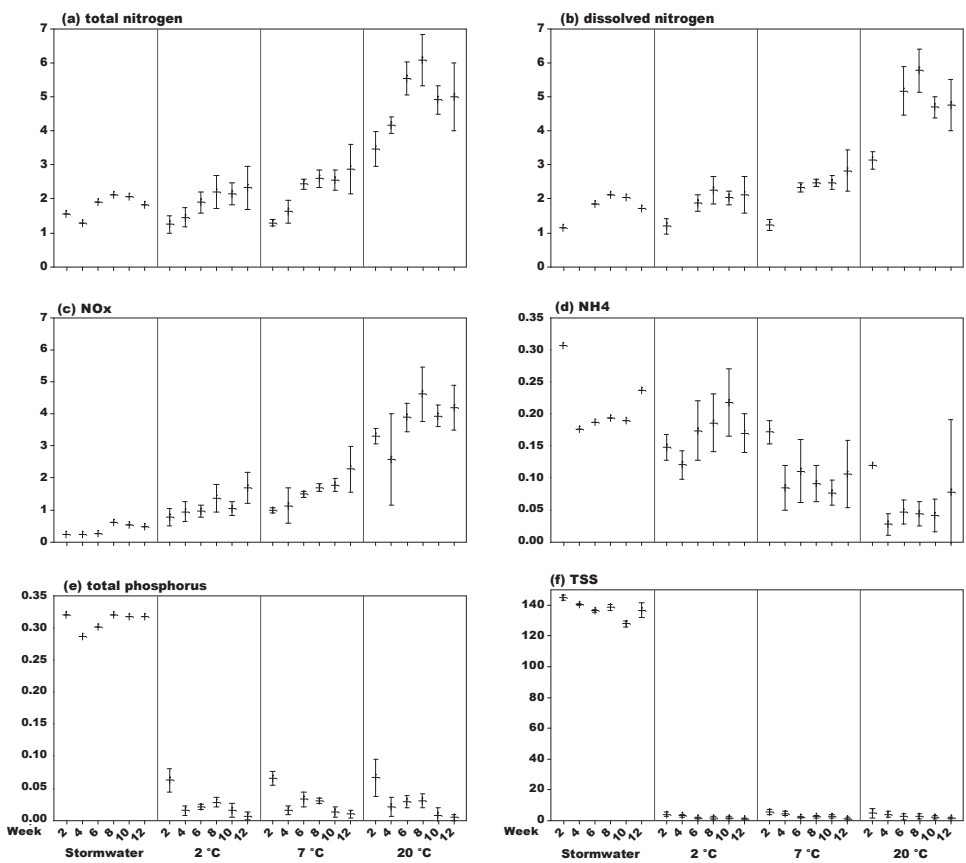
575

576 **Table 3.** Temperature coefficients derived from the Arrhenius relationship (Figure 4) for
577 different temperature steps between 2 and 20°C.

T+10 / T [°C]	Q ₁₀	θ
12 / 2	2.45	1.094
17 / 7	2.37	1.090
20 / 10	2.33	1.088

578
579

581



582

583 **Figure 1.** Interval plots of nutrient and TSS in- and outflow concentrations (mg/l) with the
584 95% confidence interval of the mean at all 6 stormwater events: (a) total nitrogen, (b) total
585 dissolved nitrogen, (c) dissolved NO_x-N, (d) dissolved NH₄-N, (e) total phosphorus, (f) TSS.
586 N.b. the different scales of the y-axis.

587

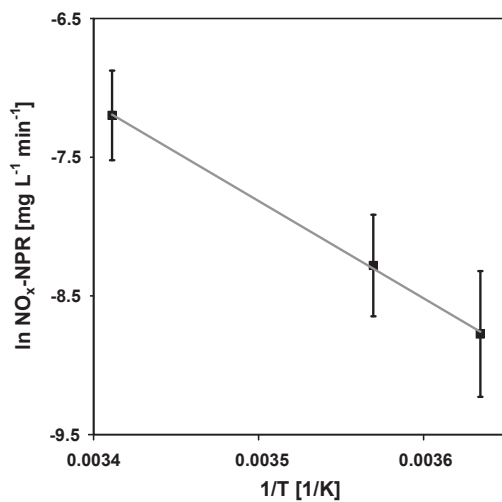
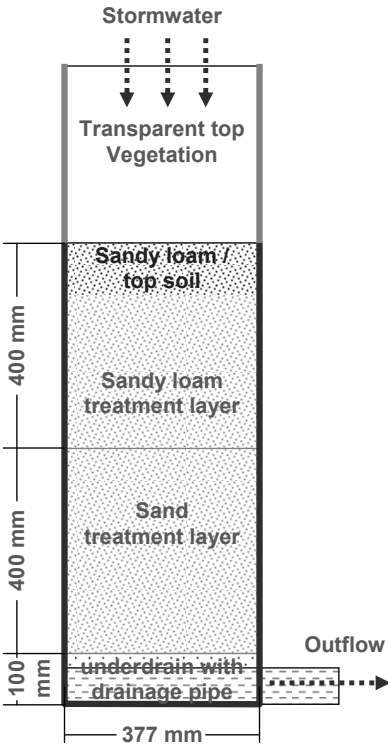
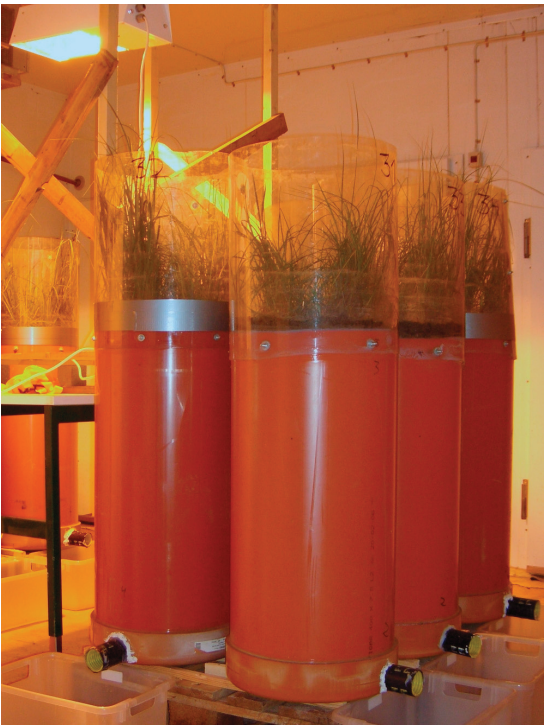


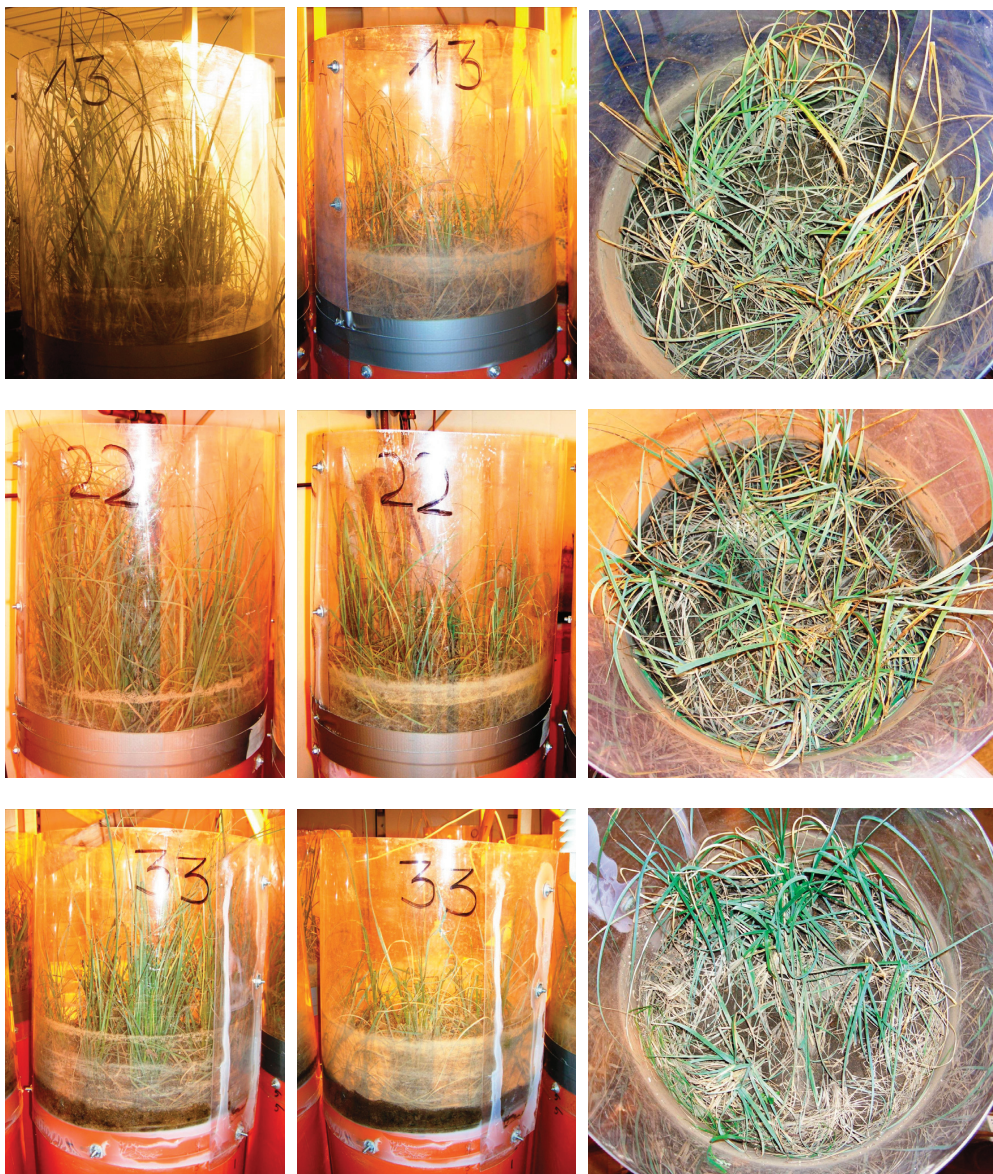
Figure 2. Arrhenius plot of NOx-N production rate versus 1/T.

SUPPLEMENTARY FIGURES



Supplementary Figure 3. Biofilter columns in climate room with greenhouse lamp.

Conceptional diagram of the biofilters.



Supplementary Figure 4. Plant development in exemplary biofilter columns in the climate rooms at 2 °C (top row), 7 °C (middle row) and 20 °C (bottom row) at the beginning of the experiment (left column) and after 10 weeks of operation (right column and top view).

Paper VI

Blecken, G.-T., Marsalek, J., Viklander, M. (submitted)

Laboratory study on stormwater biofiltration in low temperatures:
metal removal and fates

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1 **Laboratory study of stormwater biofiltration in**
2 **low temperatures: total and dissolved metal**
3 **removals and fates**

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13 **Abstract.** Stormwater biofilters, which are recommended for application in both Water Sensitive
14 Urban Design and Low Impact Development, can remove up to 80 or 90% of total metals found in
15 stormwater. However, their winter operation is a common concern. That was addressed in this
16 study by investigating the metal removal effectiveness of replicate laboratory biofilter mesocosms
17 at 2, 8 and 20°C. As recommended for cold climate bioretention, coarse filter media were
18 implemented. Cd, Cu, Pb and Zn concentrations measured in the biofilter effluent were far below
19 those in the influent and this significantly improved the treated stormwater quality. Contrary to a
20 common notion that coarse filter media impair dissolved metal sorption, satisfactory removals of
21 dissolved metals were found in this study. Most metal burdens were retained in the top layer of the
22 filter (enhanced by topsoil); some metal uptake by the plants was also detected. Temperature did
23 not affect Cd, Pb and Zn removals in general, but Cu removals increased with decreasing
24 temperatures. This was explained by increased biological activities in the filters at warmer
25 temperatures, which may have led to an increased release of Cu with dissolved organic matter
26 originating from root turnover and decomposition of organic litter and debris. Furthermore, plant
27 uptake and biofilm adsorption may also be influenced by temperature. However, even in the worst
28 case (i.e. at 20°C), Cu was removed effectively from the stormwater. Further research needs were
29 identified including the effects of road salts on stormwater biofiltration during the winter period.

30

31 **Keywords.** *Stormwater biofilter; Bioretention; Heavy metals; Low temperatures;*
32 *Water Sensitive Urban Design*

33 Introduction

34 Stormwater biofiltration (also referred to as rain garden or bioretention) is becoming
35 more and more widespread in Water Sensitive Urban Design and Low Impact
36 Development (Dietz, 2007). Stormwater infiltration into filter media leads to hydraulic
37 detention and significant peak flow reductions. In the vegetated filter media (often sandy
38 loam) stormwater is treated by mechanical, biological and chemical unit processes, and
39 its quality is further enhanced by the pollutant biouptake by the plants and biofilms
40 developing in the media and by the plant roots (Davis, et al., 2001; Davis, et al. 2003).
41 Biofilters remove a whole range of stormwater pollutants and are especially effective in
42 removing TSS (total suspended solids) and total metals, at rates often exceeding 95%
43 (Blecken, et al., 2009b; Davis, et al., 2009; Davis, et al., 2001; Dietz, 2007; Hatt, et al.,
44 2009; Muthanna, et al., 2007b). Contrary to stormwater ponds, which remove mostly
45 solids adsorbed metals by sedimentation, biofilters also remove dissolved metals
46 (Chapman & Horner, 2010; Lau, et al., 2000; Muthanna, et al., 2007a; Muthanna, et al.,
47 2007b), e.g. by sorption to the filter media or by plant uptake. This feature is ecologically
48 important, since dissolved metals are generally most bioavailable (Morrison, 1989) and
49 adversely affect aquatic life. Thus, stormwater biofilters provide multiple benefits,
50 including the control of stormwater volumes and peak flows, which would alter
51 morphology and increase flood risks in the receiving waters, and mitigation of ecological
52 deterioration of urban waters caused by stormwater pollution, and represent a promising
53 technology integrating technical solutions for stormwater quantity and quality controls
54 with creating attractive urban landscapes (Brisbane City, 2005).
55
56 However, despite the promising performance of biofilters reported so far, there are still
57 gaps in the knowledge of their performance under variable and demanding environmental
58 conditions. Since the stormwater treatment efficiency of biofilters depends on multiple
59 interacting biological, chemical and physical processes, it is uncertain how their treatment
60 performance may be affected by changing ambient conditions, e.g. due to seasonal
61 variations. In this regard, some other stormwater BMPs (best management practices) were
62 found to be less effective in removing metals during winters in a temperate climate
63 (Bäckström & Viklander, 2000). The use of stormwater biofilters in cold or temperate
64 climates with freezing temperatures may face special problems under winter conditions
65 due to temporal freezing (causing cracks in the filter media), potentially high pollutant
66 levels, de-icing salts, snowfall and snowmelt, and reduced biological activities (Marsalek,
67 et al., 2003; Westerlund & Viklander, 2006; Westerlund, et al., 2003; Viklander, 1999).
68 Although this literature indicates that also the biofilter performance could be influenced

69 by winter conditions, biofilters (as well as other BMPs) were developed in warm climates
70 and not assessed for low temperature (in this paper defined as 2 to 8°C) operation
71 (Marsalek, et al., 2003). Recently, two small-scale studies in Trondheim, Norway
72 suggested that the total removal of metals from stormwater may be satisfactory even in
73 winter conditions (Muthanna, et al., 2007a; Muthanna, et al., 2007b), thus encouraging
74 further research in regard to biofilter treatment performance in low temperatures. Such
75 research should alleviate concerns about biofilters applicability in regions with cold
76 winters (Dietz, 2007).

77

78 Concerns about biofiltration at low temperatures encompass several issues: filter
79 hydraulics, temperature effects on metal adsorption to filter media, and temperature
80 effects on biochemical processes affecting metal bio-uptake. Adequate infiltration rates
81 into, and percolation through, biofilters are fundamental for successful filter operation.
82 Water infiltration into frozen filter media is closely related to its moisture content at the
83 time of freezing, with higher infiltration rates reported for well-drained materials (Zhao &
84 Gray, 1999). Thus, cold climate biofilters need to be designed to maintain low soil
85 moisture content during storm events, in order to reduce the risk of ice formation, which
86 would reduce pore sizes and limit or even preclude water infiltration (Zhao & Gray,
87 1999). Consequently, stormwater infiltration devices operating in regions with cold
88 winters require relatively coarse filter media and an effective underdrain (Caraco &
89 Claytor, 1997; Muthanna, et al., 2008). This recommendation may cause concerns about
90 metal removal in biofilters, since metals have a strong affinity to fine materials
91 (adsorption rates ranking sand < silt < clay; Rieuwerts, et al., 1998), which may
92 contribute to a higher metal solubility in (loamy) sand soils compared to sandy loams or
93 clay soils (Bradl, 2004).

94

95 Low temperatures may have practically no influence on filtration of metals associated
96 with solid particles and the metal adsorption in the filter media (Lucan Bouche et al.
97 ,1997). However, low temperatures are likely to affect biochemical processes in filter
98 media and thus the overall metal removal. Plant and bacteria growth and activity depend
99 on temperature and vary seasonally. Even if the plant metal uptake is estimated to be just
100 around 5 to 10% of the total metal removal, it is important for achieving high removals of
101 (dissolved) metals. Varying temperatures may reduce metal plant uptake (Antoniadis &
102 Alloway, 2001; Hooda & Alloway, 1993). Furthermore, since especially Cu forms stable
103 complexes with organic matter, some biochemical processes in the filter media itself may
104 lead to changes in metal removal: varying temperatures may influence both the growth of
105 biofilms and the biological decomposition of organic matter which are both important

sinks of Cu (Martinez, et al., 2003; Rieuwerts, et al., 1998). Thus, the removal of heavy metals by biofilters may be reduced when coarse media without fine fractions are used (demonstrated for cold climate biofilters without clay in the filter media, by Muthanna, et al., 2007) and by reduced bioactivities / plant growth. Finally, dissolved metals treatment / removal appears to be particularly important during winter in the regions where applications of deicing salts contribute to increased fractions of dissolved metals in stormwater and snowmelt (Marsalek, 2003).

113

Thus, further research is needed to investigate the performance of stormwater biofilters in cold weather conditions. As a first step, this study investigates the effect of temperature variation on metal removal by laboratory stormwater biofilters with relatively coarse filter media without significant clay content. Given the importance of dissolved metal removal especially from winter runoff and the fact that the earlier biofilter studies mostly focused on total metal removals only, evaluations of dissolved metal removals should provide new knowledge for biofilter design in cold and temperate climates. Thus, the objective of this study was to determine the performance of biofilters in removal of total and dissolved metals at warm and low temperatures, and the fate of metals entering the biofilter. In this study nutrient removal was investigated as well and is presented in Blecken, et al. (2007). This work provides the basis for future studies intended to refine and optimise stormwater biofiltration technologies in cold weather regions.

126

127 **MATERIALS AND METHODS**

128 **Experimental set-up and procedures**

The biofilter experiments were conducted using 15 PVC filter columns with an inner diameter of 377 mm, an area of 0.11 m² and a height of 900 mm (Figure 1). The tops of the columns were extended with 400 mm high transparent PVC pipes to allow stormwater ponding without affecting the plants by shade. The biofilter media itself consisted of two layers, each 400 mm deep. The upper filter layer was formed by sand, with < 4% of silt (< 0.063 mm) and 14% of fine gravel (2-4 mm), D₅₀ = 620 µm, uniformity coefficient (UC) = D₆₀/D₁₀ = 6.4; the lower layer comprised fine to medium sand (D₅₀ = 280 µm, UC = 2.5). The top 100 mm filter layer was enriched by adding 20% of topsoil (a sandy loam with a high organic matter content). At the bottom the treated water was discharged to a sampling port through a drainage pipe (inner diameter: 58 mm) which was embedded in a 70 mm deep gravel (4-8 mm) drainage layer. Washout of sediment was prevented by a 30 mm transition layer (fine gravel 2-4 mm) between the filter and the underdrain. A

141 similar set-up was successfully used in earlier biofilter experiments (e.g. Blecken, et al.,
142 2009a; Blecken, et al., 2009b; Bratieres, et al., 2008). To form well-drained filter media
143 recommended for cold climate conditions (Caraco & Claytor, 1997), slightly coarser filter
144 media with a higher sand and a lower silt and clay content were chosen (the upper layer,
145 below the part with topsoil added, contained less than 4% of particles < 0.063 mm, and
146 the lower layer contained no particles < 0.075 mm), compared to the other studies. Before
147 the stormwater experiments, the filter media were saturated three times with natural water
148 from an urban bay in Luleå, Sweden, for one day each time, to flush out fines and to
149 facilitate enhanced biofilm establishment and bioactivity in the filter media.

150
151 To assess the temperature effect on the treatment efficiency, the biofilter columns were
152 placed in three thermostat-controlled climate rooms with nearly constant air temperatures
153 ($1.8 \pm 1.0^\circ\text{C}$, $7.3 \pm 0.4^\circ\text{C}$ and $20.3 \pm 1.0^\circ\text{C}$; measured by the temperature logger ebro
154 Electronic EBI 20-T at 7.3°C and EBI 2T-112 at 1.8°C and 20.3°C). At each temperature
155 (in the following referred to as 2, 8 and 20°C), five replicate columns were tested.

156
157 Each filter was planted with 8 plant of *Carex rostrata* Stokes (Bottle sedge), which were
158 grown for 5 weeks outside of the laboratory to develop a substantial root system before
159 being transplanted into the filter media. The plants were then grown for two more months
160 in the filter columns and during that time irrigated with tap water. To enable plant growth
161 in the climate rooms, the rooms were lit with high pressure sodium greenhouse lamps (G-
162 power Agro, 400 W, 55 000 Lm) for 12 h daily.

163
164 To ensure a constant quality of water applied to the biofilters during the experiments,
165 synthetic stormwater was used and prepared prior to each experimental run by adding
166 stormwater gully-pot sediment and laboratory-grade chemicals to tap water in the
167 amounts needed to achieve the target pollutant concentrations listed in Table 1. To
168 Nutrients were added as well (Blecken, et al., 2007). The synthetic stormwater of desired
169 temperatures was prepared by storing tap water in the respective climate room for at least
170 24 h before dosing, and then adding the stormwater pollutants. Consequently, the
171 synthetic stormwater had to be prepared separately for each climate room, but as
172 intended, there were no significant differences among the three stormwater mixtures, with
173 respect to TSS and metal concentrations, and pH (One-way ANOVA, $\alpha = 0.05$).

174
175 While Cu and Pb in the synthetic stormwater were mostly particle bound (85% and 98 %,
176 respectively), Cd and Zn were to a large extend dissolved (only about 25% particle bound
177 for both metals). The stormwater quality was kept relatively constant during the

178 experimental program, as documented by standard deviation values (n=15) listed in Table
179 1.

180

181 During experimental runs, each column was dosed with 15 L of stormwater (i.e.
182 corresponding to a 136 mm hydraulic head) twice weekly over 10 weeks, for a total of
183 300 L of stormwater (2727 mm) per column over the program duration. The dose volume
184 of 15 L was based on the assumption of a biofilter area occupying approximately 4% of
185 the catchment area with 85% imperviousness (i.e. one column of 0.11 m² for 2.75 m² of
186 the contributing catchment area) and the typical rainfall depth and pattern in Luleå,
187 northern Sweden (for details see Blecken et al., 2007).

188

189 **Sampling**

190 **Water sampling.** To control the synthetic stormwater quality and consistency, before
191 each run, one 0.5 L composite sample made up of 5 sub-samples was collected for each
192 temperature series.

193

194 The effluent from biofilters was collected in PE-containers to accumulate at least 12 L
195 during each run; the collected water was stirred and a 0.5 L effluent sample was collected
196 separately for each of five columns, yielding five samples for each temperature and the
197 experimental run. All equipment which was in contact with influent or effluent
198 stormwater was acid washed before each use.

199

200 During the 10 weeks of operation, 5 sampling runs (i.e. two weeks per run) were
201 conducted and labelled A to E.

202

203 **Filter media sampling.** Before starting the experiment, initial grab samples of the filter
204 media were collected. To compare the final metal concentrations in the filter media with
205 the initial ones, after completion of the stormwater application, soil samples were
206 extracted from all the biofilter columns at three different media depths: a top layer (0-50
207 mm), and at 250 and 600 mm. The top soil sample was collected manually as a grab
208 sample; the other two samples were collected by extracting horizontal cores (35 mm
209 diameter) from the filter media. The metal concentrations in the filter media were
210 analysed only for the columns used in experiments at 2 and 20°C.

211

212 **Plant sampling.** Prior to the experiments, root and shoot samples of several randomly
213 selected plants were collected to investigate the initial metal concentration in the plant

214 tissue. After the experiments were completed, from each column, a composite shoot and
215 root sample was collected and analysed for metal concentrations.
216
217 The final filter media and plant samples were collected after 12 weeks of stormwater
218 applications (i.e. in total 360 L, or 3270 mm). However, for the water analyses only the
219 first 10 weeks were included since an error occurred during water sampling during the
220 last event.
221

222 **Sample analyses**

223 The water samples were analysed for total and dissolved Cd, Cu, Pb and Zn using ICP-
224 AES (total Cu and Zn) and ICP-SFMS (total Cd and Pb, all dissolved metals) methods.
225 The detection limits for total metals were 0.05, 1.0, 0.6 and 4.0 $\mu\text{g L}^{-1}$, for Cd, Cu, Pb and
226 Zn, respectively, and for dissolved metals, 0.002, 0.1, 0.01, and 0.2 $\mu\text{g L}^{-1}$, for Cd, Cu,
227 Pb, and Zn, respectively. The dissolved metals concentrations were determined by
228 analyzing samples filtered through a 0.45 μm filter.
229

230 The leachable fraction of metals in the filter media was determined by sample leaching
231 according to the Swedish Standard Method 028183; the filter media samples were dried
232 at 50°C and leached in closed Teflon vessels using nitric acid/hydrogen peroxide.
233 Concentrations were corrected to dry substance mass at 105°C. Detection limits were
234 0.01, 0.3, 0.1 and 1.0 mg kg^{-1} of dry matter for Cd, Cu, Pb and Zn, respectively.
235

236 Prior to the analysis of the plant tissue samples, carbon, hydrogen and oxygen compounds
237 were eliminated by oxidation to carbon dioxide and water. Digestion was carried out with
238 nitric acid/hydrogen peroxide in sealed teflon containers in a microwave system, which
239 prevented the loss of volatile components. Samples were centrifuged before analysis. The
240 metal concentrations were expressed per dry sample content (mg kg^{-1} DS). Thus, the dry
241 matter content was determined separately at 105°C and the concentrations were
242 recalculated to dry weight. The detection limits were 0.005, 0.1, 0.004, and 0.2 mg kg^{-1}
243 DS for Cd, Cu, Pb and Zn, respectively.
244

245 All plant tissue samples were analysed according to the Swedish methods SS-EN
246 ISO/IEC 17025 by a SWEDAC (www.swedac.se) accredited laboratory applying its own
247 quality assurance / quality control procedures.
248

249 **Data analyses**

250 The majority of the total Cd and Zn effluent concentrations were below the detection
251 limits; i.e., in 58 and 50 cases out of 75 samples, respectively. For simplicity, those
252 values were set equal to the detection limit, recognizing that this conservative assumption
253 may have underestimated the Cd and Zn removals by less than 1.5%.

254

255 To detect possible differences in the metal influent and effluent concentrations at
256 different temperatures, a one-way ANOVA was performed with the metal concentration
257 as the response and temperature as the predictor. Since the effluent concentrations for at
258 least some metals were partly diverging for different sampling runs and the overlapping
259 effects of the repeated measurements should be avoided, the statistical test was conducted
260 separately for each experiment comprising five replicates (A to E). To detect a possible
261 influence of the varying influent concentrations on the effluent concentration, a linear
262 regression was performed.

263

264 The two-sample t-test was used to detect possible differences between the filter media
265 metal concentrations in different layers, after the completion of stormwater applications,
266 at temperatures 2 and 20°C. The metal concentrations in the filter material before and
267 after the stormwater applications were plotted to detect the metal ingress into the filter
268 media. To detect a possible influence of temperature on metal concentrations in plant
269 tissue resulting from stormwater treatment, a one-way ANOVA was performed for both
270 root and shoot tissue concentrations.

271

272 Based on the water influent and effluent volumes and the pollutant concentrations, a
273 mean mass balance was prepared for one column. Using the influent and effluent
274 pollutant masses, pollutant mass removal in the filter was calculated.

275

276 For all statistical analyses, $\alpha=0.05$ was chosen.

277

278

279 **RESULTS**

280 **Stormwater effluent concentrations and observed treatment**

281 The mean metal effluent concentrations and removal rates are presented in Table 2. The
282 effluent metal concentrations are clearly lower than those in the influent. Small variations
283 in influent concentrations during different sampling runs did not affect the effluent

284 concentrations significantly in most cases (linear regression influent vs. effluent
285 concentrations, $\alpha=0.05$). During the first sampling run, somewhat high metal effluent
286 concentrations were measured, compared to the subsequent runs; for runs B to E, no
287 differences between the single runs were detected (Figure 2). The total Cd and Zn effluent
288 concentrations were below the detection limits in 58 (Cd) and 50 (Zn) cases out of 75
289 samples in total.

290
291 The influent pH was 7.0 during the first sampling run and varied between 6.7 and 6.8
292 during the five subsequent runs. The effluent pH at all runs was slightly higher, ranging
293 from 7.3 to 7.6, without any dependence on the temperature.

294
295 The runs with statistically significant differences between the effluent concentrations at
296 various temperatures are shaded in Figure 2 (based on a one-way ANOVA, $\alpha=0.05$; for
297 Cd no statistical analyses were performed for the runs B to E since most effluent
298 concentrations were below the detection limit). Overall, the metal effluent concentrations
299 were relatively unaffected by the different temperatures and indicated good to excellent
300 metal removals in most cases and for all the temperatures tested. Only total and dissolved
301 Cu effluent concentrations in all sampling runs were affected by the temperature; higher
302 temperatures caused increasing effluent concentrations. Thus, at 20°C the dissolved Cu
303 effluent concentrations were about twice as large as those corresponding to 2°C, which in
304 turn contributed to the temperature effect on total Cu effluent concentrations. The particle
305 bound Cu concentrations in the effluent (calculated as difference between total and
306 dissolved Cu) were nearly constant at all the temperatures (mean: 3.2 $\mu\text{g L}^{-1}$ at 2°C, 3.6
307 $\mu\text{g L}^{-1}$ at 8°C and 2.5 $\mu\text{g L}^{-1}$ at 20°C). Consequently, the percentage of dissolved Cu in
308 the effluent increased with rising temperatures from 70 to 85%, which is a much higher
309 value than in the influent (14%).

310
311 In general, the total metal removals were excellent (Figure 2, Table 2). Total Cu removal
312 was > 89% and Cd, Pb and Zn removals were > 95%. Even 99% of the dissolved Cd and
313 Zn loads in the stormwater were removed by the biofilter. In contrast, dissolved Cu
314 removal (24 - 66%) and Pb removal (46 - 55%) was less efficient. Leaching was detected
315 in a very few cases (3 Cu and 2 Pb samples, out of 75 dissolved metal samples in total).
316 But since Cu and Pb in the stormwater were almost exclusively particle bound, the poor
317 removal of the dissolved fraction did not impair the total removal. Nevertheless, this
318 caused elevated fractions of dissolved Cu and Pb in the effluent compared to the influent
319 (Table 2). The increasing dissolved effluent concentrations with rising temperatures were
320 clearly reflected in the removal rates: while the mean dissolved Cu removal at 2°C was

321 64% it decreased to 24% at 20°C which in turn caused a smaller total Cu removal at this
322 temperature (Table 2).

324 **Metal concentrations in the filter media**

325 The total metal concentrations in the filter media were clearly elevated after the
326 experiments, only Pb from the top layer leached slightly (Figure 3). Especially in the top
327 layer with the added top soil a high increase in metal concentrations was observed. Thus,
328 the majority of metals did not ingress deep into the filter. No significant differences could
329 be detected in any filter media layer due to varying temperatures (2-sample t-test, $\alpha=0.5$).

331 **Metal concentrations in plants**

332 Both roots and shoots tissues showed increased metal concentrations after stormwater
333 application; only the Pb concentration in the roots was below the initial value after the
334 experiments (Table 3).

335
336 Even if there is a trend of decreasing metal concentrations in the shoots with increasing
337 temperature, no statistically significant temperature effect could be detected. For Cu, Pb
338 and Zn the metal concentrations in the roots increased with increasing temperatures;
339 however, only for Cu such increases were statistically significant. Even though
340 statistically significant differences in Cd concentrations in the root tissue were noted, no
341 trend was detected, with the highest concentration at 8°C and no difference between 2
342 and 20°C.

344 **Metal mass balance**

345 The results of the pollutant mass balance are presented in Table 4. During the 10 weeks of
346 runs included in the water analyses, a total of 300 L stormwater was applied to each
347 column and 279 L (98%) were collected in the effluent. The remainder was either
348 retained in the column or evapotranspired. The volume of the effluent from different
349 columns was not correlated with the temperature.

350
351 The total pollutant mass removal was very efficient and exceeded 93% for total metals
352 and TSS. Even the removals of dissolved Cd and Zn were in the same range, while
353 removals of dissolved Cu and Pb were less effective (correlating with the worse water
354 treatment efficiency).

355

356 The water mass balance could not be completed by including the soil and plant tissue
357 metal burdens, since those were taken after two more weeks of stormwater applications
358 (i.e., 12 weeks) which were not included in the water analyses.

359

360

361 **DISCUSSION**

362 A comparison of metal concentrations in the synthetic stormwater to the Swedish water
363 quality criteria (Swedish EPA, 2000) shows that the stormwater contamination used in
364 the experiments was far in excess of the limit value for “very high concentrations” of Cd,
365 Cu and Pb, and close to the upper limit of “high concentrations” for Zn. Highly effective
366 treatment in the biofilters contributed to Zn and Cd effluent concentrations meeting the
367 water quality guidelines and being classified as very low (Zn) or low (Cd). The total Pb
368 effluent concentration was in the range of moderately-high concentrations. However,
369 since more than 90% of Pb were particle bound, the dissolved (bioavailable) fraction
370 would be classified as very low. For Cu, the temperature effect on the biofilter treatment
371 made a difference; at lower temperatures the dissolved effluent concentrations were
372 “moderately high”, but “high” at 20°C. However, even if all effluent concentrations do
373 not meet the low pollution levels, the effect of the biofilter treatment is much better than
374 the current practice often consisting in discharging stormwater without any treatment at
375 all. Furthermore, it has to be taken into account that the guideline values refer to the
376 receiving water body as a whole. Since mixing and dilution of the effluent will occur in
377 the receiving waters, it is likely that outside the mixing zone, the receiving waters will
378 comply with the requirements of a higher water quality category.

379

380 The highly efficient removal of total heavy metals observed in this study agrees with
381 findings from other biofilter studies, as summarised in a literature review by Davis et al.
382 (2009). Excellent metal removals at all temperatures indicate good performance of
383 biofilters throughout the whole year, even when low temperatures are to be expected.
384 Provided that favourable hydraulic conditions and a sufficient percolation capacity is
385 ensured, biofilters perform well in low temperatures while other BMPs might be less
386 effective during such periods (Bäckström & Viklander, 2000).

387

388 The metal removal in the biofilter largely depends on the metal partitioning between the
389 solid and dissolved phases in the stormwater to be treated and is affected by the capacity
390 of the filter media to retain the incoming metals. While incoming particle bound metals

391 might be filtered mechanically together with the associated particles (Davis, et al., 2009),
392 the removal of the incoming dissolved metals is mainly related to cation exchange,
393 specific adsorption, precipitation and complexation by the filter media (Rieuwerts, et al.,
394 1998). Plant biouptake of dissolved metals also contributes to the overall removal, but to
395 a lesser degree than the filter media uptake (Davis, et al., 2001).

396

397 In the biofilter columns, effective mechanical filtration of fine particles and particle
398 bound metals took place and a clearly visible layer of stormwater sediment formed on the
399 top of the biofilter. However, the hydraulic conductivity of biofilters decreases relatively
400 quickly with clogging as a possible result of this layer of fine sediment on top of the filter
401 (Le Coustumer, et al., 2007). Since in regions with cold winters sediment concentrations
402 in winter runoff are often elevated due to the use of sand to enhance traction (Westerlund
403 & Viklander, 2006), the maintenance of the filter and especially the scraping of the top
404 layer is needed for maintaining an adequate hydraulic conductivity. Water saturated
405 conditions in the trapped sediment layer and concurrent freezing may greatly reduce the
406 infiltration capacity of the filter (Zhao & Gray, 1999).

407

408 The primary factor controlling the dissolved metal sorption processes and thus metal
409 dissolution and soil-surface chemistry is pH (Bradl, 2004; Rieuwerts, et al., 1998). Metal
410 solubility has the tendency to increase at lower pH and vice versa. The pH in this study of
411 around 6.8 (influent) and 7.5 (effluent) is in the range of optimal sorption of the metals of
412 concern and thus metal sorption in the filter media is likely to be very effective (Bradl,
413 2004; Davis, et al., 2001; Rieuwerts, et al., 1998). It is difficult to determine the exact
414 mechanisms leading to less efficient removals of dissolved Pb and Cu on the basis of the
415 collected data. One argument explaining differences in biofilter removals of various
416 metals could be based on the facts that specific adsorption follows some order of
417 precedence, reported as $Cd < Zn < Cu < Pb$ (Rieuwerts, et al., 1998), and this order agrees
418 with the removal efficiencies of the investigated biofilters. Metal adsorption to soils is
419 relatively unaffected by temperature (Lucan Bouche, et al., 1997; Rieuwerts, et al., 1998),
420 and that was generally confirmed in this study as well.

421

422 In contrast to other cold climate biofilters showing a net production of dissolved Zn, Cu
423 and Cd (Muthanna, et al., 2007a; Muthanna, et al., 2007b), the coarse filter media with
424 only marginal contents of, or without, silt and clay did not compromise the dissolved
425 metal removal in the biofilter columns. Efficient sorption of dissolved metals was noted,
426 since most dissolved metals were retained in the top layer with the added topsoil. This
427 arrangement is recommended for biofilters adapted to cold climates and comprises a

428 relatively thin layer with added topsoil or mulch (promoting a sufficient sorption
429 capacity), which is underlain by coarse filter media providing sufficient water percolation
430 even at (air) temperatures below 0°C. The aim of such a design is to find a balance
431 between a relatively high hydraulic capacity and sufficient removal of stormwater metals.
432 However, this study provides only a basis for developing such design recommendations
433 and further laboratory and field tests are required to develop and optimize the biofilter
434 design for cold climates.

435

436 In the soil chemistry, and especially with reference to Cu, complexation with organic
437 matter is of special importance, since Cu has the strongest affinity to organic matter
438 (Ponizovsky, et al., 2006; Yin, et al., 2002). Since Cu forms stable complexes with both
439 solid and dissolved organic matter (DOM), the ratio of these two components is of
440 importance for Cu removal in biofilters. While solid Cu-organic matter complexes
441 improve the removal of Cu, DOM mobilises Cu by forming Cu-DOM complexes
442 (Rieuwerts, et al., 1998; Temminghoff, et al., 1997). In the top 100 mm of the filter
443 media, solid organic matter was available due to the addition of humus into the sandy
444 loam filter material leading to a high Cu sorption in that layer. Furthermore, especially in
445 the root zone biofilms probably developed and would have a capacity to sorb significant
446 amounts of metals, depending on the metals affinity to organic matter (Warren & Haack,
447 2001). Below the top layer, no organic matter was added to the filter media. It has
448 previously been shown that the addition of solid organic matter (in the form of wood
449 chips and straw embedded in the filter media) increases Cu removal significantly
450 (Blecken, et al., 2009a). Hatt et al. (2007) have shown dissolved Cu leaching from sand
451 filters rich in organic matter, because of leaching of DOM.

452

453 Cu-organic matter complexation may also partly explain the temperature influence on Cu
454 removal. Martinez, et al. (2003) observed that increases in DOC (dissolved organic
455 carbon) and soluble metals correlated well with the increasing temperature in metal-
456 contaminated soils. Similarly, in stormwater biofilters, at 20°C higher biological activities
457 and thus a higher turnover and decomposition of organic matter (e.g. plant roots, bacteria)
458 take place and may lead to a subsequent flushing of DOM in the effluent. In low
459 temperatures, this phenomenon seems to be less pronounced. Complexed with DOM,
460 higher amounts of Cu will be present in the effluent from the columns at warmer
461 temperatures. Even Cu sorption by biofilms (Warren & Haack, 2001) in the root zone
462 may depend on temperature variations.

463

464 The observed dependency of dissolved Cu removal in biofilters on temperatures
465 corroborates the results of Muthanna, et al. (2007b) who reported higher leaching of
466 dissolved Cu from biofilters exposed to the local climatic conditions during August
467 (warmer temperature), when compared to April (lower temperature).
468

469 Besides Cu, Pb also has a relatively strong affinity to organic matter, which in turn may
470 mobilise Pb if organic matter is in the dissolved form (Bradl, 2004). This may explain
471 why the dissolved Pb effluent concentrations were at least partly influenced by the
472 temperature. Similar processes as for Cu might take place, although they are weaker.
473

474 In cold regions, the increased salinity of winter runoff or acidic melt water in late winter /
475 early spring (acidic shock) can increase the solubility of metals (Goodison, et al., 1986;
476 Warren & Zimmermann, 1994). These phenomena may release metals, adsorbed to the
477 filter media or bound to trapped stormwater sediment, from biofilters. Further research of
478 this issue is thus recommended to ensure reliable winter operation of stormwater
479 biofilters.
480

481 The importance of the upper biofilter layer (partly containing mulch) for mechanical and
482 chemical metal removals has been shown before (e.g. Blecken, et al., 2009b; Davis, et al.,
483 2001; Muthanna, et al., 2007a). Thus, the high metal removal in the top layer indicates
484 that the biofilters in the study at hand produced reliable results and that the metals do not
485 ingress deeply into the filter, e.g. due to preferential flow. The results show that the
486 mechanical filtration of particle bound metals works even in low temperatures. However,
487 when biofilters are exposed to freezing, cracks may occur and lead to metal penetration
488 into deeper filter layers, because of preferential flow. Furthermore, in the top layer, metal
489 sorption onto soils and organic matter is particularly relevant; the latter especially for Cu
490 because of the relatively high organic matter fraction achieved by adding top soil rich in
491 organic material to the top 10 cm of the filter column (see below).
492

493 The metal concentrations in the filter media do not exceed Swedish guideline values for
494 sensitive land use (Swedish EPA, 2009). However, these values might be exceeded after
495 longer biofilter operation (depending on the relative biofilter area and the stormwater
496 characteristics) and the material removed from the filter surface may require landfilling or
497 remediation (Anderson, et al. 1998).
498

499 The high metal accumulation in the top filter layer facilitates easy maintenance, because a
500 high portion of the accumulated metals can be removed from the filter by scraping the top

layer. Furthermore, smaller filter depths of 400 to 500 mm may be adequate for removal of metals from stormwater, rather than the commonly recommended deep filters with the depths of media from 800 to 900 mm (Melbourne Water, 2005). However, even the less deep filter has to provide enough space for the root growth.

The metal concentration in plant tissue (both shoots and roots) is significantly (two to three times) higher than in the filter media (see Figure 3). However, the total amount of accumulated metals in the filter media is much higher due to the higher filter media mass compared to the plant mass. Unfortunately, it was not possible to estimate the total plant dry mass in the filters and thus a detailed mass balance could not be conducted. Nevertheless, the comparison of the metal masses in plant shoots and roots and the filter media allows an overview of the metal fate: it follows from other biofilter studies that the filter media account for the main share of the removal, even if the concentration in plants is higher (Blecken, et al., 2009b; Davis, et al., 2001; Davis, et al., 2003; Muthanna, et al., 2007a; Muthanna, et al., 2007b).

It was noted that the plant uptake of metals depended on temperature; Cd, Pb and Zn plant uptakes were significantly higher at 25°C than at 15°C (Antoniadis & Alloway, 2001; Hooda & Alloway, 1993), partly due to increased root activity which enhances metal bioavailability (Rieuwerts, et al., 1998). In this biofilter study, the temperature dependence was confirmed for the metal concentrations in root tissue, which tended to be higher in plants exposed to higher temperatures. Even though there was a metal uptake by the plant shoot tissue as well (i.e. metal concentrations increased after stormwater applications), at higher temperatures, metal concentrations in shoot tissue were lower than at lower temperatures, which was somewhat unexpected. This may be related to a faster growth at warmer temperatures. However, in both cases the temperature dependence was not statistically significant. Longer operation of the biofilters should produce more definitive results.

Generally, it is assumed that only a smaller part of the metal burden removed by the biofilter ends up in plants; Davis, et al. (2001), Muthanna, et al. (2007a) and Sun & Davis (2007) calculated this fraction as 5 to 10%. Thus, the role of the plants in metal treatment should not be overestimated. In this study, in spite of the relatively short duration of biofilter operation, at all temperatures, significantly higher metal concentrations were found in plant tissues after stormwater applications, which confirms the beneficial influence of plants on metal removals by biofilters over a wide range of temperatures covering a large part of seasonal cycles in temperate and cold climates. Furthermore,

538 vegetation enhances the overall performance of the biofilter system in terms of
539 maintaining hydraulic conductivity and providing nutrient removal (Read, et al., 2008).
540 Thus, the role of biofilter plants during low temperatures should be further investigated.

541

542

543 **CONCLUSIONS**

544 Stormwater biofilters were found effective in removing metals from stormwater. Since
545 the most relevant processes facilitating metal removals are mostly temperature
546 independent, the stormwater biofilters tested were found to provide reliable stormwater or
547 snowmelt treatment with respect to metal removals over a wide range of temperatures (2-
548 20°C) . Thus, these biofilters are effective even at low temperatures, particularly in
549 removal of particle-bound pollutants. Concerns that coarse filter media without
550 significant clay content, adopted for cold climate conditions, may impair metal adsorption
551 were not confirmed, but large adsorption capacity was provided by the top layer
552 comprising sand with 20% of topsoil. Some biochemical processes, such as plant growth
553 or decomposition of vegetative biomass (contributing to release of dissolved organic
554 matter), are temperature dependent, but this did not deteriorate the overall metal removal
555 at any temperature. The importance of organic matter in filter media for Cu removal by
556 biofilters has to be further investigated, since in the long term, washout of decomposed
557 organic matter from the filter would increase effluent Cu concentrations after some time.

558

559 The findings of this study are not only important for biofilter applications in cold
560 climates, but also for biofilter operations in a temperate climate with a cold season, when
561 temperatures drop to the levels investigated in this study (2 - 20°C).

562

563 This study gives a first indication of the feasibility of stormwater treatment by biofilters
564 in cold weather conditions and the findings are subject to limitations imposed by the
565 nature of laboratory experiments. To obtain more robust knowledge of stormwater
566 treatment, including metal removals by biofilters in winter conditions, further research is
567 needed concerning the effects of de-icing salts or acidic shocks on pollutant removal, the
568 risk of release of metals accumulated in filter media, the selection of the most suitable
569 plant species, infiltration into frozen biofilters, and maintenance requirements.

570

571

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578 REFERENCES

- 579 Anderson, B. C., Brown, A. T. F., Watt, W. E., & Marsalek, J. (1998). Biological leaching of trace
 580 metals from stormwater sediment. *Water Sci. Technol.* 38 (10), 73-81.
- 581 Antoniadis, V., & Alloway, B. J. (2001). Availability of Cd, Ni and Zn to ryegrass in sewage
 582 sludge-treated soils at different temperatures. *Water Air Soil Pollut.*, 132(3-4), 201-214.
- 583 Bäckström, M.; & Viklander, M. (2000). Integrated stormwater management in cold climates. *J.*
 584 *Environ. Sci. Health. Part A Toxic/Hazard. Subst. Environ. Eng.*, 35(8), 1237-1249.
- 585 Blecken, G. T., Viklander, M., Muthanna, T. M., Zinger, Y., Deletic, A., & Fletcher, T. D. (2007).
 586 The influence of temperature on nutrient treatment efficiency in stormwater biofilter
 587 systems. *Water Sci. Technol.*, 56(10), 83-91.
- 588 Blecken, G. T., Zinger, Y., Deletic, A., Fletcher, T. D., & Viklander, M. (2009a). Impact of a
 589 submerged zone and a carbon source on heavy metal removal in stormwater biofilters.
 590 *Ecol. Eng.*, 35(5), 769-778.
- 591 Blecken, G. T., Zinger, Y., Deletic, A., Fletcher, T. D., & Viklander, M. (2009b). Influence of
 592 intermittent wetting and drying conditions on heavy metal removal by stormwater
 593 biofilters. *Water Res.*, 43(18), 4590-4598.
- 594 Blecken, G. T., Zinger, Y., Deletic, A., Fletcher, T. D., & Viklander, M. (2010). Effect of
 595 retrofitting a saturated zone on the performance of biofiltration for heavy metal removal -
 596 preliminary results of a laboratory study. *Proceedings of NOVATECH*, Lyon, France,
 597 2010.
- 598 Bradl, H. B. (2004). Adsorption of heavy metal ions on soil and soil constituents. *J. Colloid*
 599 *Interface Sci.*, 277, 1-18.
- 600 Bratieres, K., Fletcher, T. D., Deletic, A., & Zinger, Y. (2008). Nutrient and sediment removal by
 601 stormwater biofilters; a large-scale design optimisation study. *Water Res.*, 42(14), 3930-
 602 3940.
- 603 Brisbane City. (2005). *Water Sensitive Urban Design Engineering Guidelines: Stormwater*. Water
 604 Resources, Urban Management Division, Brisbane City, QLD, Australia.
- 605 Caraco, D., & Claytor, R. (1997). *Stormwater BMP Design Supplement for Cold Climates*. Center
 606 for Watershed Protection, Ellicott City, MD, USA.
- 607 Chapman, C., & Horner, R. R. (2010). Performance Assessment of a Street-Drainage Bioretention
 608 System. *Water Environ. Res.*, 82(2), 109-119.
- 609 Davis, A. P., Hunt, W. F., Traver, R. G., & Clar, M. (2009). Bioretention Technology: Overview
 610 of Current Practice and Future Needs. *J. Environ. Eng.-ASCE*, 135(3), 109-117.
- 611 Davis, A. P., Shokouhian, M., Sharma, H., & Minami, C. (2001). Laboratory Study of Biological
 612 Retention for Urban Stormwater Management. *Water Environ. Res.*, 73(1), 5-14.
- 613 Davis, A. P., Shokouhian, M., Sharma, H., Minami, C., & Winogradoff, D. (2003b). Water quality
 614 improvement through bioretention: Lead, copper, and zinc removal. *Water Environ. Res.*,
 615 75(1), 73.
- 616 Dietz, M. E. (2007). Low Impact Development Practices: A Review of Current Research and
 617 Recommendations for Future Directions. *Water Air Soil Pollut.*, 186, 351-363.
- 618 Goodison, B. E., Louie, P. Y. T., & Metcalfe, J. R. (1986). Snowmelt acidic shock study in South
 619 Central Ontario. *Water Air Soil Pollut.*, 31(1-2), 131-138.
- 620 Hatt, B. E., Deletic, A., & Fletcher, T. D. (2007). Stormwater reuse: designing biofiltration
 621 systems for reliable treatment. *Water Sci. Technol.*, 55(4), 201-209.
- 622 Hatt, B. E., Fletcher, T. D., & Deletic, A. (2009). Hydrologic and Pollutant Removal Performance
 623 of Biofiltration Systems at Field Scale. *J. Hyrol.*, 365(3-4), 310-321.

624 Hooda, P. S., & Alloway, B. J. (1993). Effects of time and temperature on the bioavailability of Cd
625 and Pb from sewage sludge-amended soils. *J. Soil Sci.*, 44(1), 97-110.

626 Lau, Y. L., Marsalek, J., & Rochfort, Q. (2000). Use of a Biofilter for Treatment of Heavy Metals
627 in Highway Runoff. *Water Qual. Res. J. Canada*, 35(3), 563-580.

628 Le Coustumer, S., Fletcher, T. D., Deletic, A., & Barraud, S. (2007). Hydraulic performance of
629 biofilters for stormwater management: first lessons from both laboratory and field studies.
630 *Water Sci. Technol.*, 56(10), 93-100.

631 Lucan Bouche, M. L., Habets, F., Biagianti Risbourg, S., & Vernet, G. (1997). The simultaneous
632 influence of pH and temperature on binding and mobilisation of metals in sand .2. lead.
633 *Fresenius Environ. Bull.*, 6(11-12), 719-726.

634 Marsalek, J. (2003). Road salts in urban stormwater: an emerging issue in stormwater management
635 in cold climate. *Water Sci. Technol.*, 48(9), 61-70.

636 Marsalek, J., Oberts, G., Exall, K., & Viklander, M. (2003). Review of operation of urban drainage
637 systems in cold weather: water quality considerations. *Water Sci. Technol.*, 48(9), 11-20.

638 Martinez, C. E., Jacobson, A. R., & McBride, M. B. (2003). Aging and temperature effects on
639 DOC and elemental release from a metal contaminated soil. *Environ. Pollut.*, 122(1), 135-
640 143.

641 Melbourne Water. (2005). *WSUD Engineering Procedures: Stormwater*. CSIRO Publishing.

642 Morrison, G. M. P. (1989). Bioavailable metal uptake rate in urban stormwater determined by
643 dialysis with receiving resins. *Hydrobiologia*, 176/177, 491-495.

644 Muthanna, T. M., Viklander, M., Blecken, G. T., & Thorolfsson, S. T. (2007a). Snowmelt
645 pollutant removal in bioretention areas. *Water Res.*, 41(18), 4061-4072.

646 Muthanna, T. M., Viklander, M., Gjesdahl, N., & Thorolfsson, S. T. (2007b). Heavy metal
647 removal in cold climate bioretention. *Water Air Soil Pollut.*, 183, 391-402.

648 Muthanna, T. M., Viklander, M., & Thorolfsson, S. T. (2008). Seasonal climatic effects on the
649 hydrology of a rain garden. *Hydrol. Processes*, 22, 1640-1649.

650 Ponizovsky, A. A., Thakali, S., Allen, H. E., Di Toro, D. M., & Ackerman, A. J. (2006). Effect of
651 Soil Properties on Copper Release in Soil Solutions at Low Moisture Content. *Environ.*
652 *Toxicol. Chem.*, 25(3), 671-682.

653 Read, J., Wevill, T., Fletcher, T. D., & Deletic, A. (2008). Variation among plant species in
654 pollutant removal from stormwater in biofiltration systems. *Water Res.*, 42, 893-902.

655 Rieuwerts, J. S., Thornton, I., Farago, M. E., & Ashmore, M. R. (1998). Factors influencing metal
656 bioavailability in soils: preliminary investigations for the development of a critical loads
657 approach for metals. *Chem. Speciation Bioavailability.*, 10(2), 61-75.

658 Semadeni-Davies, A. (2006). Winter performance of an urban stormwater pond in southern
659 Sweden. *Hydrol. Processes*, 20, 165-182.

660 Sun, X. and A. P. Davis (2007). "Heavy metal fates in laboratory bioretention systems."
661 *Chemosphere* 66(9), 1601-1609.

662 Swedish EPA. (2000). *Environmental Quality Criteria - Lakes and Watercourses*. Report 5050.
663 Swedish EPA, Stockholm, Sweden.

664 Swedish EPA (2009). *Guideline values for contaminated areas – modell description and guidance*
665 (In Swedish: Riktvärden för förorenad mark - Modellbeskrivning och vägledning). Report
666 5976. Swedish EPA, Stockholm, Sweden.

667 Temminghoff, E. J. M., Van Der Zee, S. E. A. T. M., & De Haan, F. A. M. (1997). Copper
668 Mobility in a copper-contaminated sandy soil as affected by pH and solid and dissolved
669 organic matter. *Environ. Sci. Technol.*, 31, 1109-1115.

670 Warren, L. A., & Haack, E. A. (2001). Biogeochemical controls on metal behaviour in freshwater
671 environments. *Earth Sci. Rev.*, 54, 261-320.

672 Warren, L. A., & Zimmermann, A. P. (1994). The influence of temperature and NaCl in cadmium,
673 copper and zinc partitioning among suspended particulate and dissolved phases in an
674 urban river. *Water Resour.*, 28(9), 1921-1931.

675 Westerlund, C., & Viklander, M. (2006). Particles and associated metals in road runoff during
676 snowmelt and rainfall. *Sci. Total Environ.*, 362, 143-156.

677 Westerlund, C., Viklander, M., & Bäckström, M. (2003). Seasonal variations in road runoff quality
678 in Luleå, Sweden. *Water Sci. Technol.*, 48(9), 93-101.

679 Viklander, M. (1999). Dissolved and particle-bound substances in urban snow. *Water Sci.*
680 *Technol.*, 39(12), 27-32.

681 Yin, Y., Impellitteri, C. A., You, S.-J., & Allen, H. E. (2002). The importance of soil organic
682 matter distribution and extract soil: solution ratio on the desorption of heavy metals from
683 soils. *Sci. Total Environ.*, 287, 107-119.

684 Zhao, L. T., & Gray, D. M. (1999). Estimating snowmelt infiltration into frozen soils. *Hydrol.*
685 *Processes*, 13(12-13), 1827-1842.

687 **Table 1.** Synthetic stormwater characteristics and metal sources.

Pollutant	Stormwater pollutant concentration ± SD		Percentage dissolved	Source in synthetic stormwater
	total	Dissolved		
Cd	4.2 µg L ⁻¹ ± 0.4	3.2 µg L ⁻¹ ± 0.4	76 %	CdCl ₂
Cu	151.9 µg L ⁻¹ ± 17.9	21.0 µg L ⁻¹ ± 4.2	14 %	CuCl ₂
Pb	42.3 µg L ⁻¹ ± 4.4	0.3 µg L ⁻¹ ± 0.1	1 %	PbCl ₂
Zn	275.9 µg L ⁻¹ ± 27.2	206.4 µg L ⁻¹ ± 14.5	75 %	ZnCl ₂
TSS	137.7 mg L ⁻¹ ± 12.1			Gully pot sediment <400 µm
pH	6.8 ± 0.2			H ₂ SO ₄
Temp	3.2 °C ± 1.0			-
	8.6 °C ± 0.6			-
	18.6 °C ± 1.0			-

689 **Table 2:** Mean of influent and effluent concentrations, and removals and percentages of dissolved
690 metals at the temperatures tested. Particle-bound metal concentrations were calculated as the
691 difference between total and dissolved concentrations.

		Influent stormwater	Effluent		
			2°C	8°C	20°C
Cd	Total concentration ($\mu\text{g L}^{-1}$)	4.2	0.05	0.05	0.05
	Particle-bound concentration ($\mu\text{g L}^{-1}$)	1,0	0.03	0.03	0.03
	Dissolved concentration ($\mu\text{g L}^{-1}$)	3.2	0.02	0.02	0.02
	Percentage dissolved (%)	76	39	33	42
	Total removal (%)		99	99	99
	Dissolved removal (%)		99	99	99
Cu	Total concentration ($\mu\text{g L}^{-1}$)	151.9	10.1	11.7	16.0
	Particle-bound concentration ($\mu\text{g L}^{-1}$)	130,9	3,2	3,6	2,6
	Dissolved concentration ($\mu\text{g L}^{-1}$)	21.0	6.9	8.1	13.4
	Percentage dissolved (%)	14	70	69	85
	Total removal (%)		93	93	89
	Dissolved removal (%)		64	66	24
Pb	Total concentration ($\mu\text{g L}^{-1}$)	42.3	1.9	1.9	1.7
	Particle-bound concentration ($\mu\text{g L}^{-1}$)	42,0	1,8	1,8	1,6
	Dissolved concentration ($\mu\text{g L}^{-1}$)	0.3	0.1	0.1	0.1
	Percentage dissolved (%)	1	10	9	9
	Total removal (%)		95	96	96
	Dissolved removal (%)		46	55	54
Zn	Total concentration ($\mu\text{g L}^{-1}$)	275.9	4.8	4.8	4.7
	Particle-bound concentration ($\mu\text{g L}^{-1}$)	69,5	2,9	2,9	2,6
	Dissolved concentration ($\mu\text{g L}^{-1}$)	206.4	1.9	1.9	2.1
	Percentage dissolved (%)	75	43	42	48
	Total removal (%)		98	98	98
	Dissolved removal (%)		99	99	99

692

693 **Table 3.** Mean metal concentrations (mg kg^{-1} dry mass) in plant shoot and root tissues before and
694 after stormwater application. P values of one-way ANOVA: metal concentration vs. temperature.

Metal	Sample	Plant metal concentration	
		Shoot	Root
Cd	initial	0.03	0.15
	after dosing 2°C	0.5 ± 0.2	0.3 ± 0.0
	after dosing 8°C	0.3 ± 0.1	0.6 ± 0.3
	after dosing 20°C	0.3 ± 0.1	0.2 ± 0.1
	p-value	0.063	0.015
Cu	Initial	9.88	10.60
	after dosing 2°C	22.7 ± 7.7	14.8 ± 4.4
	after dosing 8°C	17.4 ± 4.5	17.1 ± 6.3
	after dosing 20°C	14.6 ± 3.4	43.2 ± 22.8
	p-value	0.102	0.013
Pb	Initial	0.66	2.23
	after dosing 2°C	3.9 ± 1.2	0.8 ± 0.3
	after dosing 8°C	2.8 ± 1.4	1.3 ± 0.7
	after dosing 20°C	2.2 ± 1.4	1.0 ± 0.2
	p-value	0.175	0.239
Zn	Initial	42.7	24.0
	after dosing 2°C	71.3 ± 13.3	41.56 ± 5.6
	after dosing 8°C	71.3 ± 11.5	54.4 ± 20.8
	after dosing 20°C	61.5 ± 11.5	58.78 ± 15.7
	p-value	0.363	0.225

695

696 **Table 4:** Mass balance of metals entering and leaving one average biofilter column.

	Influent		Effluent		Retention	
	Total mass in (mg)	Dissolved mass in (mg)	Total mass out (mg)	Dissolved mas out (mg)	Total mass removal (%)	Dissolved mass removal (%)
Water	300 L		279 L		7	
TSS	41300		866		98	
Cd	1.3	1.0	<0.1	<0.1	99	99
Cu	47.4	6.3	3.5	2.6	93	59
Pb	12.7	0.1	0.5	<0.1	96	57
Zn	82.8	61.9	1.3	0.5	98	99

697
698
699

700 **FIGURES**



701

702 **Figure 1.** Biofilter columns in a climate room.

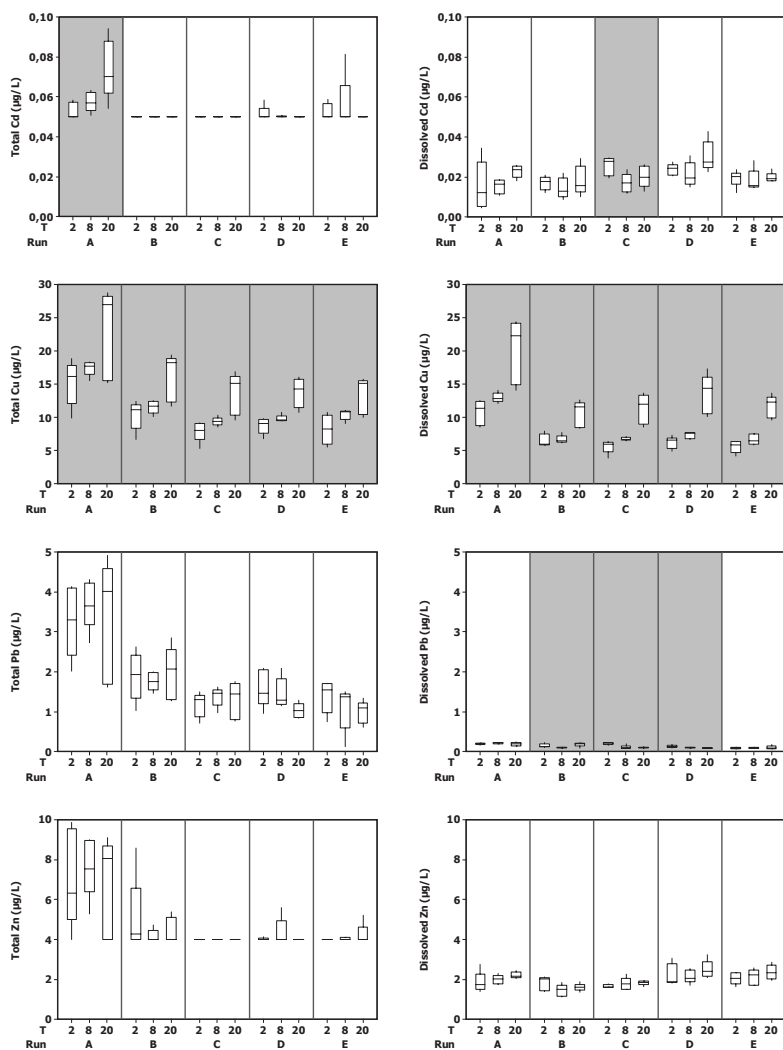
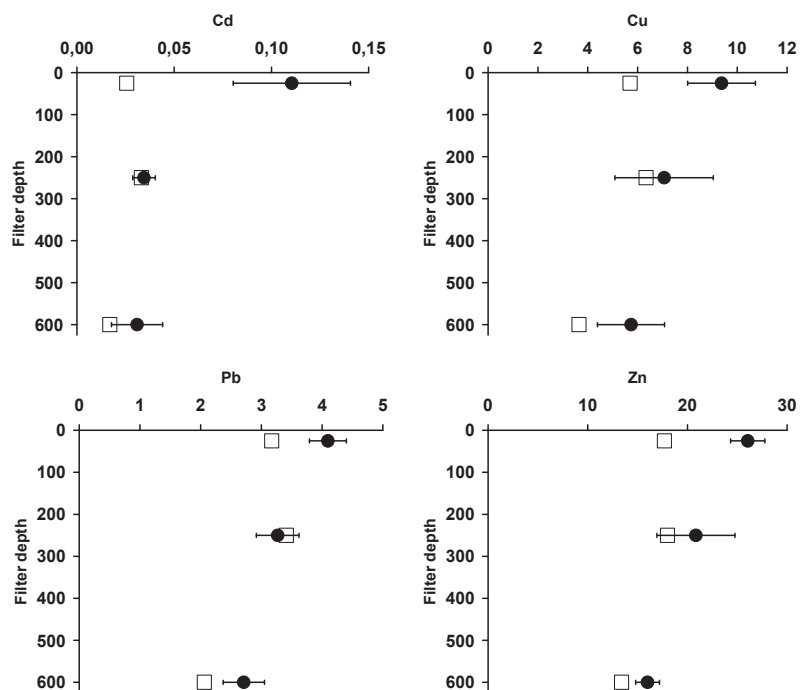


Figure 2. Effluent metal concentrations vs. temperature (2°C, 8°C and 20°C) for the different sampling runs (A to E, after every second week). Shaded background indicates sampling runs with a statistically significant ($\alpha=0.05$) temperature influence (not for total Cd due to majority of values < detection limit). The respective stormwater concentrations are presented in Table 1.

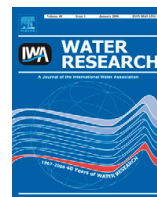


708

709 **Figure 3.** Mean metal concentrations in the filter media (mg kg⁻¹ DS) at different depths (mm)
 710 before (open markers) and after (closed markers \pm standard deviation, n=5) stormwater
 711 application.

712

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Snowmelt pollutant removal in bioretention areas

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ABSTRACT

Snow accumulating in urban areas and alongside roads can accumulate high pollutant loads and the subsequent snowmelt can produce high pollutant loads in receiving waters. This paper examines the treatment of roadside snowmelt in bioretention with respect to pollutant removal, pollutant pathways, and major sinks. Bioretention was used to treat snowmelt from three types of urban roads in Trondheim, Norway: residential, medium, and roads with high-density traffic. Metal retention in bioretention boxes had a mass reduction in zinc, copper, lead, and cadmium in the range of 89–99%, and a decrease in outflow concentrations in the range 81–99%. Cadmium was only measured in the water samples, while the other three metals were traced through the system to identify the main sinks. The top mulch layer was the largest sink for the retained metals, with up to 74% of the zinc retained in this mulch layer. The plant metal uptakes were only 2–8% of the total metal retention; however, the plants still play an important role with respect to root zone development and regeneration, which fosters infiltration and reduces the outflow load. Dissolved pollutants in snowmelt tend to be removed with the first flush of meltwater, creating an enrichment ratio with respect to the average pollutant concentrations in the snow. The effect of this enrichment ratio was examined through the bioretention system, and found to be less predominant than that typically reported for untreated snowmelt. The enrichment factors were in the range of 0.65–1.51 for the studied metals.

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1. Introduction

Bioretention facilities, and a sub-set often called rain gardens provide stormwater retention and treatment, and add vegetation to the urban environment. The active processes in bioretention facilities include infiltration, adsorption, filtration, decomposition, volatilization, organic complexation, and ion exchange (Clar et al., 2004). Metal retention in the soil media can be related to cation exchange (non-specific adsorption), coprecipitation, and organic complexation (Alloway, 1995). In addition, plant uptake of metals also contributes to the retention of dissolved metals at a slower rate. Plants, however, are important in the interaction between the plant roots, the

rhizosphere, and the surrounding soil by improving infiltration, soil texture, and preventing clogging (Gregory, 2006). Laboratory and event-based field testing of bioretention performance with respect to metal retention have shown an above 90% removal of copper, zinc, and lead. However, plant uptake accounted for approximately 5% removal by mass. In comparison, the mulch layer accounted for 20% of copper, 10% of lead, and 34% of zinc (Davis et al., 2001). Field testing of existing established bioretention areas reported herein had a wider performance range with respect to metal removal. The field test reported from 42% to 70% for a less developed bioretention facility to over 90% in a well-developed bioretention facility with good vegetation (Davis et al., 2003).

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The use of in situ infiltration practices has been recommended as a treatment for urban snowmelt with high concentrations of soluble pollutants (Oberts, 2003). Infiltration uses the ion-exchange capacity in the soil, or engineered infiltration media, to adsorb soluble pollutants (Oberts, 2003). For successful infiltration of meltwater, adequate infiltration rates are very important, 1.3 cm/h as a minimum rate and clay contents less than 30% have been reported in the literature (Caraco and Claytor, 1997). Recently, this thought has changed towards reducing the clay to less than 5%, even as far as zero (Minnesota Stormwater Steering Committee). The pre-freezing soil water content is also important, as high soil water content at the time of freezing can lead to the soil becoming an impervious layer with close to zero infiltration, also referred to as concrete frost. Granular or porous frost, however, will maintain and can even exceed the infiltration capacity of the unfrozen soil (Granger et al., 1984; Kane, 1980). The use of biological elements in treatment systems for meltwater, such as the use of vegetated swales with plant roots to enhance infiltration, and vegetated cover to promote sheet flow has been reported as recommended modifications to cold climate best management practices (BMPs) (Oberts, 2003; Caraco and Claytor, 1997). These findings suggest that bioretention offers a great possibility for use both as a snow deposit and for the retention of pollutants from the meltwater. The mixed vegetation enhances infiltration, and plant roots have been shown to be active even during the cold season for potential pollutant adsorption. The mulch layer provides an easily replaceable treatment layer that prevents clogging and retains pollutants from the snowmelt.

The main pollutants in road runoff include copper, zinc, lead, cadmium, sediments, PAHs, and de-icing salts (Makepeace et al., 1995). The sources are the same for the rain and snow; however, the residence time in the snow can be up to several months long, compared with a residence time of hours for rainfall runoff. The sources of metal in road runoff can be divided into pavement wear (40–50% of particulate mass), tyre wear (20–30% of particulate mass), and the remaining 15% comes from engine and brake parts and 3% from urban atmospheric deposition not related to road activities (Kobriger and Geinopoles, 1984). Pollutant loads and pathways in snow and snowmelt pollutant transport differ from rainfall runoff pollutant loads and pathways. Pollutants in the snowpack can be transported hydraulically during snowmelt, and also by snow drift and removal, which again are affected by other climatic and meteorological factors (Oberts, 1990). Snow can store pollutants over long periods, and in climates with a long sustained cold period in the winter, the snowpack can be several months old by the time it melts. Snow removal and road maintenance with sand and de-icing salts, vehicle and road wear and tear all contribute to accumulation of pollutants in the snowpack (Malmqvist, 1978). A study from northern Sweden comparing meltwater runoff and rain runoff concluded that the concentration of sediments was significantly higher in the melt period, and a stronger correlation between total suspended solids (TSS), particle sizes, and metal (Cd, Cu, Ni, Pb, and Zn) concentrations (Westerlund and Viklander, 2006). Snow handling and management will also greatly affect snow quality and pollutant pathways, and with snow, unlike rain,

this pathway can be selected more easily based on the management strategy (Reinosdotter and Viklander, 2005). Snow can be collected and transported to central snow deposits or stored locally in ditches and open areas, such as parking lots. Central snow deposits require transportation of the snow and could be a source of shock pollutant loadings during the melt season. On the other hand, local snow deposits could pose a traffic safety issue, limit parking availability, and cause local flooding in the melt season if it is an area of poor drainage (Reinosdotter et al., 2003).

Studies on snowmelt and pollutant pathways in snowmelt have identified an enrichment factor of dissolved pollutants in the early stages of snowmelt. In one study from Japan, 50–90% of the dissolved pollutants were transported with the first fraction of meltwater, while the tail end contained a larger concentration of particulate matter (Ecker et al., 1990). Enrichment factors measured in the first 20% of runoff volume in snow deposits in Luelå, Sweden, were in the range of 1.2–2.0 for copper, zinc, and lead (Viklander and Malmqvist, 1993). The reason for this can be found in the metamorphoses of snow, driven by thermodynamic instabilities and water vapour transport along gradients in the snowpack. This causes a concentration of dissolved phase in the liquid-like layer on the surface of the ice crystal, causing it to be washed out with the first meltwater (Daub et al., 1994). The partitioning coefficient of metals in snow controlling the amount of metal in dissolved and particulate-bound phases are affected by the temperature and salinity content of the snowpack. Increasing salinity or decreasing temperature will increase the concentration of dissolved, bioavailable metals (Warren and Zimmerman, 1994). This shift from the particulate to the dissolved phase could also affect the treatment efficiencies of traditional BMPs, such as ponds where sedimentation of particulates is one of the prime functions (Novotny et al., 1999).

The objective of this paper is to evaluate the metal retention and the fate of chloride in a bioretention facility during snowmelt. Snow from three streets with low-, medium-, and high-traffic density was used to investigate to what extent the pollutant composition and concentrations in the snow influenced the retention of pollutants in the bioretention facility. The metal retention and pollutant pathway and enrichment factors through the biofilter for the three different sites were compared with the pathways and enrichment factors of no treatment of snowmelt. The chloride concentrations in the snow and in the outflow from the bioretention boxes were also compared to investigate the fate of the most commonly used de-icing agent, sodium chloride, through the system. In addition, the chemical oxygen demand (COD) of the snow and outflow was measured for an initial screening of organic pollution retention.

2. Experimental section

The set-up of the study involved three parts, the design and construction of the bioretention boxes, the selection and characterization of the snow sampling sites, and the laboratory analysis of the water, soil, and plant samples.

2.1. Bioretention boxes and experimental set-up

Two pilot size bioretention boxes were built in September 2004 and October 2005 at the Risvollan Urban Hydrological Research Station in Trondheim, Norway. The bioretention boxes were constructed using watertight polyethylene plastic boxes (width 88 cm, length 109 cm, and depth 80 cm). Gravel (10 cm; $d_{50} = 20$ mm) was placed at the bottom and a thin plastic mesh was placed to avoid the clogging of the gravel layer due to the soil on top. The soil medium was a sandy soil placed above the gravel layer and was 50 cm thick, followed by a 5–10 cm mulch layer to cover the soil and improve pollutant retention, leaving 15 cm freeboard in the box for ponding of water in the box during runoff events. A low clay content and a high sand content were chosen to aid winter infiltration in the bioretention boxes. The mulch layer was made up of shredded bark and some leaf litter accumulated from the plants in the system. At the bottom, a 20 mm PVC tube drained the outflow from the box into a storage tank in the basement of the measuring station. The drainpipe had a minimum slope of 3% to avoid water freezing in the pipe, thus avoiding blocking the drainage. The rate of change in the water level in the tank was measured by a pressure transducer (0–160 mbar range) placed at the bottom of the outflow tank (Fig. 1).

The soil and sand were mixed to be equal in the two systems, but the final physical properties of the soil in the two boxes differed slightly (Table 1). The cation exchange capacity (CEC) was much higher in bioretention box 1 than in box 2, even though it was measured when bioretention box 2 was constructed and bioretention box 1 had already been in operation for 12 months. This rather large difference in CEC between the two boxes suggests a difference in composition of the soil. Bioretention box 2, with the lowest CEC, had a higher fraction of clay and silt, hence this cannot explain the difference. Sample contamination, or possibly mixing of some partially decomposed mulch in the sample from bioretention box 1, could explain the higher CEC value. One

reason for this could be the time of measurement; CEC was measured in the soil prior to the snowmelt study, at a time when bioretention 1 had been in operation 12 months longer than bioretention box 2. The plants used in the boxes included perennial flowers, yellow iris (*Iris pseudacorus*), and purple-loosestrife (*Lythrum salicaria*), a shrub sea-buckthorn (*Hippophae rhamnoides*), and the ground covering plant lesser periwinkle (*Vinca minor*). Plant selection was based on commonly used plants for stormwater treatment (*L. salicaria* and *I. pseudacorus*), and plants that are native to Trondheim (*H. rhamnoides*).

2.2. Snow collection sites

Snow was collected from three locations in February and March 2006. The three collection sites were chosen based on traffic density. The low-density site with a traffic density of 1550 vehicles/day was a typical suburban residential street with single-family homes and townhouses (site A).

Table 1 – Soil physical and chemical composition for the two bioretention boxes at time of construction

	Bioretention 1	Bioretention 2
Clay (%)	2.6	2.9
Sand (%)	92.7	88.3
Silt (%)	4.7	8.8
Organic matter (%)	8.7	10.7
Bulk density (g/cm^3)	0.79	0.84
Solid particle density (g/cm^3)	1.05	1.18
pH soil	6.88	6.79
pH mulch	5.5	5.6
CEC (cmol_e/kg) ^a	55.2	20.0

^a The CEC was measured at the time of construction for bioretention 2, when bioretention 1 had been in operation for 12 months already, which can explain the large difference in CEC measured in the two systems.

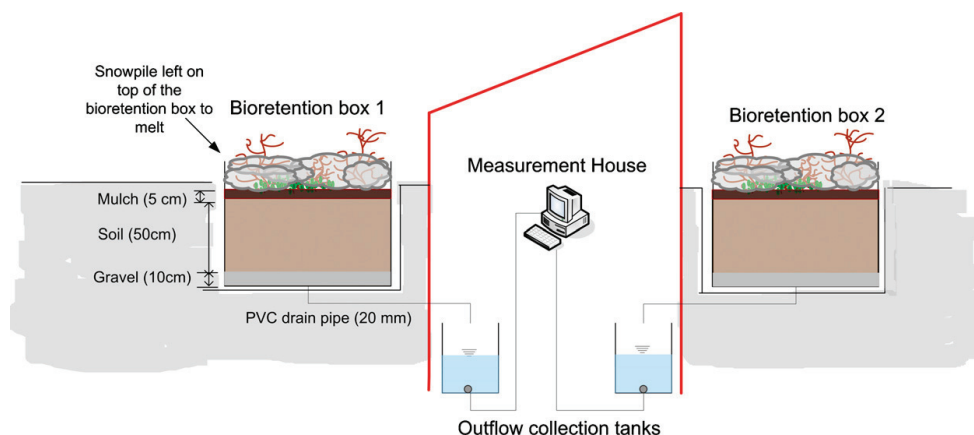


Fig. 1 – Schematic of snowmelt study set-up and bioretention box media.

The medium density site (site B) with 5000 vehicles/day was an urban collector road, and a high-density road (site C) with 47,000 vehicles/day was a main highway. The traffic density figures were obtained from the Norwegian Directorate of Public Roads. The snow was collected within 1.5 m of the road in the snowpack closest to the road. The snow pile depth was approximately 30–40 cm on collection day 1 (23 February 2006), and 50–60 cm on collection day 2 (27 March 2006). The snow was sampled over a 50 m stretch throughout the depth of the snow pile; however, ice formation at the bottom made sampling of the bottom 10 cm of the snow pile difficult.

The average annual precipitation in Trondheim is 900 mm/yr, out of which 30–40% is snow. In the main snowmelt season, March and April, the average 24 h temperature is 0 and 4 °C, respectively (Thorolfsson et al., 2003).

2.3. Sampling

Snow was collected on 23 February and 27 March 2006. Each time, approximately 75 L of snow was collected in three white plastic bags for each site and stored in freezers at –18 °C until the snowmelt study started in mid-April. During the snowmelt study, a tarpaulin was constructed over the two bioretention boxes in order to prevent precipitation contamination of the tests. The snow from site A, the residential street, was applied to the bioretention boxes first, on 14 April 2006, as this snow was expected to have the lowest pollutant concentrations. The snow from the two sampling days was mixed homogeneously and applied in equal volumes to the two bioretention boxes, i.e., 75 L each. Subsequently, at site B, the medium-density site, snow was applied on 21 April, after all the meltwater from site A was drained from the filters and allowing for a 24 h rest period for the media. Finally, at site C the snow was applied on 27 April 2006, again 24 h after the last snowmelt from site B left the boxes.

The flow from the drain pipes, the soil temperatures, and the soil moisture content were measured continuously and logged on a Campbell Scientific data logger (CR10X). In addition, meteorological data, air temperature, wind speed, solar radiation, and relative humidity were available on a 2 min resolution from the Risvøllan Urban Hydrologic Research Station, at the same location. Samples were taken based on the volume drained from the filters, and the first three samples were all sampled from within the first 15 L drained from the tank. Less frequent samples were taken, at approximately 10 L intervals for the next three and then 15–20 L intervals for the last two samples. A total of eight samples were taken from each bioretention box for each site. The time of sampling was the same for both the bioretention boxes; however, there were minor variations in the flowrate through them. To account for this, the exact time and volume were noted for each sample. These volume-based outflow samples are referred to as S1–S8 for each of the three sites. To find the mass loading of metals, an incremental summation of the partial volume for each sample multiplied with the concentration was used, as shown in Eq. (1). V_{Ai} , V_{Bi} , and V_{Ci} denoted volumes from sites A, B, and C, respectively, and X_{Ai} ,

X_{Bi} , and X_{Ci} denote the corresponding concentrations.

$$\text{Mass}_{\text{metal}} = \sum_{i=1}^8 (V_{Ai}X_{Ai}) + \sum_{i=1}^8 (V_{Bi}X_{Bi}) + \sum_{i=1}^8 (V_{Ci}X_{Ci}). \quad (1)$$

Initial soil, mulch, and plant samples (roots and shoots) were collected prior to installation of the bioretention areas. The soil and the mulch were sampled using a composite sample of 15 grab samples, and the plants were sampled by making a composite sample of all plants of the same species. Prior to the snowmelt study, after the bioretention areas had been in operation for 19 and 6 months, respectively, the mulch, top soil layer, and above-ground plant material were sampled again using composite grab samples. At this point, only the top soil layer could be sampled due to frozen soil and in order to avoid damaging the soil column prior to the experiments. The roots of plants could not be sampled due to frozen ground. Three weeks after the snowmelt experiments, complete soil column samples with 10 cm increments, plant roots and shoots, and the mulch layer were sampled again.

2.4. Analysis methods

The pH was measured as the samples were collected in the field, with a field pH meter (HI 991300, Hanna Instruments). TSS were measured using Whatman GF/C 1.2 µm pore size glass microfibre filters in three replicates (NS4733E, 1983). The metal samples were analysed using a high-resolution inductively coupled plasma-mass spectrometer (HR ICP-MS). The samples were stored in sterile 50 mL centrifugal tubes and kept in the same tube throughout the whole analysis procedure. The dissolved samples were filtered using a cellulose nitrate 0.45 µm pore size filter. The total metal samples were digested in a microwave oven with 10% HNO₃, and then diluted 16 times (0.1 M HNO₃) prior to analysis. The HR ICP-MS detection limits for copper, zinc, lead, and cadmium are 0.125/2.0, 0.2/3.2, 0.01/0.16, and 0.01/0.16 µg/L, respectively, with a relative standard deviation of less than 10%. The first number represents the detection limit for the undiluted dissolved samples, while the second number is the detection limit for the total samples that were diluted by a factor of +16 due to the solids content. The particle size classification was determined using a particle size analyser (Beckman Coulter LS 230). The COD concentrations were measured with Dr. Lange cuvettes for COD (LCK 314, 15–150 mg/L), and standard deviation of 0.6 mg/L and 95% confidence interval (CI) of ±1.5 mg/L.

The soil samples were dried and sieved to remove particles larger than 2 mm, then the sample was boiled with aqua regia. Plant samples were dried and crushed, then nitric acid and hydrogen peroxide were added and the samples were digested in a microwave. Both plant and soil samples were then analysed using an inductively coupled plasma-mass spectrometre (ICP-AES). The CEC was determined by shaking the soil sample with 1 M ammonium acetate and then extracted and analysed using an ICP-AES. Enrichment factors of dissolved pollutants in the snowmelt were calculated by the same procedure used by Viklander and Malmqvist (1993),

as

Enrichment factor

$$= \frac{\text{concentration in first 20\% of meltwater}}{\text{average concentration in meltwater}} \quad (2)$$

3. Results and discussion

3.1. Metal concentrations

The chemical and physical composition of the snow from the three sites showed highest pollution loads for the high-traffic road (site C). The zinc concentration was almost five times higher than site A, the residential area (Table 2). The conductivity and chloride concentration were highest for site B, the medium-density collector road. It might have been expected that site C should have a higher chloride concentration due to more salt applications; however site B is located at a higher elevation (64 m above sea level) and with less traffic, hence more salt is needed to keep the road free of ice and snow. Site A is at the highest elevation (ca. 125 m above sea level); however, de-icing agents are infrequently applied to residential roads in Trondheim. These roads are cleared for snow and then anti-slipping agents such as gravel and sand are used. The three roads are also maintained by three different entities; site A, the residential road is a city road, where salt will be applied based on difficult driving

conditions, but with the goal to minimise salt applications. Site B, the urban collector road, is a county road, which will be regularly salted throughout the winter with the goal to keep the driving lanes free of snow. Site C, the urban highway, is a state road, which also will be regularly salted; however, due to a lower elevation and higher traffic load the chloride is more easily washed off here.

The changes in concentrations between snow and outflow varied between the metals, between the total and dissolved phases, and between locations (Table 2), which will also be the case in a field installation. Days between events, seasonal traffic patterns, and winter salt applications will result in snow and rainfall runoff with variable inflow concentrations. The percentage reductions can often be misleading since they are usually directly related to the inflow concentration. The largest change in snow to outflow concentration for the total concentrations were seen at site C for all the metals, with more than 90% lower total concentrations in the outflow compared with the snow. The most variable change in concentrations were seen at site A where total copper only had a 24% lower outflow concentration than in the original snow, while total zinc and total lead had more than 80% reduction in outflow concentrations. Site B, the urban collector road, fell in between the residential road (site A) and the highway (site C). The changes in total concentrations followed the loadings, so that the largest change in total concentration was seen at the site with the highest total snow metal concentrations to begin with. This indicated that the

Table 2 – Chemical and physical composition of the snow collected at the three study sites and the mean outflow concentrations from the bioretention boxes

	Site A		Site B		Site C		USEPA ^a (µg/L)
	(µg/L)	RMS	(µg/L)	RMS	(µg/L)	RMS	
Snow							
Total copper	123.4	0.7	200.4	3.2	543.3	29.1	13(9)
Dissolved copper	36.4	0.7	19.0	0.2	13.5	0.4	
Total zinc	386.4	8.7	537.6	29.6	1465.3	49.8	120(120)
Dissolved zinc	7.2	0.6	6.1	0.6	2.6	0.2	
Total lead	24.6	1.6	34.8	0.9	93.7	1.5	65 (2.5)
Dissolved lead	0.30	0.003	0.18	0.001	0.19	0.007	
Total Cadmium	0.30	0.012	0.44	0.026	1.52	0.011	2 (0.25)
Dissolved Cadmium	0.02	0.000	0.02	0.002	0.01	0.001	
Chloride	48 974	1616	215 754	7336	20 863	563	860 (230) ^b
Outflow							
Total copper	92.6	10.4	75.4	8.0	52.0	6.5	
Dissolved copper	60.3	17.6	55.1	7.1	42.6	13.7	
Total zinc	72.6	14.7	85.8	22.5	36.4	13.4	
Dissolved zinc	57.1	17.7	63.0	24.9	27.1	9.2	
Total lead	1.6	0.1	1.1	0.1	0.6	0.1	
Dissolved lead	0.20	0.012	0.18	0.013	0.15	0.013	
Total cadmium	0.04	0.018	0.06	0.021	0.09	0.033	
Dissolved cadmium	0.04	0.006	0.06	0.011	0.05	0.016	
Chloride	55 785	10 205	85 923	17 203	136 005	21 143	

Root mean squares (RMS) of the average concentrations in RMS column for each site.

^a USEPA national recommended water quality criteria (USEPA, 2002). Acute values and chronic values in parenthesis. There are no applicable Norwegian water quality standards that can be used to compare the values against.

^b Chloride values are listed in mg/L.

change in total concentration through the bioretention box was a function of the loading. The dissolved concentrations had a more variable change. Dissolved copper, zinc, and cadmium as well as chloride for sites A and C all had a negative change with higher outflow concentrations than snow concentrations. Lead was the only dissolved metal that had a positive change with lower outflow concentrations. Based on the criteria given by the USEPA (2002), only total and dissolved copper failed to meet the recommended values in the outflow concentration, but for copper the outflow concentrations, especially the dissolved concentrations, were substantially higher than the recommended values.

3.2. Mass balance

An overall mass balance on the total inputs and outputs from the system was performed to investigate the overall performance of bioretention for treatment of snowmelt. In total, over the three applications on the two boxes, a snow water equivalent of 357 L was applied, 340 L of which was collected in the outflow again. This is a mass recovery of 95.3%; the remainder of the water was retained in the soil column and not retrievable. The total pollutant retention in the system was very good for metals and sediments, with an above 95% reduction in total metal mass and above 99% reduction in TSS (Table 3). Dissolved metals had a more varied result, with good retention of soluble lead, while some leaching zinc was observed. The dissolved copper masses in and out are very similar and within the overall uncertainty of the measurements (discussed in the following section), indicating that the dissolved copper mass is transported directly through the bioretention box without any adsorption. The organic substances, measured in COD were reduced by 57% mass, which is a lower reduction than a previously reported laboratory-scale study using synthetic runoff (Hong et al., 2006). A slight increase in chloride mass could be seen through the system; however, accounting for uncertainties in concentrations (discussed in the next section) the chloride remained unchanged through the system. It is also possible that continuous testing of the facility over 2 yr prior to this study had left some residual chloride in the soil column that was washed out with the snowmelt. In either case, it can be seen that chloride for the most part is transported directly through the

system without any reduction in mass loads. The total metal retention was strongly correlated to TSS reduction and all above 95% mass reduction, which is excellent retention for a full-scale outdoor study.

3.3. Pollutant accumulation in soil, plants, and mulch

The accumulation sinks for the retained pollutants were analysed to identify where the majority of pollutants were retained and whether there was any difference between the different plant species.

The accumulation of metals in the roots and shoots of the plants varied greatly between the species. *V. minor*, a ground-covering evergreen had a clear accumulation of metals in the above-ground biomass. Unfortunately, an error occurred during post-snowmelt sampling so that the below-ground sample of the *V. minor* could not be used. However, since it is a terrestrial plant the uptake must occur in the root zone, indicating a good transport of metals from the roots to the shoots in the plant. The copper concentration remained nearly unchanged between pre-snowmelt and post-snowmelt measurements, but showed an accumulation that was 250% higher compared with natural levels from the start of operation due to preceding stormwater experiments. Lead showed 250% and zinc showed 140% higher accumulation post-snowmelt compared with pre-snowmelt. *H. rhamnoides*, a small shrub, showed a lower accumulation and only minor differences between the natural and post-snowmelt results in the twigs (Fig. 2).

The top mulch layer showed a clear accumulation of all the three metals (Fig. 3b), which supports previously published studies investigating metal retention in mulch (Davis et al., 2001; Jang et al., 2005). Comparing pre-snowmelt levels with post-snowmelt levels, the metal concentrations in the mulch layer were 160%, 110%, and 120% higher, respectively, for copper, lead, and zinc. Metal concentration as a function of soil depth did not reveal a clear trend between initial soil metal concentrations and the post-snowmelt soil metal concentrations. Small increases in metal concentrations were seen at the bottom of the soil column, while no difference was measured at the top portion of the column (Fig. 3a). Davis et al. (2001) reported no apparent variation of metal concentrations in the soil core depth in the post-experiment analysis

Table 3 – Summary of mass balance of snow input and outflow metals, chloride, particles, and COD

	In		Out		% mass retained	
	Total	Dissolved	Total	Dissolved	Total	Dissolved
Snow volume (L)	357		340.7		5	
Zinc (mg)	301	1.8	11.6	8.7	96	–372
Copper (mg)	110	8.0	12.1	9.1	89	–14
Lead (mg)	19	0.1	0.2	0.0	99	59
Cadmium (mg)	290	6.3	14.7	26.0	95	–310
Chloride (g)	30		33.1		–10	
COD (g)	49		20.7		57	
TSS (g)	2112		1.8		100	

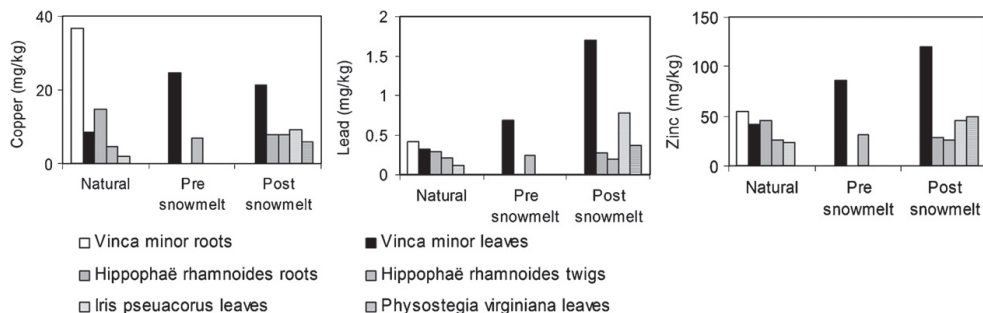


Fig. 2 – Plant metal concentrations in above-ground biomass, twigs and leaves, and roots for natural conditions, before the snowmelt experiment and 3 weeks after the snowmelt experiment.

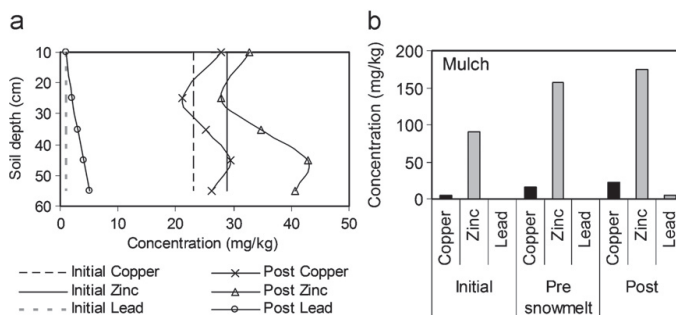


Fig. 3 – Soil depth profiles of metal accumulation in the bioretention areas (a) and in the top mulch layer (b).

of the soil and no significant soil adsorption of metals was seen. However, this can be a function of the total metal mass added to the system compared with the soil mass in the system and possibly the resolution of the measurement technique.

The dissolved copper and zinc mass in the outflow indicated some leaching from the soil column. A laboratory leaching test was performed to investigate this. De-ionized water was slowly pumped, 2 mL/min, into a column of 600 mL of soil from the bioretention boxes for approximately 6 h. The results revealed a leachate concentration of copper and zinc in the range of 30–40 µg/L. This is in the same range as the increased dissolved fraction in the outflow, except for the first few samples from site B and site A.

A mass balance on the metal mass input, output, and retention in the system was performed. Based on known volumes of soil and mulch and estimated plant biomass, the main sinks can be identified. The 5 cm thick top mulch layer retained approximately 74% of the zinc, 13% of the lead, and 66% of the copper by mass that was retained in the system. This was higher than the number reported by Davis et al. (2001). However, the snow contained a much higher concentration of TSS, and after the snow had melted a grey layer of sediments was left on the mulch. This could have contributed to a higher retention in the mulch layer initially and possibly some of the metals would be transported further down in the soil column with subsequent rain events. The plant biomass

was not harvested, making only an estimate of the plant metal retention possible. Analysing the total plant metal uptake based on the plant biomass showed that approximately 6% of zinc, 8% of copper, and 2% of lead retention can be attributed to plant uptake, which is in the same range reported by Davis et al. (2001) in a laboratory study. This would leave 20% zinc, 28% copper, and 85% lead of the retained metal mass to be retained in the soil column, possibly due to the large volume of soil compared with the small mass of metals added, although this could not be confirmed. In order to increase the plant uptake of metals, hyperaccumulating plants could be used, though the plants would also need to be cold and chloride resistant and be able to grow well in a short growing season. Most plants found to hyperaccumulate metals are either aquatic or terrestrial plants that are grown in a water solution (Kholodova et al., 2005; Fritioff and Greger, 2003).

This does not represent a complete mass balance, but it clearly indicates that the most important mechanisms of metal removal in the system are through mechanical filtration, trapping suspended solids, and adsorption onto the top mulch layer. In spite of the minor role the plants might play in metal uptake, they are still an important part of the bioretention system with respect to nutrient removal, root zone development for improved infiltration and reducing clogging, rhizosphere biofilms, and regeneration of the system. The snowpack contains a large amount of particles

and pollutants and after snowmelt in the spring a thick layer of sediments and dirt covers the ground and the winter-dormant plants. Then 2 months later this grey layer of dirt and pollution is covered by green vegetation and slowly incorporated into the top mulch layer. The plant biomass from bioretention systems can also be harvested, thereby removing metals from the system.

3.4. Inflow and outflow pollutant compositions

Having confirmed that the bioretention facility could retain pollutants from urban snowmelt by looking at the overall change in concentrations and mass reductions, the timeline and site-specific composition and concentration were investigated.

The timeline for the application of snow from the different sites started with the residential snow (site A), which lasted 6 days (14–20 April) with a 24 h rest period before the start of the application to the urban collector road (site B), which also lasted 6 days (21–26 April) following a 24 h rest period. The final application to the urban highway (site C) began on 27 April and lasted until 2 May. The average air temperatures were 4.5, 6.7, and 8.7 °C respectively for sites A, B, and C.

The total metal retention rose with increasing metal concentration in the snow, which usually is the case in stormwater treatment systems, and can be misleading in finding the true performance of the system. The best attainable outflow concentrations, defined as the best consistent outflow concentration independent of loading concentrations, will give a better indication of the actual performance that can be expected in a field installation. Analysing the outflow concentrations showed more consistent values for cadmium and zinc, while there was some larger variance for copper and lead (Fig. 4). The median values of the outflow concentrations were used as the best attainable outflow value. The best attainable outflow concentration for zinc over the three sites was found to be 64 µg/L. The cadmium concentration in the outflow showed a best attainable value of 0.07 µg/L, of which most was dissolved cadmium, with a few exceptions for site C, which also had a substantial particle-bound part. For lead, the median outflow value was 0.9 µg/L, while the mode was as high as 1.3 µg/L, with a mean value in between at 1.1 µg/L. Due to the larger variance in the outflow concentrations, the mean appears to be the most suitable description of the best attainable outflow concentration. Copper had a median value of 58 µg/L, with a slightly lower mode, and a slightly higher mean. Based on the graphical inspection of the results (Fig. 4), a best attainable outflow concentration can be found at around 60 µg/L for lead. A better consistent performance was seen for site C for all the metals; however, this site had the lowest chloride concentration and the highest traffic load. It is also possible that this could be due to a higher average air temperature for site C melt, improving the performance of the bioretention boxes.

Snow also accumulates oil and grit over the winter months that will be transported with the melt water. To obtain an initial screen result of the performance of the system with respect to organic pollutants, COD was measured in

addition to the metals. The COD in the snow showed little variation between the three sites; from 121 mg/L at the residential street (site A) to 146 mg/L for the urban highway (site C). The outflow was nearly constant for all three sites, and indicated a best attainable outflow concentration was 42 mg/L for all the three sites, which gave a 67–71% reduction. Sites A and B had a lower COD concentration for the first sample (first 20% of runoff volume) compared with the other samples (50%, 80%, 100% of volume). The same trend was not seen for site C, where the outflow COD concentrations were constant through the samples. This variation could be due to the type of organic compounds in the snowmelt. A previous study of snowmelt chemodynamics found that water-soluble organics would leave with the front of the meltwater, while the particulate-bound organics would leave with the tail of the meltwater (Schöndorf and Herrmann, 1987). A laboratory study on sustainable oil and grease removal from bioretention media found an approximately 90% removal of hydrocarbon contaminants through filtration in the mulch layer and subsequent microbial activity in the mulch layer (Hong et al., 2006). Further studies of snowmelt dynamics through the bioretention system should be investigated with respect to microbial activity in the mulch layer during the melt season compared with the summer season.

3.5. Sediments and chloride

TSS retention was more than 99% for all the sites, with an inflow concentration ranging from 2900 to more than 9600 mg/L, while the outflow concentration was less than 10 mg/L for all the samples. Looking at outflow concentrations, 5–6 mg/L was the best attainable outflow concentration on a consistent basis. Particle size distribution analysis of the inflow and outflow revealed a different particle size distribution for the snow and the outflow from the bioretention. The mean particle size for the snow was 13–17 µm, while the outflow particles were an order of magnitude larger, 144–154 µm. Analysis of some of the outflow samples for total volatile solids indicates that the outflow particles were almost all organic and probably result from detached biofilm in the outflow pipe or collection tank. Only 0.9–1.3% of the particles in the snow were less than 5 µm in size. The dissolved fractions in the snow with exception of copper for sites A and B were less than 2%. Site A had 30% dissolved copper in the snow. A strong correlation has been reported between dissolved metal fractions and suspended solids and chloride (Reinosdotter and Viklander, 2005). However, for this study, site A had the lowest suspended solids and chloride concentration of all three sites.

A Pearson correlation between total metal concentration and suspended solids in the snow revealed a strong correlation for all metals with correlation coefficients above 0.99. In the outflow from the bioretention boxes, no correlations were found between TSS and zinc or cadmium. A correlation between TSS and copper (correlation coefficient 0.566) and lead (correlation coefficient 0.749) in the outflow was found to be significant at the 95% CI.

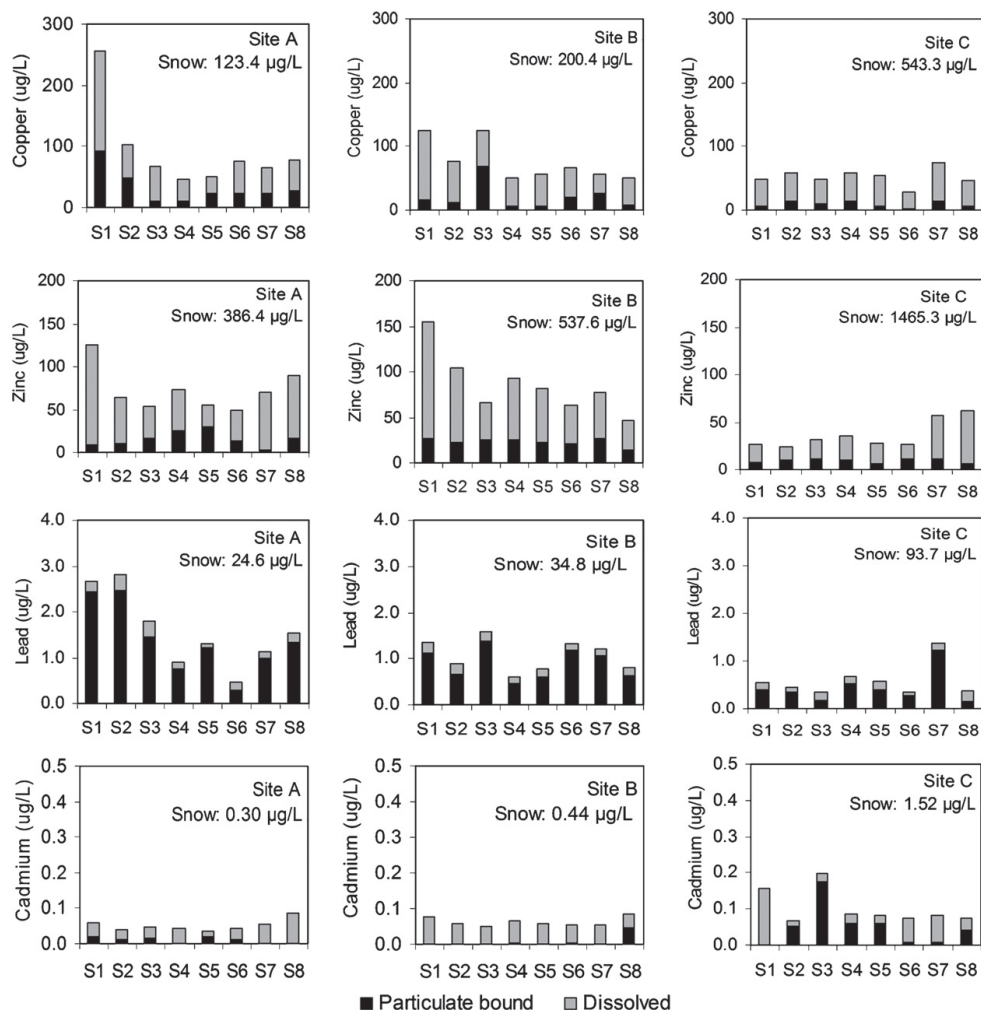


Fig. 4 – Average metal concentration in the bioretention outflow for the three snow sites, where S1–S8 represents the outflow samples collected at set volume of outflow intervals. The snow metal concentrations are listed in Table 2, but omitted here due to the large scale difference.

3.6. Pollutant pathways

The pathways of pollutants through the bioretention filter were compared with the pathways without any treatment. This comparison was done to investigate to what extent the bioretention filter changes the enrichment factor of dissolved pollutants in the front end and particulate-bound pollutants in the tail end of the meltwater flow. Comparing the mass accumulation of metals over time, both dissolved and particulate versus outflow volume gives a picture of the pathways of the pollutants through the bioretention boxes (Fig. 5). The collector road (site B), showed a positive enrichment for all the metals, while site A, the residential

road, had a more mixed picture with positive enrichment of zinc and copper, and neutral to negative for lead. For sites A and B the enrichment ratios were positive for all three metals, ranging from 1.5 to 1.1. Site C, the urban highway, showed virtually no enrichment of lead and copper, but a negative enrichment factor for zinc, 0.65 (Table 4). This could indicate an initial retention with subsequent washout of the dissolved zinc. Snow accumulating along urban highways influenced by winter storm maintenance activities has been shown to have a higher particulate-bound fraction compared with rainfall runoff (Glenn and Sansalone, 2002). A dissolution of some of the particulate-bound zinc through the bioretention box could cause a delayed dissolved fraction in the outflow.

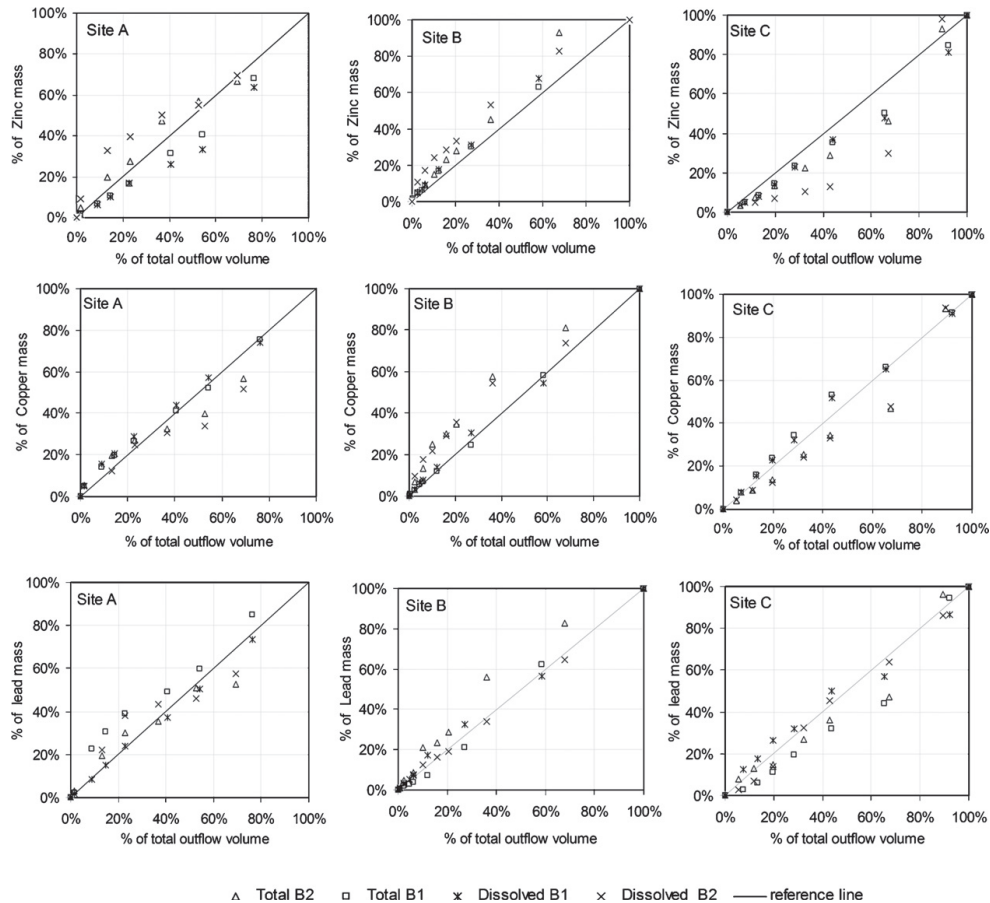


Fig. 5 – Dissolved and total metal mass fractions versus fraction of total outflow volume for zinc, copper, and lead in the two bioretention boxes. B1 = bioretention box and B2 = bioretention box 2.

Table 4 – Enrichment factors in the bioretention outflow			
	Site A (1500 vehicles/ day)	Site B (5000 vehicles/ day)	Site C (47 000 vehicles/ day)
Copper	1.51	1.17	0.97
Zinc	1.22	1.20	0.65
Lead	1.44	1.06	0.97

The enrichment ratios for sites A and B, however, were not as strong as reported in the literature (Viklander and Malmqvist, 1993; Ecker et al., 1990), indicating that the bioretention system to some extent was capable of reducing the elevated front-end concentrations of dissolved metals. The enrichment of tail-end particulates was not seen either; however,

with the high TSS removal in the system this would not be expected.

The mean chloride inflow concentrations at the three sites were very different. Site B had a chloride concentration that was 10 times higher than site C, 215.8 versus 20.9 mg/L, while site A had 50.3 mg/L. In the literature elevated chloride concentrations have been shown to be linked to the dissolved metal fraction (Warren and Zimmerman, 1994; Reinosdotter and Viklander, 2005), but this could not be found in this study. It is possible that some of the chloride had washed off the road at site C prior to collection due to the lower elevation and therefore higher average temperatures. There was also a tendency that the chloride was temporarily retained in the system between the site B and the site C snow applications. The outflow from site B had a 46% decrease in mass (from 10.7 g in the snow to 5.8 g in the outflow), while site C had a large increase in mass from 1.4 g in the snow to 7.7 g in the outflow.

4. Conclusions

The ability of the bioretention boxes to treat snowmelt from roadside snow was good overall with respect to achieving suitable concentration outflow levels and reducing mass loads. The best attainable outflow concentrations from the bioretention boxes, based on the median outflow concentrations, were 66 µg/L for zinc, 58 µg/L for copper, 1.1 µg/L for lead, and 0.07 µg/L for cadmium. The mass reductions of metals were excellent for all the sites, with 89–99% mass reduction of metals from the snow to the outflow meltwater. This clearly demonstrates that bioretention can successfully be used to treat snowmelt from urban roads; however, due to the small scale of the field set-up the performance of full-scale facilities should be further investigated. One issue could be the sheer volume of snow cleared from urban roads, which could require very large bioretention areas. Sorting and treatment only of the most heavily polluted snow could be a practical solution to this.

The top mulch layer was responsible for the most significant metal retention, with up to 74% of the zinc retained here. The plant metal uptake was found to be in the range of 2–8%, by estimating the final plant biomass; however, the function of the plants in the system to improve infiltration, and root-zone biofilms are still very important for the overall function of the system. The bioretention boxes reduced the effect of the enrichment factor of soluble bioavailable metals found in the front end of the snowmelt. Heavy loading of particles and particle-bound pollutants in the tail end of the snowmelt runoff was also not observed. However, the bioavailable (dissolved) copper and zinc concentration in the outflow increased, which should be further investigated either by the use of hyperaccumulating plants or by other retention media.

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REFERENCES

- Alloway, B.J., 1995. *Heavy Metals in Soils*. Blackie Academic & Professional.
- Caraco, D., Claytor, R., 1997. *Stormwater BMP Design Supplement for Cold Climates*.
- Clar, M.L., Barfield, B.J., O'Connor, T.P., 2004. *Stormwater Best Management Practice Design Guide, vol. 1, Vegetative Biofilters*.
- Daub, J., Förster, J., Herrmann, R., Robien, A., Striebel, T., 1994. Chemodynamics of trace pollutants during snowmelt on roof and street surfaces. *Water Sci. Technol.* 30 (1), 73–85.
- Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., 2001. Laboratory study of biological retention for urban stormwater management. *Water Environ. Res.* 73 (5), 5–14.
- Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., Winogradoff, D., 2003. Water quality improvement through bioretention: lead, copper, and zinc removal. *Water Environ. Res.* 75 (3), 73–82.
- Ecker, F.J., Hirai, E., Chohji, T., 1990. The release of heavy metals from snowpack on the Japan Sea side of Japan. *Environ. Pollut.* 65 (2), 141–153.
- Fritioff, Å., Greger, M., 2003. Aquatic and terrestrial plant species with potential to remove heavy metals from stormwater. *Int. J. Phytoremediat.* 5 (3), 211–224.
- Glenn, D.W., Sansalone, J.J., 2002. Accretion and partitioning of heavy metals associated with snow exposed to urban traffic and winter storm maintenance activities. II. *J. Environ. Eng.* 128 (2), 167–185.
- Granger, R.J., Gray, D.M., Dyck, G.E., 1984. Snowmelt infiltration to frozen Prairie soils. *Can. J. Earth Sci.* 21 (6), 669–677.
- Gregory, P.J., 2006. Roots, rhizosphere and soil: the route to a better understanding of soil science? *Eur. J. Soil Sci.* 57 (1), 2–12.
- Hong, E.Y., Seagren, E.A., Davis, A.P., 2006. Sustainable oil and grease removal from synthetic stormwater runoff using bench-scale bioretention studies. *Water Environ. Res.* 78 (2), 141–155.
- Jang, A., Seo, Y., Bishop, P.L., 2005. The removal of heavy metals in urban runoff by sorption on mulch. *Environ. Pollut.* 133 (1), 117–127.
- Kane, D.L., 1980. Snowmelt infiltration into seasonally frozen soils. *Cold Reg. Sci. Technol.* 3 (2–3), 153–161.
- Kholodova, V.P., Volkov, K.S., Kuznetsov, V.V., 2005. Adaptation of the common ice plant to high copper and zinc concentrations and their potential using phytoremediation. *Russ. J. Plant Physiol.* 52 (6), 748–757.
- Kobriger, N.P., Geinopoles, A., 1984. *Sources and Mitigation of Highway Runoff Pollutants*.
- Makepeace, D.K., Smith, D.W., Stanley, S.J., 1995. Urban stormwater quality: summary of contaminant data. *Environ. Sci. Technol.* 25 (2), 93–139.
- Malmqvist, P.A., 1978. Atmospheric fallout and street cleaning—effects on urban storm water and snow. *Prog. Water Technol.* 10 (5/6), 495–505.
- Novotny, V., Smith, D.W., Kuemmel, D.A., Mastroianni, J., Bartosová, A., 1999. *Urban and highway snowmelt: minimizing the impact on receiving water*. Water Environment Research Foundation, Alexandria, Virginia.
- NS4733E, 1983. Norwegian Standard for Suspended Particulate Matter.
- Oberts, G.L., 1990. Design considerations for management of urban runoff in wintery conditions. In: *Proceedings of the International Conference on Urban Hydrology and Wintery Conditions*, Narvik, Norway.
- Oberts, G.L., 2003. Cold climate BMPs: solving the management puzzle. In: *First International Conference on Urban Drainage and Highway Runoff in Cold Climate*, Riksgården, Sweden.
- Reinosdotter, K., Viklander, M., 2005. A comparison of snow quality in two Swedish municipalities—Luleå and Sundsvall. *Water Air Soil Pollut.* 167 (1–4), 3–16.
- Reinosdotter, K., Viklander, M., Malmqvist, P.-A., 2003. Comparison of the effects of using local and central snow deposits: a case study in Luleå. *Water Sci. Technol.* 48 (9), 71–79.
- Schöndorf, S., Herrmann, R., 1987. Transport and chemodynamics of organic pollutants and ions during snowmelt. *Nord. Hydrol.* 18 (4–5), 259–278.
- Thorolfsson, S.T., Matheussen, B.V., Frisvold, H., Nilsen, O., Kristiansen, V., Pettersen-Øverleir, A., 2003. Urban hydrological data collection in cold climate. In: *First International Conference on Urban Drainage and Highway Runoff in Cold Climate*, Riksgården, Sweden.
- USEPA (United States Environmental Protection Agency), 2002. *National Recommended Water Quality Criteria: 2002*. Office of Water. Report no. EPA-822-R-02-047.

- Viklander, M., Malmqvist, P.A., 1993. Melt water from snow deposits. In: Proceedings of the Sixth International Conference on Urban Drainage, Niagara Falls, Ont., Canada.
- Warren, L.A., Zimmerman, A.P., 1994. The influence of temperature and NaCl in cadmium, copper and zinc partitioning among suspended particulate and dissolved phases in an urban river. *Water Res.* 29 (9), 1921–1931.
- Westerlund, C., Viklander, M., 2006. Particles and associated metals in road runoff during snowmelt and rainfall. *Sci. Total Environ.* 362 (1–3), 143–156.

