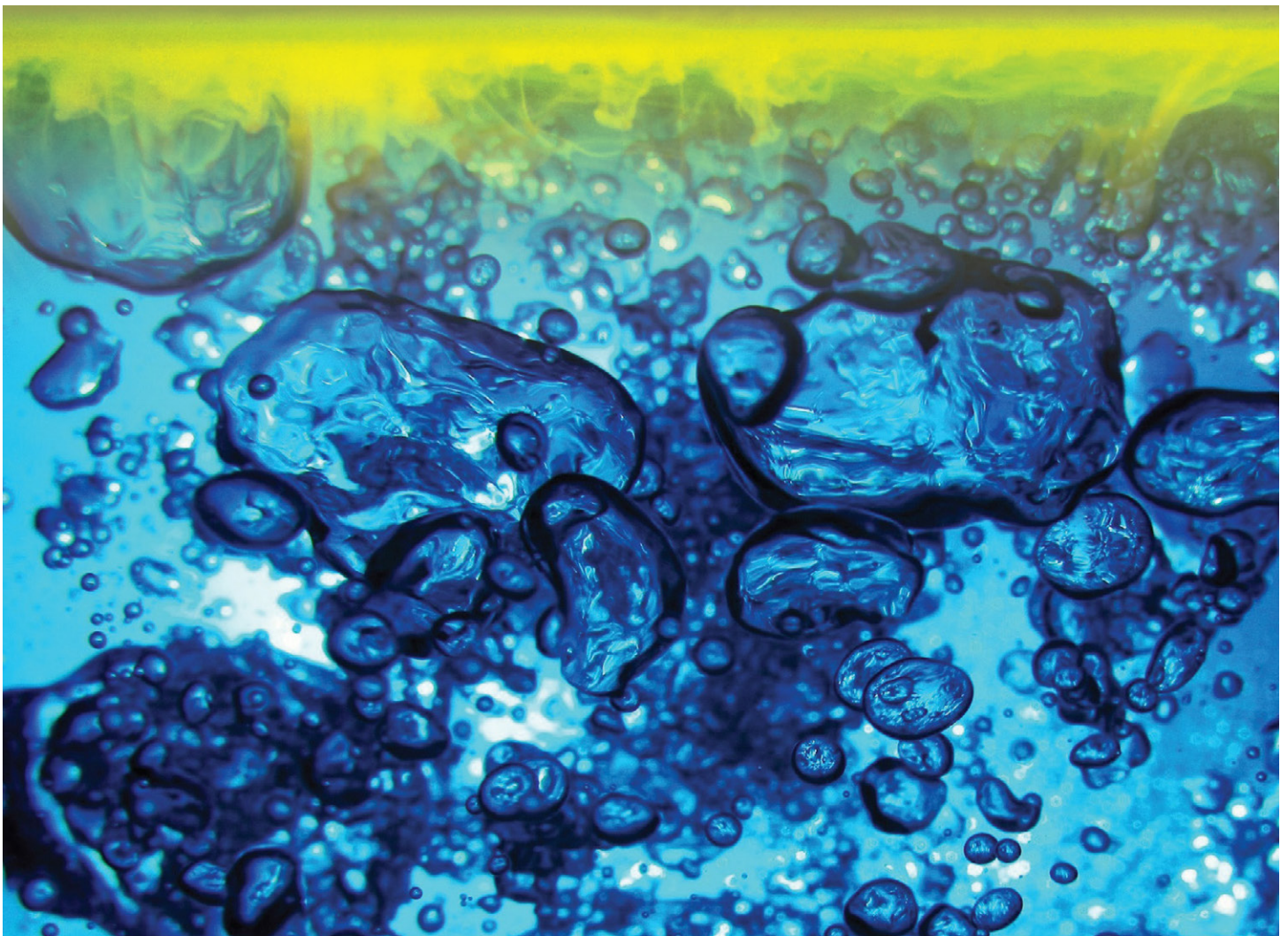




Adsorbents for infiltration based highway stormwater treatment in Norway

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Sammen drag

Denne rapporten presenterer resultatene fra et prosjekt med fokus på utvikling av avanserte infiltrasjonsbaserte løsninger for behandling av veiavrenning. Avansert infiltrasjon refererer i denne rapporten til et media, dvs. jord og eller sand, som har iblandet adsorberende medier for rensing av løste stoffer, som f.eks. tungmetaller og organiske stoffer. I dette prosjektet har fokuset vært på rensing av tungmetaller, og spesielt kobber (Cu), sink (Zn), bly (Pb), og nikkel (Ni). Fire adsorbenter (furubark, olivin, aktivt kull og bunnaske tilsatt en jernoksid blanding) ble testet i kolonneforsøk. Olivin og furubark var samlet sett de to beste alternativene basert på rensegrad og hydraulisk kapasitet. Disse to adsorbentene ble også testet ut i en fullskala laboratoriegroft/swale.

Title

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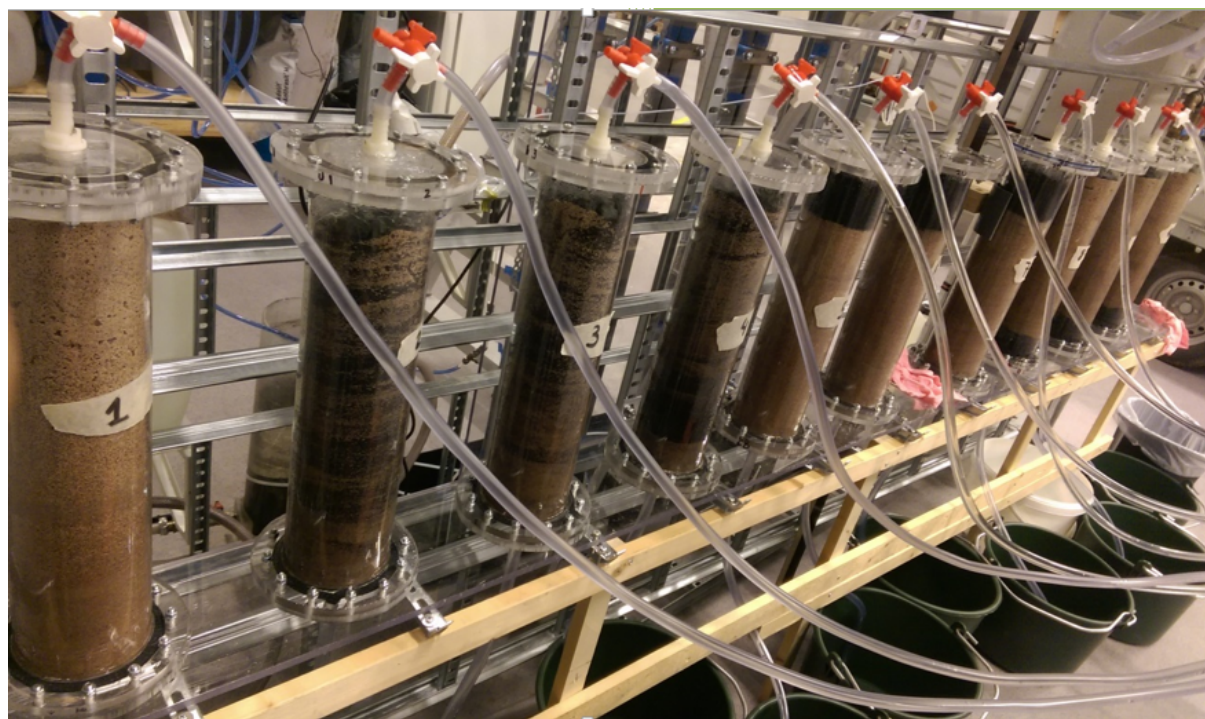
Summary

This report presents the results of a project focused on developing advanced infiltration based solutions for the treatment of highway stormwater. Advanced infiltration refers to amended infiltration media, i.e. soil and or sand amended with a suitable adsorbent media, for removal of soluble pollutants such as heavy metals and organic compounds. In this project, the focus has been on the treatment of heavy metals, especially copper (Cu), zinc (Zn), lead (Pb), and nickel (Ni). Four adsorbents (Pine Bark, Olivine, Charcoal and Bottom ash/Iron oxide mixture) were used in pilot scale column tests. The results showed that pine bark and olivine were both suitable adsorbents material due to their high performance and relatively long operational span. These adsorbents were also tested in a laboratory scale swale.

Aamir Ilyas, Carlos M. Martinez, Tone M. Muthanna

ADSORBENTS FOR INFILTRATION BASED HIGHWAY STORMWATER TREATMENT IN NORWAY

Trondheim, June 30, 2016



Statens vegvesen

 **NTNU**
Kunnskap for en bedre verden

Sammendrag

Dette prosjektet har vært et samarbeid mellom Statens Vegvesen og NTNU, finansiert under NORWAT etatsprogram i perioden 2013-2016. Det har vært en post-doc stilling og deler av en stipendiat stilling knyttet til arbeidet i prosjektet i tillegg til NTNUs prosjektleder. Hovedformålet med prosjektet har vært å se på mulige adsorbenter som kan brukes i dreneringsgrøfter til rensing av veiavrenning fra høyt trafikkerte vegstrekninger. Det har også vært en målsetning å se på hydraulisk belastning og levetid for de ulike løsningene.

Arbeidet i dette prosjektet er under publisering i fire vitenskapelige artikler. NTNU tar forbehold om at resultatene som er presentert her, og referert til manuskriptene ikke publiseres offentlig hos Statens Vegvesen før alle de fire vitenskapelige artiklene er publisert. Det vil også bli en oppdatering av referanselisten når den vitenskapelige publiseringen er ferdig, da det per i dag ikke foreligger fullstendig referanse for de artiklene.

Det kalde klimaet i Norge er en ekstra utfordring for håndtering og mulig rensing av overvann fra veiavrenning fra motorveier og annen høyt trafikkert vei-infrastruktur. Veinettets utstrakte nature er en ytterligere utfordring for drift og vedlikehold av mulige renseløsninger. Det er i dette perspektivet også viktig å se på levetid og vedlikeholdsbehov ved løsningene. Det er behov for å utvide porteføljen av mulige renseløsninger basert på ulik forurensningsgrad av veiavrenningen, og sensitiviteten til resipientene.

Denne rapporten presenterer resultatene av et prosjekt med fokus på utvikling av avanserte infiltrasjons baserte løsninger for behandling av veiavrenning. Infiltrasjon er en passiv prosess av natur, og kan med tilstrekkelig kapasitet være en plasseffektiv løsning med moderate vedlikeholdskostnader. Med avansert infiltrasjon refereres det i denne rapporten til et media, dvs jord og eller sand, som har iblandet adsorberende medier for rensing av løste stoffer, som f.eks tungmetaller og organiske stoffer. I dette prosjektet har fokuset vært på tung metaller, og spesielt kobber (Cu), sink, (Zn), bly (Pb), og nikkel (Ni). Hovedkriterier for valg av løsning ble basert på rensegrad og hydraulisk kapasitet. For dimensjonering av filter er det tatt hensyn til lokale geografiske forskjeller i klima dvs. variasjon i nedbør. Dette ble gjort med tanke på å utvikle en realistisk drifts- og vedlikeholdsregime for filtrene. Den generelle tilnærmingen i dette prosjektet var å bygge videre på eksistere vitenskapelig kunnskap igjennom bruk av litteraturstudie hvor man så på både teoretisk analyse og eksperimentell verifikasjon i utvelgelse av adsorberende media.

I den første delen av prosjektet ble flerkriterieanalyse brukt for å identifisere potensielle alternative adsorbenter som kunne egne seg til videre testing. En av motivasjonene for dette prosjektet var å bidra til å fylle kunnskapshullene om de praktiske sidene av adsorbentbruk fordi litteraturen gir lite informasjon om kostnader, vedlikehold og miljøpåvirkninger. Ved eksplisitt å kombinere de tre aspekter; høy ytelse, lave kostnader og lave miljøbelastninger igjennom en

flerkriterieanalyse, var det mulig å identifisere alternative materialer som ville være egnet for videre implementering i infiltrasjon system. I tillegg til adsorbentenes evne til å oppnå høy rensegrad og reduksjon av avrenningstoppen, ble kostnad og miljøkonsekvenser vektlagt. Resultatene av denne første del resulterte i en liste over 12 potensielle adsorbenter, som kunne tilfredsstillte de gitte kriteriene.

I den andre delen, ble de åtte beste adsorbenter fra den første delen brukt i et benkeforsøk for å bekrefte rensegrad og eventuell utlekking, miljøkonsekvenser, igjennom desorpsjonsforsøk og utvasking. For denne delen ble det brukt en runde med høye metallkonsentrasjoner (Cu, Ni, Pb og Zn), or en runde med varierende metallkonsentrasjoner. Adsorpsjonsdata og utlekkingsdata dannet grunnlaget for å redusere listen ytterligere ned til de fire mest lovende adsorbentene; furubark, olivin, aktivt kull og bunnaske tilsatt en jernoksid blanding, som videre i den neste delen ble brukt i kolonnetester. I kolonnetestene ble metallkonsentrasjonene fastsatt til 1 mg/L for hvert av de fire metallene, og en høy hydraulisk belastning. Alle de fire adsorbenter var i stand til å fjerne 90% eller høyere, og passere vannmengde tilsvarende en nedbørshendelse med et toårs gjentakintervall i løpet av 24-48 timer. Dermed oppfyller de alle målsetningen som ble satt som et av kriteriene. Virkningen av vinter salting av veiene ble testet i kolonneforsøkene ved å bruke vann med 1g/L NaCl konsentrasjon og samme høye hydrauliske belastning. Resultatene viste at adsorpsjonen var stabil selv under høy saltkonsentrasjon og samlet utlekking av metaller var under 1% totalt.

Etter belastningstestene med kort perioder med høy hydraulisk belastning ble kolonneforsøkene kjørt i ytterligere tre måneder med konstant volum gjennomstrømming i kolonnene. Disse volumene ble senere brukt i omregning av levetid, basert på nedbørsmengder etter geografisk beliggenhet i Norge. Resultatene viste, som forventet, at levetiden varierte mye. Det ble antatt en konstant forurensingsbelastning for denne delen. Dette er en konservativt antagelse, som gir en buffer i levetidsanalysen. Olivin og furubark var samlet sett de to beste alternativene. Begge hadde høy rensegrad, god hydraulisk kapasitet, og relativt lang antatt levetid. Selv om bunnaske iblandet jernoksid viste en lang operasjonell levetid, begrenset tilstoppingsproblemer på grunn av sementeringsreaksjoner i bunnasken den reelle levetiden betraktelig, som gjorde den mindre egnet i full skala drift.

Adsorbentene identifisert i dette prosjektet har alle meget god rensegrad for rensing av løste metaller. For bunnaske iblandet jernoksid og olivin ble ingen utmattelse observert i løpet av testperioden, selv om olivin kom nærmest, med en rensegrad på ned mot 60% på slutten. For furubarken ble det observert en reduksjon i rensegrad ned mot under 35% for to av de fire metallene, men uten en fullstendig utmattelse. Aktivt kull viste den dårligste ytelsen av de fire adsorbentene testet i kolonneforsøkene. Vesentlig reduksjon i rensegrad ble først observert etter vannvolumer som tilsvarer flere års nedbør, og avrenning med høye metall konsentrasjoner, som ikke tar høyde for en kjent forhøyet konsentrasjon tidlig i hendelsesforløpet, og synkende jo lengre hendelsen varere. Prøvetaking på veier av ulike trafikktetthet i Trondheims området viser en vesentlig lavere vannføringsvektet gjennomsnittskonsentrasjon (event mean concentration).

Den hydrauliske kapasiteten og infiltrasjonsrater ble testet både i kolonner og i full størrelse laboratorium oppsett. I den siste delen av prosjektet ble infiltrasjonskapasitet verifisert i en fullskala swale bygget på laboratoriet; 5 meter lang, 80 cm bred og 50 cm dype. Hydraulisk kapasitet i kolonneforsøk tar ikke høyde for den horisontale strømmingen i en grøft. Hvis vannhastigheten blir for høy vil det ikke gi tilstrekkelig tid til den vertikale infiltrasjonsprosessen. Dette bidro til å forstå den hydrauliske oppførsel i det foreslått designet i virkelige situasjoner og dimensjonere filter / swales riktig for å oppnå maksimal effekt.

Infiltrasjonskapasiteten for alle fire adsorbentene var tilstrekkelig god nok i forhold til anbefalingene for minimum infiltrasjonshastigheten for infiltrasjonsanlegg. Det er her verdt å merke seg at adsorbentene er blandet med sand som hovedmedia, som har en naturlig høy infiltrasjonskapasitet, slik at disse testene først og fremst var egnet til å identifisere hvis adsorbentene hadde en hydraulisk kapasitet under det som var nødvendig. En enkel formel er foreslått for å dimensjonere filter plassert i grøfter langs veiskulderen, basert på noen få parametere og lett tilgjengelig data. Dataene som kreves er mettet hydraulisk konduktivitet (KSAT), for filtermaterialet, og nedbørsmønsteret (nedbørsmengde for ulike gjentakintervaller). Med denne enkle prosedyren, kan infiltrasjonsanlegg dimensjoneres med utgangspunkt i både hydraulisk belastning og rensegrad.

Summary

The cold climate of Nordic countries presents a challenge with regards to stormwater quality and quantity from highway infrastructure. The nature of road construction increases the risk of contamination spreading over a wide geographic area and polluting pristine aquatic eco-system. It goes without saying that the contamination risks from highway stormwater needs to be contained and minimized to maintain ecosystem health and enhance the sustainability of transportation infrastructure. In this regard, efforts are needed to further evaluate the water quality of stormwater-i.e. type and variations of contaminants in relation to weather patterns. Understanding these interrelationships can be a useful in predicting performances of local BMPs and dimensioning new systems. At the same time, there is need to diversify existing portfolio of commonly used highway stormwater handling methods by testing low cost methods to treat contaminated stormwater.

This report presents the results of a project focused on developing advanced infiltration based solutions for the treatment of highway stormwater. Infiltration was chosen because of its low space requirement and passive nature with little to no operational control. With advanced infiltration it refers to amended infiltration media, i.e. soil and or sand amended with a suitable adsorbent media. Two main selection criteria were applied based on the objectives; the use of alternative adsorbent media, and secondly, the hydraulic behavior of the filters. Here a particular focus was dimensioning filters with regard to local geographical differences in climate i.e. variation of precipitation and hydraulic behavior. This was done with a view to develop a realistic operational and maintenance regime for the filters. The overall approach of this project was to build on exist scientific knowledge and focus on potential applications of the infiltration based solutions. Therefore the project was structured in way that it combined both theoretic analysis and experimental verification to achieve rapid implementation of the chosen solutions.

In the first part, multi criteria analysis was used to identify potential alternative adsorbent materials which could be successfully transitioned into field scale implementation. This project was carried out to fill the knowledge gaps concerning the practical aspects of adsorbent use because the literature provide little information about adsorbents costs, maintenance and environmental impacts. By explicitly combining the three aspects; high performance, low cost and low environmental impacts in multi criteria analysis, it was possible to identify a pool of alternative materials which would be suitable for implementation in infiltration system. Here along with costs and environmental impacts, the main focus was on any given adsorbents ability to achieve high removal and reduce peak flows within 24-48 hours. The results of this first part provided a list of 12 potential adsorbents, which could meet the given criteria.

In the second part, 8 of the best adsorbents from the first part were used in batch tests to verify their adsorption performance and environmental impacts-through desorption and leaching. Here adsorption performance was tested at high and variable metal (Cu, Ni, Pb & Zn) loads. The adsorption data and leaching behaviour helped narrow down this list to four adsorbents (Pine Bark, Olivine, Charcoal and Bottom ash/Iron oxide mixture), which were later used in pilot scale column tests. In the column tests metal concentrations were fixed at 1mg/L for each metal, and a rapid flow scheme. All the four adsorbents were able to remove at 90% or above and pass water volume equivalent to two year return period rainfall within 24-48 hours. Thus, meet the objectives set for infiltrating small storms locally. The impact of road salt applications was tested at the end of rapid flow tests by passing through tap water mixed with 1g/L salt concentration.

The results showed that adsorption was stable even under high salt concentration and release of adsorbed metals was below 1% overall.

After the rapid flow tests, the columns were run for another three months passing a constant volume through the columns. These volumes were later converted to equivalent numbers of years of rainfall, which was used along with catchment area and rainfall intensity to estimate potential operational life at different geographical locations in Norway. The results showed that depending chosen catchment area and geographic location the operational life varied greatly. In summary, the results showed that pine bark and olivine were both suitable adsorbents material due to their high performance and relatively long operational span. Although the bottom ash/iron oxide mixture showed long operational lifespan, it experienced clogging problems due to cementation reaction did not allow its use after a certain period, making it less suitable in full scale operations.

The adsorbent identified in this study have shown very good adsorption performance for the target metals. In case of bottom ash/iron oxide mix and olivine no exhaustion was observed within the test period, although olivine's adsorption did decrease to 60% towards the end. For pine bark, the adsorption of two out of the four metals decreased below 35% but without complete exhaustion. The charcoal showed poorest performance of all the four adsorbent. However, this performance was observed after e having passed several equivalent years of precipitation of extremely contaminated water. In real life event mean concentrations found in stormwater runoff are considerably lower than concentrations used in this study, which makes the promising results showed in this report to be conservative regarding field conditions.

The hydraulic capacity and infiltration rates of the filters were tested both in columns and in a full size laboratory setup. In all cases, the infiltration rates registered in the hydraulic tests exceeded the recommendations for minimum design infiltration rate for infiltration facilities. A simple formula is proposed in order to size roadside filters based on few and easy to obtain data. The data required is the saturated hydraulic conductivity (K_{sat}), of the filter material, and the rainfall characteristics of the location of interest. With this simple procedure, the developers can dimension an infiltration facility while taking into account basic operation factors but at the same time keeping the design still manageable for any developer.

The laboratory scale swale constructed as the last step of this project was 5 meters long, with 50 cm deep filter beds. A swale of three parallel is being finalized and initial results are shown. This setup will include three different swales made up with materials based on the results obtained in the previous column tests. This will help understand the hydraulic behavior of proposed filter design in real life situation and dimension the filter/swales correctly to achieve maximum impact.

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1. Background

Effective and sustainable management of highway stormwater entails that environmental impacts, due to pollutants, should be minimized through adoption of low cost and blue green solutions. Current highway stormwater handling relies heavily on detention basins and ponds with a dual focus of peak flow reduction and on reducing the total concentrations of contaminants, and less on the bioavailable and potentially toxic dissolved phase of contaminants. They provide effective treatment for particulate or suspended phase contaminants but lack in controlling the dissolved phase contaminants i.e. metals, nutrient and organics. Furthermore, due to the extensive nature of highways, treating highway storm water inside the existing wastewater treatment system is not a practical option.

In this regard, infiltration based solution such as bio-swales, bio-retention and infiltration trenches can be implemented to provide the desired treatment effect for particulate and dissolved contaminants, particularly heavy metals. The particular focus in this report will be on heavy metals, though highway pollutants are not limited to toxic metals. Removal of the metals can be achieved through either special adsorbent materials or high surface area soils. The challenge, however, is to find a low cost adsorbent material that can achieve both peak flow reduction and acceptable treatment performance of contaminants. A faster peak flow reduction is important as prolonged ponding in ditch or over filter area, close to roads, may adversely affect the road bed stability and traffic safety.

To develop infiltration based system, selection of proper adsorbents is important for the infiltration based solutions to ensure effective removal of contaminants. In general, the selected adsorbent should have high affinity for the target dissolved contaminants. It should not be costly or require frequent maintenance. Although, many examples of low cost adsorbents are available in the scientific literature, only few examples exist regarding their performance in the field. Therefore, it is necessary that adoption potential of adsorbents should be evaluated prior to adoption.

The choice of adsorbent materials will be determined by type (suspended vs dissolved) and variability of contaminants, in response to seasons and operations (deicing), in highway runoff. Moreover, placement of the adsorbents will have an effect on not just infiltration but also the removal performance of such infiltration systems. The chosen filter medium should provide a tradeoff between sufficient drainage and enough detention time for treatment and/or vegetation survival (Le Coustumer et al., 2009).

Furthermore, in real life, for proper function of infiltration based treatment, two aspects need to be considered: 1) treatment effect of alternative adsorbents, and 2) hydraulic behavior of proposed infiltration solution. Long-term infiltration rates in the filters and water quality variations are important hydraulic (Grebel et al., 2013) and treatment controls that can determine the life span of such systems. Amending filters with adsorbent material will also have influence over the infiltration capacity of the whole infiltration system (Paus et al., 2014). The Norwegian recommendation, for infiltration systems, is to collect and infiltrate runoff from smaller rainfall events (<20mm) locally. While runoff from medium events (20 – 40 mm) should be delayed and retained and for larger events (> 40 mm) safe flood ways and secure safe passage of runoff is required (Norsk Vann Rapport, 2008).

From a maintenance point of view, of infiltration systems, the effect of deicing salts and placement of an adsorbent within the filter need to be evaluated prior to implementation. The use of salt can have effect on adsorption process and also may desorb the contaminants from adsorbent surfaces. The adsorbent placement can determine adsorbents life span in relation to factors such as frost and erosion. Finally, determining the size of the filter with respect to the catchment size is another important aspect. Given the fact that rainfall patterns vary over geographic regions, this needs to be accounted for in the design considerations. The data on infiltration capacity can help determine the size of catchment by relating this information to rainfall characteristics such as intensity duration and frequency.

1.1. Scope and limitations

The main aim of the project was to evaluate alternative adsorbent materials that could be used in development of infiltration based treatment solution for the treatment of highway runoff; more specifically, removal of heavy metals. The approach was to build on existing knowledge both locally and internationally. Therefore, the study was not about evaluating the adsorption processes in alternative adsorbents and/or understanding the kinetics of pollutant removal, or performing long term hydrologic simulations of stormwater. A considerable body of knowledge is already available on these subjects. The overall aim is to provide practical information that could be used to implement infiltration based solution for treatment of highway stormwater.

Keeping in line project aims, the current report presents the results on following aspects of the project. It is anticipated that these results will help bridge the knowledge gap on these issues and provide authorities a practical way to design and implements low cost infiltration based treatment solutions in cold climate. Following research questions were the focus of investigations.

- ❖ What is the upscaling potential of alternative adsorbents for highway stormwater treatment?
- ❖ Can reported performance of alternative adsorbents be verified for four (Cu, Ni, Pb & Zn) commonly found metals?
- ❖ What are the effects of road salt on adsorption and desorption of metals?
- ❖ What are the effects freeze-thaw conditions on hydraulic function of the proposed filter?
- ❖ How to dimension adsorption filters with fewer data and local hydrologic conditions?

2. Alternative adsorbent materials (AAMs)

Following section is based on results presented in (Ilyas and Muthanna, 2016; Ilyas and Muthanna, 2014).

Alternative adsorbent materials (AAMs) can refer to a class of adsorbents extracted from geologic, biological and secondary wastes. One main advantage of AAM is their low cost which is an important factor for their application in treatment of highway stormwater. Because extensive spatial scale of highways limits the use of commercial treatment systems, for stormwater, that require control or frequent maintenance. There are many alternative adsorbents and abundant literature is available on identification of new materials and their evaluations under various conditions. The AAMs include: secondary wastes such as blast furnace slags, fly/bottom ashes and pine bark e.g. (Alexopoulos et al., 2013; Eichhorst et al., 2013; Gustafsson et al., 2008; Johansson, 1999; Kalmykova et al., 2010; Ronda et al., 2014; Zhou and Haynes, 2012); geologic materials such as various minerals e.g. (Gustafsson et al., 2008; Motsi et al., 2009; Norris et al., 2013; Wium-Andersen et al., 2012); biological materials such as peat and seaweed, e.g. (Alhakawati and Banks, 2004; Elangovan et al., 2008; Kalmykova et al., 2009; Kängsepp et al., 2009). These AAMs have been tested to treat landfill leachate, domestic wastewater and storm water e.g. (Genç-Fuhrman et al., 2007; Kalmykova et al., 2008; Westholm, 2010; Wium-Andersen et al., 2012). The results of these studies show that AAM have a very high specificity and removal of metals such as Cu, Pb, and Zn etc.

2.1. Finding a suitable AAM

Despite that fact that AAM are available in abundance, finding a suitable alternative adsorbent is still not easy due to lack of their performance bench marking or verification. More importantly, there few examples of their application at the field scale, which makes it risky to simply rely on studies that only focus on removal capacity in laboratory tests. The based laboratory studies do not account for differences in operational conditions. For example, Rastas-Amofah and Hanæus (2006) reported that slag removed 40-53% of P in domestic wastewater, which was significantly lower than previously reported(up to 99% P removal) in the laboratory studies. This discrepancy was due to clogging caused by higher particle load of real wastewater compared to the synthetic one, used in the lab studies. Similarly, Kalmykova et al. (2008) evaluated removal metals and petroleum hydrocarbon from the landfill leachate by several AAMs and showed that there were significant performance differences between actual leachate and synthetic solution as well as between batch tests. Using the synthetic solution and batch tests overestimated the metal removal by AAMs, due to high concentrations, and did not reproduce the competitive effects of other ions present in the actual leachate. Thus, ignoring the differences in operational conditions (i.e. saturated flow in columns vs intermittent flow in field) climate (i.e. stable room temperatures vs variable field climate) and can result in poor performance of filters using AAMs.

For a realistic assessment of alternative adsorbents to treat highway stormwater, non-technical factors such as costs, environmental impacts, end-of-life care, and application flexibility, should be integrated into the analysis. However, despite extensive research, on AAMs, one cannot find studies that provide data on non-technical factors. Generally, available data on AAM performance evaluation and ranking is solely based on adsorption performance. For example, Genc- Fuhrman et al., (2007) evaluated 11 different AAMs and developed a ranking based on

metal removal capacity by using isotherm constants. In another study, Al-Anbari et al., (2008) evaluated eight different for heavy metals(Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) removal from storm water and then ranked the adsorbents based on maximum removal of metals. However, this type of ranking may give information about an adsorbents affinity for a particular contaminants but it does not given any data above mentioned factors. This makes selection decision risky or difficult for the end users or decision makers who need to have broader assessment of an AAM.

To avoid these pitfalls, the project combined multi-criteria modelling (MCM) with experimental evaluations to evaluate the upscaling potential of AAMs and identify the most important factors that can affect the upscaling process and/or where more information is needed. The main focus was on AAMs' suitability and potential for upscaling into a real life infiltration based treatment system. To this end, from the published literature, i.e. adsorption studies, potential AAMs were identified and the relevant data were collected (i.e. removal capacity, particle sizes, desorption etc.) for the decision modelling. The steps involved in this process are described below.

Definition of criteria: technical, economic and environmental aspects, which are further subdivided under each category (see Table 1).

1. Search for adsorbent: Previous scientific literature was searched to identify potential sorbents and extract data on their performance.
2. Selection of Multicriteria model¹: for this task linear utility model given by Keeney and Raiffa (1976) was used.
3. Development of weighting method: In order to limit the bias in scoring and weighting a literature based weighting method was used. This relies on the impact of a particular study by judging its replication and/or application in field. In this way adsorbent most replicated or tested in the field would get high scores, and thus a better chance of success in our settings.
4. Computation of ranks: Using the model(present in point 2) scores and weights were combined to compute a final rank for each adsorbent.
5. Experimental verification: Batch and pilot scale column tests were used verify the performance of selected adsorbents and narrow down the choices given by the model.

$$^1 R_i = \sum_{j=1}^n S_j W_{ij} = S_1 W_{i1} + S_2 W_{i2} + \dots + S_n W_{in}$$

Where R is the rank, S is the score on a particular performance indicator, W is the weight while subscripts *i* and *j* indicate a particular score and weight in the matrix

Table 1: Definition of upscaling objectives and criteria along with explanations. Desirability is introduced to avoid scoring similarities(Ilyas and Muthanna, 2016).

Objectives	Criteria	Units	Desirability	Explanation
High Performance				
	Hydraulic Load	Liquid/Solid Ratio	High	In road settings, high infiltration is required to prevent damage to road structures.
	Removal	Percentage	High	Percentage removal for contaminant types
	Pollutant Loads	g / Kg Sorbent	Low to moderate	Storm water does not contain high concentrations of contaminants
	No of Contaminants	n.a.	Several type	Type of contaminant means - metals, organics and nutrients.
Lower Costs				
	Availability	Ton/ year	High	Preferably, locally available and should replace 20-30% of used adsorbent in a given year
	Cost €/Kg	Euro	Low	
	Operational Cost	Euro	Low	
	End of Life Costs	Euro	Low	End of life costs mean disposal or treatment after use.
Low Environmental Impact				
	Life Span	Years	High	Longer life span would cause fewer disturbances to surrounding environment through construction or maintenance activity.
	Clogging Risk	n.a.	Low	High clogging would reduce performance thus contribute contaminants to environment.
	Leaching	mg/kg Liquid	Low	Effluent should comply with EU & Norwegian Water Quality Criteria

Here some highlights of the theoretical analysis are given and results of batch and column tests are described in subsequent sections.

1. MCM was successful in integrate adsorption capacity data with other factors such as costs, operational life, clogging risk and environmental impacts etc to provide a broader evaluation of AAMs' potential for use in highway stormwater treatment.
2. Out of total of 25 MCM helped identify 10 potential AAMs (Figure 1) that could be further analysed and screened in laboratory batch tests. These adsorbents scored high because they were able to meet the set criteria for selection defined in table 1. The result also makes it easier for decision maker to compare AAM on various criteria and make trade-offs e.g. high initial costs vs long operational life.
3. This shows that low cost alternatives adsorbent such as pine barks are more likely to meet our design and operation requirement. It also highlights some choices such as bottom ash which might be considered risky. However, the model assumes that the risks could be controlled by addition of stabilizing agents. This assumption was tested, in next task, with batch tests and description is given below.
4. A sensitivity analysis was performed with the help of principal component analysis (PCA), figure 2, which identified the critical criteria, which affected both model outcome as well as the decision choice. These include hydraulic load, operational costs, clogging risks and availability etc.
5. Results of this work were published in an international conference paper (Ilyas and Muthanna, 2014) which provides detailed description of the work.

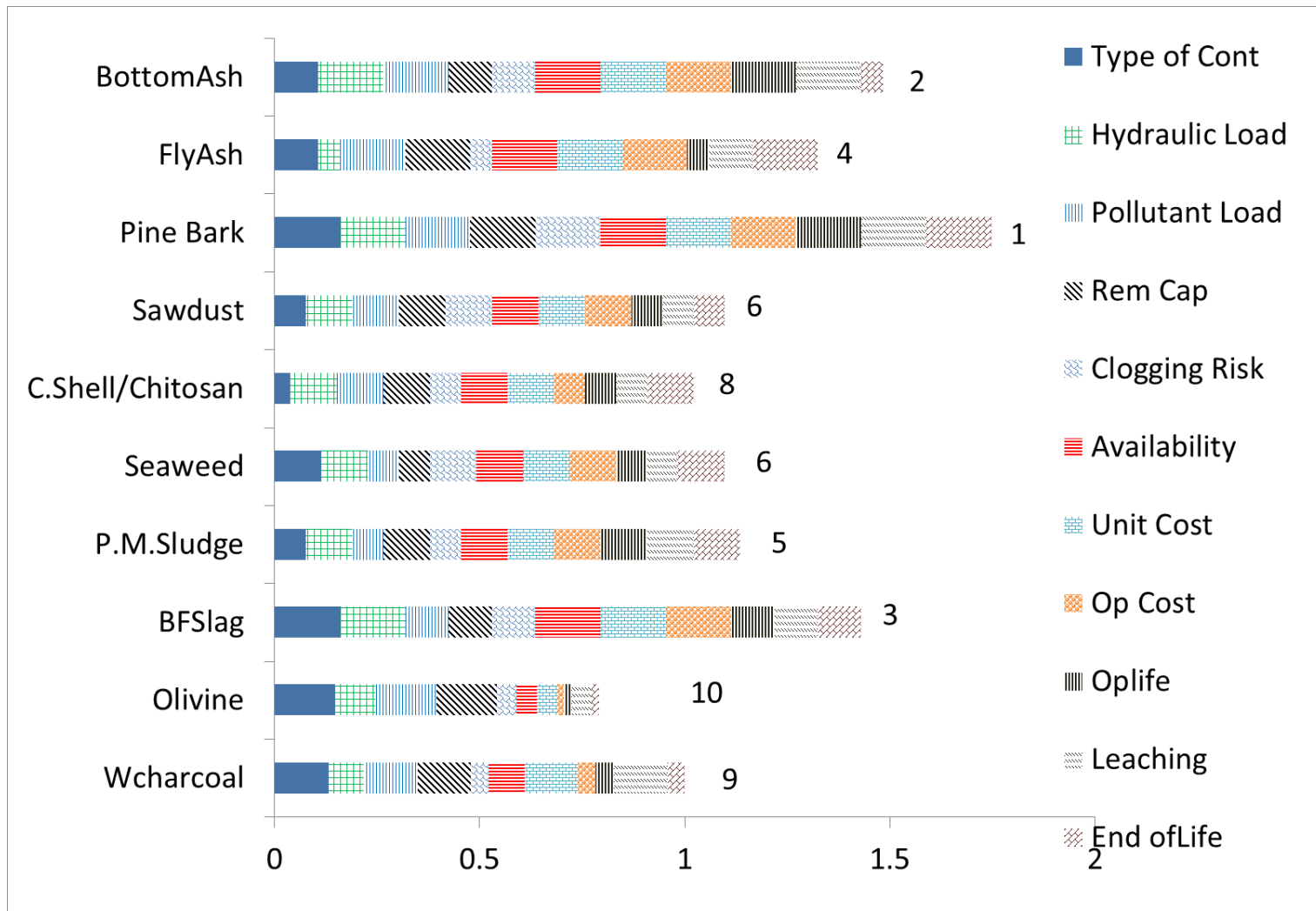


Figure 1. Multicriteria ranking of top 12 adsorbents((Ilyas and Muthanna, 2016)

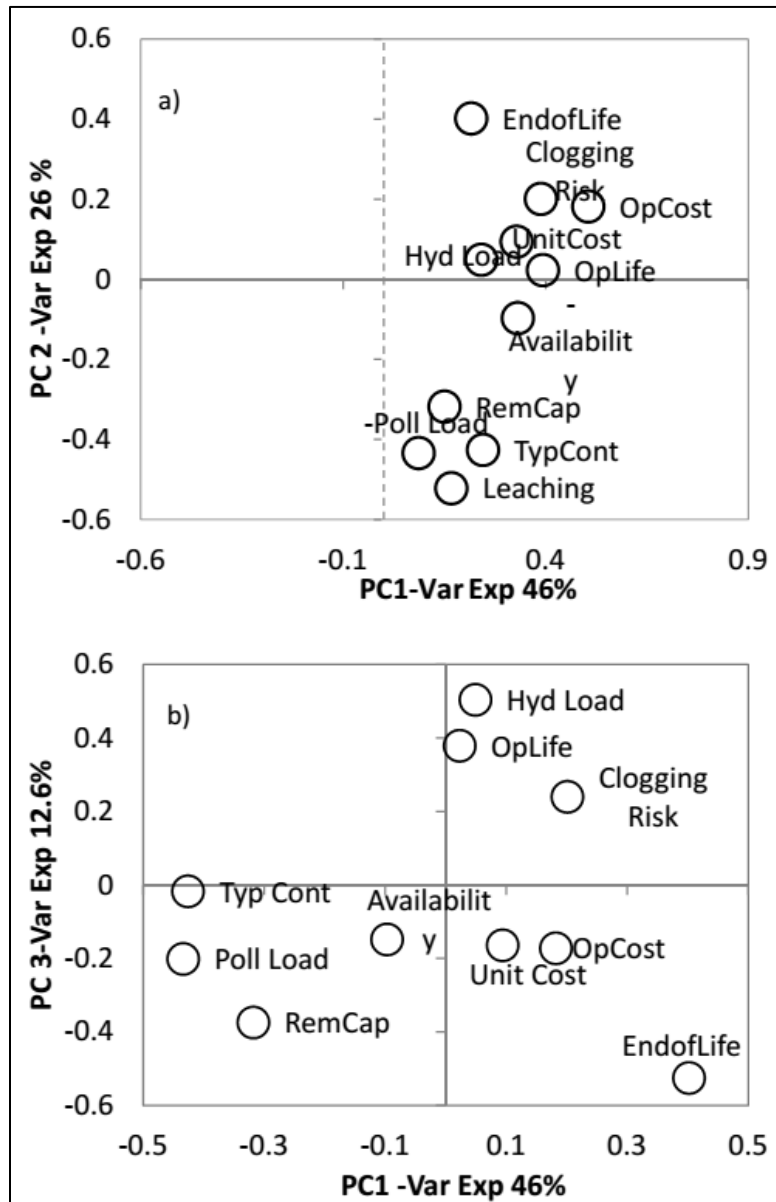


Figure 2 (a&b): The PCA factor loadings plot of various criteria(Ilyas and Muthanna, 2016).

Where follow abbreviations refer to:

PC: Principal Component;

Var Exp: Variance Explained;

OpLife: operational life;

OpCost: operational costs;

RemCap: removal capacity (%);

Typ Cont: type of contaminants (metals, nutrients, organics etc.);

Hyd Load: Hydraulic Loads

3. Experimental verification of performance

Based on the MCM 10 (8 adsorbents +2 combinations) different adsorbents were subjected to batch tests evaluation to verify their performance reported in the literatures. This sound contradictory to discussion in section 1 but batch tests were followed to keep test conditions as similar as possible to the literature. Otherwise, the verification would have no consequence or meaning.

3.1. Batch tests

The selected adsorbents were subjected to batch adsorption tests with synthetic stormwater containing four metals (Cu, Ni, Pb & Zn) with four different concentrations (table 2). The concentrations used in the experiment were kept deliberately high to achieve detection with laboratory instruments. The results of the batch tests are summarized in **Error! Reference source not found.** which shows that majority of the adsorbent performed well, achieving a very high removal of four metals. There were a couple of exceptions such as sea weed and saw dust, which did not perform as expected. This was due to difficulties in performing the experiment on these materials. For example sea weed was not stable as it quickly dissolved in a viscous solution, which hampered proper extraction and filtration of samples for the laboratory analysis. Similarly, saw dust due to low density soaked up all the solution and it was not possible to extract any samples for analysis of metals. The fly ash on the other hand presented a different problem as leached more Pb than it adsorbed. This was due to perhaps fresh state of the fly ash and due to lack of secondary mineral formed during aging process. Thus these adsorbents were excluded from the column scale tests. From the table 3, it easy to identify at least four promising adsorbents such as olivine (granules), pine bark, charcoal and bottom ash. Although, olivine powder showed very good removal but for percolation mode it is not suitable. While, Kaolinite and Molecular sieve do not show consistent removal at all the concentrations or contaminants. BA, although, has very high adsorption but is also known to leach metals and macro ions. Therefore, prior to testing bottom ash columns, a stabilization method was tested and it is described in next section.

Table 2: Target metal concentrations (mg/L), written as C1-4, in synthetic stormwater for adsorption tests

	Copper	Lead	Nickel	Zinc
C1	1.0	1.0	2.5	5.0
C2	2.0	2.0	5.0	10.0
C3	3.0	3.0	7.5	15.0
C4	4.0	4.0	10.0	20.0

Table 3. Performance of 10 different adsorbents in batch tests. The results are reported as % removal of each metal at a four different concentrations (written as C1-4).

	Pine Bark				Sea weed				Olivine-Granules				Olivine-Granules				Bottom Ash			
	C1	C2	C3	C4	C1	C2	C3	C4	C1	C2	C3	C4	C1	C2	C3	C4	C1	C2	C3	C4
Pb (II)	99.14	99.39	99.50	99.46	92.10	95.79	96.08	95.94	99.97	99.97	99.92	97.42	97.42	98.02	98.49	97.47	99.83	99.88	99.96	99.89
Ni (II)	96.53	95.48	95.55	94.66	66.94	63.60	55.16	61.24	99.86	99.85	96.27	95.97	99.99	99.99	100	99.99	99.93	99.96	99.95	99.95
Cu (II)	96.55	97.12	97.09	96.91	75.92	80.01	77.14	80.82	99.97	99.98	99.98	99.95	97.24	97.46	98.17	97.91	82.97	91.68	93.20	95.26
Zn (II)	94.69	93.82	94.69	94.59	29.77	58.81	59.15	60.70	99.98	99.98	99.77	99.71	99.08	99.17	99.44	99.24	99.96	99.99	99.99	99.99
	Kaolinite				Charcoal				Molecular sieve				Fly Ash				Saw dust			
	C1	C2	C3	C4	C1	C2	C3	C4	C1	C2	C3	C4	C1	C2	C3	C4	C1	C2	C3	C4
Pb (II)	98.59	95.24	93.04	89.47	99.91	99.92	99.95	99.94	86.53	92.62	99.27	98.81	-357	-128	-70.6	-22.9	98.76	98.92	98.90	99.08
Ni (II)	69.52	49.70	41.56	36.79	99.92	99.94	99.96	99.94	67.54	86.51	98.79	97.31	99.98	99.99	99.99	100	79.49	78.70	77.29	76.83
Cu (II)	96.21	89.56	83.64	70.45	99.95	99.73	99.94	99.89	69.78	86.94	99.00	97.92	96.36	98.35	98.50	99.47	68.51	77.84	78.58	81.21
Zn (II)	73.87	56.33	43.98	33.42	99.76	99.70	99.21	99.81	74.81	88.20	98.40	97.17	81.18	91.88	93.61	96.23	80.45	86.65	84.44	83.32

3.1.1. Stabilization of bottom ash (BA)

The results presented below are based on Ilyas and Muthanna (2016 Submitted).

To mitigate the concern regarding leaching of contaminants from incineration bottom ash, it was stabilised by testing addition of two oxides (Iron and Aluminium) at various percentages (5-20% by wt). For leaching control, alongwith four original metals(Pb, Cu, Ni and Zn, two additional metals(Cr and As) were included in the analysis. This was done because these six metals are part of water quality regulations for stormwater.

With increasing mass percentage, of both aluminium and iron oxide, metal leaching from the BA decreased, although the magnitude of reduction caused by the two oxides was not similar (see table 4). The order of reduction for the iron oxide was Pb<Ni<As<Cu<Cr and for the aluminium oxide it was Ni<Cu<Cr<As<Zn<Pb. The reduction trend for Cu, Ni, and As is linear for both oxides. For Pb, the aluminium oxide was not able to control its leaching in any significant way as indicated by negative values. Therefore, it is likely that the addition of the aluminium oxide could have caused further leaching of Pb from BA. There was one exception i.e. Cr where aluminium oxide had slightly higher adsorption than the iron oxide. However, across the board, considering all the percentages (5-20%), the difference in adsorption of Cr by the two oxides is not substantial.

Table 3: Effect of oxides on percentage reduction of leaching of six metals from bottom ash.

Amendment	Pb	Cr	Ni	Cu	Zn	As
Al ₂ O ₃ -5%	-12	9	36	16	-26	6
Al ₂ O ₃ -10%	-9	-3	42	21	-25	13
Al ₂ O ₃ -15%	-12	24	49	19	-30	15
Al ₂ O ₃ -20%	-12	30	53	35	-67	17
Fe ₂ O ₃ -5%	87	13	44	26	6	33
Fe ₂ O ₃ -10%	97	14	52	40	16	48
Fe ₂ O ₃ -15%	82	16	57	48	-47	49
Fe ₂ O ₃ -20%	83	7	59	60	-36	67

In general, these results show that the effect of iron oxide is stronger on four out of six metals (Cu, Ni, As, Pb) and moderate to low effect on the remaining two(Zn and Cr). The results for aluminium oxide were not as promising and, therefore, it was not used as leaching control amendment for the column tests. Part of the reason is that the aluminium oxide did not mix well with BA and it formed small lumps, despite vigorous shaking, which perhaps reduced the available surface area. The iron oxide, on the other hand, was completely mixed, even coating BA particles, as the ash particles acquired a distinct dark red color of iron oxide. Thus, the high

pH, combined with low solubility (Manh et al., 2011) and dispersive behavior (Liang and Morgan, 1990) of iron oxide resulted in coating of smaller BA particles, which prevented dissolution of ash particles and subsequent release of metals for BA matrix.

In final analysis, iron oxide is an effective and suitable control amendment which can be used to stabilize BA not just for the adsorption but perhaps for also other reuses such as construction of landfill covers or road sub-base layers. This assessment about BA's adsorption potential and leaching control was further tested in column tests and result is presented in next section.

3.2. Pilot scale column tests

The results summarized in this section are from (Ilyas and Muthanna, 2016 Submitted; Monrabal-Martinez et al., 2015)

Based on the batch test results four adsorbents (Pine Bark, Olivine, Charcoal, Bottom ash/iron oxide mix) were used in pilot column tests. This selection was made on the basis of adsorption performance and particle size. For example, olivine powder, kaolin and montmorillonite were excluded because of their low particle size, which would have hampered the high flow column tests. We attempted to modify these with sand but the results did not vary as all three of them either dissolved or formed a dispersive solution.

3.2.1. Surface areas of adsorbents

The surface areas of four adsorbents characterized by using the BET method are presented in table 5. Following order for surface areas was observed: Pine bark < sand < olivine < bottom ash < charcoal. The reason charcoal has high surface area is because it is activated and in contrast none of the other adsorbent have been activated. However, despite highest surface area, the charcoal showed poor performance (see next sections). This could have been due to shorter contact time and competition from other ions, not the lack of surfaces. The high surface of charcoal implies a longer life span if contact time can be optimized to have similar effects on all the metals. This essentially means using it with a pond/storage where flow could be controlled to provide sufficient contact times.

Bottom ash has a high surface especially than olivine and pine bark. It could be due to the fact that it contains several classes of minerals (carbonates, al-silicates and iron oxides). Furthermore, smaller particle size was used in the study which also contributed to high surface areas as most of the mineral content is present in this small particle fraction of BA. Mixing the bottom ash with the iron oxide reduced its surface area from 25.60 to 17.03 m²/g, because the iron oxide had a lower surface area than bottom ash. However, the role of iron oxide is based on potential for formation of new surfaces at water/solid interface and current area is prior to conduct of the experiments. Nonetheless mixing did not have any negative effect on adsorption as BA/mix achieved very removal rates for the four metals.

Olivine is also known to have high surface area but in present case it is a granulated version (approx. 2 mm particle size), which explains the low surface area. The olivine despite its high adsorption potential has not been tested as extensive as charcoal or pine bark. Finally, the pine bark although has low surface area but it achieved higher removal rates comparable to high

surface adsorbents (e.g. charcoal). This could be due to the fact that removal metals by pine bark is due to lignin and carboxyl type compound, whose interaction with metals is through complex formation not adsorption on to the surface. Similarly, the sand used in the study also has same surface area as the pine bark. This could be due to the fact that it is quartz sand with uniform particle size and very few leachable elements. As compared to other adsorbents such as charcoal and olivine, it is cheaper and, thus, it can be used to reduce costs without having to reduce the treatment effect on metals.

Table 4: Surface areas of alternative adsorbent materials (Modified from (Ilyas and Muthanna, 2016 Submitted)).

Surface Area	BA ¹	BA ²	Olivine	Pine Bark	Sand	Charcoal
Single point	24.71	16.57	4.26	0.44	0.56	881.96
BET	25.60	17.03	4.39	0.50	0.58	885.53
Langmuir	35.41	23.44	6.04	0.74	0.79	1217.26

¹Bottom ash without addition of oxide

²Bottom ash amended with 15% iron oxide

3.2.2. Infiltration tests on selected adsorbents

The main criterion for the adsorbents is to pass small storms at rapid rate and achieve high removal simultaneously. Among the factors that affect the infiltration rate in a soil are soil texture and structure, soil moisture content, type of vegetation, and soil temperature. Furthermore, clogging effect due to suspended particles found in stormwater runoff may reduce the capacity of these filters to infiltrate water. Saturated hydraulic conductivity (expressed as *K_{sat}*) data can be used to dimension these systems because it can counterbalance this detrimental effect. Furthermore, the *K_{sat}* values are often used as a conservative estimate of the infiltration rate (Paus et al. 2013). Therefore, the selected materials were subjected to hydraulic conductivity tests to verify their hydraulic performance with constant head piezometer (Figure 3). The piezometer simulates infiltration at steady state rate which is then expressed as a saturated hydraulic conductivity (*K_{sat}*).



Figure 3 Setup for measurement of K-sat at room temperature

The saturated hydraulic conductivity values, for the four adsorbents, are given in table 6. These values were later used to adjust the pump flow rates during the column experiments. In table 7 some recommendations for minimum design infiltration rate are shown. Comparing the two, one can see that all the filters tested in this study conform to these reference values and the filters with these adsorbents would be able to achieve desired infiltration rates and peak flow reduction for smaller storms. However, it is clear of the adsorbents/filter would be able to maintain desired infiltration rates after going through freezing and thawing cycles in real life. The assessment of this issue is presented in the next section.

Table 5. Mean $K_{20^\circ C}$ (mm/s) at a head constant (with coefficient of variation in brackets). In this case, all columns have sorbent on the bottom. Three measurements were taken in every column.

	Olivine	GAC	Pine Bark	BA/O
Column 1	0.14 (4.8%)	0.15 (2.39%)	0.11 (13.4%)	0.04 (17.2%)
Column 2	0.13 (6.6%)	0.17 (0.83%)	0.12 (3.99%)	0.02 (10.6%)
Column 3	0.11 (6.9%)	0.14 (0.33%)	0.11 (9.74%)	

Table 6. Recommended minimum design infiltration rate (MDIR) for infiltration facilities.

Reference	MDIR (mm/s)
(ARC, 2003)	0.00347
(OENORM, 2000)	0.01
(Melbourne Water, 2005)	0.0138
(Caraco and Claytor, 1997)	0.0036
(Beven, 2001)	0.0138
(PGC, 2007)	0.00705

3.2.3. Effect of freezing-thawing conditions on infiltration

The aim of this experiment was to quantify the diminution in infiltration capacity of the filters presented in this report under freezing/thawing conditions, and evaluate its potential in cold climate. The test was carried out in a cold chamber (Figure 4) where temperature could be monitored and adjusted as required. The columns were frozen at -2°C and fed with water at $+2^{\circ}\text{C}$ to simulate snowmelt runoff entering a frozen filter facility. Two different soil moisture contents were studied, i.e., saturated filters and filters allowed to drain for 24 hours after saturation (field capacity).

The variables measured during this test were the time needed to observe discharge from the frozen soil, i.e., breakthrough discharge time, and average discharge flow measured 24 hours from breakthrough, i.e., beginning of drainage. These variables may give an indication about the performance of such filters under rain on snow events or when snow melts. In addition, K_{sat} was measured both before and after conducting the freezing test in order to see influences on the infiltration capacity due to changes in the soil texture or structure within the column.

The preliminary results (Table 8) obtained from this study highlight the importance of a good drainage in the filter to minimize water retention prior winter/freezing temperatures and therefore reduce the formation of ice, which may deteriorate the infiltration rate down to 3 orders of magnitude compared with K_{sat} values measured at room temperature. On the other hand, breakthrough times were in every case higher than 24 hours. As a consequence first flush coming from snowmelt, which has even higher peak concentrations than a normal rainfall first flush, may be missed since no infiltration will handle it. Therefore, it is crucial to have a ponding capacity that may buffer this highly contaminated water until infiltration processes occur.



Figure 4. Columns in the cold chamber under freezing/thawing simulation

Table 7. Effects of freez-thaw on Ksat and infiltration rates of the selected adsorbents.

Material	WC	Ksat 20°C (mm/s) Pre freezing	INF _{24h} (mm/s)- (ml/min)	Ksat 20 °C(mm/s) Post freezing	Breakthrough (hours)
GAC	24h	0.174	-	0.227	39.8
GAC	24h	0.231	0.018-6		36.9
GAC	24h	-	-		37.4
GAC	24h	0.332	-		43.4
GAC	Sat	0.38	0.0277-9	0.393	55.7±5
GAC	Sat	0.124	-	-	53.0
Pine Bark	Sat	0.164	-	0.145	57.4
Pine Bark	Sat	0.175	0.024-8	0.177	54.3
Pine Bark	Sat	0.191	0.018-6	0.201	85.3
Pine Bark	24h	0.234	0.036-12	-	63.8
Pine Bark	24h	0.284	0.018-6	-	59.9
Pine Bark	24h	0.44	0.036-12	-	41.9
Olivine	24h	0.289	0.007-2.5	0.215	33.6
Olivine	24h	0.239	0.006-2	0.175	32.6
Olivine	Sat	0.413	0.032-11	0.265	39.7
Olivine	Sat	0.377	0.080-27	0.299	57.1

3.2.4. Adsorption performance of selected adsorbents

The results presented in this section are from Ilyas et al.(2016)

The pilot scale column tests were used to verify performance of four adsorbents (pine bark, charcoal, olivine and bottom ash /iron oxide mixture) by simulating condition close to real life. Stormwater was created by mixing pure metal salts in tap water and concentrations of each target metal (Cu, Ni, Pb &Zn) was fixed at 1 mg/L. The pH of this influent was not adjusted as it was similar to pH of actual stormwater. The tests were conducted in two stages; 1) short term test; 2) long term tests. In short term test the flow was controlled and exit flow rates were measured at each sampling interval. These tests were designed to verify that the selected adsorbents were capable of achieving both high removal and peak flow reduction. In the long term tests, flow was not controlled and sampling was done at longer interval. The objective, in these tests, was to simulate long term behavior of the adsorbents.

The results of short term test confirmed the adsorption performance and ability to pass peak flows. Here only the results from long term tests on four adsorbents are because are relevant for selection and eventual adoption.

a. Olivine

Figure 5 presents the removal curves of four metals on olivine which follow a non-linear decreasing trend. The removal of Pb, Ni and Zn shows a slight increase. One plausible explanation is perhaps changes in flow conditions, which may have caused this pattern. In case of olivine, spacing between granules makes it easier for the influent to bypass the olivine surfaces. Furthermore, it can also indicate that spherical shape limits the exposed surface, which when covered with metals starts to release some into the solution; therefore, recovering some of the lost adsorption capacity. Given the length of experiment (73 days), and high volume of water ($\pm 3 \text{ m}^3$), it is not unlikely that adsorptions and desorption were operating simultaneous. Previously, (Mariussen et al., 2012) have reported Cu removal (20-80%) and Pb removal (60-80%) by olivine. In this regard, our results are close their study but there is one difference, which is that they used stormwater direct from a pond. From the eluate data we did not see release of Ni from olivine as it has been reported in some cases. This could be due to that granulated form and chemical composition of the olivine. From the results it is not possible discern what mechanism are operating here, except that olivine being a mineral can remove metals by surface adsorption. Nonetheless, the olivine is relatively a new adsorbent material and nature of its charge sites/surface functional and removal mechanisms in different forms and experimental conditions have not been evaluated yet. Therefore, to elucidate main metal removal mechanisms, of olivine, and their variability, in response to operational factors, would further require further detail investigation.

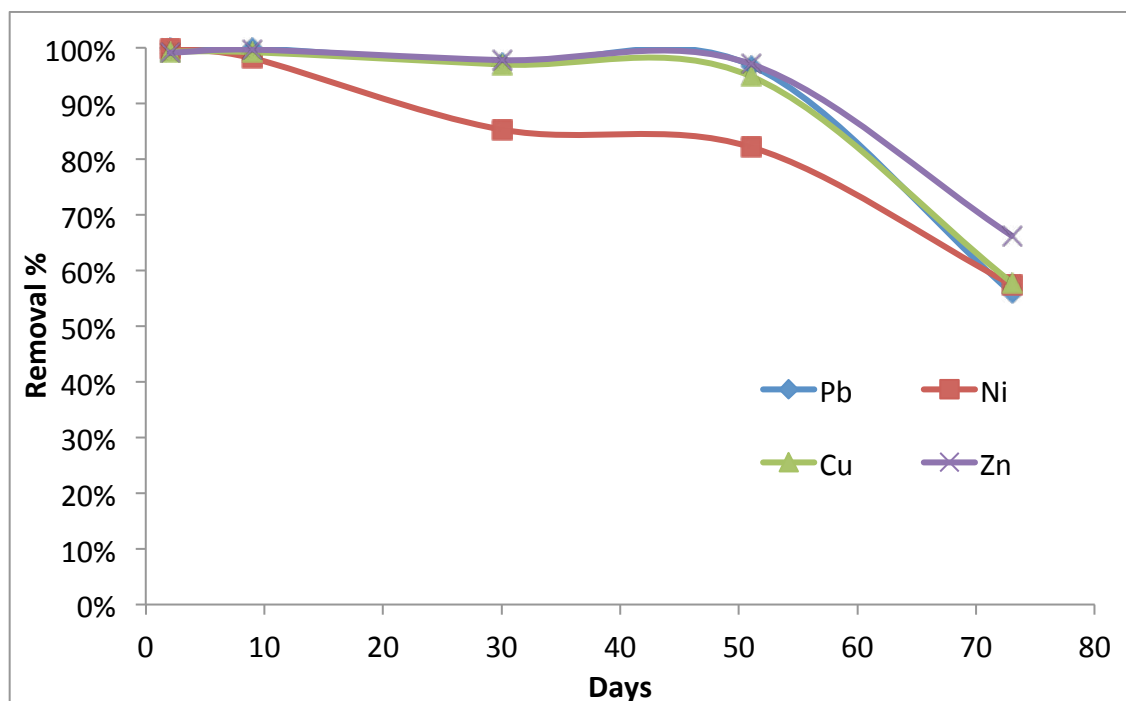


Figure 5. Percentage removal of four metals by granulated olivine.

b) Pine Bark

In case of pine bark (Figure 6), after initial high removal, a smooth and slow decrease in removal rate, for at least two metals (Pb/Cu), was observed. In contrast the removal rate for Ni/Zn declined rather sharply. After 73 days the removal Ni and Zn had decreased to 17.86 % and 32 % respectively. The other two metals Pb and Cu were being removed at higher percentages i.e. 83% and 77% respectively. This results shows that pine bark has limited affinity for Ni and Zn which decreased over time. Furthermore, because Ni adsorption has reached close to a break through; therefore, it would control the operational life and it can be assumed that pine bark has reached end use stage, even though it still has very high affinity for moving Pb and Cu. Thus, for pine bark it is the removal of Ni and Zn that would control the life span of the filter.

The different removal patterns are not surprising because it has widely varying affinities for the metals. Pine bark unlike other adsorbents has larger surfaces inside the pores than outside on exposed surfaces. This requires diffusion into pore space for surface adsorption. More importantly, the adsorption on pine bark has been attributed to compounds such as polysaccharides, lignin and tannin (Gaballah et al., 1997), which provide carboxylic and phenolic moieties for adsorption metals. But at the same pine bark can also leach some of these organic compounds which can interfere with adsorption by complexing with metals in the solution. In addition, diffusion into the pores of pine bark can be an issue especially for larger ions with ionic radii and presence of suspended solids.

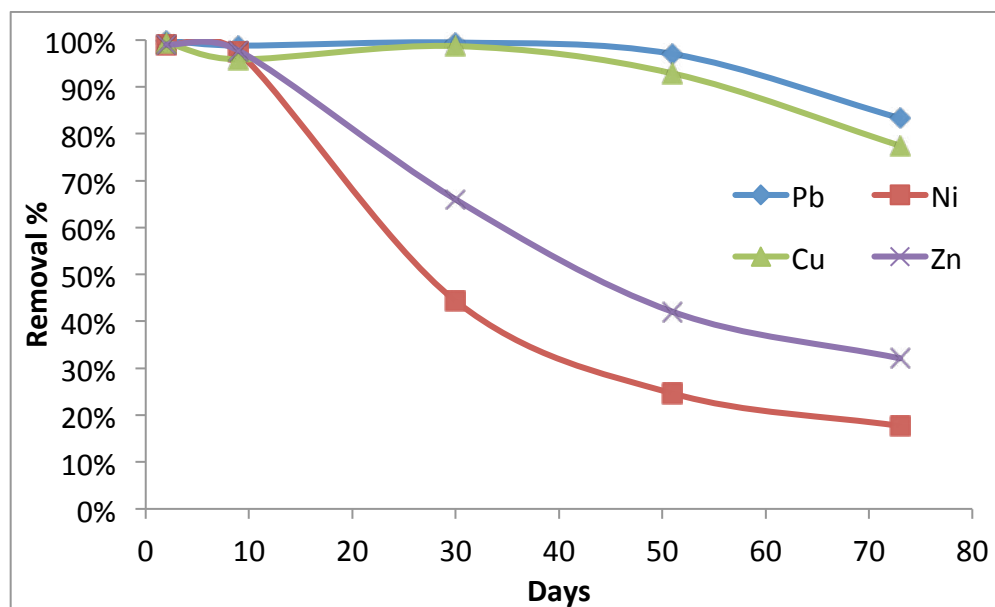


Figure 6. Percent removal for the four metals by Pine Bark.

The pore openings (641Å) of pine bark are generally larger than the ionic radii (Cu= 0.69Å Zn= 1.2 Å) of metal (Ronda et al., 2014), which rules out the difficulties with entry into the pore space. Similarly, blockage by suspended solids can also be ruled out because it would have affected metals similarly. Therefore, variable binding mechanisms and competition from other cations and dissolved organic carbon (expressed as TOC), in tap water and pine bark, could be the probable cause of reduced adsorption. Schiewer and Wong (2000) have reported that Pb and Cu form co-valent or strong bonds with bio-sorbents, while Ni and Zn usually adsorb on weak electrostatic binding sites. This kind of binding behavior can result in reduced adsorption if there is a competition from other ions (i.e. Ca). Al-ashah and Duvjak (1997) reported that presence of Ca^{2+} ion reduce the adsorption metals such as Cd, Ni and Zn on pine bark by 50%. In addition, of Ca^{2+} and dissolved organic carbon (DOC) in water and leaching from bark can also affect the adsorption metals such as Cu and Ni.

c) Charcoal

Like Pine Bark, activated charcoal is also a highly porous sorbents with pore diameters ranging from 10-300 Å and it also relies on surface functional groups. However, in terms of performance (Figure 7), the removal of metals, with the exception of Cu, decreased sharply after a week. A large decrease in removal of Ni and Zn, 7% and 17 % respectively, was observed. The low removal of Ni by Charcoal could be due to pH of the storm water solution (7.5). Previous studies e.g. (Pawluk and Fronczyk, 2015) has reported that optimal Ni adsorption occurs at pH 6. However, in present case, coal based adsorbent has point of zero charge at 7.2 (Chen and Lin, 2001), which is close to the pH of influent. Therefore, pH conditions are favorable for cationic metal adsorption. Low Ni adsorption could also be due to nature of the adsorbent which is derived from metamorphic source anthracite charcoal. The FTIR data from Liu et al. (2013) show that anthracite based carbons although have a highly stable surface but they contain low oxygen surface functional groups, which can affect adsorption metal such as Ni. They found that treating

anthracite based adsorbent with NaOH increased the Ni adsorption, perhaps due to creation of –C-O and –O-H type surface groups. Similarly, Shim et al. (2001) have reported that, at pH below 8, Ni adsorption was several orders of magnitude lower than other metals such as Cu. They attribute this behavior to oxygen surface groups on activated charcoal, which lead to the difference in the amount of adsorbed metal species under the co-existing condition.

As far other metals such as Zn and Pb are concerned their adsorption was higher initially but declined over time perhaps indicating saturation of adsorption capacities of these two metals or increased competition for limited of the binding sites at neutral pH. This indicates that metamorphic nature of charcoal is suitable for removal of Cu, Pb and Zn but not for Ni. Nonetheless, like pine bark, the use of charcoal is also controlled by Ni because its removal decreased earlier than the other metals. The removal of metal ions by charcoal follows an order (Cu<Pb<Zn<Ni), which is similar to reports from previous studies on GAC and Charcoal.

Even though charcoal performed poorly but we are not ruling it out. The above result means that charcoal is not suited for filters where peak flow and metal removal are combined. This assertion is based on the fact that high flow and low contact in current setting could have also contributed to poor performance of charcoal. Another factor is that charcoal has known affinity for organic contaminants. Therefore, its use should be further explored in different configuration e.g. in combination separate peak flow reduction (detention pond) and controlled flow which can optimise the contact time and perhaps improve performance.

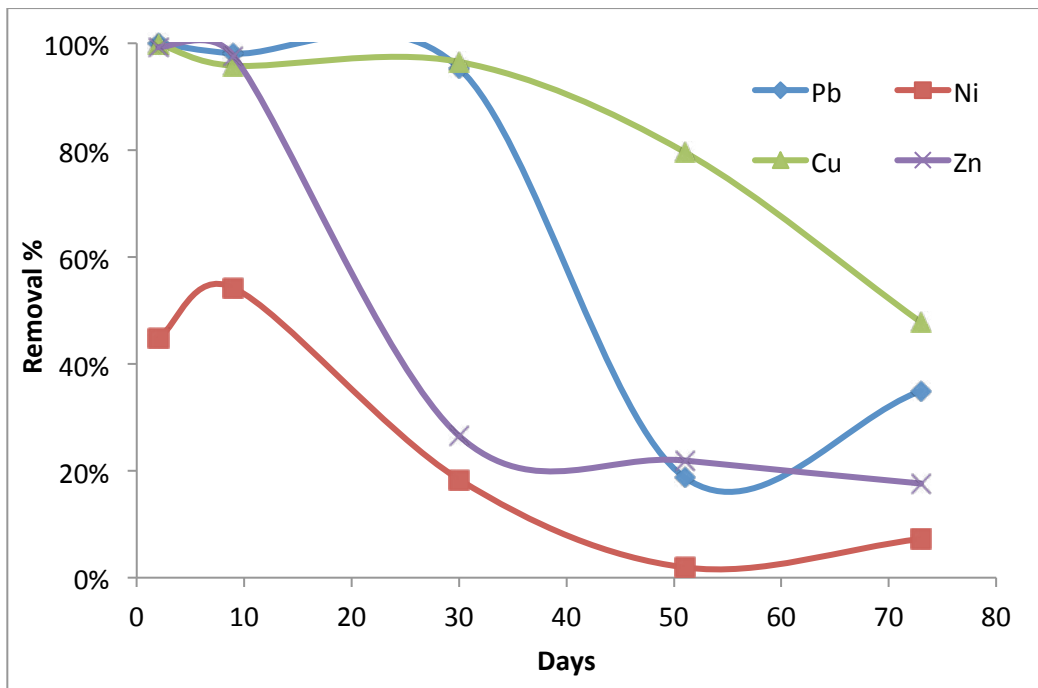


Figure 7. Removal of four metals by charcoal

d) Bottom As/IO Mix

The adsorption by BA/iron oxide mixture is presented in figure 8, which shows a high affinity for the target metals. Other than some fluctuations there was no clear trend in the results with regard to time. Given that BA is a complex mixture of several minerals, it is rather difficult to ascertain exact mechanism of the adsorption and perhaps a mix of mechanisms (i.e. electrostatic interaction/complexation, ion exchange and precipitation) could be operating here. Iron oxide is well known to form surface complexes with metal ions (Bargar et al., 1997), depending on pH, ionic strength and functional groups these dissolved metal ions can form inner or outer sphere complexes (Zhou and Haynes, 2010), and surface complexation models with double or triple layer better describe the adsorption in many cases (Davis and Leckie, 1978). For bottom ash, removal mechanisms such as ion exchange and surface sorption have been indicated by Chaspoul et al., (2008) and Apak et al., (1998). Furthermore, at a high pH, metals are hydrolyzed which facilitates their adsorption on negatively charged surfaces e.g. (McBride, 2000). Apak et al. reported that OH bearing oxides of aluminum and iron along with co-precipitation with insoluble hydroxides and flocculation caused by adsorption of hydrolytic products i.e. $[\text{Fe}_2(\text{OH})_4]_2$, $[\text{Fe}_3(\text{OH})_4]_5$ and $[\text{Al}_4(\text{OH})_8]^{4+}$ can scavenge metals. In addition, alkaline pH, well above pH_{PZC} of minerals, indicates a strong possibility of metal ion complexation with mineral surfaces.

Nonetheless, BA shows promise with regard to its use as an adsorbent and the problem of toxic metal leaching was not an issue here. That could be due to addition of iron oxide which helped it to stabilise. Only issues that remain unresolved in case of BA are problem of compaction over time and release of non-toxic species such Ca, Na, N, P and K etc. These may cause adverse impact in freshwater, which can be resolved by combining BA with rain garden etc. While former could be due to smaller particle size and it can resolved by using larger particle sizes. Nonetheless, BA is an interesting material and it should be investigated further. However, given these two issues it is excluded from large scale test for the time being.

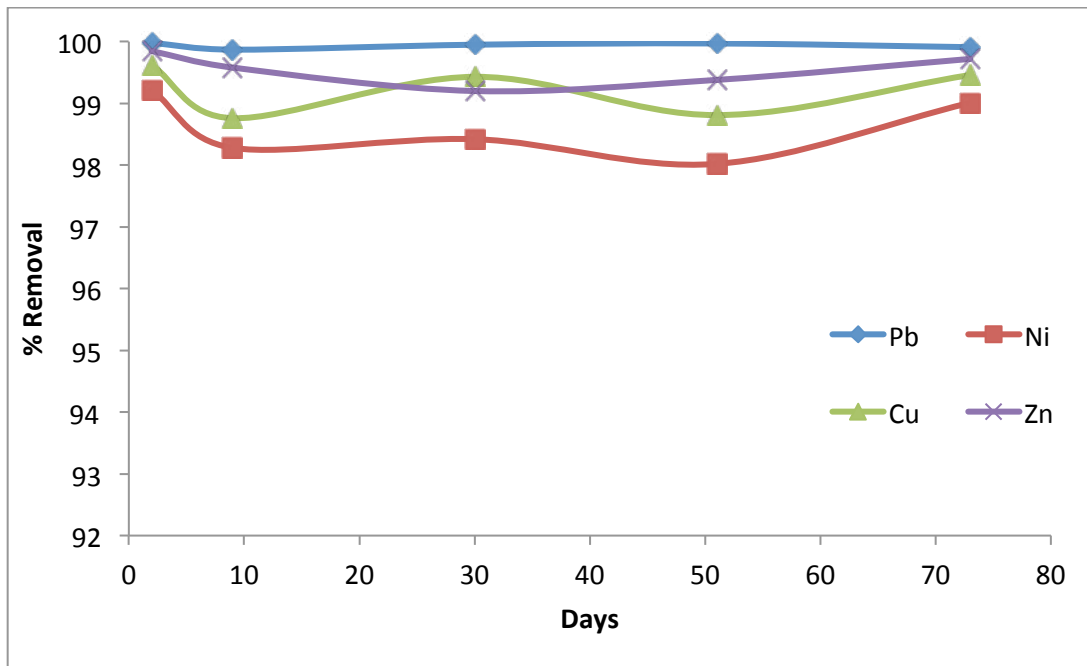


Figure 8. Removal of four metals by bottom ash/ iron oxide mix.

3.2.5. Summarising adsorbent performance

In summary, all the four adsorbent performed well within the time frame of tests. With the exception of pine bark and charcoal, break through was not achieved for olivine and BA/iron mixture. Even in these two cases, complete break through was not observed, only Ni on charcoal reached close to a break through. Nonetheless, given the time limitations the tests were terminated after approximately 90 days. For BA/ iron oxide mixture the test were stopped at 73 days due to stopping flow perhaps caused by cementation or clogging. Therefore the data presented above is for 73 to keep result presentation uniform. Since the breakthrough was not achieved the estimation of service life was achieved through a different approach, which converts the total volumes of influent into equivalent numbers of years of runoff to assess the potential life span.

In final analysis it seems that both bottom ash/iron mixture and olivine performed well and consistently with a little variability in removal. Bottom ash is promising material with high surface area and specificity for target metals. With regard to toxic metals leaching, the addition of iron oxide was successful in retarding their release from BA filter. The effect was especially strong in case of Cu, Pb and Cr which are known to leach from BA. Therefore, from environmental standard perspective, BA filter would be able to meet the target values. The leaching test data from column test was compared with target values from stormwater guidelines developed by Swedish municipalities, and all the tested metals were far below the target values (results are presented in Ilyas et al. Manuscript).

The addition of oxide had some retarding effect on leaching macro-ions (e.g. Cl, Na, Ca, Mg, K, P, and S etc), but in general it continued especially in the initially phase of experiments. These elements are not regulated as toxic metals and some of them are essential nutrients from plant growth, but high amount of salts especially Cl can negatively affect the freshwater eco-system. However, the problem of salinization can be avoided if the discharge from bottom ash filter is lead to vegetated detention ponds or swales/raingarden with salt tolerant vegetation. Therefore, use of BA as filter has to be situation specific and it should be further investigated with regard to settlement issue.

Next is pine bark, which shows very affinity and removal for at least metals. However, there is one unknown variable, which is biodegradability of pine bark. This aspect needs thorough investigation with help of respiratory tests. Finally, the charcoal with highest surface area was not performing well in case of Ni. The reason could be perhaps shorter contact time or competition. If the former is true then it may not be suitable for objective of peak flow reduction.

Nonetheless, these results present pros and cons of each adsorbent and these also show possibilities of combining more than adsorbents. For example, charcoal despite having poor performance can still be used for scavenging of organic contaminants. Finally, the final choice of adsorbent would depend on life span, initial costs, infiltration performance, need for maintenance etc. not just the removal performance. To mitigate pine bark's poor performance on Ni and Zn and high cost of olivine, it would be advisable to explore the combine use of these two adsorbents

4. Estimating service life: equivalent years of rainfall (EYR)

The question of adsorption performance and environmental were dealt above but due to lack of breakthrough, the data does not give any idea about the potential life span of any particular adsorbent. Normal approach is to use empirical models, with break through data, to estimate the exhaustion times of any particular adsorbent. However, in these cases little attention is paid to real life situation, which is storm events and infiltration process.

In present case, the break through did not happen, therefore, a different approach is adopted here. This estimates the service life of the filter by adopting a discharge threshold and modelling the amount of runoff needed to reach such concentration in the discharge. In the column tests, large volumes of influent were passed through the columns (3.7 m³/column) over 73 days. These volumes were converted to equivalent numbers of years of rainfall over our hypothetical filter, with the help of equation one. Our hypothetical filter corresponds with the column surface area, which is approx. 0.008 m². This approach allowed developing empirical relations between ratio of filter surface area to catchment (I/P) and rainfall depths. The values will vary depending on the size of the catchment (A) feeding the infiltration facility (A_{filter}) as well as the rainfall patterns of the city where this is implemented (RP). A is calculated by $A = (I/P) * A_{filter}$.

$$EYR(yr) = \frac{V(m3)}{RP\left(\frac{m}{yr}\right)*A(m2)*C} \quad Eq.1$$

The EYR estimates are present in table 9 and no final exhaustion was reached in any of the materials. The metal concentrations used in the influent were way higher than representative field storm water, therefore values showed in table 6 provides a conservative estimation of their service life.. In Bergen, in which the annual average precipitation is 2250 mm, the amount of water used in this long-term study would equal to 4.6 years of rainfall in a catchment 50 times bigger than the filter. In the case of Oslo and Trondheim the equivalent years of precipitation would be 11.7 and 14.8 years, respectively. These values will increase or decrease according to the local yearly rainfall. The ration I/P factor is another element influencing the equivalent number of years. The smaller the catchment the more years of precipitation are needed to make up the water pumped in this study. In the case of Bergen, 4.6, 2.3, and 11.6 equivalent years were passed through when I/P factor of 50, 100, and 20 are considered, respectively.

Table 8: EYR¹ estimates for different cities based on volume influent passed and I/P ratios.

Material	Volume (m ³)	I/P	Trondheim	Bergen	Oslo
Charcoal	3.7	50	11.7	4.6	14.8
Olivine	3.7	50	11.7	4.6	14.8
Pine Bark	3.7	50	11.7	4.4	14.8
Charcoal	3.7	100	5.5	2.3	7.4
Olivine	3.7	100	5.5	2.3	7.4
Pine Bark	3.7	100	5.5	2.3	7.4
Charcoal	3.7	20	29.2	11.6	37.2
Olivine	3.7	20	29.2	11.6	37.2
Pine Bark	3.7	20	29.2	11.6	37.2

¹ Assumption: runoff coefficient = 0.9, annual average precipitation in Trondheim = 895 mm, in Bergen = 2250 mm, in Oslo = 705 mm.

5. Dimensioning of filter based on infiltration capacity

The data on infiltration capacity can help determine the size of catchment by relating this information to rainfall characteristics such as intensity duration and frequency. Several design guidelines in terms of water quality volume as well as some infrequent events were considered to determine catchment size and establish a relation between catchment size and filter dimension. An even rainfall intensity throughout the duration of the storm event was assumed as well as a runoff coefficient of one since the systems are meant for managing highly impervious tributary areas. The approach used to obtain these ratios is shown below with equation two:

$$\text{RATIO} = \frac{\text{Catchment Area}}{\text{Filtration facility Area}} = \frac{K_{\text{sat filter media}} \left(\frac{\text{mm}}{\text{seg}} \right) * \frac{3600 \text{ seg}}{1 \text{ hour}}}{\text{Runoff Coef} * \text{Local Peak rainfall intensity} \left(\frac{\text{mm}}{\text{hour}} \right)} \quad \text{Eq.2}$$

A rough estimation of sizing ratios between tributary area and facility area is shown in table 10. The calculations presented in the table assume that the runoff generated in the 100% impervious catchment (i.e. road surface) is completely filtrated by the filter media. The values, in the upper part of the table 10, represent the required ratios impervious catchment area to filter area to meet national and international standards such as the American Society of Civil Engineers (ASCE), the Centre for Watershed (TCW), and the national guideline in Norway.

The ASCE recommends an 80% annual capture rate as a standard of practice for water quality volume. For example, Bergen registers 2250 mm of annual precipitation with 242 rainy days. This means 9.3 mm of precipitation every registered rainy day, on the average. Assuming that this precipitation is evenly distributed along the day it turns into 0.38 mm/h. Now considering that the filter is made up with charcoal and sand, formula (2) yields a ratio impervious to pervious area of 1781. This means that the area of the catchment feeding the filter might be 1781 time bigger for the mentioned scenario. The same procedure was followed for the rest of cities and guidelines. In the lower part of the table 10, frequency-duration based storm events were considered to size filters. The values in the table 10 are considerably location and adsorbent dependent. There are changes in the same row because a material with lower infiltration capacity will be able to infiltrate less runoff volume, assuming that no ponding water in the filter system is intended. The ratio between tributary area and facility area should therefore be smaller for the same storm event and the same runoff coefficient.

On the other hand, within the same column there are also differences in the ratios depending on the storm event that must be handled locally. The larger rainfall intensities will suppose smaller ratios in order to allow the filter system to infiltrate all of the runoff generated in the catchment area. It is worth noting that the same rainfall intensity will equate to different return frequencies depending on which city is considered. For example, an intensity of approximately 17.5 mm/h is considered a two-year 1-hour storm event in Oslo but it would be a five-year 1-hour storm event in Bergen. This fact emphasizes the importance of designing such systems by paying close attention to the rainfall patterns since the same system could deal with a moderate storm event in some cities but with extreme events in other cities. It should also be emphasized this study considered only storm water events between two and five years return period because of their frequency as well as the realization that larger events would be beyond the scope of such

infiltration system. For such events, ponding would be more suited, and escape passages would also be needed to avoid damage to the filters.

Table 9. Ratios of catchment/facility for different water quality guidelines

Cities	Guidelines	Duration(days)	D(mm.)	Charcoal	Olivine	BA/IO	P.Bark
All	Norway	1	20	662	646	130	469
Bergen	ASCE (80%)	242	2250	1781	1736	349	1260
Trondheim	ASCE (80%)	200	895	3701	3607	725	2619
Oslo	ASCE (80%)	113	705	2654	2587	520	1878
Bergen	TCW (90%)	242	2250	1583	1543	310	1120
Trondheim	TCW (90%)	200	895	3289	3206	645	2328
Oslo	TCW (90%)	113	705	2359	2300	462	1670
Cities	RP (yr.)	Duration (hrs.)	D(mm.)	Charcoal	Olivine	BA/IO	P.Bark
Bergen	2	24	62.2	213	208	42	151
Trondheim	2	24	48.4	274	267	54	194
Oslo	2	24	42.3	313	305	61	222
Bergen	2	1	14.7	38	37	7	27
Trondheim	2	1	10.7	50	49	10	36
Oslo	2	1	17.6	31	31	6	22
Bergen	5	1	17.4	32	31	6	22
Trondheim	5	1	13.2	39	38	8	28
Oslo	5	1	25.1	22	21	4	16
Bergen	10	1	19.1	29	28	6	20
Trondheim	10	1	14.8	34	33	7	24
Oslo	10	1	30.1	18	18	4	13

Configuration used in the calculations is that one with higher K_{sat} .

ASCE-American Society of Civil Engineers

TCW-The Centre for Watershed

RP-Return period in years

D-Rainfall depth in mm

P.Bark- Pine bark

6. Laboratory scale swale

The tilt-able swale setup contains 3 swales in parallel. Every swale is 5m long, 80cm wide, and 50cm deep. The swales are fed from a 1m³ tank initially filled with tap water, although addition of sediments and/or toxic metals is under consideration. A needle valve regulates the inflow rates measured by an electromagnetic flow meter (Figure 9). The discharge at the end of each swale might be split into infiltrated water and overflow. Infiltration collection is controlled with a micro sonic sensor that measure the height of water collected in the collection tank (Figure 10). Overflow rate is measured with a V-notch weir equipped with a micro sonic sensor that records the water head over the notch (Figure 11). The water head is converted into flow rate units by using a conversion formula, specifically calibrated for this setup. Swales are equipped with 6 vertical profile probes that measures soil moisture contents along the length and depth of the filters (Figure 12). All sensors will be connected to a data logger to record time series data.



Figure 9. Inlet tank with needle valve and flowmeter.

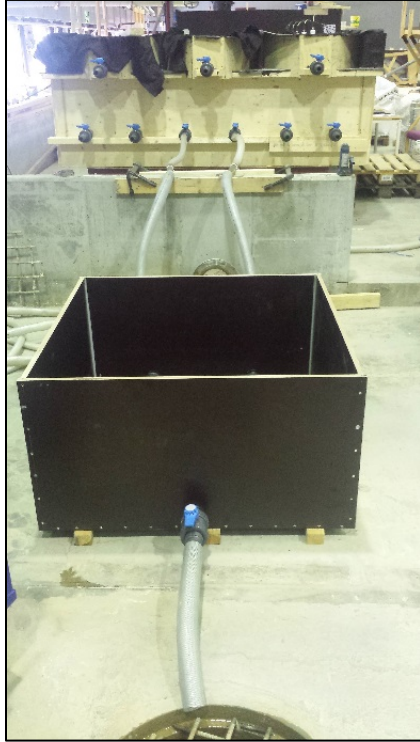


Figure 10. Tank for collecting infiltrated water.



Figure 11: The V-notch weir with microsensor.



Figure 12. Soil moisture probes along the filter protected with boulders.

The goal of this setup is to study the hydraulic balance in a swale filter meant for treating highway runoff. The composition of these swales is based on the previous column studies. One swale will have 5 cm of pine bark on the bottom and the rest will be filled with sand. The second one will have 5 cm of granulated olivine (commercially found as Bluegård G1-3) on the bottom and the rest will be filled with sand. The last swale will be composed of typical engineered soil meant for bioretention areas. Other prospective study on this setup is regarding surface processes. Filters will be tested with two different types of coverage, i.e., rock boulders and local grass able to bear salt and cold temperatures. Flow velocity attenuation and erosion control will be compared among different combinations of coverage and longitudinal slope. First runs are being performed in the swale made up with pine bark and sand. The goal of them is to understand the whole setup, compared logged to observed values, calibrate sensors, check the correct functioning of the model, and solve some general scientific questions.

6.1. Initial results

Results obtained up to now highlight the importance of having a well-maintained underdrain system. In areas with native soils with low infiltration rate such as clays or silts, it seems essential to collect the excess water that cannot pass through impervious layers and bring it out of the system. In figure 13, a runoff simulation with active underdrain system is shown. The influent rate pumped into the swale was meant at 0.7 l/s during 20 minutes, which corresponds with a 2

year return period storm intensity fall on a catchment 25 times bigger than the receiving swale. No overflow was registered over the duration of such simulation, and the infiltration started to be visible after approx. 5 min from the beginning of the run.

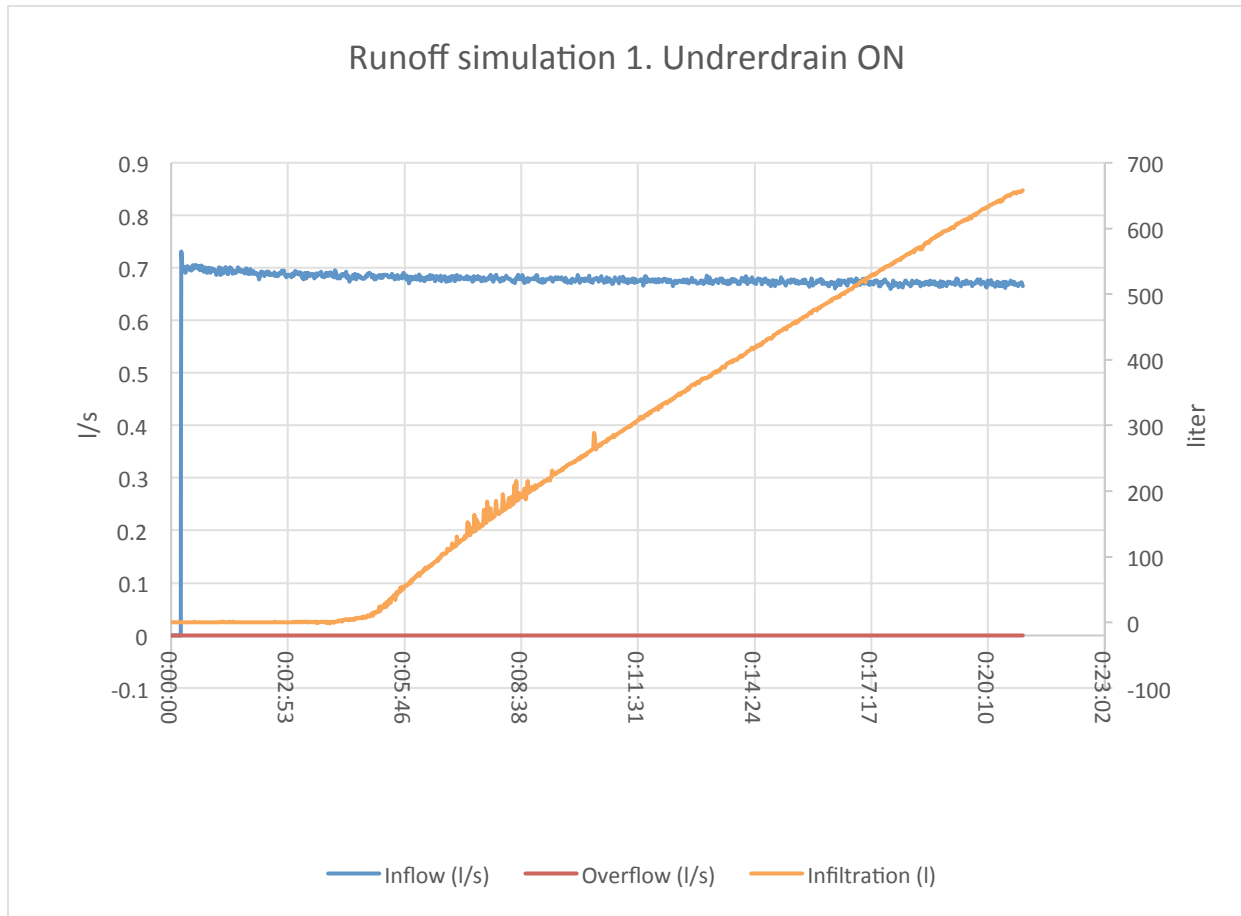


Figure 13. Simulation of runoff from filter with drainage.

On the other hand, in Figure 14 the same runoff event was simulated but in this run the underdrain system was closed. This scenario attempts to replicate an installation in which the soil underlying the filter is highly impervious and no underdrain system exists. Overflow was registered after 10 minutes from the beginning of the run, and it lasted for more than 45 minutes after the influent stopped.

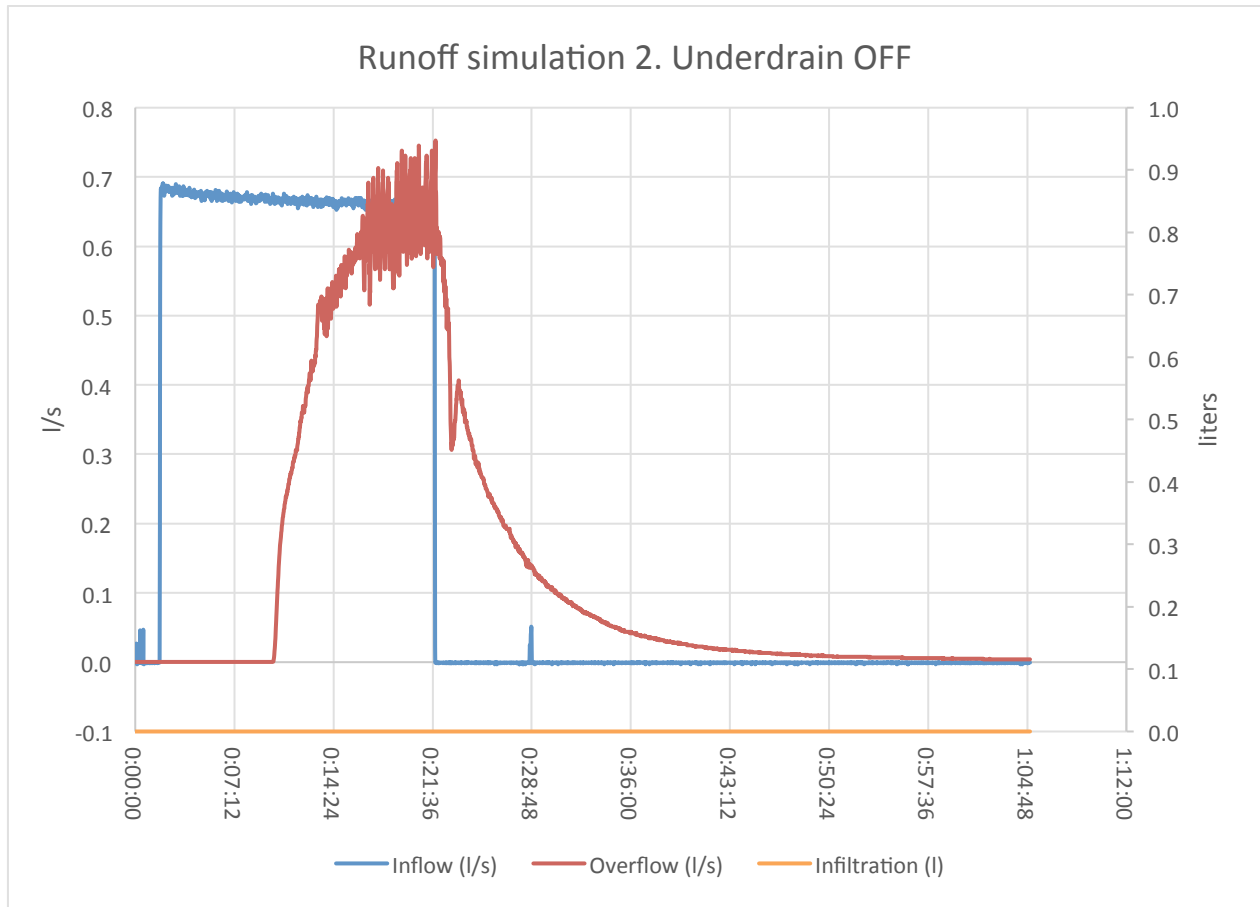


Figure 14. Simulation of runoff from filter without drainage

These results emphasize the important role of the underdrain (Figure 15). For the same runoff event, no overflow was observed when the excess of water was allowed to leave the system through the underdrain pipes placed on the bottom of the filter. This suggests a quicker drainage of the filter, therefore the storage capacity for the next event will be higher. In addition, the whole stormwater runoff generated on the feeding catchment is retained by the filter, treated and returned into the receiving water body with no environmental hazard.

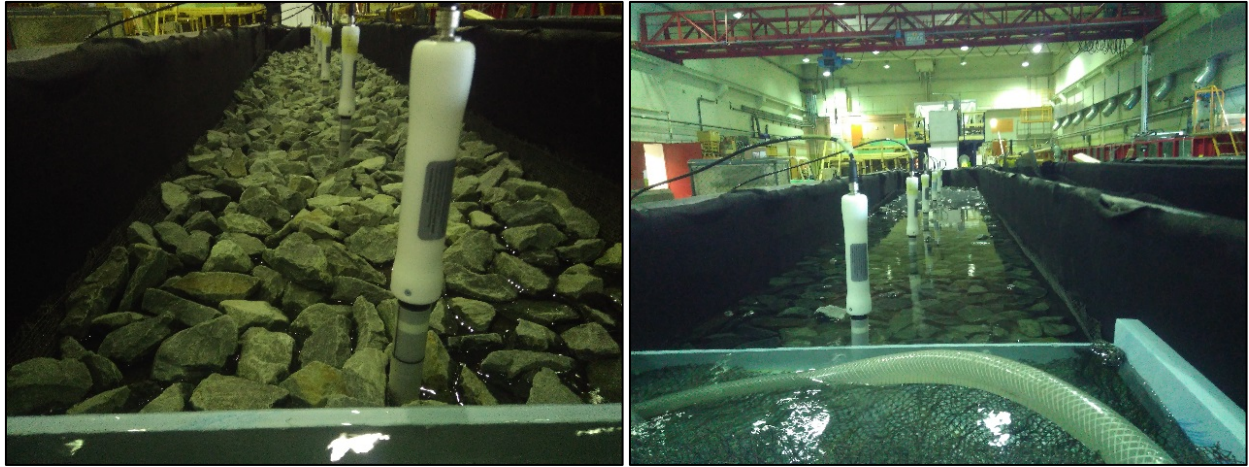


Figure 15: Swale during runoff simulation. On the left, underdrain is active. On the right, underdrain is blocked.

Looking at the soil moisture sensors from both simulations, it was noticed that when the underdrain system is closed saturation and high water contents of the soil are achieved earlier and throughout the length of the filter (Figure 16). On the other hand, when underdrain is allowed water content in the soil is reduced considerably (Figure 17), which can prevent early overflows due to small storage capacity. A good drainage is also important in order to avoid forming ice lenses throughout the filter, which will detriment considerably the general performance of the facility as it was shown in section 5.

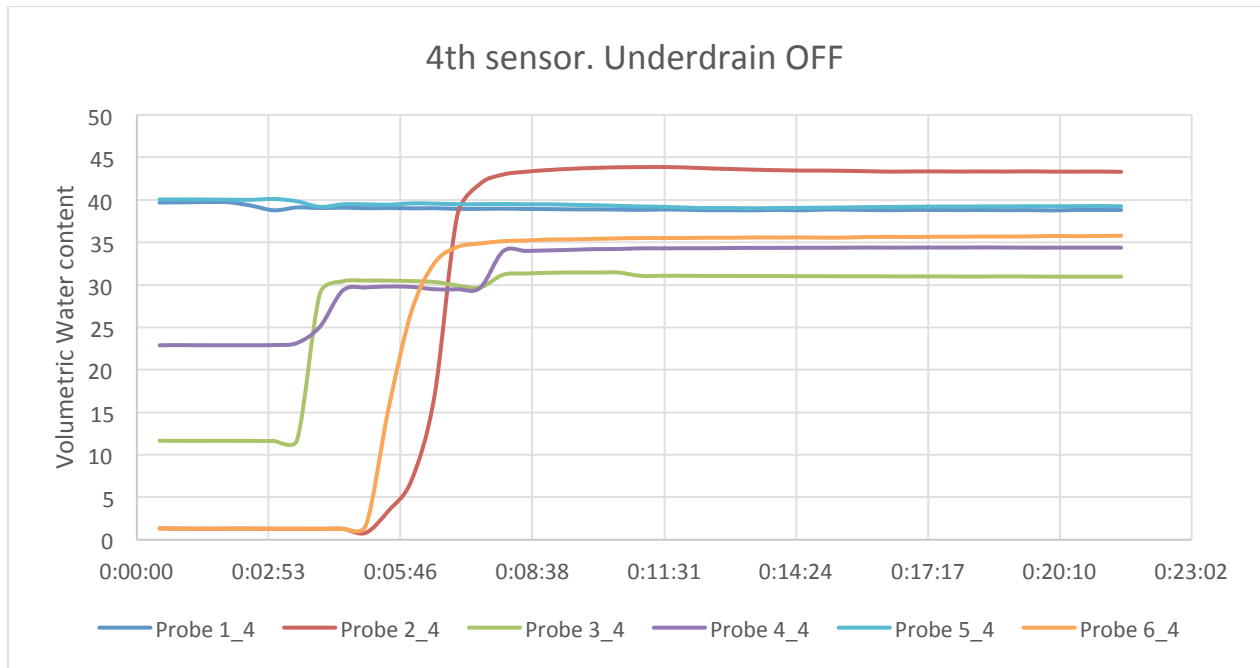


Figure 16: Soil moisture records in simulation 1

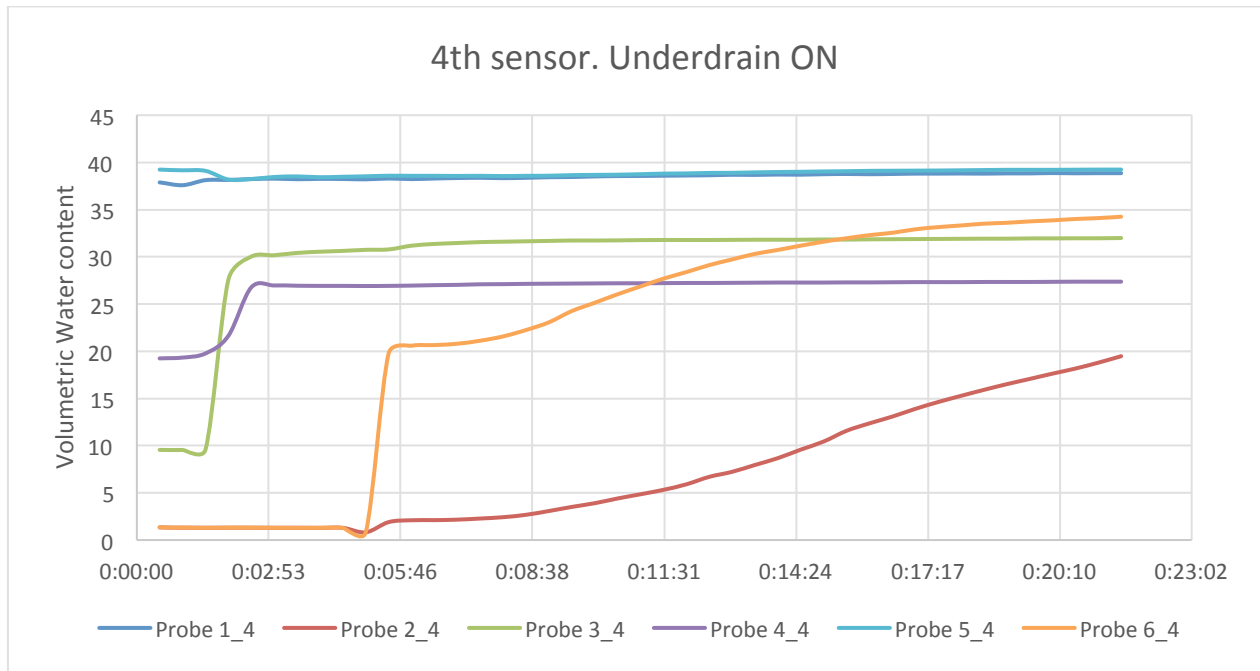


Figure 17: Soil moisture records in simulation 2

Next runs will be focused on studying the influence of several design factors on the hydraulic balance of the swale. In the beginning, the filters will be protected with boulders such those seen in above pictures. Once the tests have been performed, boulders will be removed and replaced with natural vegetation. Natural vegetation is expected to enhance the infiltration capacity because of the root network developed over time. This fact might mitigate clogging the upper part of the filter in periods such as melting season or long antecedent dry periods, with high loads of aggregates coming in from runoff. The time plan for the experiments is given in table 11.

Table 10: Time table plan for swale tests

Task	2016									
	April	May	June	July	August	Sept	October	November	December	
Filling filter										
Instrumentation										
Preliminary tests										
Tests with boulder coverage										
Planting grass										
Tests with grass coverage										

7. Some lessons learned

The project evaluated the use of alternative adsorbents for treatment of highway stormwater. For this purpose, both technical and non-technical criteria were integrated in the analysis. Theoretical

- When choosing alternative adsorbents attention should be paid to practical aspects such as costs, operational life and environmental impacts. Similarly factors such as hydraulic loads/flow regime, clogging risks and filter stability should be explicitly considered in evaluating the alternative adsorbent.
- Granulated olivine is a promising adsorbent with moderate to high removal and very high peak flow reduction potential. The granulated form also did not release any metals especially Ni. This means that it can be used directly in ditches and road side filters. However, the cost could affect its application, as the most expensive of all the four adsorbents. Therefore, the issue of cost has to be balanced with the need for treatment e.g. its use can be limited to very sensitive ecological areas or it can be combined with other lower cost adsorbents.
- Bottom ash/iron oxide mix is another novel and effective adsorbent which showed perhaps most consistent metal removal of all the adsorbents. Unlike other adsorbents its removal did not diminish over time which means it has potential long life, and least possible cost because it is available free of costs. Only cost could be from iron oxide amendment. The problem of leaching of toxic metals was effectively controlled by the use of iron oxide and it was able to meet regulatory requirements. With regard to release of nutrients (N, P, K) and other macro-ions (Ca, Na, Mg, Cl), BA should be evaluated in context of a treatment train, which can focus on removal of nutrients and others through the use of vegetation. This would limit any potential salinization or eutrophication risks in freshwater bodies.
- Pine bark is also effective adsorbent at least for two of the four metals. Only uncertainty is lack of information about biological stability, which should be investigated further. Nonetheless, given its larger particle size, metal scavenging through complexes, it can be employed in bottom and in top layers to trap organic chemicals and suspended solids.
- Charcoal did not show similar metal removal over longer periods as bottom ash or iron oxide due to perhaps shorter contact time. Therefore, it can only be used if the flow is controlled i.e. flow from detention pond or if the filter is designed to tackle both metals and organics. In the latter case charcoal could be combined with olivine or bottom ash, and its use in such setting should be investigated.

- Based on EYR approach the estimated service life all the adsorbents shows that they can last \pm 6-50 year in case of normal return period(<2 year) at various locations. Although, operational life may be shortened if higher storms were to be passed, but since the regulatory requirement is that infiltration system should pass normal storms. This means that use of these materials would not incur frequent replacement costs and would be economical for the end user.
- Preliminary hydraulic tests data suggests that a underdrain would be a necessary element of the infiltration systems containing adsorbents. Without it, there will be ponding which can result in faster deterioration of adsorbents and even may reverse the redox environment if prolonged. In winter times, the filters without underdrain would also be at higher risk of freezing than well drained filters. Therefore to avoid deterioration of adsorbents and release of contaminants it recommended that under drain should be integrated especially when adsorbents are used.
- Finally, adsorbent use should be considered in the context of local climate (e.g. rainfall depth) as the estimated service life varied greatly from location to location. This means there is no '**one size fits all**' option with regard to implementation of these adsorbents along the highways. At each locality, different relation between catchment area and filter size will have to be applied, which means that setting uniform maintenance requirements will not be possible.

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