Title: Series of studies to investigate different methods for rinsing runoff water from roads

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Abstract

Runoff from roads contains a wide range of pollutants such as inorganic compounds and organic compounds which can be dissolved or particle-bound. The dissolved contaminants are often more mobile and therefore also bioavailable which makes them compounds of concern for the environment. When the pollutants are dissolved it becomes more difficult to remove them with the methods used today. A series of studies was incorporate in this thesis study of different treatment options for road runoff, having field work on three completely different locations relevant for the assignment. The first location of field studies was in Bergen at the raingarden the municipality have constructed as a solution for urban and some road runoff including keeping the groundwater at a stable level. Even though raingardens are not an approved treatment option for road runoff, the idea was to look at passive samplers compared to manual samples and if the raingarden adsorbed any heavy metal pollution from the road. The second location of interest was a test site build simultaneously as the E18 highway between Enköping and Västerås as a location to easily measure the impact the road has on the environment. The idea was to study two different ways of road runoff treatment, as they had built an infiltration area for the runoff from the road shoulder and another well which came directly from the middle of the road. Passive samplers were used to measure the accumulated concentrations over the time period they were deployed and compare the results with manual sampling results. The third location was at the hydraulics laboratory in Trondheim. A big scale swale with three different filter materials was the study object, to investigate the ability of the materials to retain heavy metals with an increasing concentration of road salt. Passive samplers were actively used and compared to the results of manual sampling. The filter materials tested was pine bark Pinus sylvestris, granulated olivine Blueguard® G1-3 and bioretention or raingarden. A metal mix with zinc, copper and nickel were added to the water solution along with three different salt concentrations (0,100mg/L and 3000mg/L NaCl).

The raingarden in Bergen showed a decrease in heavy metal concentrations from the inlet to the outlet of the raingarden. The DGT concentrations were extremely high compared to the manual samples, which were similar to those found in previous studies from raingardens and runoff in general. Due to the very high concentration differences there could have been contamination of the DGT units, or it could be a continuous leakage of the metals that will not show in the manual samples.
The test site in Sweden resulted in concluding that there was a significant difference between the untreated well water and the water from the infiltration area, implying that with a few measures the water quality from the road runoff could improve considerably. Results from the experiment done in the hydraulics laboratory show that there is a significant difference between the sampling methods, but the impact on salt on the different material varies between the metals. Granulated olivine displays the best ability to retain metals from the runoff also, it’s the material that show best capacity to tolerate increasing a salt concentration. There is no doubt there should be more extensive studies on this subject, and more interesting would be realistic field studies.
Sammendrag

Vegvannet inneholder en rekke miljøgifter av både uorganisk og organisk opprinnelse som kan være oppløst eller bundet til partikler. De oppløste miljøgiftene er ofte svært mobile og som oftest da mer biotilgjengelig enn hva de partikulær bundne stoffene er, dette gjør dem til stoffer av bekymring for innvirkningen de har på miljøet. Miljøgifter som er oppløst i vann er det større utfordringer for å fjerne med dagens behandlingsløsninger. Denne oppgaven består av en rekke studier for å undersøke ulike behandlingsmetoder for vegavrenning, ved en rekke feltarbeid utført på tre relevante steder. Regnbedet som er konstruert ved brygga i Bergen for håndtering av avrenning fra nærliggende gater, fortøy og lignende, dette var også en metode for å opprettholde et stabilt overvanns nivå. Selv om regnbed ikke er en godkjent renseløsning for vegavrenning var idéen å se på bruken av passive prøvetakere sammenlignet med tradisjonelle manuelle vann prøvetakning. Det var i tillegg en interesse for å se på kapasiteten regnbedet har til å fjerne uorganiske miljøgifter i avrenningsvannet. The andre stedet for feltarbeid var på en «test-site» bygget i forbindelse med konstruksjonen av nye E18 mellom Västerås og Enköping i Sverige, som var et meget egnet sted for å studere en rekke ulike påvirkninger vegdekket og trafikk har på miljøet. Objektivet var å se på to ulike metoder for behandling av vegavrenning da det var bygd et filtrasjons område hvor vannet fra veiskulderen ble infiltrert før det rant ut i en brønn som var objektet for prøvetakingen. Den andre brønnen som ble testet var ubehandlet avrenning direkte fra midten av vegen. Passive prøvetakere ble brukt for å måle de akkumulerte konsentrasjonene over en tidsperiode på minst én uke og sammenligne resultatene med manuelle prøve resultater. The siste stedet var på vassdragslaben i Trondheim hvor en stor skala swale med tre ulike filter materialer var studie objektet, for å se på filterens evne til å holde blant annet tungmetaller igjen, og hvordan en økt saltkonsentrasjon påvirker denne evnen. Passive prøvetakere ble brukt aktivt og resultatene ble sammenlignet med resultatene fra de manuelle prøvene. Filter materialene som ble testet var furu bark, granulert olivin Blueguard® G1-3 og regnbed. En løsning med sink, kobber og nikkel ble tilført i vann løsningen sammen med tre ulike salt konsentrasjoner (0,100mg/L og 3000mg/L).

Regnbedet i Bergen viste en nedgang for tungmetall konsentrasjonene fra innløpet til utløpet av bedet. DGT konsentrasjonene viste ekstremt høye verdier sammenlignet med de manuelle prøvene som hadde konsentrasjoner på samme nivå som funnet i andre studier av regnbed og
vegavrenning generelt. De høye konsentrasjonene kan være på grunn av kontaminering av prøvetakerne, det kan også være en jevn lekkasje av metallene som ikke de manuelle prøvene klarer å fange opp. Resultatene fra «test-site» E18 i Sverige viser at det er en signifikant forskjell mellom infiltrert avrenningsvann og ubehandlet vann rett fra veien. Dette tyder på at med få tiltak slik som det er gjort i ved «test-siten», er det mulig å forbedre vannkvaliteten og forhindre at store mengder miljøgifter gjør skade på mottaker mediet. Resultatene fra vassdragslaben viser at det er en signifikant forskjell på prøvetakningsmetodene, men innvirkningen av salt på de ulike filter materialene varierer for de ulike metallene. Granulert olivin er det materialet som viser best kapasitet til å adsorbere metallene fra avrenningsvannet, det er også det material som er minst påvirket av en økende saltkonsentrasjon. Det er liten tvil om at rensing og behandling av avrenningsvann fra vei er noe som burde studeres nærmere og for å gjøre det enda mer realistisk.
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Abbreviations

AAM- Alternative adsorbent materials
AAS- Atomic absorption spectroscopy
AMP– Ammonium molybdophosphate
BMP Best management practice
COCs – contaminants of concern
DGT- diffusive gel in thin films
ESCO- European salt company
GC-MS- Gas Chromatography Mass Spectrometry
ICP-MS Inductively coupled plasma mass spectrometry
NGI- Norwegian Geotechnical Institute
NIVA Norwegian Institute for Water Research
NPRA Norwegian Public Road Administration
NTNU Norwegian University of Science and Technology
PAHs Polycyclic aromatic hydrocarbons
PCA- Principal component analysis
PCB Polychlorinated biphenyl
POM Polyoxymethylene
POPs Persistent organic pollutants
PPB-Parts Per Billion
PVC- Polyvinyl chloride
USA- United States of America
WFD- European Water Frame Directive
1. Introduction

A well-functioning and modernized transportation network is imperative for the modern society and economical standards today, e.g. establishing descent security for road users and an intact and secure movement of goods and services (Meland, 2010). The traffic load will increase with the expansion of the urban areas, in Norway the public transportation network increased from 44 500 km in 1948 to 92 900 km in 2008. Additionally, the transportation load increased from 2.5 to 60.6 million passenger tons in the same time period (OVF, 2008). These factors will with no doubt have a negative effect on the environment, such as local water pollution from road runoff.

Norway has many challenges when it comes to infrastructure and developing new transportation pathways, one of the main issues are the mountains and valleys, which leads to tunnel constructions. Another problem Norway endures is the variable seasonal climate, with normally hot summers and cold snowy winter, but again this is very seasonal and county dependent. It is an elongated country with 2700 kilometres from point most south to the point farthest in the north, leading to a series of challenges when it comes to the transportation network such as roads and railways. The last few decades the environmental impact caused by anthropogenic sources has been in focus and it has become a large scientific field to research the influence humans and human activities inflict on the environment.

There are multiple environmental challenges that needs to be resolved. Construction of new road networks are executed every day which results in constant release of pollutants to the environment with the construction period and the operation and maintenance. Reducing highway runoff pollution(REHIRUP) is a research project funded by the Swedish, Danish and Norwegian Road Administrations. Objective for the project is to promote the understanding of principles, processes and mechanisms associated to treatment facilities, and to incorporate the challenge concerning persistent organic pollutants (POPs) and inorganic pollutants such as metals, nutrients, chlorides (road salt) and particles (Meland, 2016).

Natural materials such as charcoal, different types of tree bark, olivine and other rock formations and bioretention ponds are among the alternatives for rinsing the excess water
form roads, pavements, rooftops etc. Several are being researched as possible filter materials in the future. Raingardens or bioretention ponds are landscape constructed depressions used for rinsing of stormwater runoff by capturing delaying and infiltrating the excess runoff water. The raingarden of interest in this study is located at Brygga in Bergen and is a solution for treatment of primary urban runoff water and to keep a stable level of groundwater. The water originates from roads with low traffic load, side-walks and roofs. Even though the runoff is not primarily road originated, it is a good opportunity to compare an outdoor located raingarden to the raingarden swale at the hydraulics laboratory. In addition, there is also a convenient way to look at any possible differences between manual and passive sampling methods for both locations.

The goal for this thesis is to improve the knowledge and understanding the behaviour of various pollutants from road runoff. Investigate the effect that different types of natural materials have on rinsing of stormwater in a series of field studies, with and without the influence of road salt. One of the objectives is to see which is most suitable as a treatment option in cold and challenging climates such as in Norway. Another intention with the studies were the use of passive samplers in addition to traditional manual samples, to look if the results are comparable and to amplify passive sampling as a good technique as the manual sampling.
2. Objectives

The present study had four objectives dependent on location for the different experiments.

Case study 1 in the hydraulics laboratory
The increasing salt load will affect the materials ability to bind metal species it will lead to more leakage of the metals to the environment. Salt increases the metals mobility which will lead to more leakage of the pollutants into the surrounding environment.

Case study 2 in Bergen
In Bergen a decrease in the metal concentrations will be apparent as the water flows through the raingarden due to the retention of metals in the dirt. The concentrations of metals will be lower in the outlet than at the inlet of the Raingarden.

Case study 3 in Sweden
In Sweden the water directly from the road will contain more pollutants in the water then the water from the infiltrated well due to water pollutants from the infiltrated area will mostly be bound to particles or bind to the particles in the infiltration material.

Case study 4 comparing sampling methods for all three locations
When comparing manually taken water samples with the passive samplers that have been deployed in water for a period of time (minimum four hours), it will become clear that the passive samplers is as good a technique for monitoring water bodies as manually taken samples.
3. Theory

3.1 Highway runoff

3.1.1 Heavy and trace metal pollutants
Heavy metals are naturally occurring elements and are found in different ratios throughout the curst of the earth. They can be harmless, but the heavy metals can also be lethally poison, it all depends the speciation, valence number and other physio-chemical properties such as charge, molar mass etc. Metals are nonbiodegradable, they cannot be broken down into less hazardous components (Walker et al., 2012). Road surfaces and systems in addition to vehicles are normally the main source of contaminants in water bodies in near proximity to the transportation network (see Table 1). Metals are the most frequent group of contaminants reported in studies of road runoff, which reflects the involvement of metal pollution due to their potentially toxicity towards aquatic organisms (Meland, 2010). Chromium and nickel are two metals that can be both essential to the body, but also extremely toxic and carcinogenic. Trivalent chromium Cr(III) ion is one of the essential nutrients, but hexavalent chromium Cr(VI) is toxic and carcinogenic, though as the Swiss scientist known as “Paracelsus” the father of Toxicology said, “The dose makes the poison” (Klaassen, 2013).

<table>
<thead>
<tr>
<th>Source</th>
<th>Contaminant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brakes</td>
<td>Ba, Cu, Fe, Mo, Na, Ni, Pb, Sb</td>
</tr>
<tr>
<td>Tire (incl. studded tire)</td>
<td>Al, Zn, Ca, Cd, Co, Cu, Mn, Pb, W, hydrocarbons, PAH (pyrene, fluoranthene, benzo[ghi]perylene)</td>
</tr>
<tr>
<td>Catalytic converters</td>
<td>Pt, Pd, Rh</td>
</tr>
<tr>
<td>Vehicle body</td>
<td>Cr, Fe, Zn (steel)</td>
</tr>
<tr>
<td>Combustion</td>
<td>Ag, Ba, Cd, Cr, Co, Mo, Ni, V, Sb, Sr, Zn, PAH (napthalene), MTBE, BTEX</td>
</tr>
<tr>
<td>Oil and petroleum spill, oil drip, used lubricant oil</td>
<td>PAH</td>
</tr>
<tr>
<td>Road surface (asphalt, bitumen)</td>
<td>Al, Ca, Fe, K, Mg, Na, Pb, Si, Sr, Ti, PAH</td>
</tr>
<tr>
<td>De-icing and dust suppression</td>
<td>Ca, Mg, Na, Cl, ferro-cyanide (anti-caking agent)</td>
</tr>
<tr>
<td>Road equipment (e.g., guardrails, traffic signs, etc.)</td>
<td>Zn (galvanised steel)</td>
</tr>
<tr>
<td>Detergents used in tunnel wash</td>
<td>Tensides</td>
</tr>
<tr>
<td>Vegetation control</td>
<td>Herbicides</td>
</tr>
</tbody>
</table>
The sources of which the human exposure and environmental contamination originates, are a result of anthropogenic activities such as smelting and mining operations, industrial production and use, and domestic and agricultural use of metals and metal containing compounds. Metal corrosion, atmospheric disposition, soil erosion of metal ions and leaching of heavy metals, sediment re-suspension and metal evaporation from water resources to soil and ground water are all sources of environmental contamination (Tchounwou et al., 2014). Highway runoff contain high concentrations of dissolved metals such as copper, zinc, lead and nickel. Accumulation of snow in cold climates during the winter season emphasize the issue of heavy metal emission when the snow melt and the pollutants which were trapped in the snow is released in the water (Ilyas and Muthanna, 2015).

There is an increasing concern about the contaminants leaching out into the environment from the roads. Copper, zinc, lead and nickel are heavy metals which are found in large concentrations in run-off water from the road infrastructures and are of great environmental and human health concern. The pollutants originate from the vehicles e.g. brakes, tires, combustion etc. and from non-vehicle related sources such as the road surface, road equipment, herbicides, detergents used in tunnel wash water, salt and chemicals used for de-icing and dust suppression. This is only the contaminants released while the road is completed, in addition the entire period of constructing the roads, tunnels and bridges involve extensive amounts of a variety of chemicals and products, and some are hazardous either to the environment and/or to human health (Grung et al., 2017). Constructions for transportation purposes such as roads, tunnels and bridges are in constant need of maintenance and rehabilitation, due to wearing and tearing. This results in additional exposure of contaminants to the environment, but this is inevitable, due to the fact that maintenance of the roads infrastructure is important for the safety of the thousands of people using the roads.

The most important factors when it comes to mobility and the danger of leaching of copper to the environment is pH and redox. Copper has a good ability to form complexes with a variety of ligands and it is known as a borderline metal. The aqua complex of copper is the principal species in natural fresh water at low pH, at high pH values deprotonation occurs and complexes involving two carbonate ions is formed. In the natural pH range complexes with hydrogen carbonate and partially deprotonated forms becomes important (vanLoon & Duffy, 2011).
Certain organic components and oxides of iron, aluminium and manganese will bind strongly to copper, the same occur when sulphur and carbonates are present with copper. The content of clay minerals in the binding medium is important for a large part of the retention. Soil which have these components can even with high concentrations of copper lead to a small or no leakage of the metal despite the pH is not too low. The copper in solution and bindings spots in soil will be taken by aluminium- and hydrogen ions (Al³⁺ and H⁺) at low pH levels. Copper in very low concentrations is toxic to fish and other water living organisms and it effects the living conditions and reproduction (Østeraas, 2014).

Zinc is one of the trace elements and is an essential component of at least 150 enzymes though as anything else in excess it can be harmful. In free ionic form in solution zinc is extremely toxic to plants, invertebrates and vertebrate fish, some organisms like Daphnia have low tolerance and just micromolar amounts of free ions can kill the organisms (Østeraas, 2014). The solubility of zinc depends largely on the pH, zinc participates at both low and high pH. In the presence of organic acids there is a formation of complexes with zinc which can have a great impact in areas where the run-off containing humic acids because organic complexes follow the water flow and participation do not occur (Østeraas, 2014).

Nickel is known to have an important role in the biology of some fungi, eubacteria, archaeabacteria and plants. Like the other metals mentioned nickel is a ubiquitous in nature, and low-level exposure by air, cigarette smoke, food and water is normal, but due to anthropogenic activities such as mining and smelting, increased concentrations of nickel into waste-water and poison fish and other aquatic organisms is of great concern. Stainless steels, batteries, pigments, catalysts and electroplating are only a few applications that contain nickel. Properties of these metal alloys are of strength, corrosion resistance including good thermal and electrical conductivity. There are various ways humans can be exposed to nickel, one of them being direct skin contact, such as with jewellery, shampoos, detergents and coins can all be routes of exposure. Nickel compounds are classified as human carcinogens, and it is the top contact allergen worldwide (Klaassen, 2013). The speciation form is what defines if nickel is toxic or not. The water-soluble ion Ni²⁺ has a minor damage impact on the other side, the non-water soluble complex Ni(CO)₄ is extremely toxic. Olivine contains nickel though the concentration is fairly low with less than 0,3 % and it’s strongly bound to the mineral grating. Though under certain conditions, such as when there is a high concentration of heavy metals like lead or copper these will replace nickel and leaching may
occur. Nickel is relatively stable when it comes to pH compared to most other metals, though there is an apparent increase in the solubility when pH is below the natural point. Under conditions were the pH is not to low organic material have the ability to retain nickel by formation of complexes (Østeraas, 2014).

3.1.2 Organic pollutants

3.1.2.1 Polyaromatic hydrocarbons
PAHs are ubiquitous environmental pollutants that are composed of two or more aromatic rings consisting of only carbon and hydrogen. Sources of release are both natural and anthropogenic primarily generated during incomplete combustion of organic compounds like oil, wood and coal. Natural sources as open burning, natural losses or seepage of petroleum or coal deposits and volcanic activities gives a background levels of PAHs in the environment. However, emissions from anthropogenic activities predominate, this are sources such as residential heating, coal gasification and liquefying plants, asphalt production and more. The fate and transport in the atmosphere and how the PAHs enter the human body is strongly influenced by the atmospheric partitioning of PAH compounds between the particulate and the gaseous phases. Several of the PAHs have toxic, mutagenic and carcinogenic properties, and since the compounds are highly lipid soluble and absorbed from the gastrointestinal tract of mammals they are rapidly distributed in tissues as body fat. (Abdel-Shafy and Mansour, 2016).

Organic compounds like these are non-charged, non-polar molecules found in coal and tar deposits, incomplete combustion of organic matter e.g. in engines and natural forest fires. The bigger the molecule the more insoluble it becomes in water. This limit their PAHs mobility in the environment, two and also three PAH rings dissolve in water which makes these compounds more available for biological uptake and degradation (Choi et al., 2010).

PAHs is one of the pollutants of concern in the runoff water from the roads, due to the moderate to high acute toxicity to aquatic life. Effects include tumours, development, reproduction and immunity which is a concern as a result of its moderately persistent in the environment and can be bio-accumulated (Grung et al., 2016). The chemical structure for the
16 PAHs which were found in the passive samplers for organic pollutants deployed at the Swedish test site are illustrated in figure 1.

Figure 1 Chemical structures of PAHs found in road runoff (Bruzzoniti et al., 2010).

3.1.2.2 Polychlorinated biphenyls

PCBs are organic chlorine compounds with chemical formula C₁₂H₁₀·xClₓ and were widely commercially produced as dielectric and coolant fluids in electrical apparatus, carbonless copy paper and heat transfer fluids. There are 209 congeners and they were manufactured and sold containing dozens of these congeners as complex mixtures. Most of the pure PCB congeners are odourless, colourless crystals and in general have low water solubility and low
vapour pressure even though the physical and chemical properties are different among the PCBs. In general PCBs are very stable which do not degrade lightly and that is one of the reasons they are classified as persistent organic compounds. The compounds are for the most part soluble in organic solvents, oils and fats. PCBs are an environmental concern even after several nations have forbidden the production, they have entered the environment through disposal and use. Due to their persistent and lipophilic properties PCBs shows tendencies to bioaccumulate and is of environmental concern (Robertson and Hansen, 2015). Several species of birds, aquatic living organisms, mammals and humans have been affected of PCB contamination which have shown results such as cancer, endocrine disruption, reproduction disruption and more.

3.2 Treatment methods of run-off water from roads
The EU Water Framework Directive (WFD) aims to protect and improve the ecological status of all water bodies. The original objectives were that all surface water and groundwater in the EU should have achieved within a six-year cycle, that of ´good status´ by the end of 2015, provided that no deadline extension or exception was petitioned. The last deadline is set by the end of the second and third management cycles which extend from 2015 to 2021 and 2021 to 2027 respectively, for the remaining member states to reach the WFD environmental objectives (European Commission, 2012). Because of road runoff may impair receiving waters, there has the last decades been larger focus to find solutions for proper and safe drainage for the environment. Tunnel wash water is particularly of concern due to the high concentrations of pollutants including detergents and should not be discharged into natural waters untreated. Unfortunately, under present circumstances some national road administrations discharge untreated contaminated wash water.

There has been a modification from conventional drainage systems into much more sustainable blue-green solutions known as Sustainable Urban Drainage Systems (SUDS) or Best Management Practice (BMPs), in figure 2 a collection of SUDS is displayed. Several applications for road water treatment exist, a few mentions are ponds, basins, infiltration systems or a combination of these, the application methods vary from country to country. The combination of an infiltration system and sedimentation if preferable due to the retention and treatment of particle associated pollutants as well as the dissolved pollutants. So far there is not one particular system that is superior to the others existing, but there is constantly new
materials and methods being researched and tested in the laboratory and in the field. The best available technology should be applied for site specific solutions, this is a crucial step to optimize the rinsing of the road water pollutants (Meland, 2016).

Figure 2. A series of Sustainable Urban Drainage systems (Hidología Sostenible).

3.2.1 Sedimentation ponds
At present there are several methods for treatment of run-off water from roads and an extensive research field to improve both quality and quantity of rinsing of pollution originating from the roads. One of the methods used in Norway is simple ponds or basins where the removal of pollutants primarily occurs by sedimentation and adsorption. Though the process considerably relies on waters residence time in the pond. Another method for treatment, are constructions such as trenches and channels including vegetation areas in close proximity to the roads and which compose transportation paths for the road water. From one rain period to another these modules can be completely or partly dry, though this is rarely the case in Norway. There are mainly ponds with permanent water levels regardless of the amount of rainfall. Areas such as these are referred to as bioretention-systems. At some locations simple wet pond constructions are developed for more advanced rinsing based on either adsorption and filters or by precipitation of pollutants by dosage of chemicals (Åstebøl, Jacobsen and Kjølholt, 2011).
Sedimentation ponds will during rainfall receive a water volume from the road and simultaneously release an equivalent water volume, which originates from previous runoff episodes. Released water from the sedimentation pond to the recipient have gone through sedimentation for removal of particular bound contaminants. Experience from Norway, USA and West-and middle Europe show that a rinsing degree in the sedimentation ponds of 70 to 80 % is achievable for of suspended matter, 55 to 65 % for total phosphorous and 45 to 75 % for heavy metals (Åstebøl et al., 2013). High concentrations of Cu, Pb and Zn which exceeded the threshold values for the compared guidelines used in the study by Karlsson et al., 2010. However, none of the samples demonstrated toxicity which could indicate that the metal species were not bioavailable. This could be related to the predominant attachment of metals to particles which results in a limitation of the bioavailability (Nordberg, Fowler and Nordberg, 2014). Regular maintenance of the sedimentation ponds is one of the issues that have an influence on the quality of the functioning of the ponds. A large number of the ponds in the Eastern part of Norway, also where there is most abundant of these ponds, is not being preserved in a good enough state. Driving on E18 from Oslo and towards Kristiansand there are multiple sedimentation ponds alongside the highway, and none of which seems to be in a good condition. What is most predominant is the extensive overgrowth of different species of plants, two of the sedimentation ponds along the highway is illustrated in figure 3.
Two of the sedimentation ponds alongside highway E18 are located approximately two kilometres apart by Statnett Tveiten, show signs of flora overgrowth.

3.2.2 Alternative adsorbent materials
Additional treatment steps to the sedimentation are required to remove larger quantities of pollutants more effectively from the road runoff, due to the high concentration of pollutants found in sedimentation ponds (Karlsson et al., 2010). The sedimentation ponds are most effective towards pollutants bound to particulate matter and have little effect towards dissolved contaminants. The necessity for infiltrating runoff as fast as possible in areas in close proximity to road surfaces or systems, is vital for safety reasons. There are several materials that have shown abilities to rinse the run-off water from the road for pollution of both organic and inorganic origin. A number of these materials are under investigation to find out if they are suitable for removal of various pollutants in road runoff. Alternative adsorbent materials (AAMs) is a class of adsorbents which are normally derived from wastes made during processing of geological materials, biomass and solid wastes. Advantages with AAMs is their low cost, very high adsorption capacity for pollutants of concern, easily available and has low maintenance requirements (Ilyas and Muthanna, 2015).
In a study done by (Ilyas et al., 2017) different materials for rinsing of road run-off were testing in pilot column tests. Four materials were selected based on adsorption performance and particle size, and two of them are of interest for this study, which are olivine and pine bark. The granulated version (approximately 2mm particle size) explains the low surface area in that particular study. Olivine has a high adsorption potential though despite this, there has not been extensive testing of the mineral such as for pine bark and e.g. charcoal. The study by (Ilyas et al., 2017) showed that pine bark achieved high removal rates compared to charcoal which have higher surface adsorbents. The removal of metals by pine bark is due to lignin and carboxyl type compound, complex formation not adsorption on to the surface is the interaction with metals for pine bark. Metal removal percentage for Pb and Cu showed similar results with respectively 83 % and 77% removal, thus for Zn and Ni the removal percentage was respectively 31 % and 18 %. The removal for the two later metals implies that pine bark has limited affinity for Zn and Ni that there is a decrease over time.

The abundant mineral Olivine is a magnesium iron silicate (Mg$^{2+}$, Fe$^{2+}$)$_2$SiO$_2$ it’s a common mineral in the earth's subsurface but when left on the surface it weathers quickly. For the ratio of magnesium to iron differs from the two endmembers forsterite Mg$_2$SiO$_4$ and fayalite Fe$_2$SiO$_4$ which is one of the reasons why the two endmembers have different properties e.g. melting temperature. Areas rich in olivine is often dry with little soil which lead to only trees and plants that can adapt to such conditions can thrive at these particular areas. Scots pine is one of those few trees which can survive on olivine rock, for Norway this is quite unique. (Brandrud, 2009). There are several applications of olivine among one of the as gemstones, the mineral has shown abilities to absorb pollutants e.g. heavy metals. The material has actively been used to clean up water runoff from a military shooting range in Hjerkinn at Dovre mountain in Norway which were highly contaminated with heavy metals like lead, copper, antimony, nickel and sink. These metals were closely looked at, properties such as transport, binding capacity and the metals solubility were very important factors to consider during the investigation. Factors that both affect speciation of the metals and in what degree they create pollution problems. There can be some issues when it comes to handling olivine and the problem is that most olivine occurrences contain asbestos which are carcinogenic and quarts which can cause silicosis by inhalation. The occurrence used in Hjerkinn did not contain asbestos and was quarts free (Østeraas, 2014).
Pine bark has shown a high removal percentage for heavy metals in particular Pb, Cd and Cu. In a study regarding the abilities of pine bark as purification method for metal contaminated water with and without microalgae activated pine bark done by (Lourie et al., 2009), the observed results show a 100 % uptake of Cu and Pb at low levels of metals content. Different retention capacities of pine bark for the following metals Cd, Cu, Ni, Pb and Zn where studied in (Cutillas-Barreiro et al., 2014). The observed results from the studies indicate that there is a rapid adsorption ranging from 70% for Ni up to 99% for Pb, there were shown faster results for low initial metal concentrations. Pb had the highest retention followed by Cu, Cd, Zn and Ni, and the conclusion was that Pb and Cu could be used to retain and remove Cu and Pb from contaminated waters, such as heavy metal polluted run-off water from roads.

3.3 Raingardens
Raingardens are flexible solutions for local treatment of excess water which allows stormwater to soak into the ground through a soil-based medium. The bioretention results in removal of particulate and dissolved contaminants (Björklund and Li, 2017) and exploit the physical, chemical and biological processes that are naturally occurring in the soil. The raingarden constructions are built as a planted area with an immersion in the terrain were the water is stored on the surface and are infiltrated to the ground or are lead to an excess water area. Natural processes in the soil contribute to retain the pollutants from the excess water, in addition the raingarden will slow the water down and relieve downstream excess water systems. There are results from studies done on bioretention systems for excess water with high concentrations of heavy metals, which show that the vegetation accumulated 0,2 to 7 % while over 80 % were retained by the filter (Paus, 2016). Stormwater contains large amounts of unwanted particles in different size ratios, contaminants such as heavy metals and organic pollutants in the water will be bound to these particles. Which initially is why removal of the particles being an effective method to retain large amount of the pollutants and why raingardens should be studied more thoroughly.

3.4 Road salt
During the winter period in several countries including Norway the need of de-icing the road surfaces is required to improve vehicle friction, which in turn results in an optimization of the traffic safety on the roads. Though there are relatively large variations in deployment the amounts of salt from season to season, it all depends on the weather that particular season. The amount of salt applied to the roads have been increased the last decades and efforts are
made to reduce the use of salt by more efficient application. During the 2009/2010 winter season a total amount of 201.000 tons salt were consumed for de-icing purposes on the roads whereas, in the season 2015/2016 the total amount was 265.187 tons of salt (Sivertsen, Skoglund and Jensen, 2016). The compound which is largely distributed to the roads is sodium chloride, there is added small portions of anti-caking agent and magnesium chloride in cases where the need to reduce dust is necessary, this is common practises in large cities (Denby et al., 2016). In Norway it will be different ratios of the components depending on which part of the country it is and how the weather conditions are. The salt enters the environment through drainage and is treated as a pollutant having a negative effect on vegetation, surface and ground water in eco-systems close to salted roads (Löfgren, 2001).

Road salt can be used in large amounts during one season and it is easily soluble in water which will indicate that the salt follows the water current, and the salt concentrations in the recipient mediums are expected to increase. High salt concentrations can lead to physical effects of water bodies receiving runoff water, such as an increased density of the salt enriched bottom layer due to altered circulation patterns in ponds and lakes (Meland, 2010). This leads to an oxygen free zone on the bottom due to the oxygen which is on the bottom is quickly consumed and because of the lack of circulation no more oxygen will enter this part of the lake (Bækken and Haugen 2006).

In (Bækken & Færøvig 2004 as sited in Bækken and Haugen 2006) the run off from roads that contains heavy metals and PAH are largely bound to particles, due to this they will be held in ditches and road shoulder. A large amount will reach the sediment on the bottom of the lakes and ponds, smaller amounts will be able to stay soluble in the water phase, but this depends on the type of metal and the chemistry of the water. The mobility of the heavy metals will increase with high concentrations of salt in the melting water in ditches, which results an easier transport to the recipients. Increased salinity is a consequence of salt application on the roads which can affect the chemical properties of metals through ion exchange processes. In (Löfgren, 2001) ion exchange increased the mobility of H+ ions and trace metals such as Zn and Cd and reduced the alkalinity as well as increasing the Zn and Cd concentrations in the streams.

Salt SMART was a research- and developmental project completed by The Norwegian Road Administration in the period from 2007 until 2011. The goal with the project was to find ways
to reduce the use road salt simultaneously maintain a god navigability and traffic security through the winter. It concludes that environmental damages on larger parts of the road net and can be avoided with a general low salt use on the roads, and where the environmental is special sensitive for road salt necessary measures should be enforced (Sivertsen et al., 2012).

3.5 Passive samplers

3.5.1 Passive samplers for heavy and trace metals

_Diffusive gradient in thin films_ are simple but accurate plastic devices accumulating dissolved substances in a controlled way. The component consists of a piston or a base, a cap and a window where the gels are placed, and the elements of interest can diffuse in, see figure 4. The conventional analysis in the laboratory provides the in-situ concentration at the time of deployment. This device and analysis method was invented in Lancaster by William (Bill) Davison and Hao Zhang. Components like these can be used for measuring trace metals, phosphate, sulphide, radionuclides in water, sediments and soil. Measures average concentration (hours to weeks) in freshwater and seawater. Measures effective solution concentrations (bioavailable fraction) the uptake is controlled by the concentration gradient between the outside of the membrane and the absorbent on the inside. Measures at high spatial resolution (microns to centimetres) (Davison, 2016).

![Figure 4. Basic construction of a DGT component with exploded view of the diffusion and the binding layers, illustrating the concentration gradient of the analyte (Davison, 2016).](image-url)
Different types of gel discs are available, for this type is six types: diffusive gel, restricted gel (restricted pore for measuring labile inorganic only), Chelex gel (for metals), Fe-oxide gel (for phosphorus), AMP gel (for Cs) and AgI gel (for sulphide).

Metals bound to colloids will not be able to be determined because they cannot cross the diffusive gel and they are not labile enough. Temperature influences accumulation in DGTs because of the diffusion over the diffusive gel is temperature dependent, the flux varies with temperature. The flux of analyte over the diffusive gel will increase with increasing temperature due to the increased diffusion gradient, this leads to higher accumulation of the labile forms of analyte (Davison, 2016).

The DGTs in water works as follows: a layer of chelex resin impregnated in a hydrogel to accumulate the metals, this layer is overlain by a diffusive layer of hydrogel and a filter. Ions will have to diffuse through the filter and diffusive layer to reach the resin layer. It is the establishment of a constant concentration gradient in the diffusive layer that forms the basis for measuring metal concentrations in solution quantitatively without the need for separate calibration (Zhang and Davison, 2000).

The plastic components are deployed for a known time and then the mass of metal in the resin layer is measured after elution with nitric acid by e.g. AAS or ICP-MS. If the temperature is known the concentration in the solution can be calculated precisely due to temperature have an effect on the speciation of the elements of interest. They are simply deployed into water or sediment by using a rope or a string. It measures all labile species in water which are in equilibrium with the species that can bind to the binding agent. For instance, Cu2+ binds to the chelex resin, in natural water Cu exists as inorganic species e.g. CuOH+ and CuCO3 and as organic complexes that can dissociate quickly (labile) or slowly (inert). DGT measures all the inorganic species and the labile organic species which are the forms that can be bioavailable (Zhang & Davison, 1995).

The components currently measured are total or total dissolved metals, but ideally the species that should be measured is those available to organisms. The uptake of trace metals across living membranes is determined by free ion concentrations when membrane transport is slow and by the total concentration of labile species when membrane transport is fast. In the events
of deployment of twin DGT devices with different diffusive gel layers can provide an in-situ measurement of both the labile inorganic and the total labile species. The labile inorganic concentration can be used to calculate free ion activities. In this particular case only one type of diffusive gel was used in all the experiments (Davison, 2016).

Substances that can be measured by DGT devices are any dissolved species which there is a selective binding agent. For the trace metals that data are available includes aluminium, arsenic, cadmium, copper, chromium, iron, manganese, nickel, lead, zinc, many more metals are possible including rare earth metals. Calcium, magnesium, phosphate, sulphide and caesium, have results that have been published. Other inorganic species are under investigation. (Zhang, DGT® Research)

3.5.2 Automatic water sampling
An alternative to DGTs and manually taken samples is automatic water sampler system which can be computed to take water samples at given times of the day, for a preferred weather events or even remote collection. The control unit usually has the ability to vary a series of factors e.g. the length of the sampling period and the number of samples in the given time period. This device is usually placed in situ which decreases the amount of human handling the samples, even though there are factors that should be taken into considerations that could interfere with the concentrations in the water. Automatic water samples are recommended for sampling compounds that do not change or degrade rapidly (Gulliver, Erickson and Weiss, 2010)

3.5.3 Passive samplers for organic contaminants
It is challenging to directly measure the truly dissolved and bioavailable fractions of contaminants of concern (COCs) in the water column, porewater and sediments. Remediation of contaminated sites is important to reduce the exposure and risk to human and ecosystem receptors. In fact, understanding the concentrations of COCs in the media of contamination is a key component, though measuring the contamination is not without difficulty. Particularly the hydrophobic organic contaminants such as Polycyclic aromatic hydrocarbons (PAHs), Polychlorinated biphenyls (PCBs), dioxins and others are among the contaminants that are difficult to directly measure the dissolved and bioavailable fractions. A large majority of the contaminant mass for the hydrophobic organic contaminants are adsorbed to particulate matter in a water sample. The analysis of water samples as surface or pore water measures the
dissolved contaminants and those adsorbed to suspended particulate matter. Dissolved contaminants loss can occur during filtration of water samples, partitioning to the apparatus or filter, etc. Filtration removes particles above a defined particle size and the contaminants they are bound to. Large volumes of water to measure detectable concentrations of the hydrophobic organic contaminants are imperative due to these compounds low solubility. Volumes of water in a large quantity can be problematic to collect especially when the sampling from porewater bodies. A traditional water sample will only give an overview of the concentration at the time of sample collection, while a passive sampler can provide the average dissolved concentrations for the deployment period. Calculating the freely dissolved hydrophobic organics contaminants from the chemicals accumulated on the sampler will give an average of the concentration during time of deployment (Stout and Wang, 2017).

(Parkerton and Maruya, 2013) refer to passive samplers as deceives that in general are composed of an organic polymer that sorbs contaminants from the dissolved phase.

Passive samplers for the organic compounds include among a few mentions Polyoxymethylene (POM), Polyethylene (PE), solid phase micro extraction (SPME) fibers and semipermeable membrane devices (SPMDs) these are used to monitor organic pollutants in the environment e.g. an aquatic environment.

POM (do not confuse this with particulate organic matter) is a polymerization product of formaldehyde. This material is widely used, a series of applications uses polyoxymethylene. It’s a sampler which can be used to determine freely dissolved concentrations of organic contaminants (Josefsson et al., 2015). The passive samplers have no issue being deployed in freshwater or saltwater systems. The uptake of contaminants of concern by passive samplers like POM is more or less the same regardless of the salinity of the water except one difference. The contaminants will accumulate into the organic polymer more readily in saltwater than in freshwater because of the presence of salt dissolved in seawater. Deployment gear is an issue that has to be well organized, due to the potential for corrosion of any metal objects in particularly seawater. In (Thompson et al., 2015) and (Gschwend et al., 2011) it’s described that the passive samplers have to be deployed until it reached equilibrium, usually this process carry on for days to week depending on the properties of the medium. The time period prior to reaching equilibrium is the “uptake” phase and a series of factors can affect equilibrium. Being the type of contaminants and hydrophobicity as one of the more important factors. Equilibrium is reached faster for those contaminants that are less hydrophobic than the more hydrophobic compounds. Other factors that will affect the equilibrium are the shape
and thickness of the passive sampling material, the sampled medium, salinity as already mentioned and temperature. Polymers that have a high density and are thicker will reach equilibrium slower than those which are of less density and have a thinner material. Once at equilibrium the sampler maintains a time-integrated equilibrium concentration with the surrounding water (Stout and Wang, 2017).

3.6 General statistics

3.6.1 Mean and standard deviation
The mean in statistics is summarizing all the object and then dividing it on how many objects originally in the data set. The standard deviation in statistics quantify the amount of variation or dispersion of the objects in the data set, and it is the square root of the variance. Are the objects similar to the mean of the set it indicates a low standard deviation, and on the other hand with a high standard deviation the objects are widely spread out. It is applied to measure confidence in statistical conclusions (Løvås, 1999).

The mean is given by:

$$\bar{x} = \frac{1}{N} \sum_{i=1}^{N} x_i$$

And the standard deviation is:

$$\sigma = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (x_i - \bar{x})^2}$$

3.6.2 Principal component analysis
Originally PCA was invented by Karl Pearson in 1901 and has been re-invented multiple times ever since. PCA is a powerful method which gives the ability to inspect multidimensional data sets using the idea of projecting data from a higher dimensional space to onto a lower dimensional space in order to simplify visualisation and interpretation. The production of an alternative set of variables to those given in the original data table is the result of the projection on to a lower dimensional space. The new created variables are linear
combinations of the original variables which often are referred to as latent variables. Interesting patterns, clusters and relationships becomes easier to discover with PCA, such as for data tables with hundreds or thousands of variables underlying patterns can be discovered (Alsberg, n.d.). PCA plots especially loadings plots can detect variables that are correlated, and which are not important. Outliers are usually detected by data analytical methods and by analysing the geometrical distribution of variables in different plots which may appear unusual and out of place.

4. Study locations

The results that are presented in this thesis were obtained by filed work and sample collection at two different locations in Norway and one location in Sweden.

4.1 The hydraulics laboratory in Trondheim

An indoor laboratory at NTNU in Trondheim were the base for a big scale swale construction, to study the effects of different natural filter materials ability to remove heavy metals from runoff water, and if an increasing salt concentration will have an impact. Tap water with an added metal mix were used to simulate runoff water from roads.

4.2 The raingarden in Bergen

At Brygga in Bergen there is constructed a raingarden as a treatment option for urban runoff including water from rooftops, pavements and roads with low traffic load. The raingarden has also function to keep the groundwater flow constant, a measure taken so the ground will not descend. Pictures from the source of the runoff water to the raingarden is displayed in appendix A.

4.3 Test site E18, Sweden

The Swedish road administration, The Royal Institute of Technology (KTH), the Swedish Meteorological and Hydrological Institute (SMHI) and Swedish National Road and Transport Research Institute (VTI) are all involved in the cooperative effort in the planning and construction of the site. It is a large-scale test site along the new highway E18 between Västerås and Enköping see figure 5. One of the purposes with the construction was to have an easy access to monitoring different aspects of the highway such as contamination of runoff
water. For this thesis the difference between two methods of treatment were studied at the site with traditional manual sampling and passive sampling.

![Test site E18 map](image)

**Figure 5 Map displays the location of Test site E18 in Sweden between Västerås and Enköping.**

### 5. Materials and methods

The water sampling was done on the three locations described in 4. Study locations. The experiments in Trondheim were executed in November of 2017. Field sampling in Bergen were done on two occasions in April of 2017 one on the 6th and one on the 20th. In total 10 field trips were made to test site E18 in Sweden.

#### 5.1 The hydraulic laboratory in Trondheim

##### 5.1.1 The swale construction

Experiments that were performed at the Norwegian hydraulic laboratory in Trondheim, extended around investigating ability of three different materials to rinse runoff stormwater. This was executed in a big scale experiments with the use of a construction made of three different swales. The materials were all natural and the study were designed to investigate the impact of the use of road salt and heavy metals on the different types of materials. Copper, zinc and nickel were the heavy metals added in the water solution that was used in all the experiments. During the early stages of the project planning, it was intended to use lead and a selection of organic pollutants such as some types of PAHs, but this were considered too dangerous regarding Health Safety Environment regulations. The reason for using these particular metals is because they mimic other metals of interest in cases regarding pollutant from anthropogenic sources, and they are of great concern due to their potential toxicity.
The three swales were constructed of a tiltable 500 cm long, 45 cm deep and 80 cm wide construction, pictures are available in figure 6. Swale number one was composed of a layer of 40 cm clean homogeneous quartz sand (d50=0.33 mm), then a layer of geotextile covering 5 cm of pine bark. The second swale had the same composition of the 40 cm layer of sand then a layer of geotextile covering 5 cm of granulated olivine (d50=1.4 mm) commercially found as Blueguard G1-3. Swale number three was entirely composed of 45 cm of traditional soil for rain gardens (Ilya et al., 2017). Beneath the sand, geotextile and material (bark or olivine) there was another layer of geotextile covering 10 cm of gravel that was made as an underdrain. This third swale was also constructed with an underdrain composed of gravel. There was placed moisture sensor in each swale form previous studies, these sensors were not used in this particular study.
5.1.2 Modification of the swale
In addition to this construction there was placed three special designed PVC pipes for the experiments in each swale with approximately 1.25-meter distance from each pipe. In figure 6 there is a picture of the set-up. The pipes where designed with holes so that water could come through and as little particles as possible, due to the original set-up of the swale was not constructed for sampling in each swale. Illustration of the pipes made by staff engineer Robert Karlsen at the workshop for natural sciences is in appendix B. Due to some misunderstanding about the structure of the swales the pipes were made with more holes than needed in addition the pipes needed to be reduced in size. Due to the fear of sand contaminating the DGTs by leakage into the pipes if no measures were taken. The solution was to tape the excess pipe holes with duct tape, that way the holes were only open the area of the materials (bark and olivine) which was 5cm. The pipes were cut approximately 5 cm at the bottom end of the pipe with assistance from senior engineer Arne Grostad at the hydraulics laboratory. This was not an issue for the pipes intended for the raingarden swale and the pipes were not modified any further.

5.1.3 Experimental methods and equipment
The purpose with the experiments in the hydraulics laboratory were to study if an increasing concentration of road salt (0, 100mg/L and 3000mg/L), in this case purely NaCl, had an influence on each of the materials in the swale with metal spiked tap water. First experiments
were done on all three materials without any added NaCl, then increasing the concentration of salt to 100mg/L for all materials and finally all three materials were tested with 3000mg/L added road salt. In every experiment there was also added a metal mix consisting of copper, zinc and nickel, which was made in the laboratory to have a concentration of 30 \( \mu g/L \). This metal mix was made by adding 30mL of each of the metals into a clean 1 litre Teflon bottle and filling it to 1 litre which correspond to 910mL of miliQ water was added to get 1 litre. The Teflon bottle was cleaned three times with MiliQ water from one of the laboratories in the department of chemistry at NTNU, both before and after use. The metals used in the solutions were issued from Teknolab A/S, Drøbak, Norway. Spectrscan ® Certified, Element standard for atomic spectroscopy. The element standards were stored in the ICP-MS laboratory at the department of chemistry at NTNU, and the concentrations for the standard of nickel was 1000 \( \pm 3 \) \( \mu g/mL \) in 20°, the standard for zinc was 1000 \( \pm 3 \) \( \mu g/mL \) in 20° and the copper standard had a concentration of 1000 \( \pm 3 \) \( \mu g/mL \) in 20°. These standards where used for six of the nine experiments, only the remaining experiments with the 3000mg/L NaCl added into the solution had different standards issued from another laboratory in Trondheim due to lack of standard. These standards were issued from Inorganic ventures CGNI1-1, the concentration for nickel was 1002 \( \pm 4 \) \( \mu g/mL \), for zinc it was 998 \( \pm 5 \) \( \mu g/mL \) and the concentration for copper was 999 \( \pm 5 \) \( \mu g/mL \).

For all of the experiments a great deal of equipment from the laboratory at the department of chemistry at NTNU had to be brought to the hydraulics laboratory at the department of Civil and Environmental Engineering. Syringes, 0,45\( \mu m \) pores filters, 15 mL ICP-MS tubes, 50mL glass pipette, pipette balloon, gloves (all the already mentioned from VWR), DGTs, clean zip plastic bags, fishing wire, polyester pantyhose.

5.1.3.1 Experimental setup
The 1000 liter water tank was filled completely with tap water from the hydraulics laboratory. The metal mix solution was added approximately when the water level had reached 200, this was done to get a more homogeneous solution due to no circulation was used in fear of contamination. The influent rate pumped into the swale was set to 0,9 l/s until the water tank was empty. An influent rate of 0,7 l/s for 20 minutes corresponds with a 2-year return period storm intensity fall on a catchment 25 times bigger than the receiving swale (Ilya et al., 2017). There was no water flow out of the swale until the water was visible in the pipes and the DGTs were put down, then the shuts were manually opened to a quarter of an opening. It took
approximately 20 minutes from starting the water pump until sampling and the shuts were opened. The water tank used around 3 hours to be fully empty. After the water tank was empty it took more than 45 minutes before the water from the pipes ran out and no more water flowing out of the outlet in the swale.

5.1.3.2 Application of road salt and metal mix

Road salt from European salt company (esco), siede-speisesalz, food grade pure dried vacuum salt. This was issued from the hydraulic laboratory at NTNU in Trondheim. The salt was weighed on two different scales due to the high weight for the concentration of 3000mg/L NaCl experiments. For the experiments with a concentration of 100mg/L, a scale at the laboratory at the department for chemistry were used to measure 100 grams into small plastic bags. The last three experiments a kitchen scale was required to measure three kilograms of NaCl in plastic bags. During the six experiments involving adding of salt to the water, there was favourable to get a homogeneous solution in the water tank. Therefore approximately 200 litres of water were filled and then the salt was added, thereafter the metal mix solution also supplied into the tank, and the tank was filled up.

5.1.4 Sampling

For each experiment one manually water sample were taken with a syringe that had been cleaned and homogenised with the water in the tank three times before putting on a 0,45 μm pore filter and filtering water into one marked ICP-MS 15 ml tube. The time it took from the pump was started until it was enough water in the pipes to take water samples and put down DGTs were approximately 20 minutes. First the manually taken samples from each pipe (1, 2 and 3) was taken by using a 50mL glass pipette and a pipette balloon to suck up water to fill up the syringe, the syringe was cleaned three times with the water in the particular pipe that the sample was taken from, then a 0,45 μm pore filter was put on the syringe to filter the water sample. Thereafter three DGTs were put into a polyester pantyhose, which was to minimize the risk of contamination of the passive samples, and they were placed in pipe 2 and 3 until it was visible that the water in the swale started running out. The passive samplers were taken out and put in clean plastic zip bags, before a new round with manual samples done just as already mentioned. All the ICP-MS tubes was thoroughly marked with a number which corresponded too what experiment it was, where the sample came from in the swale and if it was a DGT or a manual sample.
5.1.5 Pre-treatment of samples prior to analysis
The samples were taken back to the laboratory at the department of chemistry for pre-treatment before analysis on the ICP-MS. Pre-treatment of the manual water samples consisted of acid conservation with three drops of ultra-pure nitric acid (HNO₃) before the samples were put into storage until analysis. The passive samplers were taken apart by using a small flatiron to take the cap off, then a clean plastic tweezer was used to remove the filter and the diffusive gel from the chelex gel. The chelex gel was then placed in a 15 mL ICP-MS tube and weighed before a known amount (weight) of 1M nitric acid were applied until it covered the chelex gel. The gel was emerged in acid for at least 12 hours before an aliquot of approximately 1 gram were transferred into a new 15mL ICP-MS tube and diluted roughly 10 times, everything was weighed and registered for later calculations of concentration gained from the ICP-MS analysis. The samples were stored in room temperature until analysis on ICP-MS.

The procedure above was done on the samples from all the experiments in the hydraulics laboratory at NTNU, in total 54 DGT samples and 63 manual samples were collected during the experiments. There was made method blanks for each day of sampling as a quality assurance. Some days two experiments were executed, while other days only one experiment was finished.

5.1.6 Experimental test period
Experimental data were collected from the swale in April and May of 2016 by having a trial period during one of the doctoral experiments by Carlos Monrabal Martinez. At that time there was not possible to deploy the DGTs in the swale due to the pipes were constructed in September 2017, only in the input tank and the output tank(s) were tested. These are not relevant for this thesis only for the experience with sampling, pre-treatment of samples and to learn how the swale works.

5.2 Bergen
The raingarden in Bergen was a good opportunity for comparing results from sample collection with the results from the study done at the raingarden swale at the hydraulics laboratory at NTNU, regarding sampling method and metal concentration differences.
5.2.1 Sample collection
Collection of water samples from the raingarden at the Brygga in Bergen were done two times, April 6th and April 20th. Equipment was brought to the site from NTNU, such as syringes, 0.45μm pore filters, DGT (made the day before), ICP-MS tubes which was given a sample number, clean plastic bags for storage of the samples after retrieval, gloves and polyester pantyhose. On the first visit samples from three different location in the raingarden were obtained (well before inlet, at the inlet and an overflow pipe, even though it was raining, and the inlet had plenty of water, the outlet had none. Due to the lack of water in the outlet water samples were taken from an overflow pipe and not the actual outlet. Pictures from the raingarden and sample sites is illustrated in figure 7. Manual water samples were taken from all three locations before deployment of DGTs and when they were retrieved. The sampling was executed with the same procedures as for the samples in the hydraulics laboratory (detailed description above).
5.2.2 Pre-treatment prior to analysis

The three DGTs in were placed in a polyester pantyhose before they were emerged in water for approximately four hours. The first time there was three DGTs in three different locations. Inlet, a pipe before the raingarden and one in the outlet of the garden. There was taken manually water samples from all the locations both before and after the deployment of the passive sampler units for comparison. The second sampling day the sampling was only done at two locations, the inlet and the overflow pipe, but the same sampling methods for manual and passive samplers were applied as for the previous sampling day. Pre-treatment of the samples were done accordingly as for the samples from the hydraulics laboratory at NTNU. All the ICP-MS tubes were marked with a sample number which corresponded to the location and when the sampling took place (before deployment or at retrieval for the DGT). In total 13
DGT samples and 13 manually taken samples were collected during the two days of sampling in Bergen. Additionally, one method blank was made by adding 3 drops of ultra-pure nitric acid (HNO₃) in an ICP-MS tube with 10 mL of Milli-Q water.

5.3 Test-site E18, Sweden
Test site E18 in Sweden is a measurement station located in Sweden between Västerås and Enköping managed by the Swedish Transport Administration. Environmental data can be collected by the various of sensors, gauges, and data loggers that are located at the test site, see figure 8.

Figure 8. Illustrates the construction of the Test site E18 in Sweden.

5.3.1 Sampling preparation and equipment
A sampling period of 10 weeks during the autumn of 2017 were conducted at Test-site E18 in Sweden from September 12th to November 21th. In addition, one trip was made the 4th of December to retrieve the passive samplers for organic pollutants. The fieldtrips to Sweden consisted in deploying and collecting DGTs each time and comparing with manual water
samples from two different wells with run-off water. Equipment for water sampling were brought from NTNU which included a 500mL Teflon bottle, ICP-MS tubes with sample numbers, syringes, 0.45\(\mu\)m pore filters, fishing wire, DGT devices prepared the day before, PVC-pipe for the DGTs, clean plastic zip bags, bolt cutter (to cut the fishing wire) and gloves. The passive samplers were deployed in water for at least one week until they were retrieved and placed in clean plastic zip bags. At the E18 test site there were several wells containing runoff water with different treatment, the water came directly or indirectly from the road. For this particular project two of the wells were chosen for further investigation, one well contained water that came directly from the middle of road. The other well stored water that originated from the road shoulder and went through an infiltration area with stone and gravel, before the water was collected into a pipe and lead into the well. At the first visit to the test-site employees from the Swedish road administration was there to show the different aspects of the site. A PVC pipe similar to the pipes used in the hydraulics laboratory experiments were placed in the well with the infiltrated water so that the DGTs would be kept safe from any particles that may have had contaminated the samples. The two sampling wells and the infiltration area are illustrated in figure 9.

5.3.2 Sample collection
In the well that contained infiltrated water there was taken manual water samples and passive samples, the manual samples were both filtered and unfiltered. Two samples before and two after deployment of DGTs were collected from the infiltrated well, one filtered and one unfiltered. Collection of the unfiltered samples were done by cleaning the sampling bottle with the well water three times as well for the syringe, then approximately 10mL of unfiltered water was put into a 15mL ICP-MS tube. The unfiltered water was not filtered until minimum 24 hours later (did not realise this before the end of the project, so the samples on the first travel period were not filtered until the week before analysis). One filtered manual sample and one unfiltered sample were collected from the well water which originated directly from the road. All the samples where marked prior to arrival or at arrival at the test site, and a log of the numbers, location and type of sample were written down in a notebook.
Figure 9. Sampling site at test site E18 (a) illustrated representation of the two wells used for sampling at E18 Test-site. (b) The infiltration area before the well. Photos: Ingeborg Farnes

5.3.3 Pre-treatment prior to analysis
The water samples and the DGTs were placed in separate clean plastic bags and put in a backpack and carried in hand baggage on board the plane back to Trondheim (on one occasion to Oslo). Samples were untreated except the filtered samples until arrival at either NTNU or Tønsberg, immediately upon arrival to the two destinations the water samples were preserved with concentrated ultra-pure nitric acid. Passive samplers were dissembled carefully with a screw driver, the filter and diffusive gel were removed by a plastic tweezer and the chelex resin gel were taken out with a clean plastic tweezer and put in empty 15ml
ICP-MS tubes. The tubes were filled with roughly 1g, until the chelex gel were covered, with 1 M nitric acid. Chelex gel were emerged in nitric acid for at least 24 hours before an aliquot were from the sample tube were pipetted out and transferred to a new ICP-MS tube. Then the sample in the new tube was dissolved approximately 10 times (e.g. 0.8 g acid → 8.0 g acid and water) with miliQ water.

5.3.4 POM
The four POM samples were used as passive sampler for collection of organic pollutants in the experiments in Sweden to establish the levels of particularly PAHs in the runoff water from the road, but in addition the POM samples were also tested for a selection of PCBs. The POM samples used are of the POM-55 format which are very flexible when it comes to deployment options. Two POM samples were placed in the infiltered water well and two in the well containing run-off water directly from the road. The contamination risk from organic material was of concern when figuring out what kind of material the POM samples should be attached to for deployment in the water. Two polyoxymethylene rods were issued for this particular purpose from the mechanical workshop for the institute of natural sciences.

5.3.4.1 Sample collection and analysis
The four samples of POM were ordered and analysed by the Environmental laboratory at NGI in Oslo. The samples retrieved in the field were wiped clean before extraction. The normal procedure for extraction of the organic passive samplers are to weigh the samples and then they are soaked sequentially for 24 hours with acetone and dichloromethane (DCM) on an orbital shaker for the reason of light agitation. The only information concerning the analysis of the POM samples were that of a ratio between Hexan: Aceton to 3:1. 350 mL, shake extraction for 3 days before analysed on high-resolution gas chromatograph (GS-MS).

5.4 Total amount of collected samples
21 DGT samples, 48 manual samples and 4 POM samples were collected at the test site in Sweden, in addition one method blank was made during the pre-treatment of the samples after each trip as a quality assurance.
5.5 Analytical methods
All the DGT samples, manual samples and method blank samples from every experiment were analysed on the ICP-MS located in the Department of Chemistry at NTNU. The environmental lab at NGI Oslo supplied and analysed the organic passive samplers after deployment by extraction then analysed on GS-MS.

5.6 Data treatment

5.6.1 Calculations of concentrations from DGT samples
The concentrations from the DGTs gained from the ICP-MS were found by inserting the use of a pre-made excel file. There were different factors that needed to be added to the file before the final concentration were given. The dilution factor, sample volume, deployment time and temperature and the concentration measured by the ICP-MS was plotted in the form. The temperature was different from each location and sampling period. The rest of the properties needed to do the calculations were already in the excel file, such as gel volume, diffusion constant, diffusive gel thickness, filter thickness, elution factor and membrane area. The only property varying between the different metals are the diffusion constant, and due to fact that not all metals have an existing satisfactory elution factor e.g. arsenic and mercury, they were not calculated. As a quality assurance a few samples of each metal were controlled by manually calculating the concentration by using equation (1) and (2).

Calulation of the DGT measured concentrations given by two equations given by DGT® Research prepared by Hao Zhang.

The mass of the metal accumulated in the resin gel layer were calculated with equation one given by

\[ M = \frac{C_e (V_{HNO_3} + V_{gel})}{f_e} \]  

(1)

Were Ce being the concentration of metals in the 1M HNO\(_3\) elution solution (in*g/L), \(V_{HNO_3}\) is the volume of HNO\(_3\) added to the resin gel, \(V_{gel}\) is the volume of the resin gel, and \(f_e\) is the elution factor for each metal.

The concentration of metal measured by DGT were calculated using equation two

\[ C_{DGT} = \frac{M\Delta g}{(DtA)} \]  

(2)
5.6.2 Statistical methods

Calculation of DGT concentrations

DGT samples were deployed in sets of three for all locations, except the sampling on the 20th of April 2017 in Bergen. The mean of the three replicates of DGTs were calculated from each sample site and every sampling (expect the last time in Bergen with only two DGTs in inlet and outlet).

The mean of the infiltered well manual water samples were calculated in a way that the water sample collected at the deployment of the DGT and the recovery of the device became one value. This was the case for all the locations sites.

The mean was also calculated for the samples collected from the road well both as a comparison to the DGTs and also to the infiltrated water well samples.

Calculation of the mean of the samples from Bergen where the manual samples taken at the deployment moment of the DGTs and the sample collected during recovery of the passive samplers where put together to make one value, this was done to investigate the mean value of the concentration of the deployment time for the DGTs. The standard deviation of each the three (two the last visit to Bergen) DGT replicates was investigated.

Quality tools

Primarily log transformation is used to improve the normal distribution of the data, which is desirable. Issues when it comes to analysing different types of metals together is that they will have different concentrations dependent on their presence in the sampling media, which makes it difficult to compare in statistical diagrams etc. In this study all the data except from the POM concentrations were log transformed (base 10). When log transformation was not sufficient enough a Johnson transformation was done in Minitab to see if that improved the normal distribution.

Multivariate analysis

All the data both raw and log transformed were analysed with principal component analysis, except from the POM sample results. Primarily explain the maximum amount of variance in the data with as few number of principal components as possible. It is also a good approach to find patterns, correlation and identifying any observations that could be outliers.
One-way ANOVA and Two-way ANOVA

A confidence interval of 95% was chosen for all the analysis, meaning that if the p-value of any test is lower than 0.05 the two values are significantly different from each other with a 95% certainty. Where used as analysing methods to see if there were any significant differences between the samples tested e.g. is there a difference between manual sampling and passive water sampling and if so is the difference significant. This was the general case for all the location site. For the experiments at the hydraulics laboratory the impact of salt on the filter material was one of the main objectives. At the raingarden in Bergen the difference between the DGT samples and the manually taken samples were tested, and if the difference was significant or not. The analysis done on the samples from test site E18 were to see if there was a difference between the infiltrated well and the road water well and if there was a significant difference. Also, the comparison between DGT samples and manual sampling were tested if was of significant difference. Two-way ANOVA was used to see main effects, potential interaction effects and whether they were significant or not.

Data treatment of concentrations of PAHs and PCBs from POM

The results from the POM strips extraction were only data that were excluded from any analysis due to the low number of samples. Only two strips from each well makes four in total which is the reason why they excluded from statistical procedures. Some of the PAHs results had concentrations below the detection limit. To achieve a scientifically result from the detection limits stated in the analysis report from NGI, these limits were divided with by two, which is one of the common practises to do in the scientific research field. The lower detection limit for PCBs are down to 0,1pg/L and 0,1ng/L for PAHs. Due to the low sample size for POM, it was favourable to investigate if there were any difference within the wells. For this reason, one of the strips was placed lower down in the well compared to the one on top.
6. Results and discussion

The results from the three study locations are listed up below in the same order as for the materials and methods chapter. Due to the large amount of sampling data, discussion will be incorporated within the results section.

6.1 Results for the experiments at the hydraulic laboratory at NTNU

In the series of experiments done on the three different filter materials there is obvious differences in the behaviour of the various metals in the solution. The results of the samples are distributed in various graphs and diagrams dependent on what kind of statistics have been executed on the data. Some of the plots are representations of the raw data results and some are from log-transformed values of the original data. The log-transformation was done due to large concentration differences for the various metals, also it used as a tool that can make the data more normally distributed, but this is not always the case. Figure 10 displays a representation of the original concentrations of Ni, Cu and Zn in a box plot with filter material and salt concentrations as categorical variables. In appendix C the time series plots displaying the original data concentration of Pb, Fe, Co, Al, Cr, Mn and Cd with salt concentration and filter material as categorical variables. The first value is from the water tank, the three second value points are representations of the mean concentrations of the manual samples from pipe 1, 2 and 3 respectively, and the two last value points are the mean concentrations of the DGT samples from pipe 2 and 3, respectively.
The time series plot in figure 10 the concentrations of the first value point is high due to the metal mix start concentration had 30 ppb of copper, nickel and zinc. The concentrations of the manual samples compared to the DGT samples varies to some point, and the difference become more apparent with 3000mg/L added NaCl solution. Though olivine displays a good retention capacity for copper. The DGT samples show higher concentrations compared to the water tank and the manual samples taken from pipe 2 and 3 in the experiment with pine bark and 3000mg/L added NaCl. The raingarden displays the same tendencies with the different salt concentrations to retain copper. The concentrations of manual samples taken from pipe 2 and 3 are higher than the concentration of the DGTs from pipe 2, but the DGT concentration increases in the sample from pipe 3.

In figure 11 the same type of time series plot is displayed as in figure 10, but the nickel concentrations are distributed with filter material and salt concentrations as categorical variables. The order of the points is the same as in figure 10, the water tank sample is representing the first point, then average concentrations of manual samples from pipe 1, 2 and 3, and the last two points are the mean concentration values of the DGT samples from pipe 2 and 3.
Figure 11. The concentrations (ppb) of nickel displayed in a time series plot with salt concentration and filter material as categorical variables.

The time series plot of nickel concentrations displays a very high peak is characterized as an outlier, but because of the low sample amount the point has not been removed from any analysis. Olivine display good retention tendencies towards nickel concentrations, though with 100mg/L added NaCl, the DGT samples have higher concentrations compared to the manual samples, the concentration from pipe 3 are even higher than the water tank. There could be some leakage of nickel as a consequence of the NaCl influence, but the olivine displays good tendencies once again toward the highest salt concentration. The raingarden does not seem to be able to retain nickel, the manual samples from pipe 1 are low for all salt concentrations, but a steep increase for the manual and DGT samples from pipe 2 and 3. It can seem like the pine bark is influenced by the salt concentration due to the decreasing ability to retain nickel. Figure 12 displays the time series plot of the zinc concentrations with filter material and salt concentration as categorical variables.
It is quite clear from the time series plot of zinc concentrations from the experiments in the hydraulics laboratory that the DGT samples concentrations are extremely high compared to the manual samples. It may seem like the increasing salt concentration have an impact on the DGT samples from pine bark and raingarden, as these are very high compared to the water tank. The zinc found in the soil from the raingarden could also have been affected by the metal mix solution with increasing salt concentration and leached into the runoff water gradually and that is why the manual samples do not cover these high zinc concentrations.

Taking the manual samples in consideration and comparing them with each other, all the filter materials show good tendencies to retain zinc, also it looks like the salt concentration have a small impact, especially on the pine bark. When examining the three previous figures (10, 11 and 12) the start concentration in the water tank for copper (average 45 ppb) is higher than what the start concentration of nickel and zinc, which have more or less the same start concentrations average of 20 ppb.
PCA results

In figure 13 the score plots from the principal component analysis is shown with different factors expressed. The results from the PCA show that most of the variance is explained in PC1, see loading plot displayed in figure 14, and small portions in PC2. The two first principal components explain 80.7% of the variation in the data. The Kaiser criterion only include principal components with an eigenvalue greater than 1, the two first PC fulfil these requirements. In appendix C the result table from the PCA shows the eigenvalues for all the principal components.

Figure 13. PCA scores with different subdivision of the factors. (A) Score plot with separating the different location sites. (B) Score plot of the experiments in the hydraulic laboratory looking at sampling method. (C) Score plot dividing the different types of material from the experiments done in the hydraulic laboratory. (D) Score plot concerning the salt concentration form the experiments in the hydraulic laboratory.
The score plots are showing to some degree clustering such as in score plot (A) where all the samples from the water tank is located in the positive corner of PC2. It is quite clear from score plot (B) that the DGT samples is responsible for the most variance in PC1 and for the manual samples are spread around the negative corner of PC2. There seems to be no distinct clustering for the samples when looking at the filter material, there is some groups from the manual sampling, but the DGTs are spread around with no apparent pattern. The samples do not seem to show any apparent patterns.

As seen in figure 14 the component for copper and nickel is largely explained by PC2, a better representation of the principal components explained for each variable is shown in appendix C.

PCA scores of the sampling method indicate that the data is spread over PC1 and PC2. In the loading plot most of the heavy metals are correlated but Ni and Cu is correlated with each other but have no effect on the other metals (no correlation). The most logic reason to the direction of the loadings for Cu, Ni and Zn, is due to the fact that these three metals were used to spike the tap water to make it more realistic when looking at road runoff. As shown in the score plots the samples from the water tank is clustered away from the other samples, and the loadings are drawn towards that cluster.
ANOVA analysis

Two-way ANOVA analysis were done on Pb, Ni, Cu, Zn, Fe, Co, Al, Cr, Mn and Cd comparing the metals concentrations with the different filter materials and increasing salt concentration to see if there were any underlying interaction or main effects.

Table 2 shows the results of a One-way ANOVA for PCA-scores versus salt concentrations. The p-value was 0,700 before Johnson transformation and 0,874 after, which is higher than 0,05, indicating the difference between the means are not statistically significant. The different salt concentration is categorized within the same group providing the information that there is no significant difference between the salt concentrations.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt 1</td>
<td>2</td>
<td>0,2853</td>
<td>0,1427</td>
<td>0,14</td>
<td>0,874</td>
</tr>
<tr>
<td>Error</td>
<td>51</td>
<td>53,7380</td>
<td>1,0537</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>53</td>
<td>54,0233</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

With residual plots it is possible to determine whether the data do not follow the specified distribution, in most cases the normal distribution. Two hypothesis, a null hypothesis which states that the data follow a normal distribution, and an alternative hypothesis that the data do not follow a normal distribution. If the p-value is the same or smaller than the significance level (normally 0,05) than the data do not follow a normal distribution and the null hypothesis can be rejected. In cases where the p-value is higher than the significance level the conclusion cannot reject the null hypothesis. The higher the p-value for residual plots the more normally distributed are the values, that is if normal distribution is the type of distribution chosen.

Figure 15 illustrates the results from residual plot before and after Johnson transformation of PCA scores and the different salt concentrations, material and sampling method. The residual plot before the Johnson transformation show a p-value of 0,008 which indicate that there is no particular distribution in the data, the H₀ hypothesis can be rejected. However, after the Johnson transformation on the PCA scores the probability plot p-value for the same factor were 0,736 indicating a much higher distribution than before the transformation.
Figure 15. residual plots before (left) and after (right) Johnson transformation respectively between PCA scores and the different salt concentrations.

The residual plot for PCA scores and the different material factor show an increasing p-value after the Johnson transformation. Before the transformation the p-value was <0.005 and after it was 0.127, none of which is counted as a good representation for a normal distribution. The same goes for the residual plot for PCA scores and the sampling methods. There is an improvement on the p-value before and after the Johnson transformation, with a p-value of 0.046 before the transformation and 0.321 after. The figure 16 shows the residual plots for both the different filter materials and sampling methods, comparing before and after the Johnson transformation.
PCA1 sample scores versus sample material show that there is no significantly difference between the means of the two, the p-value is 0.352.

Comparing the PCA1 scores with sampling method however is showing a significantly difference due to the p-value of 0.021. The groupings show that there is a significant difference between DGT in pipe 3 and manually taken samples from the water tank and pipe 1. Summary report indicate that there is no normal distribution and the probability plot for both material and sampling method shows poor normal distribution trends. with p-values of 0.034 and <0.005 respectively.

After a Johnson transformation of the PCA1 scores the normal probability plot appears more in line and the histogram more normally distributed. And comparing the new transformed PCA1 scores with the sampling method there is significantly larger differences between the DGT samples and the manually taken samples. DGT samples from pipe 3 have A grouping DGT sample from pipe 2 have AB grouping. Manual samples from pipe 2 and 3 have BC
grouping and manual sample from the water tank have CD and manual sample from pipe 1 have D grouping. still after the Johnson transformation there is no significant difference between the mean of the material and the PCA1 scores with a p-value of 0.539.

The sampling methods are significantly different with a p-value of 0.000, and with the Tukey pairwise comparison they fall into different groups. The confidence interval comparing DGT and manual sampling technique in figure 17 do not contain zero, which indicate that the corresponding means are significantly different.

![Figure 17. Illustrates the Tukey confidence interval comparing the two sampling methods used in the experiments.](image)

6.1.1 Lead

The concentrations of lead are displayed in two box plots in figure 18 and 19, which represent the original data and the log-transformed data respectively. Figure 18 present the lead concentrations with the filter material and salt concentrations as variables. In figure 19 the lead concentrations are displayed as in figure 18, but the data is log-transformed. When increasing the salt concentrations up to 3000mg/L the spread of the concentrations of the samples varies a great deal. The same tendencies are shown in the raingarden swale, but not for the olivine which is more or less stable with all the different salt concentrations. An outlier is indicated in the log-transformed plot in figure 19, this does not necessarily mean it is an outlier and to remove without any further investigation is not wise. The reason is due to potential loss of important and explanatory data.
Figure 18. Lead concentration of the raw data with filter material and salt concentrations as variables. All the concentrations are ppb.

Figure 19. The log-transformed concentrations of lead with filter material and salt concentrations as variables.
The mean concentrations of lead in road runoff with yearly day traffic load (Årsdøgntrafikk), which is the average traffic volume per day based on total, actual or calculated, traffic volume for the whole year divided by the number of days of the year, is shown in table 3. The concentrations found in the experiments in the raingarden is much lower than the average concentrations shown in table 3. The water used in the experiments was only tap water and the concentrations originates from natural levels in the tap water.

Table 3. Average concentrations of copper, lead and zinc in road runoff (Lindgren,2001).

<table>
<thead>
<tr>
<th>ÅDT</th>
<th>Cu (µg/L)</th>
<th>Pb (µg/L)</th>
<th>Zn (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-15000</td>
<td>35</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>15-30000</td>
<td>45</td>
<td>25</td>
<td>150</td>
</tr>
<tr>
<td>30-60000</td>
<td>60</td>
<td>30</td>
<td>250</td>
</tr>
</tbody>
</table>

The variance analysis after doing a Two-way ANOVA is show in table 4, the results for lead show that with a p-value of 0.735 for the salt concentrations meaning that the salt concentrations are not associated with the concentrations of lead. Regarding the different filter materials, the p-value was 0.832 which also indicate that the different filter materials are not associated with the lead concentrations. The p-value for the interaction between salt concentration and filter material is 0.645, indicating that the relationship between filter material and lead concentrations do not depend on the salt concentration. There is a collection of a main effect plot and several interaction plots for the concentration of lead in figure 20.

Table 4. The analysis of variance table from the Two-way ANOVA analysis.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt 1</td>
<td>2</td>
<td>0,2845</td>
<td>0,14225</td>
<td>0,31</td>
<td>0,735</td>
</tr>
<tr>
<td>Material</td>
<td>2</td>
<td>0,1701</td>
<td>0,08504</td>
<td>0,18</td>
<td>0,832</td>
</tr>
<tr>
<td>Salt 1*Material</td>
<td>4</td>
<td>1,1550</td>
<td>0,28874</td>
<td>0,63</td>
<td>0,645</td>
</tr>
<tr>
<td>Error</td>
<td>45</td>
<td>20,6920</td>
<td>0,45982</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>53</td>
<td>22,3015</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 20. (A) main effect plot for lead comparing the different factors in separate graphs. (B) Interaction plot comparing the lead concentration with filter material and salt concentration. (C) interaction plot for the concentration of lead between filter material and sampling method. (D) The interaction plot comparing the lead concentration with salt concentration and sampling method.

In Figure 20 (B) There are no parallel lines which indicate that the relationship between the lead concentration and salt concentration depends on the material type. When there is no added salt in the solution olivine has the highest mean concentration lead, when there is 100mg/L and 3000mg/L added NaCl the highest mean concentration of lead is in the raingarden, and the least for bark at 100mg/L and at olivine for 3000mg/L.

Figure 20 (C) show the interaction plot for lead concentration compared to sampling method and filter material. The lines are not parallel which indicates that the relationship between sampling method and mean concentration of lead depends on the type of the filter material.
For example, if you use DGT, bark is associated with the highest mean concentration of lead. However, if you use manual sampling Olivine is associated with the highest mean concentration. For figure 20 (D) the interaction plot shows no parallel lines. This interaction effect indicates that the relationship between sampling method and mean concentration of lead depends on the concentration of salt added. For example, if you use DGT, 3000mg/L added salt is associated with the highest mean concentration of lead. However, if you use manual sampling, no added salt is associated with the highest mean concentration of lead.

6.1.2 Nickel

The concentrations of nickel found in the different filter materials with increasing salt concentrations are displayed in figure 21 and 22. The concentrations from the raw data is presented in figure 21 and the log-transformed data concentrations in figure 22. In the first box plot there are two outliers suggested, that is in the first experiments with no added salt concentrations for both pine bark and olivine. The concentrations increase in the 100 mg/L added salt experiment for olivine compared to pine bark and raingarden, but the concentration decreases again in the experiment with 3000 mg/L added salt. possibly due to some form of contamination due to the lower concentration in the last experiments with a higher salt concentration. The concentrations of nickel found is similar to the concentrations found in runoff in the UK (Shutes et al., 2001), during snowmelt in northern Sweden (Westerlund and Viklander, 2006) and experiments with treatment of tunnel wash water (Paruch and Roseth, 2008a,2008b).
Figure 21. Box plot of the nickel concentrations in the experiments with filter material and salt concentration as variables.

Figure 22. The box plot of the log-transformed nickel concentrations with filter material and salt concentrations as variables.
The variance analysis table from the Two-way ANOVA analysis between the concentrations of nickel compared to the increasing salt concentration and filter material is shown in table 5. For the different salt concentrations there is no association with the nickel concentration due to a p-value of 0.854. The p-value for filter material is 0.009, which indicates that the different filter materials is associated with the nickel concentration. For the interaction between salt concentration and filter material with a p-value of 0.646, indicating that the relationship between filter material and nickel concentration do not depend on salt concentration. The different interaction plots and main effect plot are displayed in figure 23.

Table 5. Variance analysis from the Two-way ANOVA of nickel concentrations compared to filter material and salt concentrations.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt 1</td>
<td>2</td>
<td>0.1126</td>
<td>0.05629</td>
<td>0.16</td>
<td>0.854</td>
</tr>
<tr>
<td>Material</td>
<td>2</td>
<td>3.7420</td>
<td>1.87101</td>
<td>5.27</td>
<td>0.009</td>
</tr>
<tr>
<td>Salt 1*Material</td>
<td>4</td>
<td>0.8911</td>
<td>0.22277</td>
<td>0.63</td>
<td>0.646</td>
</tr>
<tr>
<td>Error</td>
<td>45</td>
<td>15.9833</td>
<td>0.35518</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>53</td>
<td>20.7290</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 23. (A) Main effect for the concentration of nickel compared to salt concentration, type and material and sampling method. (B) Interaction plot between nickel concentration, filter material and sampling method. (C) Interaction plot comparing material and salt concentrations. (D) Interaction plot comparing sampling method and salt concentrations.

In figure 23 (A) the main effect plot for nickel have no horizontal lines, which indicate there are main effects present between Ni and the three different factors. The angle reveals how large the main effect is. (B) Interaction plot for the concentration of nickel interactions between sampling method and material have lines that are not parallel. The interaction effect plot indicates there is a relationship between sampling method and nickel concentration which depends on the type of material. For both bark and olivine, the mean is highest for DGT, but that is not the case for the raingarden, which has the highest mean for manual sampling. In figure 23 (C) show no parallel lines, there is an interaction effect between nickel and salt concentration and it depends on type of filter material. There are no parallel lines, which indicate that there is a relationship between sampling method and nickel which depends on the salt concentration. Figure 23 (D) there are no parallel lines, there is a relationship between sampling method and nickel which depends on the salt concentration.
6.1.3 Copper

Box plots displaying the copper concentrations with filter material and different salt concentrations added as variables is shown in figure 24 and 25, with the raw data and the log-transformed concentrations respectively. In the box plot for the raw data show four outliers but only one in the box plot for the log-transformed data. The reduction of possible outliers can be a consequence of the log-transformation, which in most cases are favourable.

![Box plot displaying copper concentrations with filter material and different salt concentrations](image)

*Figure 24. The box plot for the copper concentrations divided in filter material and salt concentrations as variables.*
The copper concentrations found in the experiments in the hydraulics laboratory are similar to the concentrations found in other studies (Lundgren, 2001) and (Shutes et al., 2001). See table 3.

Copper concentrations is not associated with the salt concentration with a p-value of 0.367, but with a p-value of 0.007 for the filter material indicating that there is an association between filter material and copper concentration. The interaction between filter material and salt concentrations have a p-value of 0.605, which indicate that the relationship between filter material and copper concentration is not dependent on the salt concentration.

Figure 16 is a collection of the main effect plot for copper concentrations compared to the factors which are salt concentration, filter material and sampling method. And interaction plot between the copper concentration and the different factors.
Figure 26 A) Main effect plot between the copper concentration and the different factors. (B) interaction plot comparing copper concentration with filter material and salt concentration. (C) filter material and sampling method compared with copper concentrations in an interaction plot. (D) the interaction plot where the copper concentration is compared to salt concentrations and sampling method.

Figure 23(A) shows a main effect plot for the mean concentration of copper. There is no horizontal line which indicate there is a main effect. Different levels of the factor affect the response differently. The steeper the slope of the line, the greater the magnitude of the main effect. (B) is an interaction plot for copper concentration. No parallel lines which indicates that the relationship between salt concentrations added and mean concentration of copper depends on the type of material. For example, the highest mean concentration of copper for all salt concentrations is the raingarden. The lowest mean concentration of copper for no added salt is bark, but for 3000 and 100mg/L added salt it is Olivine with the lowest mean concentration. (C) Interaction plot copper concentration. Lines are not parallel. This interaction effect indicates that the relationship between sampling method and mean concentration of copper depends on the type of the material. For example, if you use DGT,
bark is associated with the highest mean concentration of copper. However, if you use manual sampling, Olivine is associated with the highest mean concentration of copper. (D) Interaction plot for nickel concentration. No parallel lines. This interaction effect indicates that the relationship between sampling method and mean concentration of lead depends on the concentration of salt added. For example, if you use DGT, 3000mg/L added salt is associated with the highest mean concentration copper. The same for manual sampling. The lowest mean concentration of copper for DGT are no added salt, and for manual sampling olivine.

6.1.4 Zinc

The zinc concentrations are displayed in box plots in figure 27 and 28 with the raw data and the log-transformed concentrations respectively. And the average concentrations are similar to those found in other studies (see table 3) (Lundgren, 2001) and (Westerlund and Viklander, 2006).

![Figure 27. Box plot of zinc concentrations with material and salt concentrations as variables.](image-url)
In table 6 there is a variance analysis report from the Two-way ANOVA. There is no association of zinc concentration for both salt concentration and filter material with p-values of respectively 0.610 and 0.342. The p-value for the interaction between filter material and salt concentrations are 0.970, which indicates that the relationship between filter material and zinc concentration do not depend on the salt concentration.

Table 6. The variance results from the Two-way ANOVA for zinc comparing salt concentrations and filter material.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt 1</td>
<td>2</td>
<td>0.2676</td>
<td>0.13379</td>
<td>0.50</td>
<td>0.610</td>
</tr>
<tr>
<td>Material</td>
<td>2</td>
<td>0.5871</td>
<td>0.29354</td>
<td>1.10</td>
<td>0.342</td>
</tr>
<tr>
<td>Salt 1*Material</td>
<td>4</td>
<td>0.1417</td>
<td>0.03542</td>
<td>0.13</td>
<td>0.970</td>
</tr>
<tr>
<td>Error</td>
<td>45</td>
<td>12.0360</td>
<td>0.26747</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>53</td>
<td>13.0324</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The Two-way ANOVA results are illustrated as main effect plots and interaction plots in figure 29.

Figure 29. (A) Main effect plot of zinc comparing the different factors in the Two-way ANOVA. (B) Interaction plot between filter material and salt concentration with the concentration of zinc. (C) Interaction plot comparing salt concentration with sampling method and zinc concentration. (D) Interaction plot between filter material and sampling method with the concentration of zinc.

Mean effect plot (A) for the mean concentration of zinc. There is no horizontal line which indicate there is a main effect. Different levels of the factor affect the response differently. The steeper the slope of the line, the greater the magnitude of the main effect. Interaction plot for copper concentration (B) have no parallel lines. This interaction effect indicates that the relationship between salt concentrations added and mean concentration of zinc depends on the type of material. For example, the highest mean concentration of zinc for all salt concentrations is the bark material. The lowest mean concentration of zinc for all salt
concentrations is olivine. The interaction plot zinc concentration (C) have lines are parallel between olivine and raingarden which means no interaction occur, but the line of bark and the two others are not parallel, interaction occurs. Interaction plot for zinc concentration (D) have no parallel lines. This interaction effect indicates that the relationship between sampling method and mean concentration of zinc depends on the concentration of salt added. For example, if you use DGT, 3000mg/L added salt is associated with the highest mean concentration copper. The same for manual sampling. The lowest mean concentration of copper for DGT is no added salt, and for manual sampling its 100mg/L added salt.

6.1.5 Iron, cobalt, aluminium, chromium, manganese and cadmium

Figure 30 and 31 displays boxplots of the concentrations of iron, cobalt and aluminium, with the salt concentrations and filter materials as variables. Figure 30 is the raw data while figure 31 present the log-transformed concentrations.

Figure 32 and 33 shows the box plots for the concentrations of chromium, manganese and cadmium with variables such as filter material and salt concentrations. The box plots display both the raw data and the log-transformed concentrations. The concentrations for cadmium are similar to those found in the study from northern Sweden (Westerlund and Viklander, 2006).
Figure 30. The concentrations of iron, cobalt and aluminum with filter material and salt concentrations as variables. Note that the plots have different scaling and the concentrations are ppb for all metals.

Figure 31. The log-transformed data for the concentrations of iron, cobalt and aluminum with filter material and salt concentrations as variables.
Figure 32. The box plot for the concentrations of chromium, manganese and cadmium with salt concentrations and filter material as variables. Note that plots have different the scaling with concentrations in ppb.

Figure 33. The log-transformed concentrations of chromium, manganese and cadmium with salt concentrations and filter material as variables. Note that plots have slight different the scaling.
**A summary of the Two-way ANOVA analysis for the remaining metals**

The analysis from the Two-way ANOVA for the concentration of iron show that there is no association between iron concentration for both salt concentration or filter material with p-values of 0.842 and 0.195 respectively. The interaction between filter material and salt concentration have a p-value of 0.562, which indicate that the relationship between filter material and zinc concentration is not dependent on the salt concentration.

For the p-value for filter material is 0.023, indicating that there the different filter materials are associated with the cobalt concentration. With a p-value of 0.982, there is no association between the different salt concentrations and cobalt concentration. In addition, with a p-value of 0.598 there does not seem to be a dependent relationship between the filter material and cobalt concentration with the salt concentration.

For the concentration of aluminium there is no association or dependent relationship between the filter material and salt concentration with the concentration of aluminium. With a p-value of 0.510 for filter material, for salt concentration the p-value was 0.499 and the p-value for the interaction between filter material and salt concentration is 0.537, indicating that the relationship between filter material and aluminium concentration is not dependent on the salt concentration.

Chromium concentration seems to be associated with the filter material which have a p-value of 0.047. The p-value for salt concentration is 0.998, indicating that the different salt concentrations are not associated with the concentration of chromium. There seem to be no dependent relationship between the different filter materials and the concentration of chromium with different salt concentrations, with a p-value of 0.467 for the interaction between filter material and salt concentration.

The p-value for filter material is 0.042, which indicates that the different filter materials is associated with different concentrations of manganese. A p-value of 0.705 for salt concentration indicates that there is no association between different salt concentrations and manganese concentrations. Interaction between filter material and salt concentration have a p-value of 0.884, indicating that the relationship between filter material and concentration of manganese is not dependent on the salt concentration.
There seems to be no association between the different concentrations of salt with different concentrations of cadmium, with a p-value of 0.510. There is however an association between the different filter material and the concentration of cadmium due to the p-value of 0.003, but the interaction between different filter materials and salt concentrations have a p-value of 0.900, indication that the relationship between different filter materials and the concentrations of cadmium is not dependent on the salt concentration.

6.2 Results Bergen

The concentrations of the various metals for the DGT samples were calculated with equation (1) and (2) shown in material and methods, the results show extremely high values compared to the manual samples. A polyester pantyhose around the DGT samplers was a preliminary measure taken to avoid particle contamination of the devises, though it may seem due to the high concentrations of heavy metals in the samples from the DGTs that it was not sufficient enough.

Samples from the raingarden at the Brygga in Bergen where collected at two occasions, the 6th of April and 20th of April 2017. The results from Bergen shows a decrease in concentration for both heavy metals and ions as the water runs through the raingarden. Figure 34, 35 and 36 show the distribution of the different metal concentration by box plots. It makes it possible to examine the center and spread of the data and observe any possible outliers. The manual samples show the same values as found in other studies (Westerlund and Viklander, 2006).
Figure 34. Box plot of the concentrations (ppb) of nickel, copper and zinc in the raingarden in Bergen with sampling method as a variable. Note that the plots have different scaling due to high concentrations from the DGT samples.

Figure 35: Box plot displaying the log-transformed distribution of Ni, Cu and Zn concentration in the samples collected in Bergen.
Figure 36. The box plots for the concentrations (ppb) of Cr, Cd, Co and Pb in the raingarden in Bergen. Note that the plots have different scaling due to high concentrations from the DGT samples.

Figure 37. Displaying box plots of the log-transformed concentrations of Cr, Cd, Co and Pb in the samples from the raingarden in Bergen.
Figure 38. Box plot of the concentrations (ppb) of aluminum, manganese and iron from the raingarden in Bergen. Note that the plots have different scaling.

Figure 39. Illustration of the log-transformed concentrations found in the raingarden for Al, Mn and Fe.
As shown in the box plots the spread of the DGT concentrations are quite large, but there is no apparent sign of outliers from the sampling, which applies there is not one or a few samples that have very extreme values, instead the spread of the values is not so large. The concentrations of Cr, Co and Pb are especially high compared to what they normal (Westerlund and Viklander, 2006).

**PCA**

Several statistical procedures were performed on the data issued from the ICP-MS analysis, principal component analysis was one of them. The sample size of the collected samples from Bergen were not as extensive, but large enough to do some statistical analysis. Illustrated in figure 40 (A) and (B) is the score and loading plot respectively from the PCA. The scores are categorized after which sampling method that were used for each value, either manual or passive samples. Both the loading and the score plots are from log (base 10) transformed data values of the original concentrations from the Raingarden in Bergen. As shown in the loading plot almost all of the variance (0.921) is explained by the first principal component. The DGT score values are explained by the first principal component and are widely spread apart, on the other hand the manually taken samples are not as spread, but they are explained on the second principal component. This indicates that within the DGT samples, most of the variance explained in the PCA. The loading plot give information of which loadings correlates either positively or negatively to each other or not at all. From the loading plot in figure 40 (B) there are several of the metals that are closely together that indicate a strong positive correlation. It seems that lead is the only heavy metal which do not cluster together with the other metals. All the loadings are pointing towards PC1 (away from PC2), this is due to the heavy metal concentrations measured from the DGT samples were much higher than the manually taken samples.
After the PCA the next step in the statistical analysis were to investigate further whether there were any significant differences between the sampling method, the location and if the concentration of metals were in fact lower at the outlet of the raingarden. The Two-way ANOVA analysis showed there were a great difference between the DGT sampling and the manual sampling. In figure 41 (A) and (B) there are schematic overview for the main effects of sampling method vs. location and interaction plot were the sampling method is plotted against location to verify if there is any interaction that should be looked into with further analysis.

Figure 40. Schematic overview of the scores plot(left) distribution for PC1 and PC2 of the sampling method for the log transformed values for the concentration of the metals detected in the raingarden in Bergen. And the loadings (right).

Figure 41. (A) Main effect plot and interaction plot (B) Interaction plot comparing sampling method and sampling location
Results from PCA indicates that most of the variance in the data set is explained in PC1. In the scores plot the manually taken samples is in a tight cluster while the DGT samples is widely spread out. One-way ANOVA analysis gives the conclusion to the raw data from Bergen that there is a significant difference between water sampling with DGT and with manual sample method. The P-value where calculated to be 0.025 which means that the null hypothesis is wrong, and we use the alternative hypothesis and conclude that there is a difference in the means of the two sample methods.

The log transformed data shows a larger spread in the scores, but there is still a significant difference in the two sample methods, the P-value was less the 0.000.

One issue with the samples from Bergen is that they are showing much higher concentrations then what the manually taken samples do. It can be contamination when deploying, uptake or pre-treatment to analysis of the samples, but that is not very likely due to the fact that all the metals have high concentrations, and the calculations is checked more than three times. DGT devices accumulate over time so it’s quite peculiar that in approximately 4 hours the accumulation has reached such high concentrations. The problem could be a combination of different factors like the ones already mentioned, another factor can have an impact on the concentration is the compatibility of the DGT units. Through several years various students have been using and reusing these passive samplers, which could have had an influence on the units either by not being sufficiently cleaned, or by possible damage on the base and cap. The damage can have led to particles getting inside the device through the window or the opening between the base and the cap and contaminating the samples. In the user manual from DGT research it is stated that these devices are reusable. Though there is always a risk of contamination transfer when using equipment again, though it can happen with new equipment as well. During the DGT deployment these samplers were fitted in a polyester pantyhose to avoid contamination from dirt and other particles, this may not have been satisfactory enough, and the DGT where influenced by particles in the water stream.
6.3 Results test site E18, Sweden

6.3.1 Heavy metals and trace metals in highway runoff

The concentrations of various metals form the test site E18 in Sweden are presented in different plots and there was done statistical analysis such as PCA. In figure 42 there is box plots of the concentrations of Ni, Cu and Zn with sampling method as a variable.

![Box plots of the concentrations of Ni, Cu and Zn](image)

*Figure 42. Box plot of the concentrations of Ni, Cu and Zn dividing the different sampling methods. Notice the concentrations are different for each metal.*

It is clear from the box plot that the spread of the samples is more or less satisfactory, but there are outlier indications for both nickel and zinc. One DGT sample and one filtered manual sample for Ni and one sample from filtered manual sample and one not filtered manual sample are presented as outliers in the plot, meaning that there is one sample with an extreme value compared to the other samples. The log-transformed concentrations are displayed in figure 43 and here it is one outlier for the DGT samples for each metal.
Figure 43. The box plots displaying the distribution of the log-transformation concentration values for Ni, Cu and Zn in the samples from Sweden.

Figure 44 and 45 show the concentrations of Cd, Pb, Cr and Co in box plots with the sampling method as a variable. The raw data is presented in figure 44 while the log-transformed data is shown in figure 45. There are several outliers presented in the plots, which indicates there are some sample that have extreme values compared to the mean of the other samples. The log-transformation reduces some of the outliers, but still there are quite a few outliers left. Note that none of the outliers indicated in the box plots have been removed from the data.

Figure 46 and 47 displays the box plots for the concentrations of Mn, Fe, Al and V with the sampling method as the variable. The first figure is the concentrations from the raw data and figure 47 is showing the log-transformed concentrations. There are a few outliers in both plots, but the number of outliers is reduced in the log-transformed plot.
Figure 44. The concentrations of Cd, Pb, Cr and Co displayed in box plots. Note that the plots have different y-axis.

Figure 45. Box plots displaying mean concentrations and the spread in the log-transformation data for the concentrations of Cd, Pb, Cr and Co.
Figure 46. The concentration of Mn, Fe, Al and V distributed in box plots with sampling method as a variable. The y-axis is different for each metal.

Figure 47. The distribution of box plots for Mn, Fe, Al and V log-transformed concentrations from test site E18.
6.3.1.1 Lead

The concentrations of lead through the Autumn season of 2017 is represented in figure 48, which shows the different concentrations for unfiltered water samples from both the road well and the infiltrated well. As seen in the figure the concentrations vary, on all occasions except two, which was the 26th of September and the 3rd of October, the water from the road well is higher than the infiltrated well. Figure 49 displays a time series plot of the lead concentrations found in DGT samples, the values vary in the beginning of the season, but evens out towards the end. Note that the concentrations are quite low.

Figure 48. The lead concentrations for unfiltered runoff water from the untreated well and the infiltrated well.

Figure 49. The DGT concentrations of lead from test site E18.
In figure 50 the comparison of the lead concentrations from the DGT samples and the filtered manual samples from the infiltrated well is displayed in a time series plot. The DGT sample concentrations is only higher during the first sampling, the rest of the sampling period, the manual samples have higher concentrations.

![Figure 50. Lead concentrations of DGT samples compared to filtered manual samples.](image)

### 6.3.1.2 Nickel

The concentrations of nickel are displayed in various time series plots, in figure 51 the comparison of unfiltered manual samples from the road well with the infiltrated well is displayed. It would have been easier to draw any conclusion to why the concentrations vary the way they do with more parameters included, such as pH, accurate temperature, rainfall, conductivity and more. Figure 53 displays the lead concentrations of the DGT samples for the whole sampling period. It looks like it increases quite extensive between the 18th of October and 14th of November, but in-between this two sampling dates there is no way to know what the concentration was. But from the 7th of November to 14th of November compared to 18th of October the increase in lead concentration is high (from 0.5ppb to 3.5ppb).
The concentrations of lead comparing DGT samples with filtered manual samples from the infiltrated well is displayed in figure 53. The concentration of lead from the DGT samples is higher at the beginning and at the end of the sampling period, which may indicate that in the period between the sampling days the average concentration has been quite high. Due to the manual sample is only a representation of the concentration in the well at the time of sampling while the DGT accumulates the metals over the time of deployment.
Figure 53. Concentrations of nickel comparing DGT samples and filtered samples

Figure 54 and figure 55 show box plots of the nickel concentrations with sampling method and location as variables with the raw data presented in figure 54 and the log-transformed data in figure 55. The outlier from the infiltrated well of DGT samples is still present at the log-transformed plot. Overall the DGT samples seems to be more spread than manual samples, it is more obvious in the log-transformed plot.

Figure 54. Box plot comparing sampling method and location for the mean and spread of the concentrations of nickel from the raw data.
6.3.1.3 Copper

The concentrations of copper are displayed in various time series plots and box plots. In figure 56 the time series plot comparing the unfiltered manual samples from the road well and the infiltrated well is displayed. The copper concentrations are higher at most sampling days in the road well, except the 12th of September and 7th of November. They are the same concentrations found in road water in other studies (see table 3) (Lundgren, 2001 and Westerlund and Viklander, 2006). Figure 57 is the time series plot for the copper concentrations from the DGT samples collected in the sampling period. The concentrations are quite low if compared to the concentrations in the road well water.
Figure 56. The concentrations of copper in a time series plot between the unfiltered samples from the infiltrated well and the untreated well.

Figure 57. Copper concentrations of DGTs from the field trips to Sweden

Figure 58. A time series plot comparing the concentrations of copper in the DGT samples and the filtered manual samples from the infiltrated well. The DGT samples is lower and have stable values through the whole sampling period.
Figure 58. Comparison of copper concentrations of DGT samples and filtered samples from the infiltrated well.

Figure 59 and 60 show the box plots for the copper concentrations in the different well and with different sampling method. For the copper concentrations the DGT samples have a low spread of values compared to the manual samples from both well for filtered and not filtered samples.

Figure 59. The box plot displays the mean and spread in the copper concentration between sampling method and location of the raw data.
6.3.1.4 Zinc
The zinc concentrations found in the samples from the sampling period at test site E18 in Sweden is displayed in various time series plots and box plots. Figure 61 is a time series plot comparing the unfiltered samples from both the infiltrated well and the road well. The concentrations are similar to what have been found in previous studies see table 3 (Westerlund and Viklander, 2006). The concentrations in the two wells vary, but most of the sampling days the samples from the road well had higher concentrations. Figure 62 shows a time series plot for the concentrations of zinc in the DGT samples collected. The concentrations are quite low compared to the unfiltered samples.
Figure 61. Comparison of zinc concentrations from unfiltered water samples from untreated road water and infiltrated road water.

Figure 62. The DGT concentrations of zinc through the sampling period in Sweden.

Figure 63 shows the concentrations of zinc comparing the DGT samples with the filtered samples from the infiltrated water. The manual samples show much higher concentrations for most sampling days. But as stated earlier the manual sample is only a picture of the concentration at the moment of sampling.
Figure 63. Zinc concentrations comparison between DGT samples and filtered water samples from Sweden.

Figure 64 and 65 displays box plots of the zinc concentrations found at the test site E18 in Sweden during the sampling period. The DGT sample values are very similar and the variance is low compared to the manual samples from both wells, though the both the filtered and unfiltered samples from the road well displays more spread in the values. In the log-transformed data there is an outlier for one of the DGT samples.

Figure 64. The box plot displaying the raw data concentration of zinc dividing the sampling method and location.
Figure 65. Box plot of the log-transformed zinc concentrations with sampling method and location as variables.

**PCA**

Comparing differences between the not filtrated manually water samples from the infiltrated well and the road water well. Doing first a PCA analysis, see figure 66, on the data which is not log transformed. See that most of the variance is explained by 3 PCs (90.7%), but only uses 2 of them. From the loading plot it appears that there is correlation between most of the heavy metals. Zn, Co and Mn are placed together the same are Cu, Pb, Fe, Ni and Cr.

Then a one-way ANOVA was executed on the PCA1 scores and the analysis indicate that there is a significant difference between the infiltrated well and the road water well. The p-value was 0.047. Null hypothesis says all means are equal and alternative hypothesis that not all means are equal, the results from the analysis indicate that the null hypothesis is wrong and that there is a difference.
Figure 66. display the score plots and the loading plot for the samples collected at testsite E18 Sweden. There are two scores plot displaying the same scores but are divided with different variables e.g. sampling method and location. By viewing the score plots there are two scores opposite of each other that are far apart from the rest of the scores, which could turn out to be outliers. The PCA provides an outlier plot (see Appendix B), this plot gives an indication of observations that might be outliers, for this particular case there are three observations that are above the line indicating outliers. From the scores plot it seems like it is only two obvious outliers, one is a DGT sample and the other is a filtered sample from the road water well.

The summary report for the PCA1 scores shows that the p value is very low which in this case is not good also the probability plot shows the same tendency that is the reason why a Johnson transformation of the PCA1 scores was done, this is a quality tool to fit the data more satisfactory. Before the Johnson transformation the p value was <0,005 after it was 0,939 which is a positive transformation, due to the fact that the we want a value close to 1. Doing a new one-way ANOVA with the transformed PCA1 scores resulted in a more fitted model and a p-value of 0,012. And the normal probability plot and the histogram is more normally distributed.
The p-value for the Probability plot of the Residuals after transformation is 0.968
After completion of a test of equal variances between PCA1 transformed and the source (road water well and infiltrated water well) there was no indication that the variances were different between the two sample sites.

The log transformed for unfiltered water samples shows a different pattern than the raw original data. After a PCA which was quite unusual and following the one-way ANOVA analysis of the PCA1 scores there was no significant difference between the two sample sites, with a p-value of 0.653.

From figure 67 it is apparent that the sampling methods is significantly different from each other. The confidence intervals do not cross over each other in figure (B), and the all the intervals in the Tukey confidence interval plot do not contain zero which is an indication that they are in fact significantly different.
Figure 67. (A) shows the Tukey 95% confidence interval from One-way ANOVA analysis. (B) Displays the confidence interval plot for the different sampling method compared with one another.
During the sampling of the water there were noticeable differences between the two wells, first the water directly from the road had much darker colour, if the turbidity had been measured it would most likely be higher in untreated road water than in the water from the infiltrated well. The 0.45 \( \mu m \) pore filters used became black during sampling, picture of the filters used in shown in figure 68. Second, there were more challenging to filter the samples from the infiltrated well than from the well containing untreated run-off water. This is most likely due to small particles entering the well from the infiltration area and blocking the filter. At the retrieval of the POM strips the temperature was close to zero degrees Celsius and it was snowing. It was visible slush in the well with untreated run-off water and the strips from that particular well were covered in black water slush residue see figure 69. The two POM samples from the infiltrated well had not any noticeable signs of discoloration. The POM samples were deployed for a month, from November 7\(^{th}\) to December 5\(^{th}\).

Figure 68. Picture of two filters used for filtration of the samples from the road water well (to the left) and from the infiltrated well (to the right).
6.3.2 PAHs and PCBs

The deployed POM samplers that were delivered to NGI in Oslo for analysis the same day as retrieval from the wells at the test site E18 in Sweden. Due to the low sample collection of only two pieces in each well, it becomes difficult to make any conclusive statements, but it gives an idea of the difference in the organic compound distribution in the two wells. In both wells the POM samples were placed on the lower water level displays higher concentrations for all of the organic compounds tested. And as shown in the results table it is quite a large difference in the concentration level from the infiltrated well and the well with water directly from the road. This gives a strong indication that the infiltration material prior to the well is retaining the compounds in a most effective way. The concentrations found at the test site are higher than what is found in a study looking at tunnel wash water concentrations of PAHs and other pollutants (Paruch and Roseth, 2007). The total concentration of PAHs found in (Paruch and Roseth, 2007) were 3.35 ppb while at the test site for untreated water had a concentration of 60.6 ppb for POM placed on the lower half and 35.2 ppb for the POM sample placed on the upper layer of the rod. The POM samples that were placed in the infiltrated well had a total PAH concentration of 23.2 ppb for the sample on the bottom of the well, and the sample on the top had a concentration of 8.74 ppb. A study investigating the accessibility of PAHs in particulate matter from road impacted environments, found concentrations of the same 16PAHs analysed in this study, ranging from 670 ppb up to 26000 ppb from a mobile road sweeper from River Alna in Oslo. Particulate matter usually contain higher concentrations of pollutants and for the study investigating the exact topic it is indisputable that the concentrations are exceedingly higher than the concentrations for dissolved PAHs (and other pollutants).
Figure 69. (A) The two POM strips collected from the infiltrated road water well, (B) two POM strips samples retrieved from the road water well the 5th of December 2017.

The POM analysis results of the distribution of the concentrations of PAHs and PCBs are displayed in figure 70 and figure 71 respectively. Phenanthrene is the compound which have the highest concentrations in both strips from both wells. Of the groups of PCBs found from the analysis of POM samples, PCB-28 is the compound with the highest concentration level, which is known for its toxic effects towards aquatic life (ECHA, 7/6-2018). Overall the PCB concentration is fairly low and are similar to the concentrations found in Huston ship Channel, Texas (Howell et al., 2008). The occurrence of the PAHs are similar within the same well and display the same scattering of compounds. The distribution of PCBs have similar patterns for both the well, though the infiltrated well has lower concentration compared to the road water well.
Figure 70. Graph presenting the concentration of the PAHs from the POM analysis.

Figure 71: Concentrations of the PCBs analyzed from the POM analysis.
6. Conclusion

The DGT sampling and the manual sampling is not comparable in this study. Every sampling location showed that there is a significant difference between these two sampling techniques. In Bergen the DGT sample concentration show way higher concentrations then the manually taken samples. This could have been contamination, transfer of some kind, or there was contamination that did not show up on the filtered manual samples due to the manual samples is only the concentration in the media at the sampling moment.

Data from the two different wells at Test site E18 in Sweden show that there is a significant difference between samples from the infiltrated road water well and from the road water well. There was also a significant difference between filtered and unfiltered samples from the wells. Unfiltered samples usually contain higher concentrations of pollutants compared to filtered samples which was an expected result for the samples collected in Sweden. Even though the concentrations varied during the sampling period, the DGT samples had lower concentrations compared to the manual samples from the same well. One explanation for the low concentrations is that the DGT samples were shielded by the PVC pipe they were lowered in, and maybe the circulation of the water in and out of the holes in the pipes were not as good as anticipated.

The organic compounds from the POM strips analysis show higher concentrations in the bottom of the two different wells compared to the strips located at top layer of water, close to the surface. This could be due to that organic compound and other pollutants often tend to bind to particulate matter, which can lead to descending of the pollutants in the wells.

For the experiments at the hydraulics laboratory olivine seem to be the filter material which is the most stable of the three tested and is the material that retains the most metal contaminants. Also, olivine is the filter material that is the least affected by the increasing salt concentration. The two other filter materials show satisfactory capability to retain the metals and withstand any increasing salt concentration. There should be more studies on these filter materials that are more realistic in a way that climate and original source of contamination are implicated in the study.
6.1 For future consideration

I would have done several more experiments at all locations. The same experimental set-up at
the hydraulics laboratory, with experiments for all the different salt concentration to increase
the sample size and achieved better representation.
If there where anyway I could test with organic compounds as well as metals to simulate more
realistic conditions and see how they interact with each other.
In connection with the construction of new E6 in Trondheim a test site should have been built
to do realistic studies on the run off water and look at the influence of the salt use.
Used lead in the metal mixture which was the initial plan.
I would have taken water samples on the test site E18 in Sweden during a whole year and not
just a season.
There should have been a clear plan over which parameters I should have measured so that I
would have more data to back up my results and make conclusions.
Maybe there is an issue that we did not plan exactly how fast the waters should flow through
the swales. The plan was initially just to empty the 1000 litre tank in four hours, I used 3
hours the first time, but there was still water in the swale. I would have turned down the flow
on the water pump, so it would take longer before the tank was empty.
On the E18 test site in Sweden there were two auto samplers that could have been used if
there was more time for cooperation and planning. This could have given results from both of
the wells and shown interesting differences. These samplers would have most likely collected
water every day for a week.
Measure different species of the metals to look at which species that are bioavailable, due to
the concern of polluting the environment close to the roads that receives the runoff.
7. Recommended future work

- Study the effect of increasing salt amounts in a metal solution in the same material, pine bark, olivine and raingarden in the field outside to get more realistic data.
- Measuring several other chemical parameters like temperature, conductivity, turbulence, pH to get more information to be able to make better conclusions.
- Take continuous water samples during a whole year to see the seasonal effects (I only took from September to November. Depends on how you characterise the seasons but normally autumn is from September to November and winter starts in December. So really, I only sampled through the whole autumn season.
- Investigate the effects of magnesium chloride on the environment like sodium chloride. And how metal species reacts.
- Study the anticaking agent that is used in the road salt mixture and figure out what relevance that has on the environment and pollution. Does it affect metal and/or organic pollutant mobility?
- Investigate each materials capability to rinse the runoff water and see for how long they have an efficient cleaning ability.
- Study the combined effects when applying both metals and organic pollutants like PAHs to the mixture. (since it was characterised as too dangerous to experiment on in the large-scale study)
- Do a study which looks at organic pollutants during a whole year.
- Microplastic study
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Appendix A

Additional information about the raingarden in Bergen.

Figure A.1. Pictures of where the runoff water in the raingarden originates Photos: Ingeborg Farnes.
Figure A.2 The street leading down to the raingarden in Bergen. Photos: Ingeborg Farnes
Appendix B

Additional information about the study done at test site E18 in Sweden.

Figure B.1. The illustration of the PVC pipes used in the experiments at the hydraulics laboratory and one pipe in Sweden.
Figure B.2. Outlier plot for the PC analysis of the results form test site E18.
Appendix C

Additional information from the hydraulics laboratory experiments.

Figure C.1. Time series plot for the concentration of lead in the experiments at the hydraulics laboratory with filter material and salt concentrations as categorical variables.
Figure C.2. Time series plot for the concentration of iron with filter material and salt concentrations as categorical variables.
Figure C.3. The concentration of cobalt distributed in a time series plot with filter material and salt concentrations as categorical variables.
Figure C.4. Time series plot for the concentration of aluminum in the experiments at the hydraulics laboratory with filter material and salt concentrations as categorical variables.
Figure C.5. The concentration of chromium distributed in a time series plot with filter material and salt concentrations as categorical variables.
Figure C.6. Time series plot for the concentration of manganese with filter material and salt concentrations as categorical variables.
Figure C.7. Time series plot for the concentration of cadmium in the experiments at the hydraulics laboratory with filter material and salt concentrations as categorical variables.
Table C.1. The principal component analysis with eigenvalues and description of eigenvectors.

**Eigenanalysis of the Correlation Matrix**

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**Eigenvectors**

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<td>0.636</td>
<td>-0.058</td>
<td>0.122</td>
</tr>
</tbody>
</table>