



Norwegian University of  
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# Investigation of the adsorption and biodegradation capacity of filter media towards airport de-icing chemicals

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## Abstract

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At airports in Norway, propylene glycol (PG) and potassium formate (PF) are used as de-icing chemicals to provide safe air traffic. Expected climate changes will lead to temperatures more frequently around zero degrees, when de-icing chemicals consumption is at its highest. In addition, air traffic is expected to increase. De-icing chemicals degradation has a finite capacity, mainly dependent on nutrients, oxygen and temperature. In this thesis, some filter media have been tested to evaluate adsorption and biodegradation capacity of de-icing chemicals. Filtralite media is today used for drinking- and wastewater treatment. Filtralite media is a promising media in a bioretention system, due to low head loss and high storage capacity. Batch experiments and column experiment have been conducted to investigate adsorption and biological degradation of the de-icing chemicals propylene glycol and potassium formate.

Batch experiments were performed to investigate adsorption onto granular activated carbon (GAC), Filtralite NC 0-2 and Filtralite NC 0.8-1.6. Adsorption was shown onto GAC. Linear isotherm was found as best-fit for both chemicals (PG,  $R^2 = 0.99$  and PF,  $R^2 = 0.94$ ). PG and PF showed similar power indexes with Freundlich isotherm, close to 1 ( $1/n$  of 0.883 and 0.871 respectively), which indicate that adsorption onto GAC was not very high for any of the de-icing chemicals. Second order kinetics fitted best for both chemicals. No adsorption onto the Filtralite media was observed.

Columns were filled with Filtralite NC 0.8-1.6 (Column 1) and Filtralite NC 1.5-2.5 (Column 2). Synthetic stormwater was prepared with concentration of 20 mg/l PG and 13.4 mg/l PF. Degradation in a 1 m<sup>3</sup> feed tank was investigated prior to the column experiment, to find that 50% of the de-icing chemicals were degraded after 5 days. This resulted in changing the synthetic stormwater every day to prevent the risk of degradation. Degradation in the columns was shown to be significant in the upper ~15 cm for both columns, while degradation in the lower parts of the columns were not significant. Initial removal in the upper ~15 cm was 20% for column 1 and 15% for column 2. Increased phosphorous and nitrogen in the synthetic stormwater showed improved degradation (C:N:P=24:7:1), with the average of 50% removal through both the filters in the columns. Results from Iwasaki

modelling showed increased filtration coefficients after nutrient addition. Clogging occurred in the top 15 cm of the filter.

From these results it was found a lifetime of 2 years for the filters tested in the column experiment, which is relatively low, probably due to high sediment loading. In reality the sediment load might actually be less than in the column experiment, however sediment loading was necessary due to the need of bacteria for the biofilter form the sediments. A top layer of GAC in the biofilter was considered, however a biofilter with a GAC layer on top reduces the lifetime of the filter due to clogging, and is therefore not recommended due to low adsorption capacity. Filtralite media showed interesting results and recommended to be further investigated.



## Sammendrag

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Propylen glykol (PG) og kalium format (engelsk: potassium formate, PF) brukes i dag ved avising av fly og rullebane for å sikre forsvarlig fly-trafikk i Norge. Forventede klimaendringer gjør at vinter-temperaturene i Norge oftere vil være rundt null grader, hvor bruk av avisingskjemikalier er høyest. Flytrafikk er også forventet å øke. Avisingskjemikalier blir nedbrutt i jorden, men jorden har begrenset nedbrytings-kapasitet, avhengig av næringsstoffer, oksygen og temperatur. Adsorpsjon og biologisk nedbryting av avisingskjemikalier for noen filtermaterialer er testet i denne oppgaven. Filtralite materiale brukes i dag i vann- og avløpsbehandling, og er et lovende materiale for et biofilter fordi materialet har høy lagringskapasitet grunnet den porøse strukturen. Batchforsøk og kolonne-eksperiment er utført for å undersøke adsorpsjon og biologisk nedbryting av avisingskjemikaliene propylen glykol og kalium format.

Batchforsøkene ble utført for å undersøke adsorpsjon på granulert aktivt kull (GAC), Filtralite NC 0-2 og Filtralite NC 0.8-1.6. Adsorpsjon på GAC ble påvist, hvorav Lineær isotherm passet best for begge kjemikaliene, (PG,  $R^2 = 0.99$  and PF,  $R^2 = 0.94$ ). Indikasjon for lav adsorpsjon av PG og PF på GAC ble funnet, da indeksen  $1/n$  ble funnet til nærme 1 (0.883 for PG og 0.871 for PF). Det ble ikke funnet adsorpsjon av avisingskjemikalier på Filtralite materialene testet.

Kolonneforsøket bestod av to høye kolonner, hvorav kolonne 1 var fylt med Filtralite 0.8-1.6 og kolonne 2 med Filtralite NC 1.5-2.5. Overvann med kjemikalier og sedimenter ble forberedt, hvorav konsentrasjonen var satt til 20 mg/l PG og 13.4 mg/l PF. Nedbryting i en tank som rommet  $1\text{m}^3$  overvann ble undersøkt, hvor det ble funnet at 50% av avisingskjemikaliene var nedbrutt etter 5 dager. Dette resulterte i beslutningen om å bytte overvann for kolonneforsøket hver dag, for å unngå nedbryting i tanken. Nedbryting i begge kolonnene viste signifikant forskjell i de øverste ~15 cm, mens nedbryting i de nedre delene av kolonnene ikke viste signifikant forskjell. Initiell nedbryting i de øverste ~15 cm ble funnet til 20% for kolonne 1 og 15% for kolonne 2. Tilsetning av fosfor og nitrogen viste økt nedbryting (C:N:P=24:7:1), med 50% nedbryting som et gjennomsnitt i hele filteret for begge kolonnene. Resultater fra Iwasaki modellering viste økt filtrasjonskoeffisient etter tilsatt fosfor og nitrogen. Fortetning av filteret skjedde i de øverste ~15 cm.

Funnene fra denne oppgaven resulterte i en levetid for filtrene testet på 2 år. Dette er sannsynligvis grunnet stor mengde sediment i overvannet. Mengden sediment er muligens høy i forhold til hva som er realitet for et fullskala filter ved flyplass. Det var uansett nødvendig å tilføre sedimenter i overvannet grunnet behov for bakterietilførsel i filteret. Et topp-lag av GAC i biofilter ble vurdert, men da det vil forårsake raskere tetting av filteret og grunnet lav adsorpsjonskapasitet er dette ikke anbefalt. Filtralite materiale viste lovende resultater og bør bli videre undersøkt i laboratoriet og fullskala.

## Preface

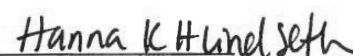
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This thesis is a product of the master thesis course TVM4905 at the Department of Hydraulic and Environmental Engineering at Norwegian University of Science and Technology (NTNU).

The thesis has been written during the spring 2016 as a part of the project Klima2050. Klima2050 is a Centre for Research-based Innovation (SFI) financed by the Research Council of Norway and the consortium partners. The thesis is a part of Work Package 2.4. The collaboration partners are Saint-Gobain Weber, that has provided the media, as well as Avinor that has provided the chemicals.

I would like to express gratitude to Kamal Azrague and Gema Raspati, researchers at SINTEF, for being my supervisors and for discussions and help with laboratory experiments. I would like to thank Tone Muthanna, Associate Professor at the Department of Hydraulic and Environmental Engineering for being my supervisor from NTNU. I am very thankful for the help and guidance in the analytical laboratory I have received from Trine Hårberg Næss and Gøril Thorvaldsen. I would also like to thank Jaran Wood from Weber Saint-Gobain for supplying Filtralite media used in the experiments.

The project has been a continuation from the Student thesis written in January and February this year, and has been an interesting experience. I have learned how much time lab work takes, and it has been a great experience to be a part of this research project. When finalizing the thesis one always see some improvement for the laboratory set up that could have made the results different or more accurate.



Trondheim, July 12, 2016

Hanna Kristine H Lindseth



## Project description

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**Candidate name:** Hanna Kristine Haug Lindseth

**Subject:** Stormwater

**Title:** Investigation of the adsorption and biodegradation capacity of filter media towards airport de-icing chemicals.

**Start:** 29th of February 2016

**Due date:** 25th of July 2016

### Background

Airports in Norway are facing real environmental challenges due to climate change. The greatest challenge in the area of soil and water relate to traffic increase, which with a changing winter climate, will result in higher consumption of de-icing chemicals (Avinor, 2013). Propylene glycol (PG) is the main component of aircraft de-icing fluids and potassium formate is also used for de-icing of runways and taxiways. These chemicals infiltrate the soil surface along the runways when the melting of snow begins around April. It is important to ascertain that these chemicals do not contaminate the groundwater, because they would lead to oxygen consumption during their decomposition (Greco et al., 2008). Indeed, PG and potassium formate are easily degraded by soil bacterial communities. However, they still constitute a threat to the groundwater due to potential overloading of the degradative capacity of the system, namely if biodegradation rates are not sufficient compared to velocities in the unsaturated zone (French et al., 2010).

Filtration treatment systems are considered as promising methods for reducing dissolved and particulate phase pollutants provided that the selected filter media has high adsorption capacity during the initial operation phase. In longer run, once the media is coated with biomass, the stormwater is then treated by biofiltration (also known as rain garden or bioretention), which provide water quality improvement and flow retention (e.g. Dietz, 2007). Chemicals at airports infiltrate during the snowmelt period, and biodegradation activity is limited by temperature (French et al., 2001). When the temperature in soil is rising during the summer, biodegradation of propylene glycol is efficiently degraded due to higher temperatures in soil (Lißner et al., 2007).

**The main objectives of the project are:**

- 1) Literature review on previous studies of de-icing chemicals removal by adsorption and biofiltration.
- 2) Determination of adsorption kinetics and isotherms for selected media based on laboratory tests.
- 3) Conclude on the adsorption capacity of these media for the removal of de-icing chemicals used in airports.
- 4) Investigation of biodegradation of selected media along the filter bed in column experiment at room temperature.
- 5) Investigation of pressure along the filter bed in column experiment.

**Collaboration partners:** Klima2050, SINTEF, Weber Saint-Gobain

**Location:** The project thesis will be conducted at the Department of Hydraulic and Environmental Engineering. The candidate should have regular meetings with advisors(s). The laboratory work will be conducted at the laboratories at the Department of Hydraulic and Environmental Engineering.

**Advisors:** Kamal Azrague, Gema Raspati, Tone Merete Muthanna

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## Nomenclature

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- $A_s$  Cross-sectional area of the column [ $\text{m}^2$ ]  
 $b$  Langmuir adsorption equilibrium constant [ $\text{L}/\text{mg}$ ]  
 $C$  Intercept which represent the rate-limiting factor [ $\text{mg}/\text{g}$ ] (adsorption kinetics)  
 $C$  Concentration of suspension [mass/volume] (Iwasaki model)  
 $C_0$  Initial concentration in the solution [ $\text{mg}/\text{L}$ ]  
 $C_e$  Equilibrium concentration in the solution [ $\text{mg}/\text{L}$ ]  
 $h$  Length of media whose hydraulic conductivity is being tested [ $\text{m}$ ]  
 $H$  Total hydraulic head across the filter [ $\text{m}$ ]  
 $h_{0,2}$  Initial adsorption rate [ $\text{mg}/\text{g min}$ ]  
 $k$  Hydraulic conductivity [ $\text{m}/\text{s}$ ]  
 $k_1$  Rate constant [ $\text{g}/\text{mg h}$ ]  
 $k_2$  Rate constant [ $\text{g}/\text{mg h}$ ]  
 $k_{id}$  Intraparticle diffusion rate constant [ $\text{mg}/\text{gh}^{1/2}$ ]  
 $K_F$  Adsorption capacity of the sorbent [ $\text{mg}/\text{g (L}/\text{mg)}^{1/n}$ ]  
 $L$  Media depth [length]  
 $\lambda$  Filter coefficient [ $1/\text{length}$ ]  
 $n$  Indicates change in adsorption strength with change in adsorption capacity [-]  
 $Q$  Volumetric flow rate [ $\text{m}^3/\text{s}$ ]  
 $Q_0$  Maximum adsorption density when surface sites are saturated with adsorbate  
[ $\text{mg adsorbate}/\text{g adsorbent}$ ]  
 $q_e$  Adsorption density [ $\text{mg}/\text{g}$ ]  
 $q_t$  Amount of solute adsorbed in the adsorbent at time  $t$  [ $\text{mg}/\text{g}$ ]  
 $R$  Gas constant [ $8.314 \text{ J}/\text{mol K}$ ]  
 $R_L$  Constant for separation [-]  
 $T$  Temperature [ $\text{K}$ ]  
 $t$  Time  
 $V$  Volume [ $\text{L}$ ]  
 $W$  Mass of media [ $\text{g}$ ]  
 $z$  Depth [length]



## Abbreviations

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ATP	Adenosine triphosphate
DIC	De-icing chemicals
DOC	Dissolved organic carbon
GAC	Granular activated carbon
PF	Potassium formate
PG	Propylene glycol
SS	Suspended solids





# 1 Introduction

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## 1.1 Background

De-icing chemicals are applied on airplanes and taxiways to provide safe air traffic in cold climates during winter. Expected climate changes will lead to temperatures more frequently around zero degrees. This is when consumption of de-icing chemicals is at its highest (French et al., 2010). At the same time, airplane traffic is expected to increase, which also leads to increased consumption of de-icing chemicals. An example of a de-icing operation is illustrated in Figure 1-1.



Figure 1-1: Aircraft de-icing (Gurandsrud, n.d.)

De-icing chemicals are naturally degradable in soil. The amount of chemicals degraded in soil is dependent on temperature and thickness of soil. The degradation capacity is finite, limited by degradation rates, nutrients and oxidation levels. With the future increase in consumption of de-icing chemicals and increased air traffic, this will cause a larger pressure for the nature to degrade the chemicals if nothing is done.

Some airports have systems for collecting stormwater at airports today, however many airports do not have such a system for the polluted stormwater. Filters and infiltration

systems have become more popular for treating different kinds of runoff the recent years. A filter system is one possible approach to solve the problem, hence this is further investigated in this thesis.

Today, Filtralite media is used for treatment of drinking water, wastewater and industrial water. One of the aims of the project Klima2050 Work Package 2.4, is to look at a new application of Filtralite media. It will be investigated if it is possible to treat runoff from airports as well as runoff from highly trafficked roads. This thesis is focusing on runoff from airports, specifically looking at the de-icing chemicals commonly used in Norway. Propylene glycol is used for de-icing of aircrafts, and potassium formate is used for de-icing the runways and taxiways. Filtralite media come in many fractions and with different treatment properties. The part of the thesis that investigates the adsorption capacity of media is focusing on Filtralite NC 0-2, Filtralite NC 0.8-1.6 and granular activated carbon (GAC), as these fractions were used in the study by Andersen (2016). For the column tests, it was decided to focus on commercially available media, therefore Filtralite NC 0-2 was left out and Filtralite NC 1.5-2.5 was included together with Filtralite NC 0.8-1.6.

## **1.2 Objectives addressed in the thesis**

The main goal is to assess applicability of biofilter treatment of de-icing chemicals from airport runways. To reach this goal the thesis is divided into five objectives, which are addressed in the same order:

- Literature review on previous studies of de-icing chemicals removal by adsorption and biofiltration.
- Determination of adsorption kinetics and isotherms for selected media based on batch experiment in the laboratory.
- Conclude on the adsorption capacity of these media for the removal of de-icing chemicals used in airports.
- Investigation of biodegradation of Filtralite media NC 0.6-1.8 and NC 1.5-2.5 in room temperature
- Investigation of pressure along the filter bed in column experiment, to determine the lifetime of the filter as well as where clogging will occur.

## 2 Stormwater pollution and climate change

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### 2.1 Stormwater pollution at airports

Stormwater at airports will contain different substances from airport traffic. Both the aircraft traffic and the de-icing operations in winter contribute to contamination of the stormwater. As mentioned, the focus in this thesis will be on de-icing chemicals. There are various selections of de-icing chemicals for aircraft and runway de-icing. For this project the main focus is on propylene glycol and potassium formate.

#### 2.1.1 De-icing chemicals

De-icing chemicals are used on airplanes and taxiways to guarantee safe air traffic during winter (Lißner et al., 2007). Propylene glycol (PG) is used for de-icing the aircraft and is degradable in soil (Lißner et al., 2007). Potassium formate is used for de-icing of runways and taxiways. As an example, de-icing chemicals are used from October to April at Gardermoen airport in Norway (French et al., 2001). De-icing chemicals are mixed with snow due to mechanical removal of snow from runways and taxiways and airborne drift of chemicals from airplanes at take-off (French et al., 2001). It is considered that approximately 20% of the chemicals will mix with the snow and melt with the snow in spring (Lißner et al., 2007). Chemical composition of the two de-icing chemicals is illustrated in Figure 2-1.

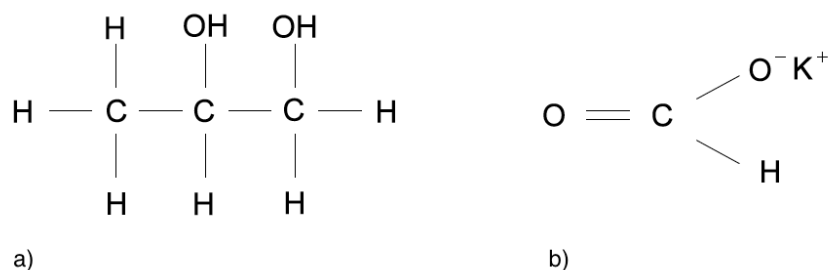


Figure 2-1: Chemical formulas, (a): propylene glycol and (b): potassium formate

During the snow-melting period, de-icing chemicals are infiltrated in the soil. This usually starts in April. At Gardermoen airport, more than 50% of the recharge to the groundwater occurs during the snow-melting period, which is usually 3-5 weeks (Jørgensen and Østmo, 1990).

Studies have previously been done regarding the development of Gardermoen airport, because of the large unconfined aquifer that is situated under the airport (French et al., 2001). Contamination of groundwater might in general have large consequences. At Gardermoen, the thickness of the unsaturated zone varies between 1-30m (French et al., 2001). The de-icing chemicals used are naturally degradable by microbial biomass at the soil surface (French et al., 2001). However, the degradation requires a high oxygen demand and this may affect the natural state of the soil (Liβner et al., 2007). Degradation of glycols has a high biochemical oxygen demand and can influence receiving waters. Comparing glycols and potassium acetate, it is found that the potassium acetate is a less polluting alternative for the equivalence de-icing power (Revitt and Worrall, 2003). Low temperatures limit the rate of degradation. Residence time of chemicals in the unsaturated soil influences the degradation rate (French et al., 2001). Water containing de-icing chemicals is infiltrating during snowmelt and may bypass the upper zone with largest degradation potential during the snowmelt period due to high flow velocities and low temperatures (Liβner et al., 2007).

### **2.1.2 De-icing chemicals concentration found at airports**

Concentrations of de-icing chemicals found in runoff connected to airports vary, dependent on climate and airport traffic. The concentration of pollution is highest for first flush when accumulated particles at impermeable surfaces are flushed into surface waters, permeable surfaces or sewer system. Trondheim Airport Værnes is monitoring the de-icing chemicals in the surface water from the airport. The highest concentration found in period 2013/2014 was 83 mg/L for propylene glycol and 109 mg/L for potassium formate. Average values were detected to be 20 mg/L for propylene glycol and 19 mg/L for potassium formate (Andersen, 2016).

## **2.2 Impact of climate change**

The climate is expected to continue to change in the following years. In cold regions like Norway, winter temperatures are expected to increase. This means that temperatures will more frequently be around zero degrees. Temperatures in the winter might also be more variable. A statistical model of Oslo Airport Gardermoen indicates more wind, precipitation and flights. This, combined with low temperatures, results in an increased use of de-icing chemicals in the future (French et al., 2010). In addition, consumption of de-icing chemicals is highest when temperatures are around the freezing point. However, it is foreseen that there

will be a reduced consumption in the long term (2071-2100) due to higher temperatures (French et al., 2010).

Climate change will also cause heavier rainfalls more often. The reduced permeability due to development of taxiways, runways and buildings leads to more surface runoff. The first flush describes the flow that occurs at the beginning of a rainfall. As for airports, there will be pollution on taxiways and runways. During the first period of a rainfall, most of the substances will be flushed into collecting systems or into receiving water and nature. The first flush will hence be most polluted.

During the snow-melting period, water will infiltrate into the soil. Water will flow through the pores in the soil, and eventually end up as ground water. Ground water is in an important source for clean water in the world in general. Once the groundwater is polluted, it is difficult to recover to the initial state. If the ground water gets polluted, it will have long time consequences and water courses and local streams that receive the polluted water will be affected (Øvstedal and Wejden, 2007).



## **3 Filter and biofiltration systems**

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In this section, literature on biofiltration systems for removal of de-icing chemicals will be presented. The focus for the literature study is to investigate propylene glycol and potassium formate degradation in biofilter, and its possible limitations. However, some studies with other chemicals give an indication of performance in general, and are therefore included. The literature section has a base from the project thesis of Lindseth (2016), and is further developed and improved.

### **3.1 Filter systems**

Filtration is defined as the removal of particles in a fluid when the solution passes through a porous medium (Crittenden et al., 2012). Filtration stages in a typical drinking water system is illustrated in Figure 3-1.

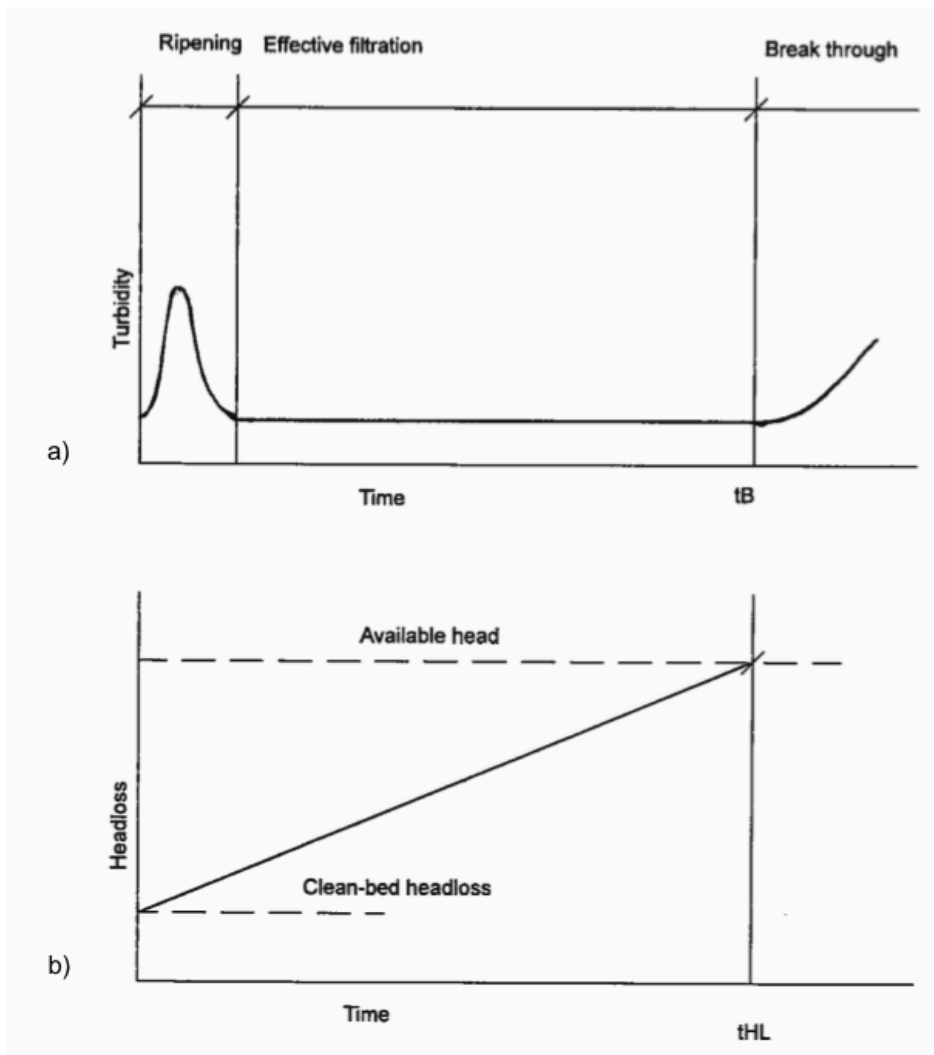


Figure 3-1: (a): Filtration stages, (b): head loss curve, adapted from Crittenden et al, 2012.

Filtration systems are often used to treat drinking water, and the filter is behaving as shown in the graph. In rapid filtration, backwashing is important. The water is flushed by reversing the filtration flow in such that the retained particles are flushed out of the filter (Crittenden et al., 2012). Ripening period (Figure 3-1a) is defined as the period after backwashing, when particles from backwashing are still in the filter. The breakthrough ( $t_B$ ) defines when the filter is no longer operating effectively and needs to be backflushed (Crittenden et al., 2012). In a biofiltration system for the airport, the filter will most probably not have a backwashing system, however the curve can indicate something about the lifetime of the filter before replacement is needed. The head loss curve (Figure 3-1b) is describing the head loss over time for a filter with constant flow. As seen, head loss increases with time as particles settle in the filter.



### 3.2 Biofiltration

Biofiltration includes biological activity in the granular filtration process. Filter media commonly used are sand, anthracite and GAC. Biofilm can form at the surface of the media, and is able to degrade some organic compounds at the surface of the filter (Crittenden et al., 2012). Temperature, oxygen and substrate are important factors in a biofiltration system. If these factors are favourable, a biofilm will establish itself in granular media (Crittenden et al., 2012). As in conventional filters, the head loss will build up over time and needs to be backwashed to maintain a sufficient head loss, or changed if backwashing is not possible (Crittenden et al., 2012).

Biofiltration, also called a bioretention facility, is defined as depressed areas in the landscape that are designed to accept stormwater (Dietz, 2007). Differences between sand filters and biofilters are mainly that the biofilter supports vegetation and have a different media mix designed with high permeability (Water Environment Federation, 2012). The hydrology of the biofilter is closer to the original hydrology at the site due to evapotranspiration by the surface vegetation (Water Environment Federation, 2012). Biofilters decrease the surface runoff, increase the groundwater recharge and treat pollutants (Dietz, 2007). An example of a bioretention system is illustrated in Figure 3-2.

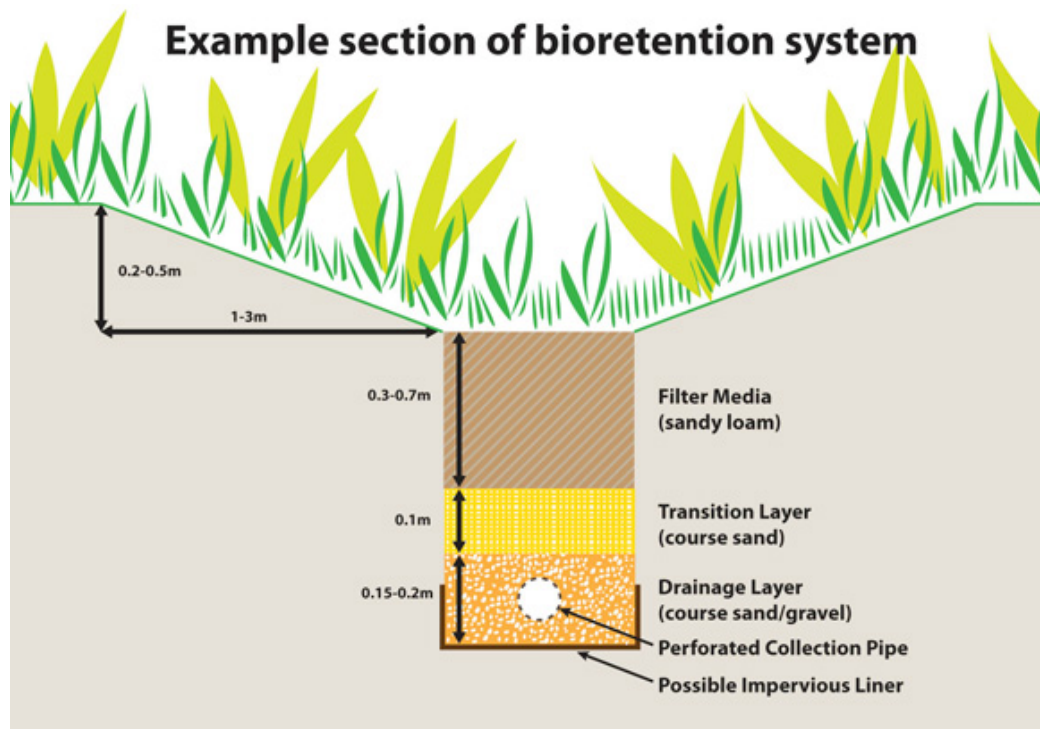


Figure 3-2: Example section of bioretention system (Land8, 2012)

Biological activity is dependent on the temperature and will vary through the year depending on the climate (Crittenden et al., 2012). French et al. (2001) evaluated how fast the de-icing chemicals are degraded under realistic conditions. Degradation rates in the melting period is measured as low, because chemicals bypass the zone with highest degradation potential (French et al., 2001). A higher zone will have a higher degradation potential compared to a lower zone in the biofilter. The melting period of snow cover at Gardermoen area normally starts from the beginning of April and lasts for 3 to 5 weeks. 3-5 weeks. The soil is degrading the de-icing chemicals, but the degradation is limited by temperature. The degradation rate is dependent on snow cover volume and thickness of the unsaturated zone. The simulations done by French et al. (2001) showed that less than 1% of the infiltrated water was likely to enter the groundwater before the summer. During the summer, the degradation continues and is higher due to higher temperatures and stagnation of water in the unsaturated zone. They concluded that the degradation at Gardermoen Airport would continue all summer in the unsaturated zone, if the ground water table was not reached. This is because precipitation is equal to evapotranspiration during the summer months at Gardermoen airport.

Chemical degradation is dependent on the temperature in the soil. A study in microcosm experiment has shown that propylene glycol degradation is clearly slower at low temperatures (4°C and 7°C), compared to a reference temperature at 22°C (Libisch et al., 2012). Half-life of propylene glycol was about four times higher at 22°C compared to the low temperatures. Temperatures for this experiment were chosen to represent conditions during and after melting period (Libisch et al., 2012).

### **3.2.1 Propylene glycol biodegradation**

Propylene glycol removal was investigated in 15-cm deep columns in room temperature by Bielefeldt et al. (2002). The columns contained saturated sand and gravel. The propylene glycol-degrading bacterial culture was taken from Denver International Airport and grown before entering the columns. The water containing propylene glycol was pumped vertically upwards in the column. A degree of propylene glycol degradation occurred in the feed flask and tubing before entering the column, in other words before the solution entered the columns (Bielefeldt et al., 2002).

The columns were loaded continuously with water containing propylene glycol. It was observed that the hydraulic conductivity decreased for all columns. This is due to biological growth in the filter media, which cause an increased resistance. When the propylene glycol load was stopped, it was observed that the hydraulic conductivity increased. This was due to biological washout and endogenous decay (Bielefeldt et al., 2002).

For the column with continuous loading of propylene glycol, the hydraulic conductivity flattened out. The final biomass concentrations in the continuously loaded and the intermittent loaded column were not significantly different. The results of the experiments show that the intermittent loading of propylene glycol can help to prevent clogging of sand biofilters. It also shows that the degradation of propylene glycol is likely to be rapid also after periods with no propylene glycol exposure. Biodegradation of propylene glycol was achieved to be greater than 99% for all the conditions tested (Bielefeldt et al., 2002). The hydraulic conductivity also dropped with time.

Nutrients addition was one of the conditions tested by Bielefeldt et al. (2002). The removal of de-icing chemicals was greater than 99% and showed nearly identical performance. Different C:N ratios were tested, and the primary difference was the effluent biomass. The column with the highest available nitrogen had the highest effluent biomass, which indicates that there may have been more cell growth in this column.

### **3.2.2 Potassium formate biodegradation**

Degradation of potassium formate was investigated in a lysimeter study by Hellstén et al. (2005). Lysimeter barrels were 1.7 m tall with a diameter of 2 m and a sample collector connected to a data logger to observe the percolated water. They found that 98% of the formate was effectively retained in the sandy lysimeter after a cold winter period. However, the potassium formate might leach into ground water if it is applied as de-icer for several years. In reality, the runoff will be more diluted than what has been investigated in the experiment. The increased temperatures during spring resulted in an efficient removal of chemicals from the lysimeter. Low correlation was found between microbial growth and formate concentrations. The reason for this might partly be low phosphorous concentration (<0.002 mg/l) and low nitrogen concentration (0.02 mg/l) in the percolated water (Hellstén et al., 2005).

### 3.2.3 Removal rate with the Iwasaki model

The Iwasaki model, dating back to 1937, describes the decrease in concentration within the filter depth. The decrease in concentration is described as a function of the input concentration and the filtration coefficient. The Iwasaki model was developed for slow sand filtration and is calculated as follows (Shandalov et al., 1997):

$$\frac{\partial C}{\partial L} = -\lambda C \quad \text{Eq. 3-1}$$

$C$  is the concentration of suspension [mass/volume]

$L$  is the media depth [length]

$\lambda$  is the filter coefficient [length<sup>-1</sup>]

The non-differential equation is written as follows:

$$-\ln \frac{C}{C_0} = \lambda z \quad \text{Eq. 3-2}$$

Where  $C_0$  is the initial concentration of suspension and  $C$  is the final concentration of suspension [mass/volume] and  $z$  is the filter depth [length]. Filtration coefficient can be used to evaluate effectiveness of a filtration process by comparing different layers in a filter or different filter media.

### 3.2.4 Limiting factors in a biofilter

Degradation in biofilter is limited by many factors like clogging, temperature, light, oxygen and nutrients.

#### **Clogging**

Clogging is considered the main limiting factor for filtration systems. If the particles are larger than the voids in the filter, the particles will form a filter cake at the surface of the filter (Crittenden et al., 2012). The filter cake can provide a high head loss. To avoid a rapid forming of the filter cake, filters are designed to remove particles continuously through the depth of the filter. Literature suggest that particles might cause significant clogging with the

accumulation of 1.2-5 kg/m<sup>2</sup> sediment per filter surface media (Water Environment Federation, 2012). Media size, media depth and flow rate influence the filter performance (Crittenden et al., 2012). Biological growth in the filter can also affect the hydraulic characteristics of the filter, and extensive biological growth can plug the biofilter (Cunningham et al., 1991).

The hydraulic gradient is the head loss per unit depth. Head loss can be high at the top of the filter, because of settlement of particles at the surface. As shown in Figure 3-3, the pressure in the filter can be negative if the hydraulic gradient is higher than the static head gradient (Crittenden et al., 2012).

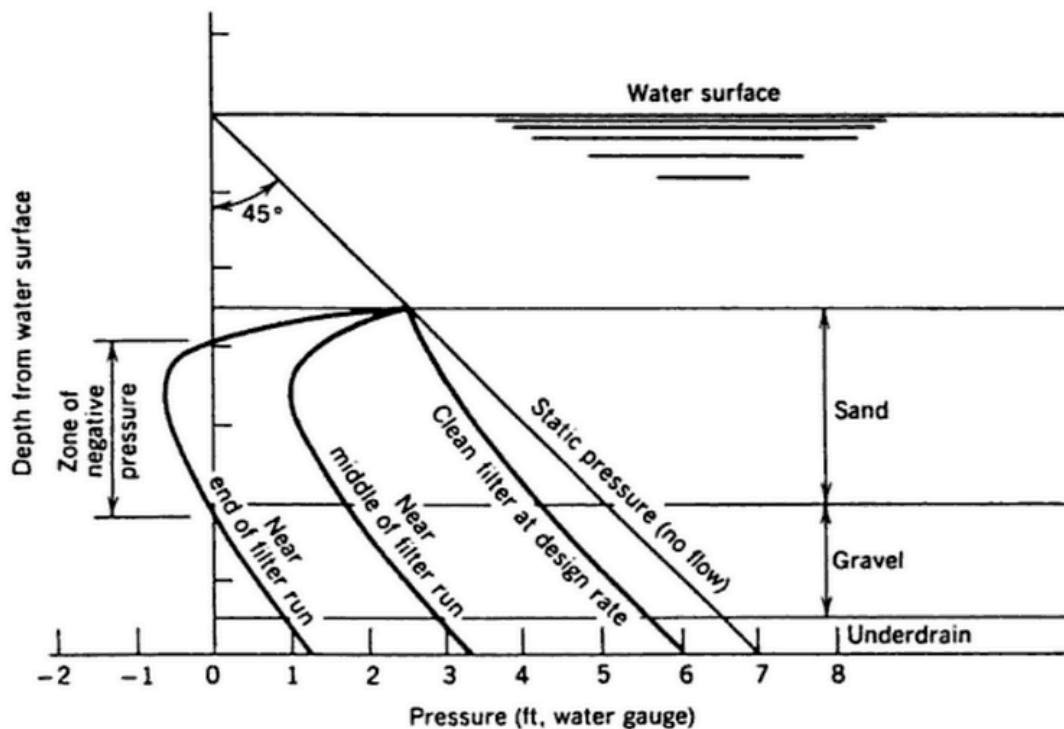


Figure 3-3: Pressure in filter (Kawamura, 2000)

Clogging phenomena was investigated by Kandra et al. (2014). Different materials with different flow through rates of semi-synthetic stormwater were used in the column test. Flow through rate significantly affected the clogging and removal rate. Different filter materials of 2 mm diameter were used for the column test.

Treatment efficiency is dependent on residence time between influent and filter media. It has been shown that treatment efficiency is increasing with residence time (Kandra et al., 2014).

Different outlet designs of the columns varied the residence time in the experiment. The four different filter media used for the test had about the same effectiveness on stormwater treatment for the same outlet size. It was found that low flow through rates improve the overall performance of the filter system (Kandra et al., 2014). Low flow through rates lead to high contact time between the water and the media.

Hydraulic conductivity in a column experiment can be calculated as follows:

$$k = \frac{h}{A_s} \times \frac{Q}{H} \quad \text{Eq. 3-3}$$

*k*: hydraulic conductivity [m/s]

*Q*: volumetric flow rate [m<sup>3</sup>/s]

*A<sub>s</sub>*: cross-sectional area of the column [m<sup>2</sup>]

*H*: total hydraulic head across the filter [m]

*h*: length of the filter media whose hydraulic conductivity is being tested [m]

### **Oxygen limitations**

Degradation is dependent on the oxygen available in the soil. Oxygen is consumed during biodegradation and chemical oxidation (Wong et al., 2000). It has been shown that propylene glycol will degrade slower in anaerobic conditions compared to aerobic ones. Aerobic conditions require a high oxygen demand. Anaerobic metabolism may release toxic compounds such as ethanol or methane. If there is presence of sulphates during aerobic degradation, mercaptans, a toxic compound which smells, might be produced (Greco et al., 2008).

### **Phosphorous and nitrogen limitations**

Phosphorous is usually the limiting nutrient for most inland waters, while in many marine coastal areas the limiting factor appears to be nitrogen (Stumm and Morgan, 1996). The elemental ratio, given in moles, of carbon:nitrogen:phosphorous (C:N:P) in planktonic biomass is used to understand the nutrient cycles. Studies have shown that low concentrations of phosphorous and nitrogen in water during biofiltration might limit the microbial activity.

Concentration of 0.02 mg/l for nitrogen and <0.002 mg/l for phosphorous was found in the study of propylene glycol degradation by Hellstén et al. (2005).

The well-recognized Redfield ratio for marine ecosystems is empirically developed. The molar elemental ratio was found to be C:N:P = 106:16:1. This ratio seems to be consistent globally in marine waters. Research has been done to investigate if there is a similar pattern for forest ecosystems worldwide. The ratio calculated for foliage was found to be 1212:28:1 and for litter 3007:45:1 (McGroddy et al., 2004). The high carbon is due to terrestrial vegetation. Cleveland and Liptzin (2007) indicate that element concentration of individual phylogenetic groups within the soil microbial community may vary. It was also indicated that the average atomic C:N:P ratio was found to be 186:13:1 in the soil and 60:7:1 in the soil microbial biomass at the global scale (Cleveland and Liptzin, 2007). Fine roots takes up nutrients in plants, and it was found that the global C:N:P ratio in living fine roots is 450:11:1. (Jackson et al., 1997)

In wastewater treatment plants the optimum C:N:P ratio is found to be in the range between 100:10:1 and 100:5:1 (Forster, 2003). When treating wastewater, it is important to monitor the nutrient ratio carefully. The carbon quantity will vary, hence the necessary addition of nutrients will vary dependent on the carbon. When designing a degradation system, it is possible to have a certain amount of nitrogen and phosphorous added on the media for an optimized process. However, there might be a risk of leaching of nutrients that might affect the natural ecosystem and cause eutrophication, if not consumed by the biomass. This needs to be considered carefully.





## 4 Adsorption

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Adsorption is defined as the accumulation of matter at the solid-liquid interface. Adsorption is schematically illustrated in Figure 4-1.

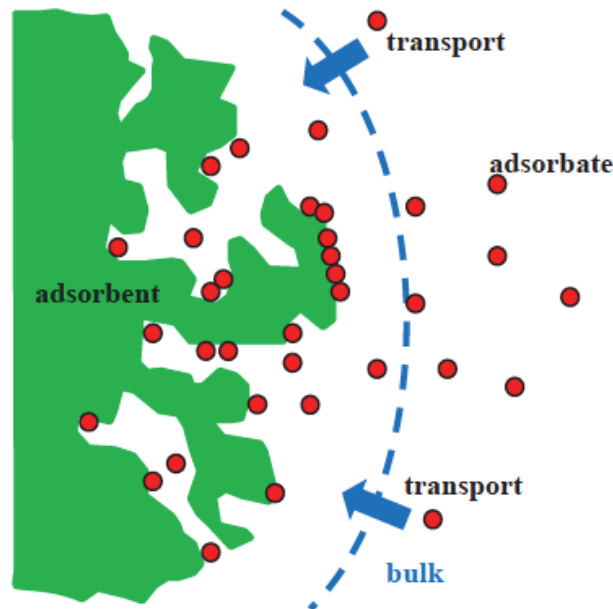


Figure 4-1: Adsorption to media

Adsorbate is the substance that adsorbs, and the solid that can bind this substance is called adsorbent (Benjamin, 2015). The reverse of adsorption is called desorption i.e. when the substance is released to the bulk solution (Benjamin, 2015). Depending on the type of forces between the adsorbate and adsorbent, adsorption can be classified as physical (physisorption) or chemical adsorption (chemisorption). Physical adsorption might be either monolayer or multilayer, where the adsorbent and adsorbate is preserved. Van der Waals forces are the bonding forces that keep adsorbate adsorbed onto the adsorbent. In contrast, chemical adsorption is based on transfer or sharing of electrons. Chemical adsorption forms a monolayer on the adsorbent, due to separate binding on each adsorption site between the adsorbate and the adsorbent.

## 4.1 Adsorption isotherms

At equilibrium adsorption and desorption reactions proceed at equal rates. Adsorption can be described by adsorption isotherms. The isotherm represent the relationship between the concentration of adsorbate and the amount adsorbed at constant temperature (Stumm and Morgan, 1996). Adsorption density is calculated as follows (Hameed et al., 2008):

$$q_e = \frac{(C_0 - C_e)V}{W} \quad \text{Eq. 4-1}$$

Where  $q_e$  is the adsorption density [mg/g],  $C_0$  and  $C_e$  is the initial and equilibrium concentrations in the solution [mg/L],  $V$  is the volume of solution [L] and  $W$  is the mass of the media [g].

Linear isotherm is the simplest adsorption isotherm and is given as follows:

$$q_e = K_F C_e \quad \text{Eq. 4-2}$$

Where  $q_e$  [mg/g] is the amount of adsorption at equilibrium,  $K_F$  is the adsorption capacity of the sorbent and  $C_e$  is the equilibrium concentration of the solution.

The Langmuir relation assumes monolayer coverage at equilibrium, that one site can hold at most one adsorbed molecule (Hameed et al., 2008). It also assumes that all adsorption sites are equally probable with no interaction between adsorbate molecules. The Langmuir isotherm is expressed as follows (Hameed et al., 2008):

$$q_e = \frac{Q_0 b C_e}{(1 + b C_e)} \quad \text{Eq. 4-3}$$

Where  $Q_0$  [mg adsorbate/ g adsorbent] is the maximum adsorption density when surface sites are saturated with adsorbate, and  $b$  [L/mg] is the Langmuir adsorption equilibrium constant (Crittenden et al., 2012). A linear relationship between  $C_e$  and  $C_e/q_e$  gives the Langmuir relationship. A dimensionless constant separation factor  $R_L$  [-] describes the essential characteristics of the Langmuir isotherm. The separation factor  $R_L$  describes the shape of the

isotherm, which can be favourable ( $0 < R_L < 1$ ), unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), or irreversible ( $R_L = 0$ ). In the equation,  $C_0$  is the highest initial concentration of adsorbate and  $b$  is the Langmuir constant [L/mg] (Hameed et al., 2008):

$$R_L = \frac{1}{(1 + bC_0)} \quad \text{Eq. 4-4}$$

Freundlich isotherm is an empirical equation, expressed as follows (Hameed et al., 2008):

$$q_e = K_F C_e^{1/n} \quad \text{Eq. 4-5}$$

Where  $K_F$  is the adsorption capacity of the sorbent and  $n$  indicates the change in adsorption strength with change in adsorption capacity. Values of  $n > 1$  is representing favourable adsorption conditions. Constants are determined when plotting  $\ln(q_e)$  versus  $\ln(C_e)$ , where  $1/n$  is determined from the slope of the plotted line. Similarly to the Langmuir isotherm, Freundlich isotherm also considers monolayer adsorption. Linear isotherm is a special case of Freundlich where  $n$  equals 1.

Temkin isotherm is a fourth model that is used to describe adsorption (Hameed et al., 2008).

$$q_e = \frac{RT}{b} \times \ln(AC_e) \quad \text{Eq. 4-6}$$

Where  $R$  [8.314 J/mol K] is the gas constant,  $T$  [K] is the temperature.  $A$  and  $b$  are constants that can be determined by plotting  $q_e$  versus  $\ln C_e$ .

Adsorption isotherm relations are illustrated in Figure 4-2. The corresponding isotherm models are potted dependent on the adsorption density and dissolved concentration of adsorbate, which represent the equilibrium concentration.

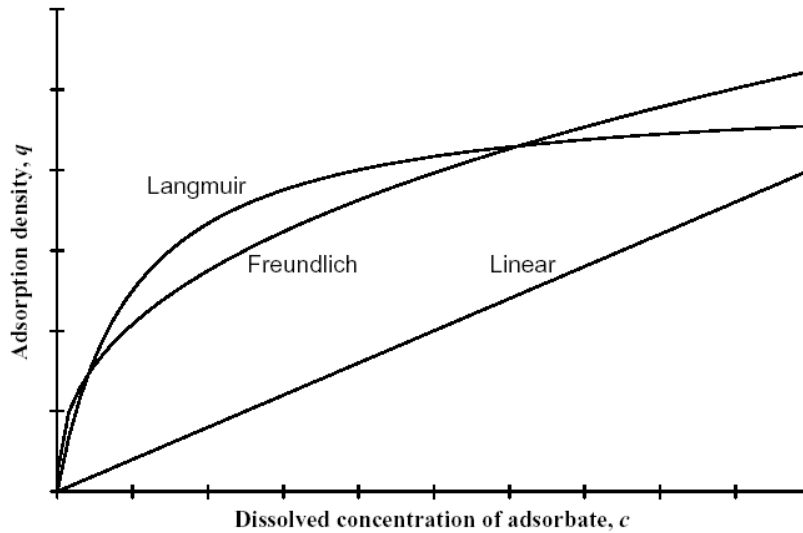


Figure 4-2: Adsorption relations (Faculty of Washington edu, 2012)

## 4.2 Adsorption kinetics

Adsorption kinetics describe the uptake rate of the adsorbate (Lin and Wang, 2009). The kinetics describe the resident time in the adsorbent-solution interface (Lin and Wang, 2009). For the kinetic studies, adsorption might be investigated as a function of time. Adsorption at time  $t$  is  $q_t$  [mg/g] and can be calculated with the concentration of in the solution at time  $t$ :

$$q_t = \frac{(C_0 - C_t)V}{W} \quad \text{Eq. 4-7}$$

Two widely used kinetic models are linear and non-linear pseudo-first-order and pseudo-second-order equations (Lin and Wang, 2009). To find the best-fit equation, correlation coefficients ( $R^2$ ) are compared.

Adsorption kinetics is described by pseudo-first-order and a pseudo-second-order equation as from Lin and Wang (2009):

*Pseudo-first-order:*

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \text{Eq. 4-8}$$

*Pseudo-second-order:*

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \text{Eq. 4-9}$$

Where  $q_t$  [mg/g] is the amount of solute adsorbed on the adsorbent at time  $t$  and  $k_1$  and  $k_2$  are rate constants [g/mg h]. Ho and McKay (1999) evaluated pseudo-first-order and second-order model, to find that the highest correlation coefficients were obtained for the pseudo-second-order kinetic model.

Linear relations can be expressed (Lin and Wang, 2009). These relations are the most popular for use in the recent years:

*Linear pseudo-first-order:*

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right)t \quad \text{Eq. 4-10}$$

*Linear pseudo-second-order:*

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{Eq. 4-11}$$

Initial adsorption rates can be calculated from the pseudo-second-order model, with the same rate constant  $k_2$  (Hameed et al., 2008):

*Initial adsorption rates:*

$$h_{0,2} = k_2 q_e^2 \quad \text{Eq. 4-12}$$

Where  $h$  is the initial adsorption rate [mg/g min].

To describe the mechanisms that are affecting the kinetics, the intraparticle diffusion model can be used for analysis:

$$q_t = k_{id} t^{1/2} + C \quad \text{Eq. 4-13}$$

Where  $k_{id}$  is the intraparticle diffusion rate constant [ $\text{mg}/\text{gh}^{1/2}$ ], and  $C$  is the intercept which represent the rate-limiting factor [ $\text{mg}/\text{g}$ ] (Hameed et al., 2008). A plot of  $q_t$  versus  $t^{1/2}$  determines the  $k_{id}$ , which should be the slope of the straight line in the plot. If the only rate-limiting step is the intraparticle diffusion, the plot of  $q_t$  versus  $t^{1/2}$  will be linear through the origin, i.e.  $C = 0$  (Cheung et al., 2007). Adsorption kinetics might as well be controlled by liquid film diffusion, hence the slope will not go through the origin (Qiu et al., 2009).

### 4.3 Adsorption of de-icing chemicals in literature

Many studies has been conducted on adsorption of organic species onto activated carbon, however there are relatively few studies of small organic molecule adsorption onto activated carbon (Peereboom et al., 2007).

Langmuir and Freundlich isotherms are often found to represent the adsorption relationship of organic species onto activated carbon (Peereboom et al., 2007). Activated carbon as an adsorbent has shown to be very effective for removal of many pollutants from aqueous solution (Hameed et al., 2008). Activated carbon consists of small grains and has a very large surface area. The smaller the pores compared to the size of the molecules that should be adsorbed, the stronger the adsorption. Activated carbon is considered as an expensive adsorbent, and the higher the quality is, the higher the cost (Hameed et al., 2008).

Aqueous-phase adsorption of glycerol and propylene glycol onto activated carbon was investigated by Peereboom et al. (2007). It was found that propylene glycol was adsorbing more strongly onto the activated carbon compared to the glycerol. They conclude that this might be because the propylene glycol is of a greater organic character compared to glycerol. Langmuir isotherm was found to represent the adsorption of individual species. The extended Langmuir isotherm was found to represent competitive adsorption of the two species (Peereboom et al., 2007).

French et al. (2001) calculated the combined effect of degradation and adsorption in the soil at Research Station Moreppen, Gardermoen. Inactive tracers were observed as well as de-icing chemicals in the soil. French et al. (2001) found that the concentration reduction of propylene glycol was from degradation. Acetate showed signs of adsorption. The overall reduction of propylene glycol and potassium acetate was due to both adsorption and

degradation. They were also expecting the adsorbed acetate to degrade at the same rate as the acetate in the solution.

Adsorption onto GAC and Filtralite NC 0.8-1.6 was investigated by Persson et al. (2007). Gemosmin and 2-methylisoborneol (MIB) were tested, and the findings show that the adsorption onto Filtralite NC 0.8-1.6 was negligible. Adsorption was found onto the GAC, as similar to other studies already mentioned.





## 5 Laboratory experiments

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In this chapter laboratory experiments are described. Batch experiments have been conducted in the analytical laboratory, to observe the adsorption on different media. An analysis of the synthetic stormwater degradation in the feed tank was also done, for verification with results obtained by Andersen (2016) and decision making for some of the set up for the column study. Investigation of the biofiltration along the column depth was done in a column study with two tall columns. Method for the analysis as well as material for the laboratory study is further described in this chapter.

### 5.1 Materials

The aim of the thesis is to look deeper into the characteristics of filter media provided by Leca in treatment of stormwater containing de-icing chemicals. Filtralite media of different fractions (Filtralite NC 0-2, Filtralite NC 0.8-1.6 and Filtralite NC 1.5-2.5) were used as well as granulated activated carbon (GAC). The de-icing chemicals used for the experiments are propylene glycol and potassium formate.

#### 5.1.1 Filtralite material from Weber Saint Gobain

Filtralite NC 0-2, Filtralite NC 0.8-1.6 and Filtralite NC 1.5-2.5 were provided by Leca. Filtralite material has low density and high porosity, and is made by burning clay at 1200 ° C. After burning, the media is crushed and sieved. When the material is crushed, a large surface area is exposed (Saint-Gobain Byggevarer as, 2015). The large surface area for biofilm growth is essential for the biological filtration process. Compared to traditional media like sand, Filtralite is able to have up to 500% longer operating time between backwashes in a water treatment plant. Figure 5-1 illustrates the porous structure of LECA.

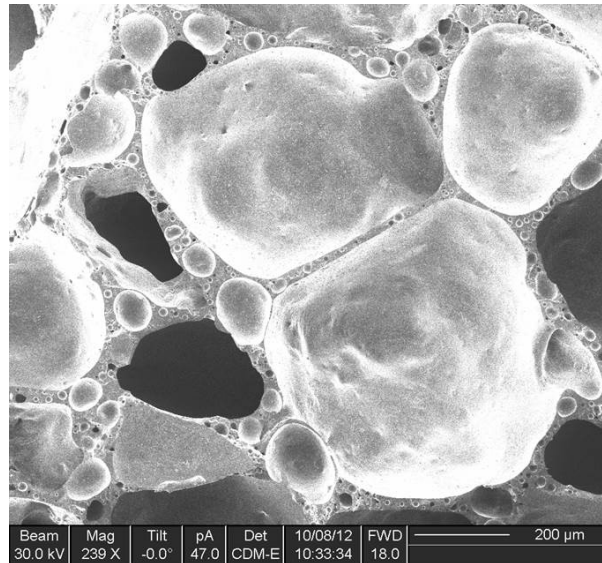


Figure 5-1: SEM picture, LECA as for Filtralite (Saint-Gobain Byggevarer as, 2012)

Filtralite is used in many parts of the world for water and wastewater treatment as well as industrial water treatment. Filtralite is found in many different fractions as well as different treatment features. Filtralite can be used both as single media treatment as well as dual media (two different media in the same filter). Compared to sand filters, Filtralite has longer filter runs between backwashing, and can therefore save water and energy compared to having a filtration water treatment plant with sand filters (Klavestad et al., 2016).

Filtralite NC 0.8-1.6 and Filtralite NC 1.5-2.5 is used for purification of water and residual and industrial effluents (Saint-Gobain Byggevarer as, 2015). It might be used as a single media or as a top media in multimedia filters. The dry particle density is 1000-1200 kg/m<sup>3</sup> and typical application is dual media filtration and biological filtration (Saint-Gobain Byggevarer as, 2015). Low head loss and high storage capacity for sludge, means that the filter can be operated for a long time before the filter needs to be backwashed (Saint-Gobain Byggevarer as, 2015). The differences between the filter media are the fractions. Filtralite NC 0.8-1.6 consists of particles from 0.8 mm to 1.6 mm and Filtralite NC 1.5-2.5 consists of particles ranging between 1.5 mm and 2.5 mm, as illustrated in Figure 5-2.

Filtralite NC 0-2 consists of smaller grains, as the name indicates, between 0-2 mm. It is not yet a commercially available material, hence there is a lack of information and research done for this material. It is therefore interesting to investigate the properties of this material further, however this is not done in this thesis. The focus is on the commercial fractions.

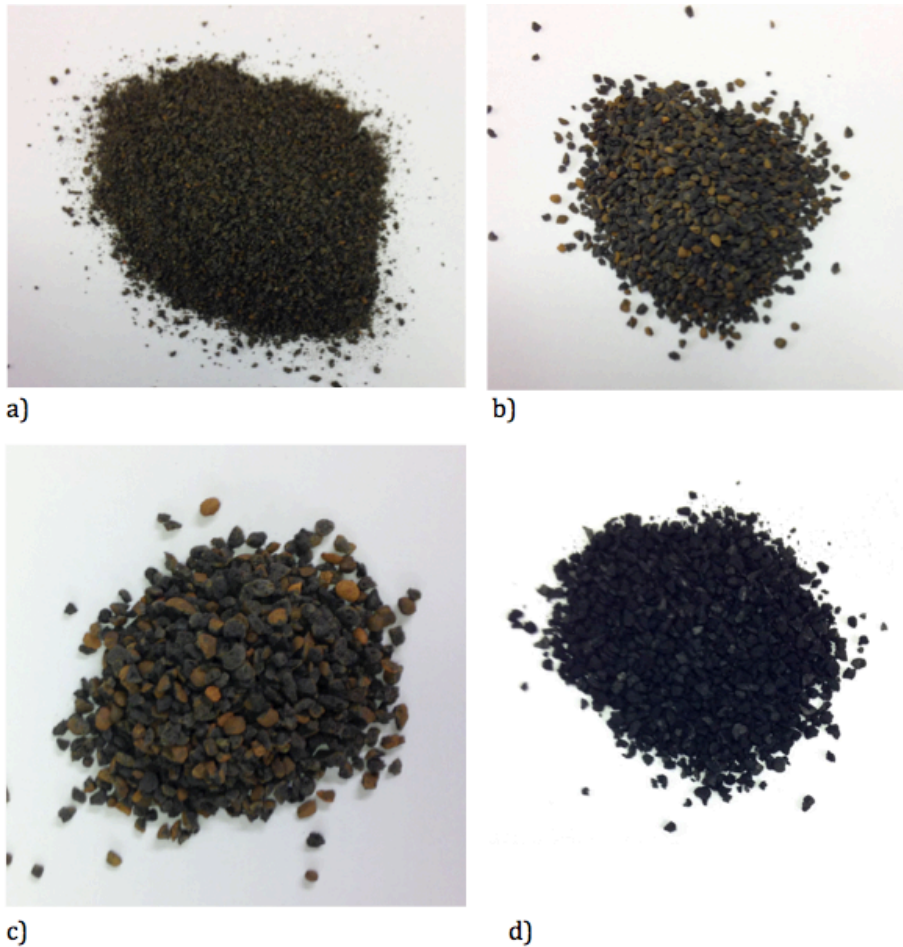


Figure 5-2: (a): Filtralite NC0-2, (b): Filtralite NC 0.8-1.6, (c): Filtralite NC 1.5-2.5, (d): GAC

### 5.1.2 Granular activated carbon (GAC)

Activated carbon has a high surface area and is an effective adsorbent (Crittenden et al., 2012). GAC is commonly used in drinking water treatment to adsorb organic compounds, taste and odour as well as synthetic organic chemicals. GAC is considered as a good, but expensive adsorbent. A study by Persson et al. (2007) shows that the GAC was able to adsorb also in colder temperatures, hence it was not that dependent on the temperature as a biofilter has shown to be.

Activated carbon for the experiments is delivered from Miljøkalk AS. The carbon delivered from Miljøkalk AS has a porosity of approximately 48.5%, and has a bulk density of approximately  $450 \text{ kg/m}^3$ . There are two types of activated carbon, granular activated carbon (GAC) and powdered activated carbon (PAC). Granular activated carbon with grain size

ranging from 0.5-1.8mm, with effective diameter  $d_{10}$  0.9mm, is used in the experiments in this report.

### 5.1.3 Sediments

Sediments for the degradation experiment in the large feed tank were collected at Trondheim Airport, Værnes in November 2015. The sediments are the same as the ones used in the column experiment conducted by Andersen (2016). The sediments were collected from the ground right beside the runway, and a variety of chemicals was found in the sediments collected. Analyses of sediments in Table 1 are performed by Eurofins Environment Sweden AS.

Table 1: Soil measurements from Værnes

<b>Substance</b>	<b>Concentration [mg/kg TS]</b>	<b>Measured uncertainty [%]</b>
Arsenic (As)	3.5	30
Lead (Pb)	6.1	40
Cadmium (Cd)	0.15	25
Copper (Cu)	82	30
Chromium (Cr)	20	30
Mercury (Hg)	0.002	20
Nickel (Ni)	17	30
Zinc (Zi)	44	25
Total TCH (>C5-C35)	340	25
Total PAH (16) EPA	0.52	30

Sediments for the tall column experiment were collected at Valgrinda Campus NTNU, due to the results from the soil analysis from Værnes. Comparing the measured values with the standard TA-2553, all the measured values are classified as class 1: Very good (in Norwegian: tilstandsklasse 1: meget god) (Norwegian Pollution Control Authority, 2009). Since the soil was considered to be in good conditions, it was not necessary to travel to Værnes to get more sediments. Only the fine particles were used for producing the synthetic stormwater. The sediments were mixed with distilled water to reach turbidity around 15 NTU. This corresponds to approximately 50 mg SS/L.

#### **5.1.4 Chemicals**

De-icing chemicals (DIC) used for the experiments are propylene glycol and potassium formate. Applications of these chemicals are described in chapter 2.1.1. Propylene glycol was delivered from Værnes in a concentrated form, consisting of ~100% propylene glycol with a density of  $1.04 \text{ g/cm}^3$ . The potassium formate solution was delivered in a diluted form consisting of ~50% potassium formate and ~50% water that gives the solution a density of  $1.33\text{-}1.37 \text{ g/cm}^3$ . Average DIC concentrations found in the runoff water from Trondheim Airport Værnes were chosen for the column experiment.

## 5.2 Batch experiment

Objective for the batch experiment was to investigate the adsorption capacity of different filter media. If adsorption was found, the goal was to evaluate the adsorption isotherms and kinetics for the media.

Adsorption of de-icing chemicals onto GAC, Filtralite NC 0-2 and Filtralite NC 0.8-1.6 was studied in a batch experiment. The Filtralite media were delivered directly from the factory and soaked for some time in distilled water. The experiment was carried out in 1 l beakers with 2 g media for each beaker. Different concentrations of de-icing chemicals were prepared by diluting chemicals with milli-Q water.

Dissolved organic carbon (DOC) was monitored to quantify the amount of de-icing chemicals. For both propylene glycol (PG) and potassium formate (PF) the stock solutions were prepared in 2 l volumetric flasks. Propylene glycol solutions were further diluted to concentrations of approximately 64, 32, 16, 8, 4 and 2 mg PG/l. The corresponding carbon content is shown in Table 2.

Table 2: Propylene glycol concentration, batch experiment

Propylene glycol concentration [mg PG/l]	Corresponding carbon concentration [mg C/l]
64	24
32	12
16	6
8	3
4	1.5
2	0.8

Potassium formate concentration was chosen to fit with the propylene glycol concentration, considering the carbon content. Concentrations are given in Table 3.

Table 3: Potassium formate concentration, batch experiment

Potassium formate concentration [mg PF/l]	Corresponding carbon concentration [mg C/l]
128	18
64	9
32	4.5
16	2.3
8	1.1
4	0.6

Kemira Kemwater Flocculator 2000 provided continuous mixing of media and solution in each beaker. Flocculators were rotating at a speed of 200 rpm through the experiment, as seen in Figure 5-3 and Figure 5-4. The flocculators provided constant mixing through the experiment, and they were stopped for a short time when sampling. A sample of 30 ml was taken from each beaker to be analysed in the DOC analyser. The samples did not need dilution because they were in the range for the DOC analyser to give good results. The only exception was the sample of 64 mg PG/l and 128 mg PF/L that was diluted 1:2.

It is assumed that the solution and the media is properly mixed at all times, that the media is intact throughout the experiment, and that the only decrease in chemical concentration is due to the adsorption onto filter media.

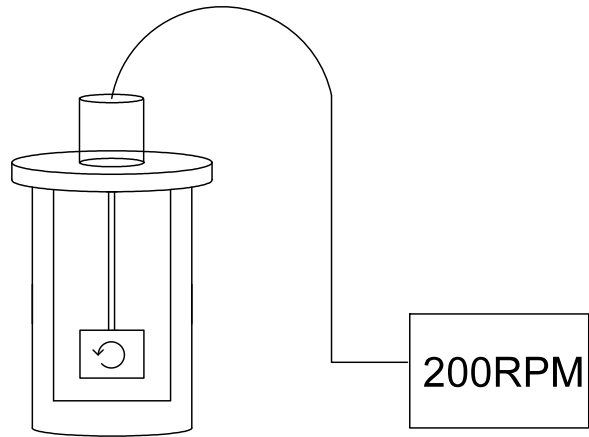


Figure 5-3: Batch experiment



Figure 5-4: Batch experiment, setup



### **5.3 Degradation in feed tank**

Column studies were conducted both by Andersen (2016) and Lindseth (2016). Due to the probability of chemicals degradation in the feed tank before the synthetic stormwater reached the filter, this needed to be investigated.

Monitored water quality parameters for the batch experiment:

- DOC analysis
- Turbidity measurement

Synthetic stormwater was prepared with a concentration of 20 mg/l of propylene glycol and 13.4 mg/l of potassium formate. The synthetic stormwater was prepared in a 1000 l tank. Sediments were added, and turbidity of the final solution was measured to 51 NTU. Propellers were installed to keep the solution mixed at all times. An IKA labortechnik RW 20.n pump was circulating the water in the tank, as in the test conducted by Andersen (2016) and Lindseth (2016).

Sampling of the water was done every day, to investigate if there was degradation of chemicals in the feed tank. DOC and turbidity was monitored, as in the reference experiment. Set up for the experiment is shown in Figure 5-5 and Figure 5-6.

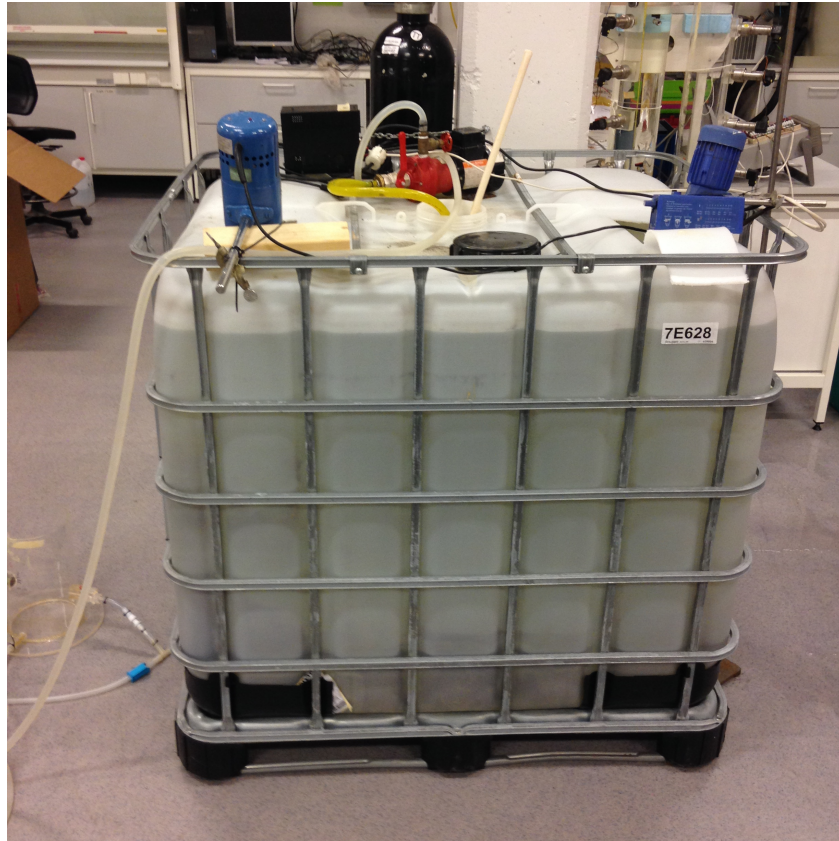


Figure 5-5: Feed tank, 1m<sup>3</sup>

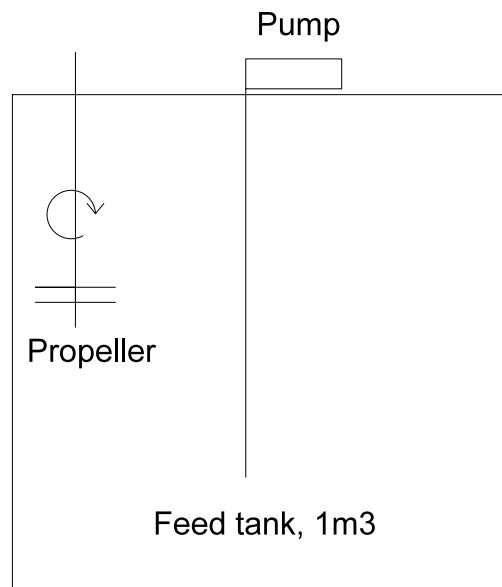


Figure 5-6: Feed tank, set up

## 5.4 Column study

The goal of the column experiment was to evaluate the biodegradation in the filter media along the depth. This was done by conducting a column experiment with two tall columns.

The column tests were done in different phases:

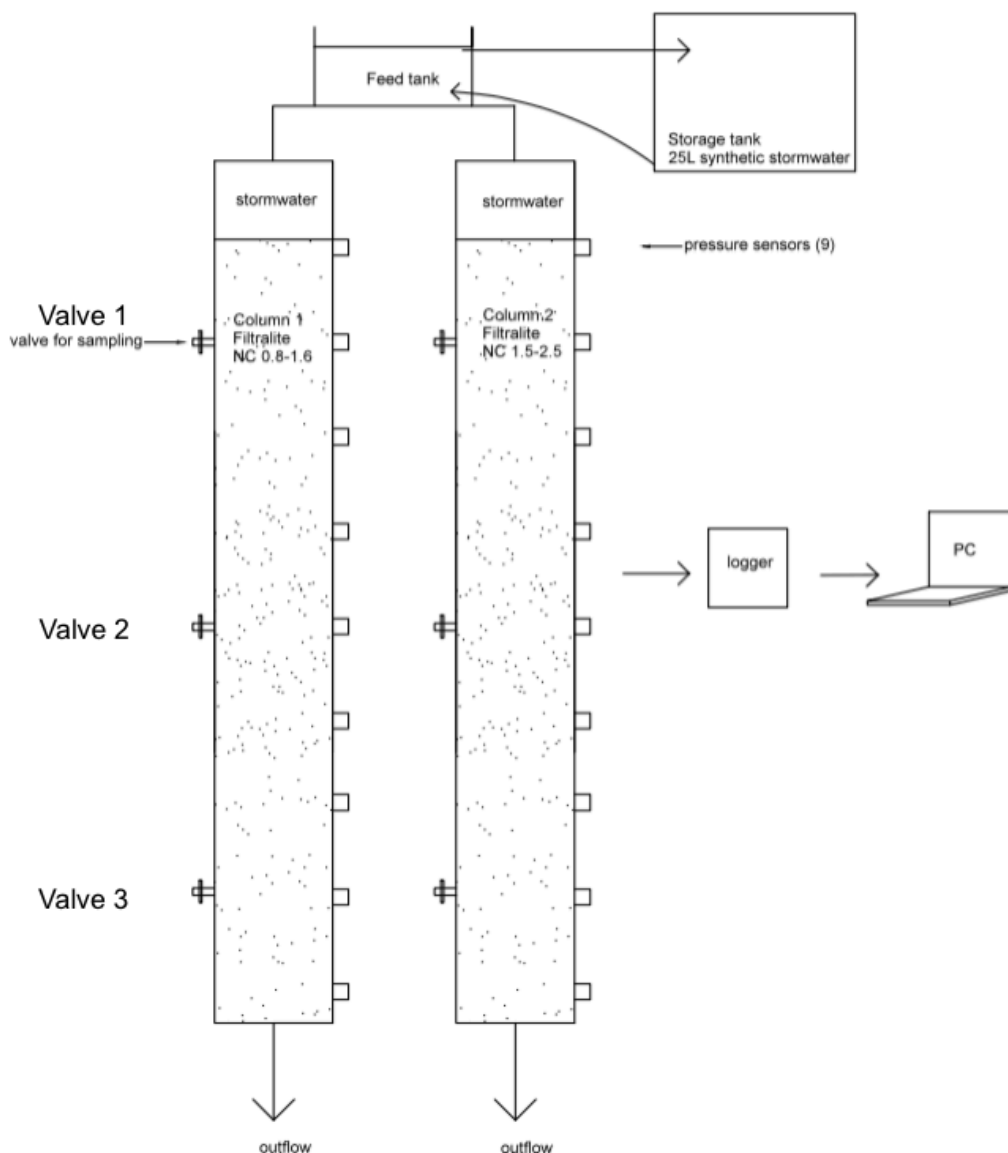
- 1) The first part of the column study was done with constant chemicals concentration as well as flow adjustments every day.
- 2) Nitrogen and phosphorous was evaluated and optimized for removal of chemicals by changing the C:N:P ratio (day 20).
- 3) The nitrogen and phosphorous concentration was increased, keeping the ratio N:P=5:1 (day 29).
- 4) Flow was increased (day 39).

Monitored water quality parameters for the column experiment:

- Flow measurement, adjustment
- DOC measurement
- Turbidity
- ATP test
- Pressure measurement along the filter depth
- Oxygen measurements
- Phosphorous and nitrogen measurements

### 5.4.1 Column set-up

The column study consisting of two tall columns was performed in the laboratory. Water containing de-icing chemicals was fed through the filters while pressure and flow were monitored, and samples were taken. Temperature of inlet water in the small tank was around 10 °C, and outlet temperature for both columns was approximately 23 °C. For the fourth phase of the experiment, a 1000 l tank was used instead of the 25 l synthetic stormwater tank, as well as one Master Flex LS Easy-load II pump was installed for suction in the end of each column. Column set-up is shown in Figure 5-7 and Figure 5-8.



Pumps installed for suction for phase 4

Figure 5-7: Column setup, flow sheet

As seen from the column set up, synthetic stormwater is fed through the columns, and pressure is monitored and stored by a computer. Pressure sensors are shown on the left hand side of Figure 5-8.

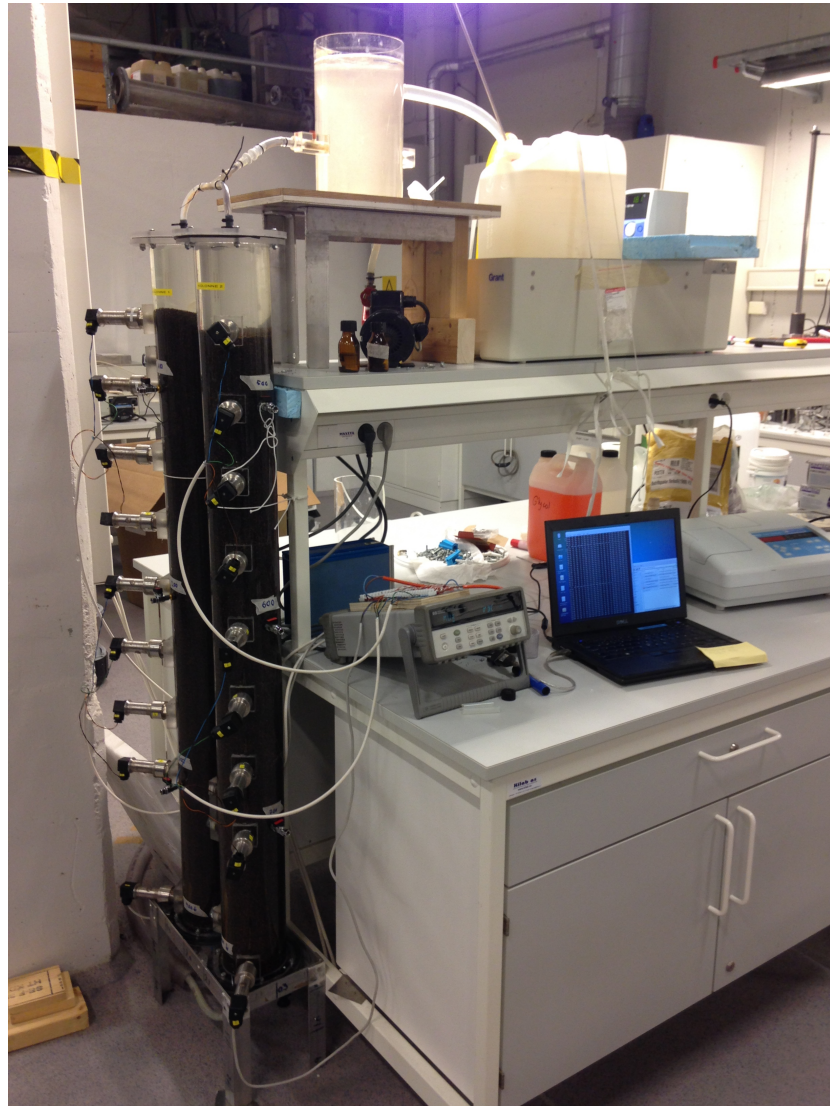


Figure 5-8: Column set up

#### **5.4.2 Filtralite media used in the column test**

Filtralite NC 0.8-1.6 and Filtralite NC 1.5-2.5 were used in the column experiment. Column 1 was filled with Filtralite NC 0.8-1.6 and column 2 was filled with Filtralite NC 1.5-2.5. The filter media Filtralite NC 0.8-1.6 was directly delivered from the factory and soaked in distilled water for three weeks. The filter Filtralite NC 1.5-2.5 was delivered some months before the experiment started, and was soaked in tap water for three months. The goal of soaking the media is to wet the surface and pores of the whole media, to ensure available adsorption and sedimentation sites. The media were installed in the filter with geotextile in the bottom to make sure the filter media were not flushed out of the column during filtration.

#### **5.4.3 Preparation of synthetic stormwater**

For the column experiment, the concentrations were therefore 20 mg/L for propylene glycol and 13.4 mg/L, to match with concentrations from previous experiments by Andersen (2016). The concentrations represent the average values from obtained from the measurements done at Trondheim Airport Værnes Airport during the winter 2013-2014. The concentration used in a similar experiment by Bielefeldt et al. (2002) was constant of 120 mg/day of propylene glycol. With the low flow used in the experiment, these two concentrations are comparable. A consumption of 5-6 l a day per column with the concentration of 20 mg/l for propylene glycol gives a total 100-120 mg/day, which is around the actual consumption for the experiment for the first three phases of the experiment. Suspended solid content was set to 50 mg SS/l, which gives turbidity of around 15 NTU in the turbidimeter.

Synthetic stormwater was prepared every day to prevent degradation of de-icing chemicals in the storing tank, before the water was filtered through the column. For the first three parts of the experiment, the stormwater was prepared in 25 l cans with distilled water to minimize the risk of degradation. For the fourth phase, a larger feed tank of 1000 l was prepared.

The water from the storage tank to the feed tank was continuously circulating to make sure the water level was steady at all times. The water was further transferred to the columns through pipes from the feed tank. The water in the feed tank of 25 l was cooled down to around 10 °C throughout the experiment with a Grant GD100 cooling apparatus. The temperature was however increasing with depth in the columns. The pressure level for the

water was chosen similar to the pressure level of the column studies conducted by Andersen (2016).

The filters were first stabilized to see the degradation of chemicals through the depth of the filter. ATP was measured to investigate the bacteria level as function of depth, in addition to the phosphorous, nitrogen and oxygen level to investigate the limiting factors.

The C:N:P ratio was changed to optimize the conditions in the filter to investigate if the degradation increased. The C:N:P ratio was chosen as the same ratio used for wastewater treatment (100:5:1). A 0.5 M phosphorous stock solution was made using monopotassium phosphate ( $\text{KH}_2\text{PO}_4$ ). The phosphorous solution was added to the feed water up to the desired ratio. The feed water contained 0.381 mg/l of  $\text{KH}_2\text{PO}_4$  after addition of the monopotassium phosphate. This gives a phosphorous concentration of 0.088 mg P/l.

When the C:N:P ratio was changed again for phase 3, the nitrogen and phosphorous concentrations were increased, but still considering the N:P ratio 5:1. The phosphorous was increased 5 times. Calculating via mole gives a concentration of phosphorous of 0.7 mg P/l added from the stock solution. For nitrogen the goal was to reach 1.58 mg N/l which means that 0.735 mg N/l needed to be added. Nitrogen was added from a 0.5 M solution ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ). Salinity increase can be an issue if inorganic salts were added, but due to relatively low concentrations added this was not considered a problem.

#### **5.4.4 Flow**

At Trondheim Airport Værnes, the recorded rainfall for the calendar year 2015 is 930 mm/year (www.met.no). This implies almost a meter of rainfall a year. The water quality volume, which is considered to capture most of the pollutants, is corresponding to 90% of the daily rainfall. The water quality volume is found by sorting and plotting the daily rainfalls in ascending order. Only the days with rainfall is considered, which in this case was 221 days. The first 90% of the rainfalls are added and accounted for the water quality volume. The largest rainfalls are therefore not considered when calculating the volume. For Værnes, this gives an annual water quality volume of 550 mm/year, which is the sum of the 90% daily rainfall as shown in Figure 5-9. Snow and rain are both considered precipitation for this calculation.

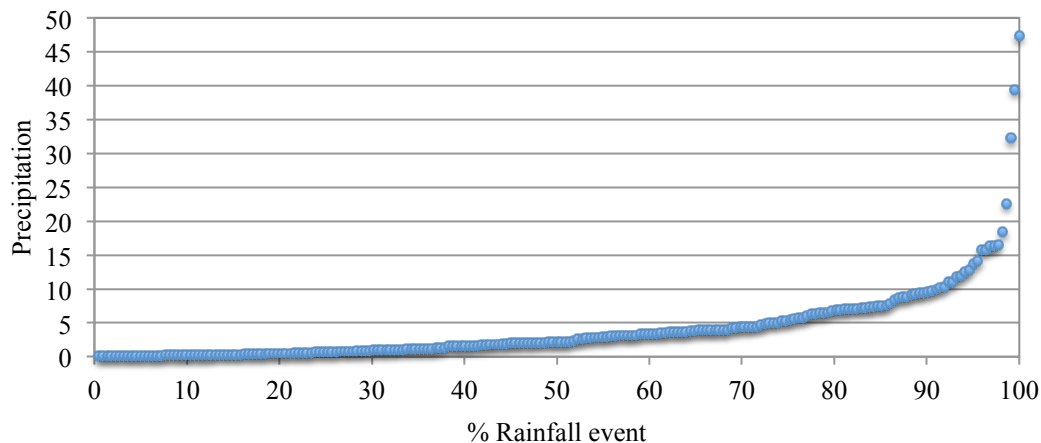


Figure 5-9: Precipitation for Værnes, daily values (based on data from [www.met.no](http://www.met.no))

The diameter of the column used in the test is 0.12 m, which gives a surface area of 0.011 m<sup>2</sup>. A low flow was chosen for the first part of the experiment, to prevent biomass washout. A flow of 7 ml/min was chosen for the first three parts of the column test. 7 ml/min gives a volume consumption of stormwater of 10 l/day per column. Calculations had to be done to be able to compare the chosen flow of 7 ml/min with the water quality volume found at Værnes Airport, Trondheim.

For the first three phases the flow was reduced every day, which led to a consumption of almost half of the initial water consumption. Filtration of 7 ml/min gives a filtration capacity of 0.9 m/day per column. With the actual flow this gives 0.45 m/day. The filter needs to take the capacity of the drainage area of the runway or taxiways. Further examples will be considering the runway. Considering the runway including shoulders to be 60 m wide, and a filter strip of 1m at each side, the filter needs to handle 30 times the rainfall. The filter is run with a low flow for the first 38 days. The volume of flow through the columns is therefore approximately 0.45 m/day for 38 days which gives around a year of rain considering a filter strip of one meter at each side of the runway. Empty bed contact time (EBCT) for the flow of 7ml/min is 34 hours. For the actual flow used in the experiment, the contact time will be higher. EBCT is the ratio between the volumes of particles in bed over volumetric flow. This corresponds to the amount of time the water is in contact with the media for this exact flow.

The study by Bielefeldt et al. (2002) used a flow around 80 cm/day for the different parameters tested, and 140-1130 cm/day for the high flow rate. The 80 cm/day is comparable



to the flow used for the first three phases of this experiment. The flow was chosen to 40 ml/min for the fourth part of the experiment, which gives a flow of 5200 cm/day. This is remarkably higher than what is used in the experiment by Bielefeldt et al. (2002). The high flow was chosen to investigate the impact of suspended solids and high relative chemical loading on the filter.

For the experiment, the columns are continuously soaked in water. For a real application, wet periods will be followed by dry periods. However, the highest loading on the filter will be during snow melting period, where the snow cover is melting, and the filter is loaded with water from snowmelt more or less constantly.

When designing a filter, it is important to consider the local precipitation pattern. The approach for estimating the lifetime of the filter for this report considers the flow through volume of the filter, compared with the rainfall pattern found for Værnes Airport, Trondheim. If designing a filter in Bergen, the rainfall pattern will be different, hence the lifetime will be different with the same conditions as tested in this experiment. Larger events like a 2-year storm are beyond the scope of this thesis, however hydraulic capacity corresponding to such an event is discussed in the thesis by Andersen (2016).

#### **5.4.5 Hydraulic parameters**

##### **Flow measurement**

Flow is measured at the end of the columns by collecting the water for one minute in a beaker and measured with a Mettler Toledo Classical PB8001-L weight scale with the accuracy of 0.1 g. The measurement is duplicated to verify the flow. The flow is monitored every day, and adjusted to have the same flow during the whole experiment. Flow was adjusted at the pipe at the outlet on the bottom of the columns. Flow measurements for the fourth part of the experiments was done by adjusting a suction pump at the end of the columns. This provided a constant flow out from the columns.

##### **Pressure monitoring in the columns**

Pressure along the column depth was measured using pressure transmitters along the column. They were installed in different vertical levels along the column to monitor the vertical pressure distribution as in Figure 5-8. The pressure transmitters are from ABB, 51T series, made of stainless steel (Jensen, 2016) as shown in Figure 5-10. Pressure transmitters were calibrated from the range of -60 to 600 cm H<sub>2</sub>O, because of the possibility that there will be negative pressure in the column during the experiment (as described in 3.1 Filter systems). Electrical signals from the pressure transmitter ranges from 4-20 mA. All the pressure sensors were calibrated to  $R^2 > 0.998$  (Jensen, 2016), as exemplified in Figure 5-11. Data from pressure transmitters are collected with an Agilent 34970a logger and a PC for storing and displaying data.



Figure 5-10: Example, pressure sensors

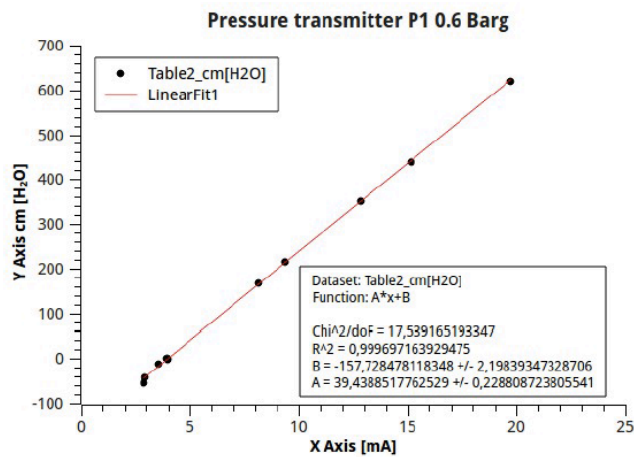


Figure 5-11: Example of pressure transmitter calibration (Jensen, 2016)

Filters were glued on each pressure sensor to prevent sand infiltration into the pressure sensor. The filters are not considered to affect the pressure measurements. A total of 18 pressure sensors were connected to the two columns, with a tape to make sure there was no leakage from the columns. A logger transferred and stored the data locally. Pressure sensors were calibrated and adjusted for the offset value in a final check with water level in the columns prior to the experiments.

#### 5.4.6 Sampling along the column

Sampling was done through the depth of the columns. Three valves were installed through the column depth. Sampling was done at the outlet as well as in the feed tank. Sampling had to be done with a flow less than the outlet flow, to prevent disturbances in the flow pathways in the filters. DOC, ATP, Turbidity, phosphorous and nitrogen were measured through the columns. Monitoring of pressure was done with pressure sensors connected to an Agilent 34970a logger and a PC for storing the data. The pressure was logged every 15 minutes, and stored locally on a computer.

#### 5.4.7 Water quality parameter

##### Turbidity measurement

Turbidity is an optical property of water. Turbidity is measured with a turbidimeter, which is based on nephelometry. Nephelometry is based on light scattering of the sample. Turbidity is mainly caused by suspended solids for the laboratory tests for experiments conducted in this thesis. The turbidity is measured in NTU, which is a relative number. Turbidity measurement is used to adjust the suspended solid concentration in the synthetic stormwater tank, for both the tank experiment and the column experiment, as shown in Figure 5-12.



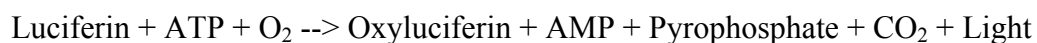
Figure 5-12: Turbidity measured with a turbidimeter

### **Dissolved organic carbon (DOC)**

Dissolved organic carbon (DOC) is defined as the carbon content of organic molecules that can pass through a filter, normally a 0.45 µm filter (Kolka et al., 2008). For the DOC measurement, 0.45 µm syringe filters were used when filtering the samples. Filtration is used to distinguish between particulate and dissolved fraction of organic carbon. After the filtration, the samples are acidified and analysed in a DOC analyser.

### **ATP (Adenosine triphosphate)**

ATP is commonly used to quantify viable biomass in biofilters, and is a rapid and easy method (Pharand et al., 2014). ATP is a molecule found in and around all living cells. The measurement of ATP is based on the energy released from ATP that is transferred to light with bioluminescence. The reagent is extracting the ATP out from the cell, and the enzyme luciferase is reacting with ATP and produces light (Aquateam, 2006).



Concentration at the top of active biofilters will typically range from  $10^2$  to  $10^3$  ng ATP/cm<sup>3</sup> in an acclimated biofilter for drinking water treatment. This gives a value from 100 nmol ATP/l to 2000 nmol ATP/l. Normally, the ATP concentration decreases with depth in the filter (Pharand et al., 2014).

### **Nitrogen and phosphorous**

Total nitrogen (TN<sub>b</sub>) was measured using LCK 138 from Hach as shown in Figure 5-13. Nitrogen is oxidized to nitrate, which reacts in a solution of sulphuric and phosphoric acid to form a nitrophenol. The solution in the cuvette is mixed with reagents and heated according to the specifications from Hach. The solution is measured with a DR2900 Benchtop VIS Spectrophotometer, where the reading shows total nitrogen.

Phosphorous is measured using LCK 349. The samples are mixed with reagents and heated according to the specifications from Hach. Total phosphorous was measured in the spectrophotometer, as similar to the nitrogen measurement.



Figure 5-13: LCK 138 for measuring total nitrogen

#### 5.4.8 Basic assumptions

- Sampling from columns is done slowly, hence it is assumed that the sampling will not create preferred streams in the filter media, and the water is flowing equally in the filter media.
- Pre-soaking the media by tap water containing DOC does not contribute to pre-adsorption of DOC onto the media.
- Flow through the columns is only affected by the changes in the filter. The decrease in the flow and the flow adjustments are negligible for the degradation.

## 6 Results and discussion

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Results and discussion from each of the three experiments conducted in this thesis are described and evaluated separately in the order the experiments were conducted. Batch experiment results are presented and discussed considering the literature findings already addressed. The same is done for the tank experiment and the column experiment.

### 6.1 Batch experiment

Adsorption of propylene glycol was tested on the media activated carbon, Filtralite NC 0-2 and Filtralite NC 0.6-1.8. Both propylene glycol and potassium formate showed some adsorption onto the granular activated carbon. Adsorption of propylene glycol onto activated carbon was shown in the pre-master project (Lindseth, 2016). Results from the improved laboratory method led to results that are more viable. Filtralite media did not show any sign of adsorption, which was also as expected from findings in literature.

#### 6.1.1 Adsorption isotherms and kinetics for propylene glycol onto activated carbon

The experiment was conducted twice. The reason was that the stock solutions were made the day before the experiment started for the first attempt. The concentration was measured during the preparation of the solutions, and one hour into the experiment. The fact that the concentration had increased remarkable from the preparation of the solutions the day before experiment start to the first measurement one hour into the experiment, resulted in a doubtful initial concentration.

The replicate experiment showed improved and viable results. The decline of carbon content in the solution is clear in the first hours until equilibrium is reached after less than twenty-four hours (Figure 6-3).

Adsorption isotherms were calculated according to the literature. Adsorption isotherms were evaluated and the isotherm with the highest  $R^2$  value was chosen as the best-fit isotherm, as shown in Table 2. The best-fit isotherm is presented in Figure 6-1, which in this case is the

Linear isotherm. Linear isotherm represents a linearly increasing adsorption capacity with respect to adsorbate.

Table 4: Isotherms for propylene glycol onto activated carbon

Isotherm	R <sup>2</sup> value
Linear	0.994
Langmuir	0.003
Freundlich	0.959
Temkin	0.893

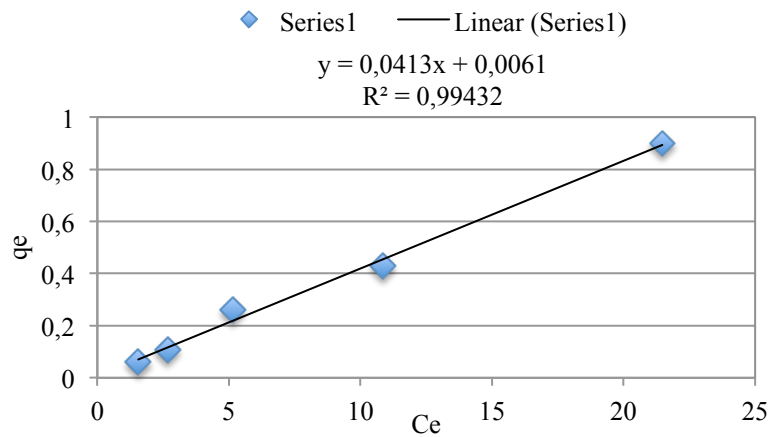


Figure 6-1: Linear isotherm for propylene glycol onto activated carbon

However, the Freundlich isotherm is almost as well fitted as the Linear isotherm. Linear isotherm is the same as Freundlich isotherm when  $n$  is 1 as described in the literature. Freundlich isotherm is shown in Figure 6-2.



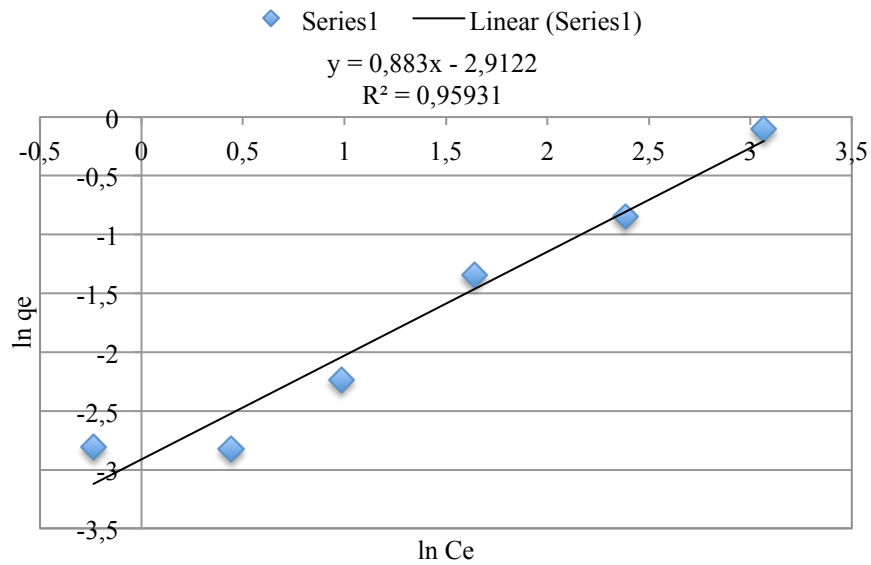


Figure 6-2: Freundlich isotherm, adsorption of propylene glycol onto activated carbon

Pseudo-second-order sorption kinetics was found to fit best for the experimental data, as seen in Figure 6-3. Measured values are presented as points, and calculated values are presented as dotted lines. Pseudo-second-order kinetics denotes that the concentration is the driving force for the adsorption. The larger the concentration, the more adsorption is observed. Adsorption onto the media is observed, as the carbon content is decreasing with time in each solution. However, the adsorption capacity of the de-icing chemicals by the media is low.

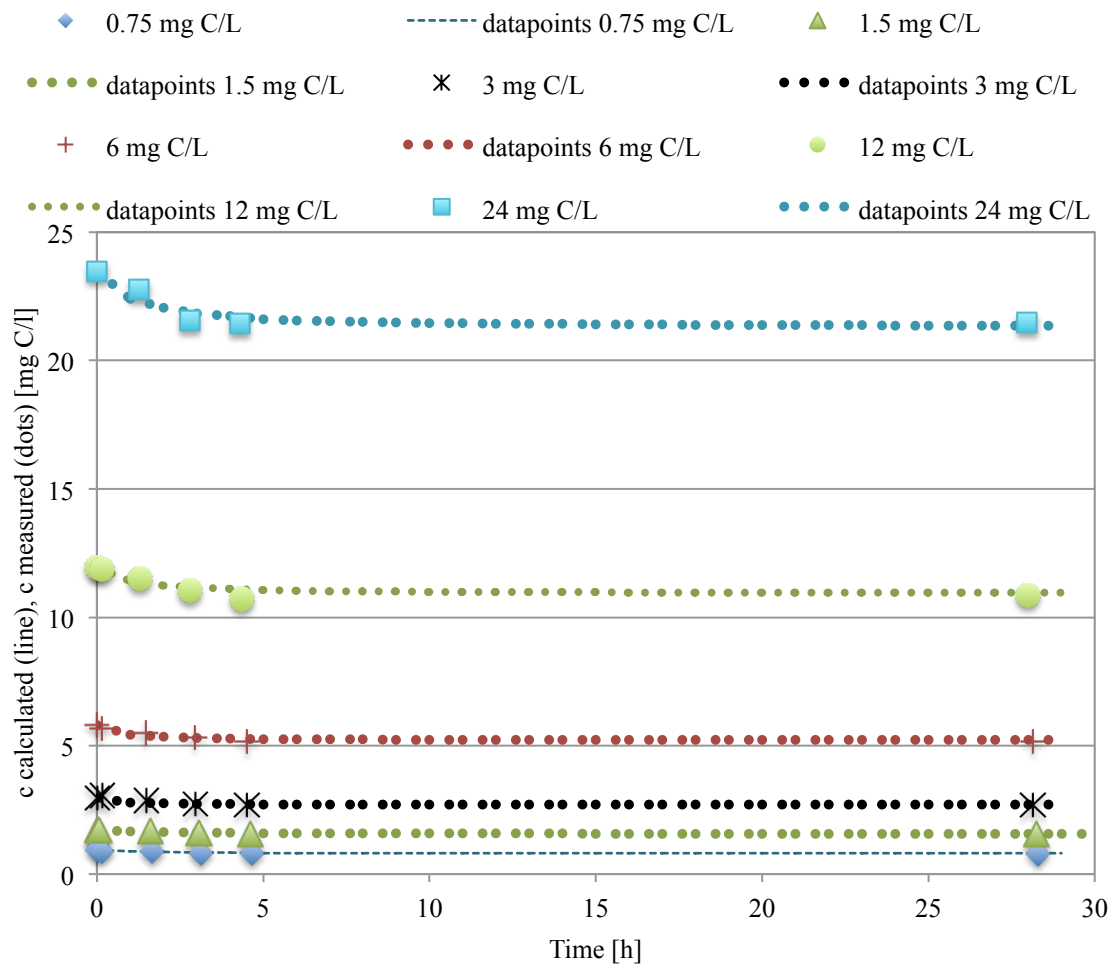


Figure 6-3: Pseudo-second-order kinetics for propylene glycol onto activated carbon

### 6.1.2 Adsorption isotherms and kinetics for potassium formate onto activated carbon

Adsorption isotherms for potassium formate were calculated according to the literature section (Chapter 4), as for propylene glycol, and shown in Table 5. The same tendency is found for the isotherm calculations, that Linear isotherm is best-fit as presented in Figure 6-4.

Table 5: Isotherms for potassium formate onto activated carbon

Isotherm	R <sup>2</sup> value
Linear	0.936
Langmuir	0.032
Freundlich	0.786
Temkin	0.649

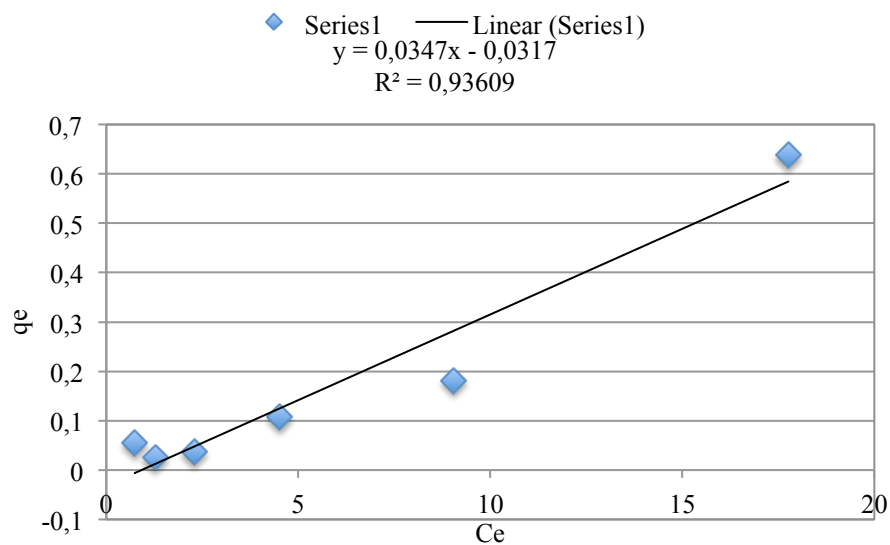


Figure 6-4: Linear isotherm, for potassium formate onto activated carbon

Due to the possibility of comparing the adsorption capacity between chemicals with the Freundlich isotherm, it is presented in Figure 6-5.

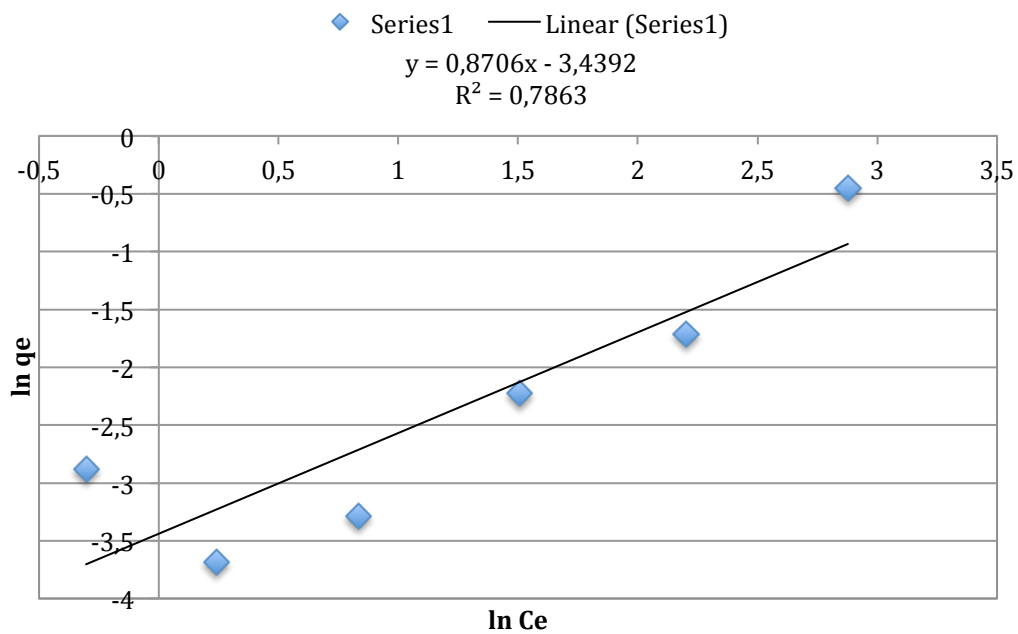


Figure 6-5: Freundlich isotherm, adsorption of potassium formate onto activated carbon

Pseudo-second-order kinetics was also found to fit the data best in this case as similar to the propylene glycol, as shown in Figure 6-6. It is observed that propylene glycol and potassium formate show the same trend, that the adsorption is not significant. The equilibrium for the batch experiment in both cases was reached after less than a day.

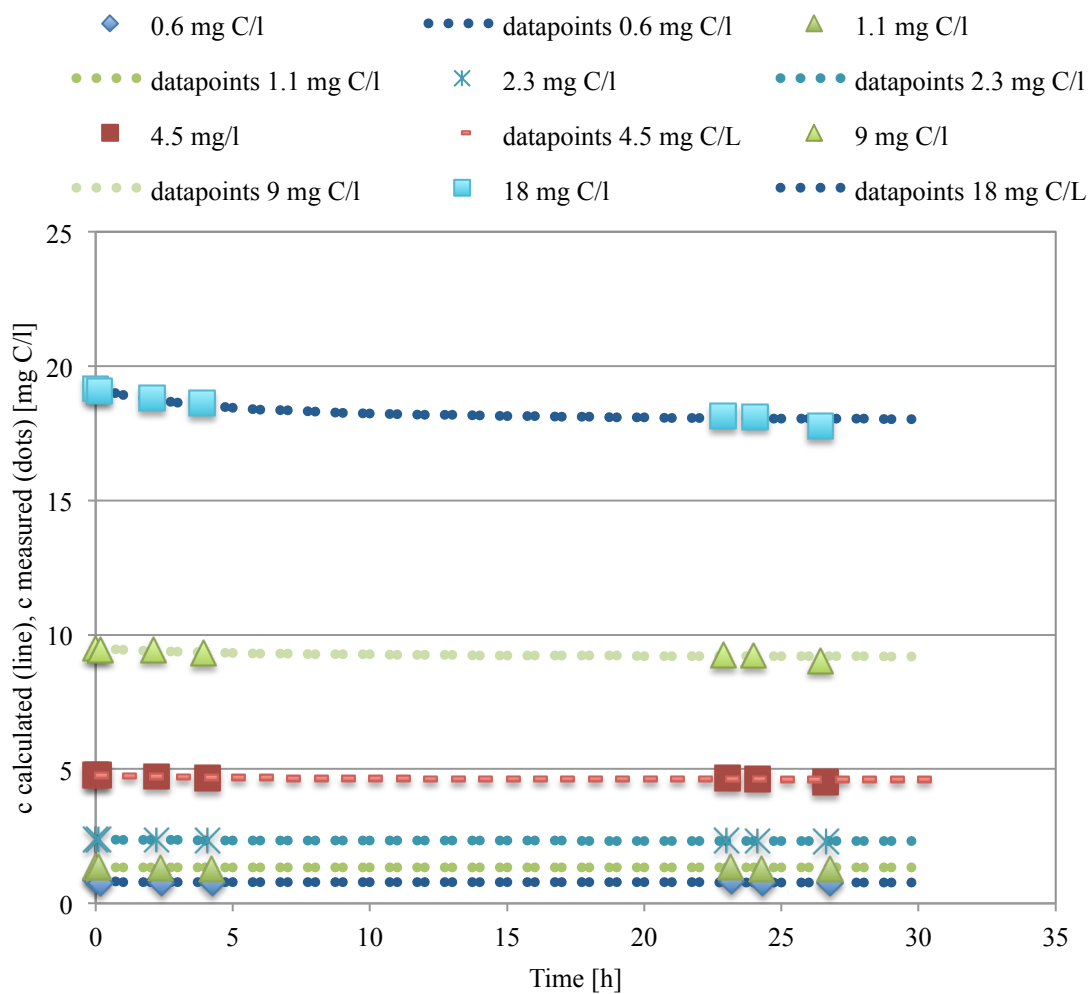


Figure 6-6: Second order kinetics for potassium formate onto activated carbon

### 6.1.3 Adsorption onto Filtralite

Adsorption onto Filtralite was not found in the batch experiments, neither for Filtralite NC 0-2 nor for Filtralite NC 0.8-1.6. As seen in Figure 6-7, no adsorption is found on Filtralite NC 0-2 for propylene glycol. The same trend was found for potassium formate. The measurement fluctuations seen in the figure are within the standard deviation of the DOC measurement.

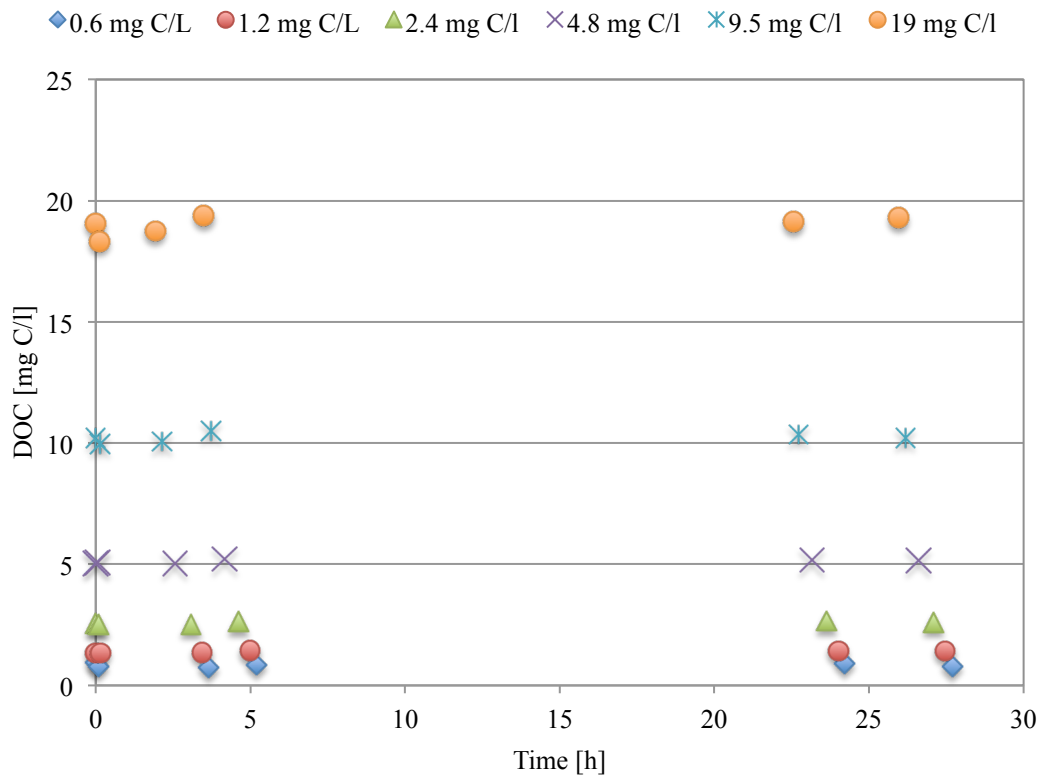


Figure 6-7: Batch experiment, Filtralite NC 0-2 and propylene glycol

## 6.2 Discussion, batch experiment

For the adsorption study, the tests were only carried out once. This means that only one temperature condition was tested, as well as one media weight. Different concentrations were used for each chemical in the experiment. The chemicals were tested separately and not tested together for the total adsorption in a solution with both chemicals. Only one DOC test was taken for each sample. The DOC analysis is considered accurate with three measurements per sample, and only with a small standard deviation. However, some of the  $R^2$  values for the isotherms are similar. Small errors in the DOC measurement and sampling might therefore affect the isotherms and kinetic calculations, and the evaluation of these. However, the Linear and Freundlich isotherms fitted remarkably better than the other isotherms evaluated.

### 6.2.1 Comparing adsorption of propylene glycol and potassium formate

Which substance that is most preferably adsorbed by the GAC can be evaluated by using the power index if using the Freundlich isotherm. The power index  $1/n$  is determined from the slope of the plot  $\ln(q_e)$  versus  $\ln(C_e)$ , and shown in Table 6.

Table 6: Power index, Freundlich isotherm

Chemical	$1/n$
Propylene glycol	0.883
Potassium formate	0.871

As seen from Table 6, propylene glycol and potassium formate have similar power index. Potassium formate shows slightly more favourable adsorption, however the results are similar and the difference can be neglected. Adsorption is favourable if  $n > 1$ . The  $n$  values are close to 1 (PG 1.13 and PF 1.15), which means that the de-icing chemicals are not preferable for adsorption onto activated carbon. This is in line with the second order kinetics, where adsorption is not significantly observed. If the constant  $1/n = 1$ , this means that the Freundlich isotherm is the same as the linear isotherm. This demonstrates why the  $R^2$  values for the Freundlich and Linear isotherms are close, especially for propylene glycol.

### 6.2.2 Adsorption study compared to the literature

For both chemicals tested in the batch experiment, it was found high  $R^2$  values for the Linear isotherm. High correlation was also found with Freundlich isotherm for adsorption on propylene glycol onto activated carbon. Adsorption can be thought to form a single layer of adsorbate on the adsorbent surface, as suggested by the Freundlich isotherm.

Peereboom et al. (2007) investigated adsorption models on the chemicals glycerol and propylene glycol onto activated carbon. It was found that the Langmuir isotherm fitted the adsorption of individual species, while the extended Langmuir model fitted the multicomponent adsorption well. It was found that the  $R^2$  value was relatively high for both Freundlich and Langmuir models for both cases (0.916 and 0.997 respectively). As observed in the experiments conducted in this thesis, Langmuir isotherm does not fit well with the obtained results. However, the study by Peereboom et al. (2007) reported a relatively high correlation for the Freundlich isotherm as well.

Affinity for adsorption is dependent on the hydrophilic nature of the adsorbed species. Propylene glycol is a hydrophilic chemical with a dielectric constant  $\delta$  of 32, while water has  $\delta$  of 80. Solvents might be classified as semi-polar for  $\delta$  between 20 and 50, hence propylene glycol can be classified as semi-polar. This might be a reason for the relatively low adsorption shown in the batch experiment.

Ho and McKay (1999) tested systems from the literature, to find that the highest correlation coefficients were obtained for the pseudo-second-order kinetic model. They also concluded that the pseudo-first order model fitted well for the initial period for the first reaction step only (Ho and McKay, 1999). Hence, the finding of pseudo-second-order kinetic model as the best-fit is in line with the literature.

As seen from the adsorption test, GAC is adsorbing de-icing chemicals. Persson et al. (2007) investigated removal of geosmin and 2-methylisoborneol (MIB) by biofiltration with filters of Filtralite NC 0.8-1.6 compared to GAC. Good removal of the chemicals were shown in both filters during biofiltration when concentrations were low (Persson et al., 2007). It was also shown that the degradation of chemicals in the GAC filter was due to both adsorption and biodegradation. For the filter with Filtralite NC 0.8-1.6 the degradation was completely



due to biodegradation. This conclusion supports the finding of no adsorption onto Filtralite NC 0-2 and Filtralite NC 0.8-1.6

Persson et al. (2007) also found that removal of de-icing chemicals with GAC was not temperature dependent compared to Filtralite media for the biodegradation.

### **6.2.3 Possibilities of a GAC layer on top in a biofilter**

In the study conducted by (Persson et al., 2007) it is concluded that GAC can be used to give extra robustness to a system. Column experiments conducted by Andersen (2016) indicated that filter media with a top layer of GAC clogged faster for all the conditions tested for Filtralite NC 0.8-1.6 + GAC. This needs to be taken into consideration when designing a filter, due to the possibilities of reducing the lifetime of the filter depending on how much GAC that is used and how much de-icing chemicals is adsorbed on the GAC with respect to the capacity of biodegradation in the filter. GAC is costly, and as seen from further results obtained by Andersen, it seems that the GAC has an adsorption capacity at the beginning of the stormwater loading, while after short time the main process will be biodegradation.

### 6.3 Tank experiment

As described in the method chapter, degradation in the tank was analysed due to indications of biodegradation in the 1m<sup>3</sup> tank from the experiment conducted by Andersen (2016). This observation is also reported in literature, where degradation of chemicals in the feed flask is occurring before entering the columns (Bielefeldt et al., 2002). Consequently, degradation was found in the tank in this experiment.

#### 6.3.1 Comparison of Andersen's results and tank experiment

Degradation in the tank was 50% after 5 days, and 65% after 8 days. This implies bacteria growth in the tank. The tank was filled with tap water, thus the initial temperature was 7°C. After a week the water in the tank had reached room temperature around 22 °C. As reported in the literature, temperature influences the degradation rate in general. Studies by French et al. (2001) shows that degradation of de-icing chemicals are higher in the summer, when temperatures are higher, compared to lower temperatures in the winter.

The data from the experiment of Andersen (2016) (Filtralite NC 0-2 + GAC and Filtralite NC 0.8-1.6 + GAC) is plotted with the data from the tank experiment in Figure 6-8.

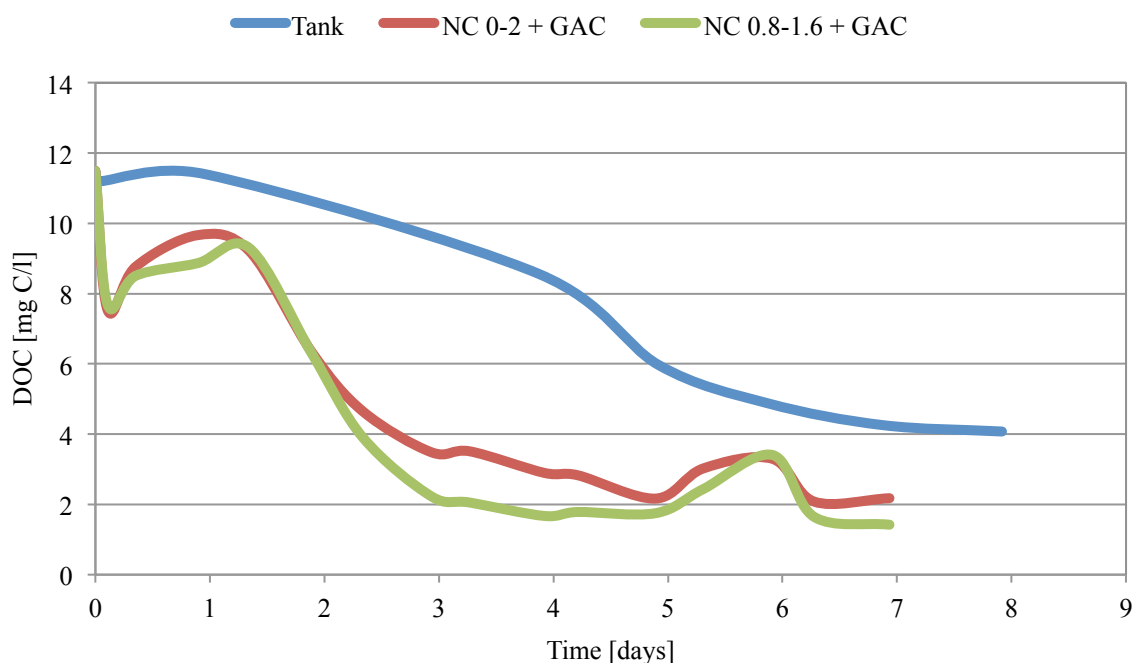


Figure 6-8: Tank experiment with data from Andersen (2016)

The data representation is developed from two individual experiments, which means that there might be deviations between the two experiments. It is illustrated that there is clearly degradation in the feed tank, and that this needs to be considered for column experiments.

As seen from the data generated by Andersen (2016), there is an indication of adsorption onto the activated carbon layer during the initial part of the experiment. This might be because the GAC is able to adsorb some chemicals at the beginning of the test, until the capacity is reached. This is further discussed in the thesis by Andersen (2016).

#### **6.4 Discussion, tank experiment**

Degradation was evaluated in a large feed tank, the same as was used in the column experiment by Lindseth (2016) and Andersen (2016). Due to the relatively high biological degradation in the tank, it was decided to have a smaller tank for the column experiment where the water was changed every day, and cooled to 10°C to lower the growth and degradation. However, the new water in the 25 l tanks showed a small variation in the chemicals concentrations of the solution. This was taken into account, but this still represents one more variable to consider. However, it is considered as a better solution than using a larger tank with degraded stormwater solution for the experiment.

## **6.5 Column study**

The column study was conducted in the laboratory at Valgrinda from 3rd of May 2016 until the 15th June 2016. The study was done in different phases.

- 1) The first part of the column study was done with constant chemicals concentration as well as flow adjustments every day (~the first 20 days)
- 2) The test was optimized for removal of chemicals by changing the C:N:P ratio (day 20)
- 3) Nitrogen and phosphorous was increased, while keeping the ratio N:P=5:1 (day 29)
- 4) The flow was increased (day 39)

The results of the experiments are presented as days after start.

## **6.6 Column study phase 1: initial measurements from stabilized filter**

Acclimatisation of the filter was done in the first part of the experiment. The feed tank was changed every day, due to findings from the tank experiment. Degradation in the feed tank was considered negligible due to change of the water every day. However, the initial concentration of de-icing chemicals somehow showed variation. This might be due to inaccuracies when mixing the synthetic stormwater, due to the sticky solution of propylene glycol that affected the accuracy of measured chemicals volume with the pipette. This is taken into account and the data are thus presented relatively dependent on the initial concentration in the feed tank. Due to a long EBCT, the initial variation of initial chemicals concentration might have some effect on the obtained data, when the samples along the columns are plotted at sampling time. However, the variation is considered small and negligible when plotting the normalized data.

### **6.6.1 Chemicals degradation in the column**

During the first four days, stronger chemicals degradation was indicated compared to the rest of the initial period. The initial high values are probably due to dilution of chemicals during the first days. However, the degradation in both columns was observed to stabilize at a lower degradation rate. The initial degradation was observed to 20% at the first valve in column 1 and 15% at the first valve in column 1. Measurements were done in the tank and at three valves along the column depth as well as the outlet. The last valve (Third valve) is not presented, due to overlapping with other values as well as no significant difference was seen

at the end of the column (as described in 6.6.2). Normalized DOC for column 1 and column 2 is presented in Figure 6-9 and Figure 6-10 respectively.

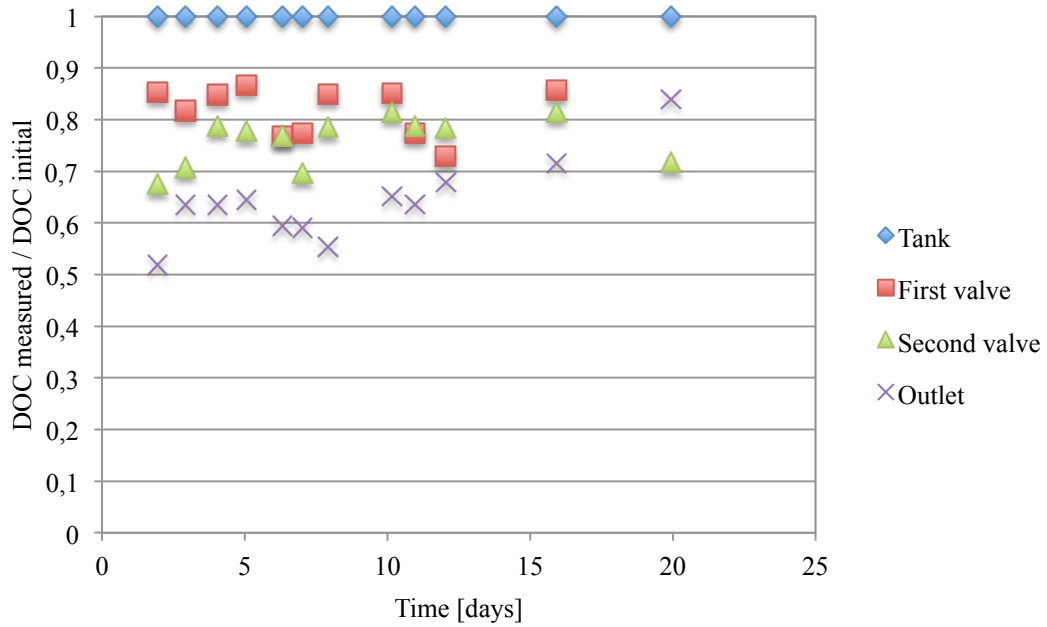


Figure 6-9: Normalized DOC removal first phase, column 1

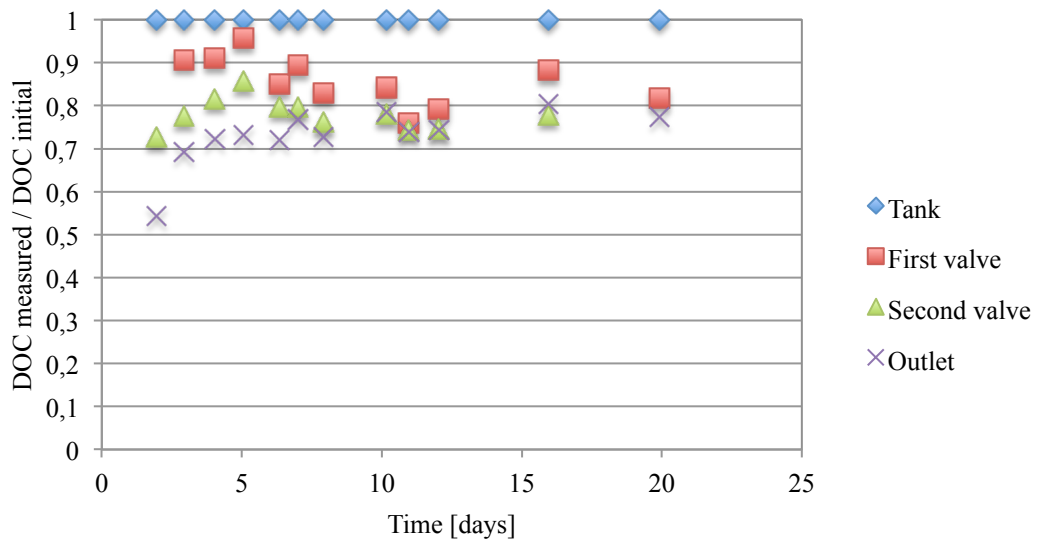


Figure 6-10: Normalized DOC removal first phase, column 2

As the removal is shown relatively, a value of 0.8 at the y-axis represent a removal of 20%.

### 6.6.2 ANOVA test

After the filter had been stabilized for the chemicals concentration, an ANOVA test was performed to investigate if there was a significant difference in concentration along the column depth. ANOVA test is an analysis of variance test that can be used to compare datasets. The results show that there is a significant difference between the feed tank and the first sampling port in both columns. A t-test was performed between the sampling ports to investigate if the degradation was significantly changed with depth. To account for the analysis of multiple datasets, the Bonferroni correction was taken into account, which is the 0.05 probability divided by the number of hypothesis tested. In this case, the number of hypothesis is five. Results from ANOVA test performed in Minitab Express are shown in Figure 6-11 and Figure 6-12, where each sample set represent the feed tank, the sample valves and the outlet for each column.

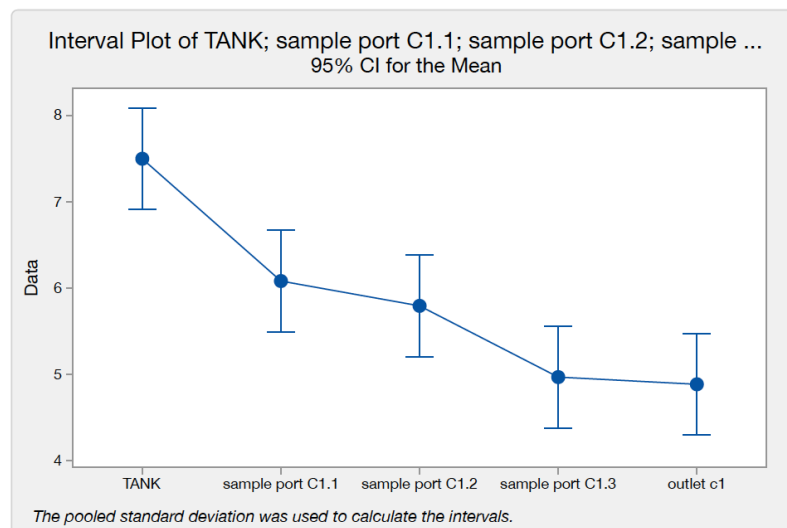


Figure 6-11: ANOVA interval plot from Minitab Express, column 1

As the interval plot of column 1 shows, there is a significant difference between the sample sets. The P-value is  $<0.0001 \ll 0.05/5 = 0.01$ , hence there is a significant change in the concentration with respect to depth. T-tests were performed for each sample set, and show that there are significant differences between the tank and all the sampling ports for both columns.

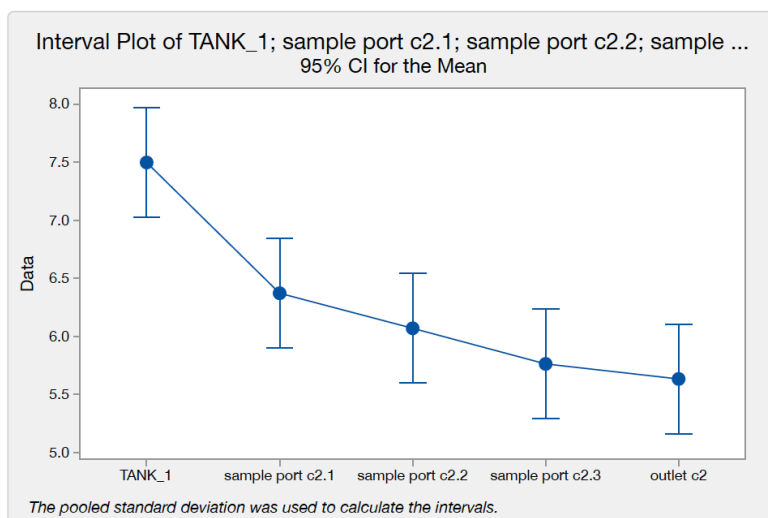


Figure 6-12: ANOVA interval plot from Minitab Express, column 2

Interval plot for column 2 shows the same trend as for column 1. The p-value between the sample sets is as well  $p < 0.0001$  that shows a significant difference. T-tests performed for the sample have proven that there is a significant difference between the feed tank and all the sampling ports. These results show the same trend as column 1. Hence, the columns are behaving somewhat similarly, regards to degradation rate, and the removal is mainly in the upper part of the column (upper 15 cm).

### 6.6.3 ATP measurements

As seen in Figure 6-13, there is observed more bacteria in the end of column 1, compared to column 2. The flow was presumed to be stable through the whole experiment, but due to clogging, the flow had almost stopped after twenty-four hours. The tendency found with more bacteria in the end of the column 1 is possibly due to longer contact time for the water flowing through this column. The ATP in the end of the column 1 is clearly higher than what is found in the feed tank, which indicates more bacteria growth in the end of the media.

Bacteria in column 2 are observed to decrease with depth. The flow was steadier for this column, which means lower bed contact time for the water, compared to column 1. As also the DOC indicates from the ANOVA analysis, there are no significant differences in the degradation of chemicals between the sampling ports one, two, three and the outlet. This indicates that there is degradation only at the upper part of the column (upper 15 cm). A more steady flow was observed for column 2 compared to column 1. Higher flow in column 2

might affect the bacterial growth in the filter, due to risk of washout in column 2. However, the flow was chosen low to prevent this risk.

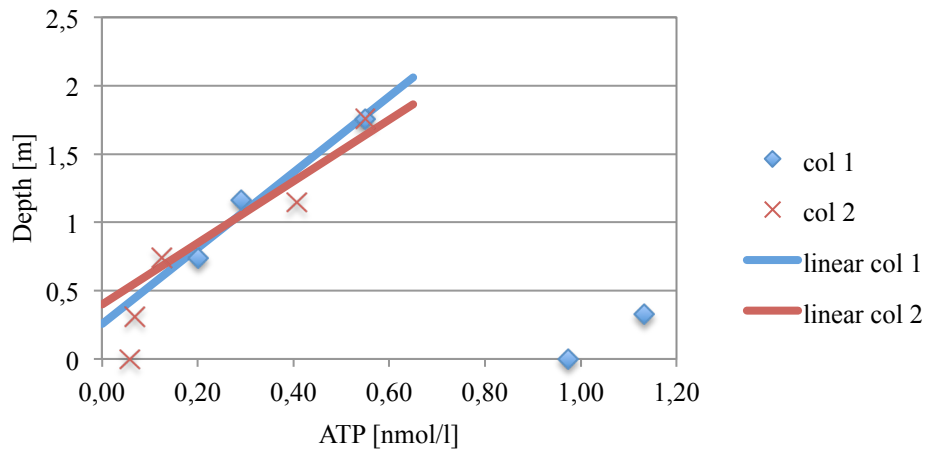


Figure 6-13: ATP after ~16days

#### 6.6.4 Phosphorous, nitrogen and oxygen measurements

As DOC measurements show relatively low degradation in the columns, nutrients were investigated. It is observed that one reason for the low degradation is due to limited amount of phosphorous. Higher phosphorous content was found with depth in the filter. A possible explanation for the higher phosphorous concentration in the end of the column might be due to leaching of phosphorous from the material. However most of the values are under the detection limit of 0.05 mg P/l, thus the measured number is only considered as an indication. Most nitrogen values were measured under the detection limit of 1.00 mg N/l as well. Phosphorous measurements are presented in Figure 6-14 and nitrogen measurements are presented in Figure 6-15.



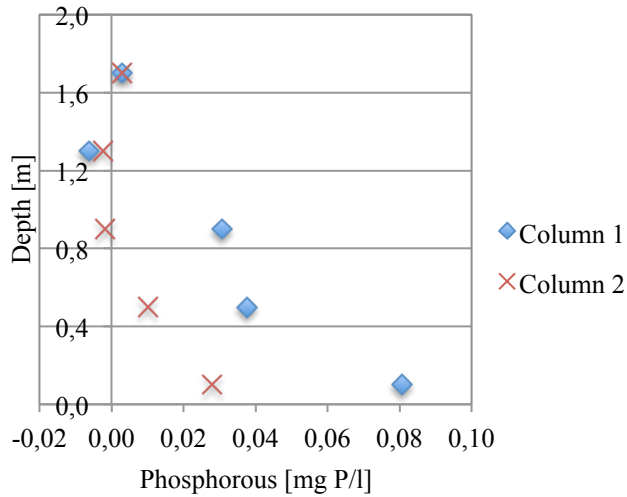


Figure 6-14: Phosphorous after ~ 16 days

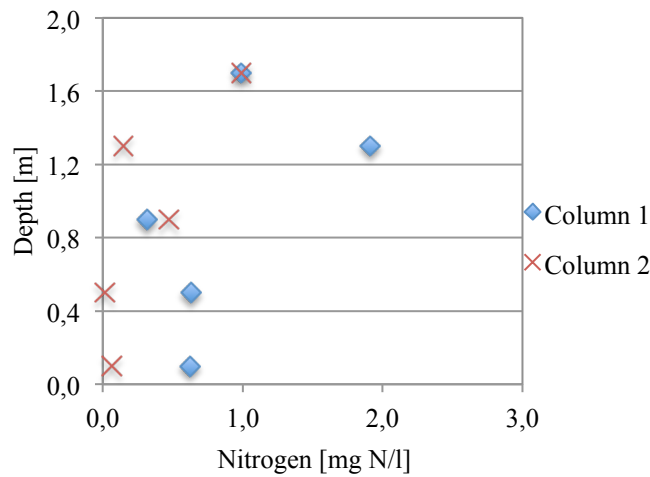


Figure 6-15: Nitrogen after ~ 16 days

Oxygen is a possible limitation for degradation of chemicals in this study. Oxygen measurements were not measured accurately due to a non-functioning oxygen probe, thus the data are not presented. However, the relatively measurements between the tap water, feed tank and the outlet of the two columns were measured. The measurements indicates that the oxygen consumption is not a limiting factor, due to the relatively high oxygen at the outlet of the columns, compared to the oxygen in the feed tank. Results also indicate that more oxygen is consumed in the first column, which is in line with ATP measurements. However, measurements are approximate, thus not reliable for final statement of the oxygen conditions in the columns.

## 6.7 Column study phase 2: Change C:N:P ratio - P addition

The carbon:nitrogen:phosphorous (C:N:P) ratio was changed when the first results of chemicals degradation was considered low. The first measurements of the carbon, phosphorous and nitrogen showed that the limiting factor was phosphorous. The synthetic stormwater contained very low phosphorous, in the zero range. This is in line with what is found in inland waters as mentioned in the literature (Stumm and Morgan, 1996). Oxygen was also measured, but was not considered a limiting factor for the degradation.

To optimize the conditions, phosphorous was added to reach a ratio close to C:N:P = 100:10:1. Carbon was measured to 8.5 mg/l and nitrogen to 0.99 mg/l. It was therefore decided to add phosphorous from a solution of monopotassium phosphate as described in chapter 3.

The C:N:P ratio was measured after some days with the new condition. The water in the feed tank was measured to be C:N:P ~ 137:15:1. The C:N:P ratio is given relatively in moles.

The degradation was slightly improved after increasing the phosphorus, however not remarkably. The decline in DOC concentration was seen in both columns (Figure 6-16, Figure 6-17). To improve this further, it was decided to add more of both nitrogen and phosphorous into the synthetic stormwater solution.

### 6.8 Column study phase 3: Change C:N:P ratio - N and P addition

In order to increase the removal of chemicals further, it was decided to increase both nitrogen and phosphorous. It was decided to increase phosphorous 10 times and keep the molar ratio N:P of 5:1. The nitrogen was added in form of a solution of 0.5 M nitrogen from ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ). The measurements from the feed tank showed that the molar ratio after the nutrient addition was C:N:P = 24:7:1.

After the nutrient addition, the removal increased as seen in both Figure 6-16 and Figure 6-17. Average values from measurement at day 34 and 36 show a removal rate of 50% at all ports, in both columns. However, the removal rate declined in the middle of phase 3. It was expected that the decrease as seen in the first measurement after adding and N would continue.

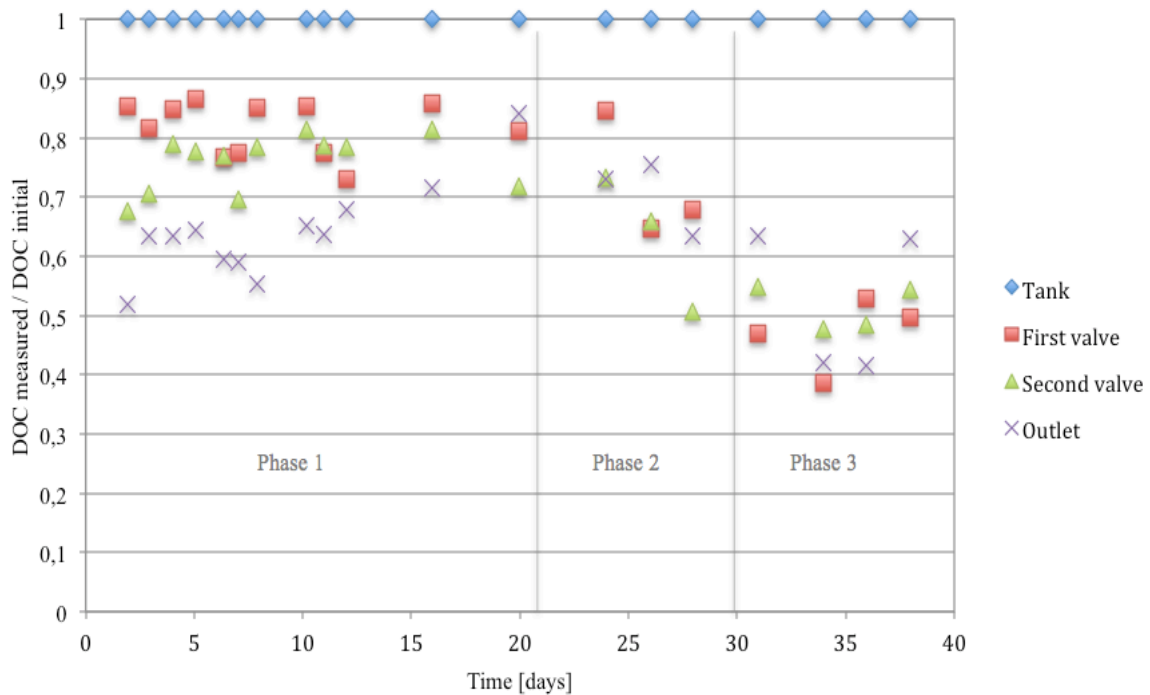


Figure 6-16: Normalized DOC, column 1

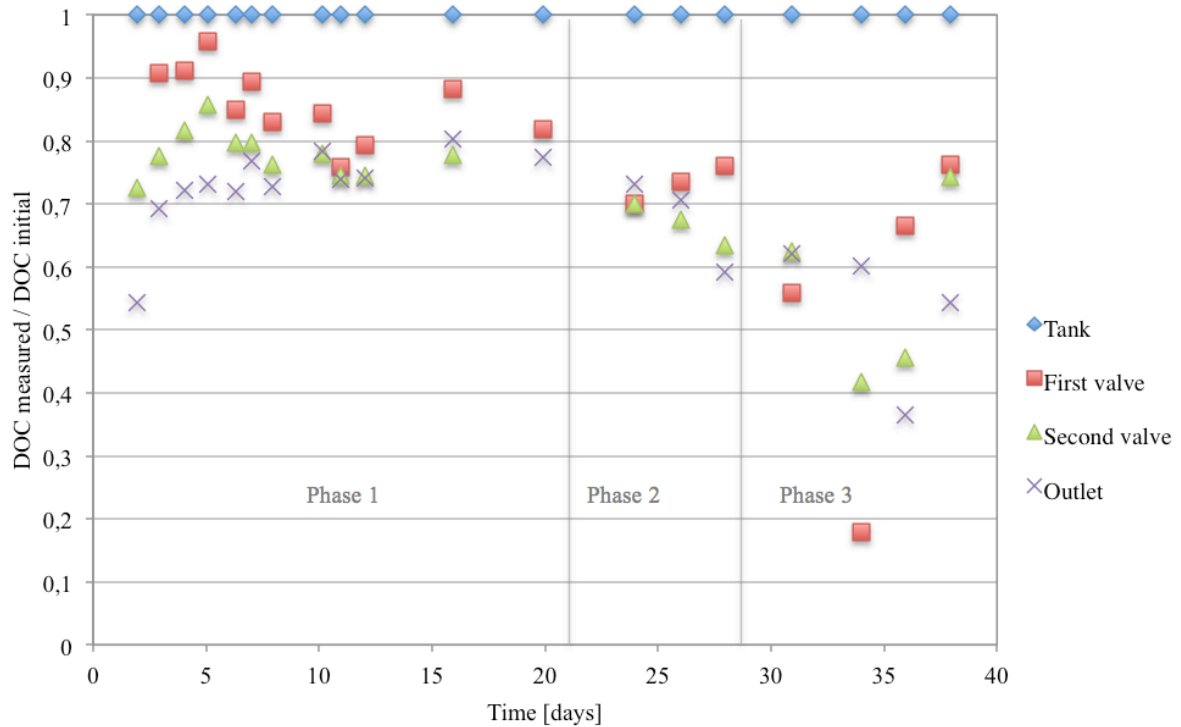


Figure 6-17: Normalized DOC, column 2

As seen from the results, a plateau or a stable situation in the column was not obtained before the conditions were changed. The biological degradation was not stable before changing the conditions, which is unfortunately a weakness for the experiment. As seen from the values, the measurements are not stable and have a large variation within the column, however the results give indications of the conditions in the filter.

### 6.8.1 Filtration coefficients by Iwasaki model

Iwasaki model was used to calculate the filtration coefficients as visualized in Figure 6-18 and Figure 6-19. As shown, the filtration coefficients are decreasing with depth (length in filter). The filtration coefficients are larger for column 1, compared to column 2 for initial conditions as well as after nutrient addition.

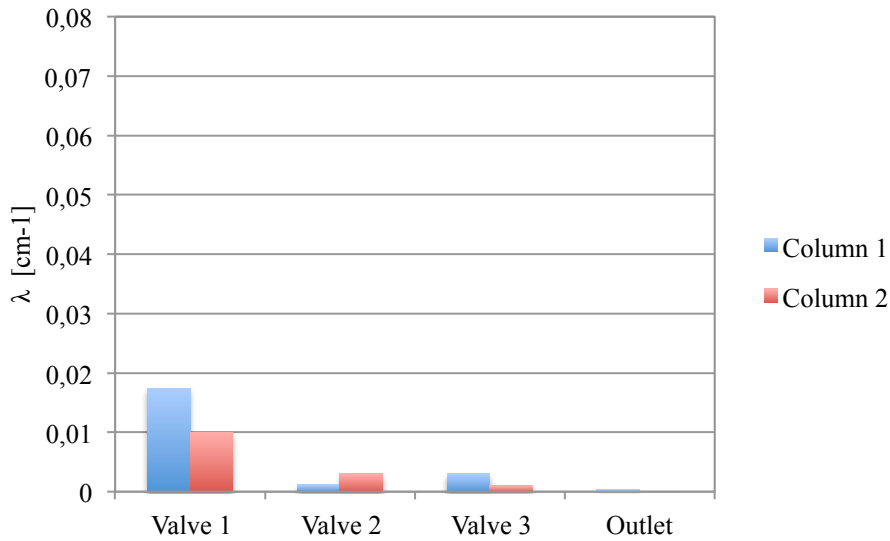


Figure 6-18: Filtration coefficient, initial values

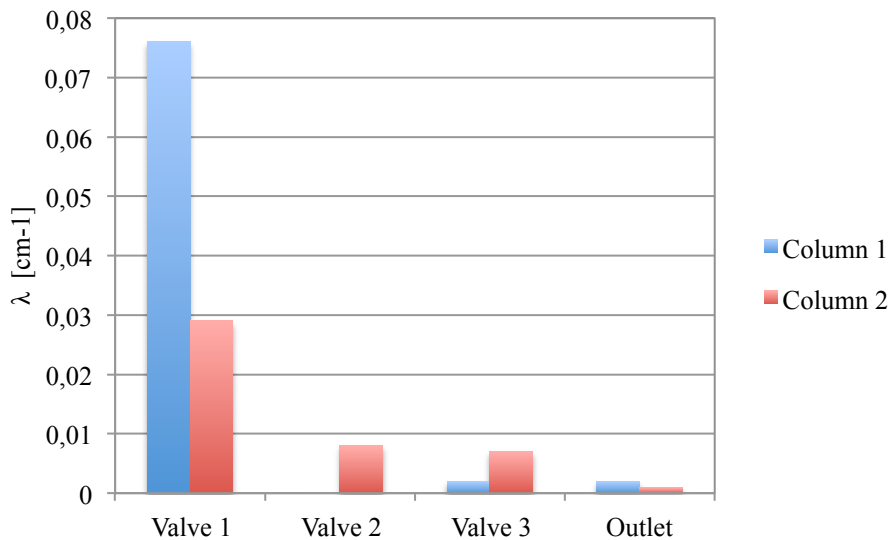


Figure 6-19: Filtration coefficient, after nutrient addition

An increase in filtration coefficient is observed for both columns after nutrient addition. This tendency is also seen in the plot for measured DOC concentrations which represents higher removal after nutrients addition (Figure 6-16 and Figure 6-17). From these results, it is seen that column 1 has better removal capacity compared to column 2. Filtration coefficients after nutrient addition are calculated with the two last measurements done for the phase (after 36 and 38 days).

### 6.8.2 ATP measurements

ATP was measured after the nutrient addition. When nutrients were added, the biological growth was increasing. Intracellular ATP (unfiltered sample) is measured as well as extracellular (filtered sample). The extracellular is ATP that has been released from stressed or dead cells. The amount of extracellular ATP decreases when the biological growth is increasing. The extracellular ATP was measured as low, which shows that there is biological growth in the media. ATP measurements are in the same range after nutrient addition, as before nutrient addition, as shown in Figure 6-20. The ATP shows an increase in bacteria at the top of the filter for column 2, compared to column 1, and increased bacteria in the feed water, compared to the first phase of the experiment.

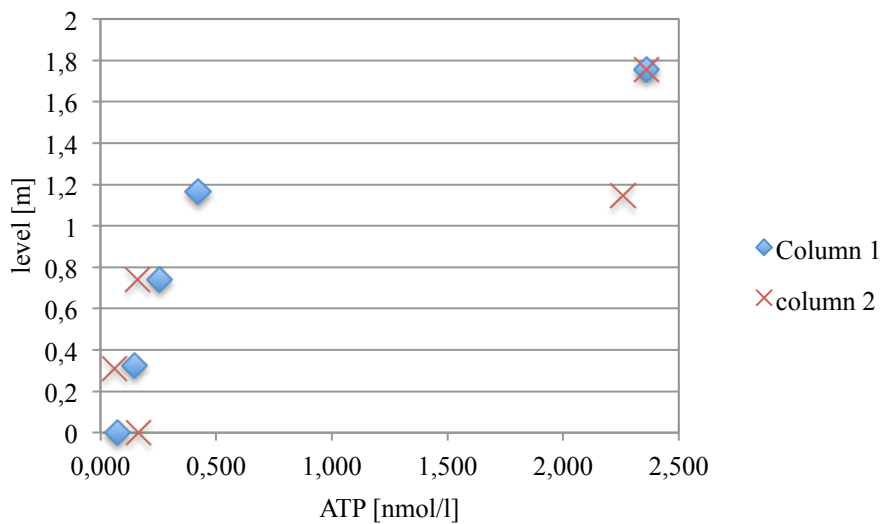


Figure 6-20: ATP after ~37 days

## **6.9 Column study phase 4: Flow increase**

Flow was increased to 40 ml/min, and held stable by suction with pumps. DOC measurements are not shown due to the mistake of not adding nutrients in the stormwater for the large tank, as well as chemicals degradation in the feed tank. Flow was increased to 40 ml/min, and held stable by suction with pumps.

Higher flow leads to a lower EBCT. For a flow at 40 ml/min, the EBCT is 6-7 hours. This means that the synthetic stormwater has less contact time with the filter media. The synthetic stormwater contained suspended solids, and the water measured turbidity around 8 NTU, which is around 25 mg/l of particles. The particles were expected to affect the flow capacity of the filter, and contributing to clogging.

### **6.9.1 Pressure in the filter**

Pressure was monitored in the filter bed. Pressure change was not observed for the first three phases of the experiment due to the low flow. When the flow was reduced during the adjustments, the pressure was stabilized to the initial conditions. After the pumps were installed for suction and flow increased, the pressure change in the columns was visual. A reason for the relatively fast clogging is that there is a high flow through the columns, containing suspended solids that will block the pores of the filter. With a flow of 40 ml/min, 5m of water will flow through the filter a day. This implies that 3 days of column operation represents one year of operation in reality, when considering flow through volume.

As seen from the pressure measurements, the clogging is observed on the top of the filter at the first 15 cm, where most particles will settle. Pressure is shown as days after experiment start. As seen from Figure 6-21, clogging occurs after 43 days in the experiment. Clogging is continuing to increase due to the suction with the pump. Clogging is observed when pressure in the filter is measured to less than the pressure at the water level.

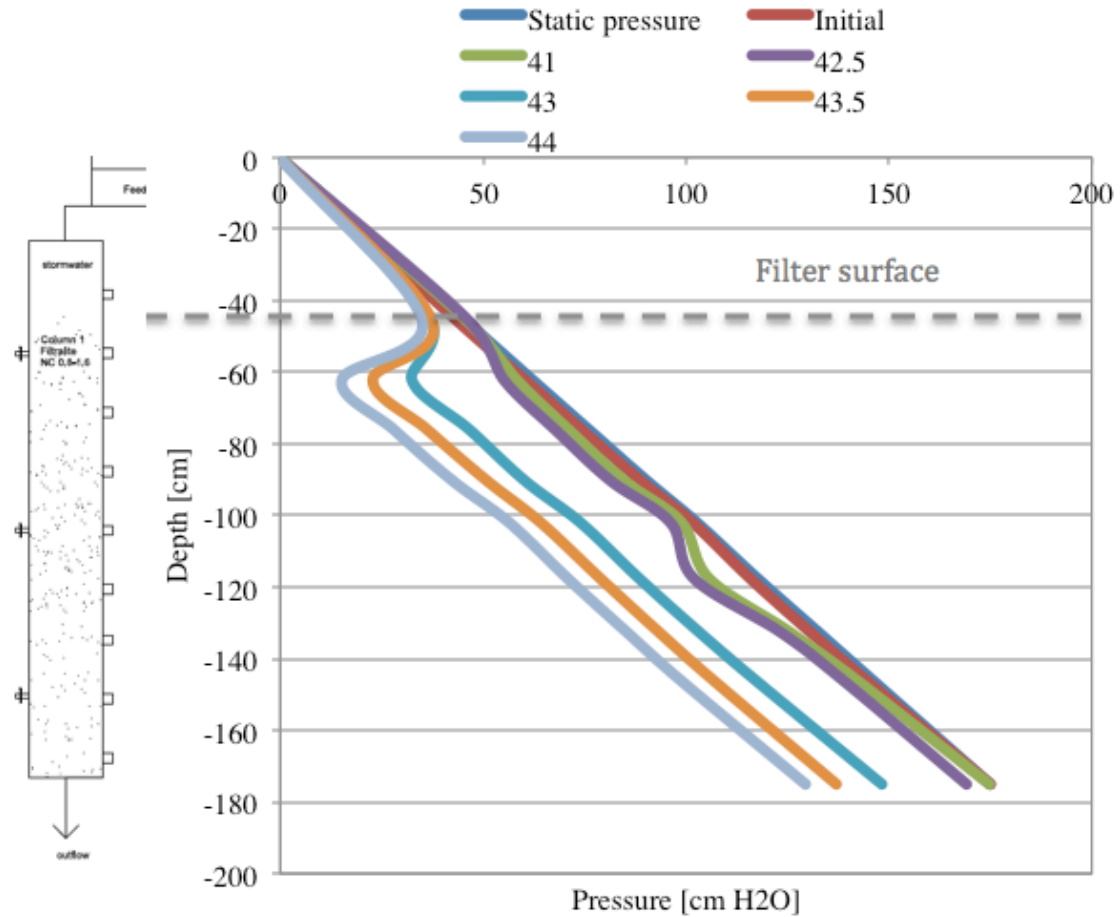


Figure 6-21. Pressure shown as days after start, column 1

Lifetime of the filter before clogging is found considering the total volume through the filter. The flow through the filter for the first 39 days of the experiment was averaging approximately 4 ml/min. After the flow increase, the filter was operating for four days with the constant flow of 40 ml/min. This implies a volume of 0.345 m<sup>3</sup> for the period before clogging, which gives 30 m water per area into the filter. Considering the water quality volume of 0.5 m/year, the lifetime of the filter is 2 years. However, as will be discussed later, clogging is due to both suspended solids and bacteria growth. When installing a grass strip in front of the filter, most suspended solids will settle in the grass strip before entering the filter, which gives a higher lifetime of the filter.



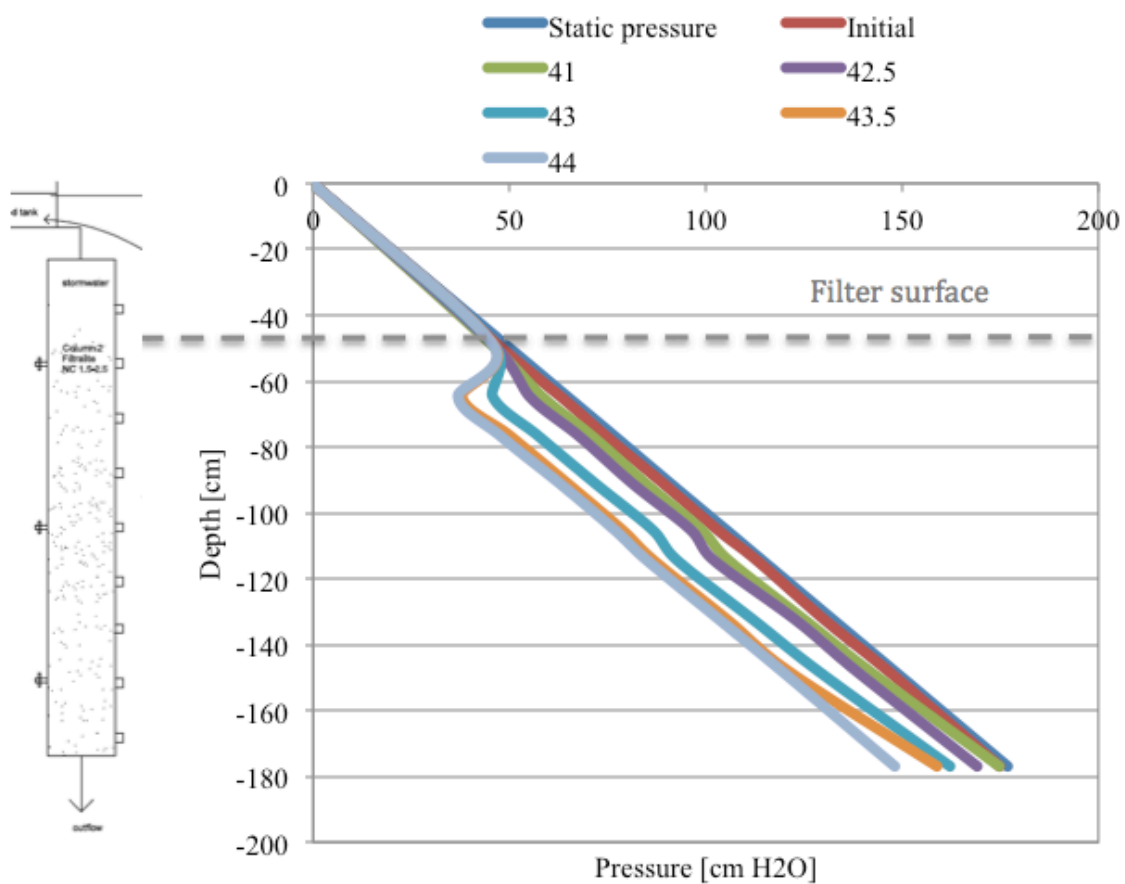


Figure 6-22: Pressure shown as days after start, column 2

Clogging in column 2 is seen after the same period in column 1, as shown in Figure 6-22. Due to the slower decrease in flow for column 2 in the first three phases, the volume through the column at this time is  $0.403\text{m}^3$ , which gives 35 m of water per area. This is in the same range as for column 1, and imply a lifetime of approximately 2 years.

Clogging tendencies are larger for column 1 compared to column 2. The media in column 1 is Filtralite NC 0.8-1.6, while the media in column 2 is Filtralite NC 1.5-2.5. The media in column 2 consist of larger grains, hence it has a larger filtration capacity and shows less clogging tendencies.

## **6.10 Discussion, column study**

### **6.10.1 Stabilisation of biofilter**

The stabilisation time for the biofilm needs to be considered. Crittenden et al. (2012) state that a steady state biological performance is reached after a maximum period of 1-2 months for a drinking water filter. As seen from the DOC measurements from the first phase, the filter was considered as stable after around 16 days. It was observed that the degradation of the chemicals was stabilized. This indicates that acclimatization time might not be that long, considering the de-icing chemicals are readily degradable. Compared to a filter used for drinking water treatment, the concentration of chemicals is much higher for this type of study. It was therefore decided to change conditions in the filter, and add nutrients to obtain a more favourable C:N:P ratio. When this was done, change in the degradation was immediately shown, however a stable condition was not obtained for phase two, before conditions were changed again. One of the reasons for changing the conditions is that the degradation of de-icing chemicals can be considered low compared to other studies e.g. (Bielefeldt et al., 2002).

### **6.10.2 Removal of de-icing chemicals**

For the initial conditions of the column experiment it was shown that the de-icing chemicals were removed by 20% in column 1 and 15% in column 2 in the upper 15 cm. This is considered as a low rate of removal, which is why the C:N:P ratio was changed. Bielefeldt et al. (2002) investigated the removal of propylene glycol in sand filter, which showed a removal of 99% for all the conditions tested in the experiment. Comparing this result with the degradation in the columns with Filtralite media, it does not show good removal for the initial period. A reason for this is probably that the sand was mixed with grown bacteria for the experiment from Bielefeldt et al. (2002). This was not done in the lab experiment performed for this thesis, thus the obtained results are not necessary low considering the conditions for the experiment.

After the C:N:P ratio was changed, indications of improved removal was shown for both media. Due to the lag time between DOC measurements and DOC results obtained from the analytical lab, conditions were changed before stable conditions were obtained. Overall, the removal after the nutrients addition was improved. Other studies have shown better removal after nutrient addition with comparable ratio as used for this study, e.g. (Bielefeldt et al.

2002). It is therefore unexpected not to have a much better removal with nutrient addition. However, this might be linked to the bacteria content in the soil.

Iwasaki modelling is determining the filtration coefficient. As seen in Figure 6-18 and Figure 6-19, the filtration coefficients are increasing after nutrient addition in both columns. It is also observed that the filtration coefficients are decreasing with depth, which is in line with literature. Literature reports that filtration the coefficient was decreasing with volume, which is related to depth in the column study (Rebhun et al., 1984).

As already stated, de-icing chemicals are naturally degradable in soil. It cannot be determined how much better a solution with Filtralite media is compared to a natural soil, however an engineered biofilter is considered a better option than natural degradation in soil. As well, Filtralite media has shown a longer operational time between backwashes compared to a sand filter for drinking water and wastewater treatment. This will probably give a longer lifetime for an application for stormwater treatment with these media compared to sand filtration or naturally degradation in soil.

### **6.10.3 Limiting nutrients**

The initial degradation is considered as low, but stable. It was therefore decided to add nutrients. After adding phosphorous for the second phase of the test, results showed improvement, however stable conditions were not obtained. Even better removal was found when increasing the phosphorous and nitrogen concentration. However, the removal rate decreased to a surprise. Oxygen was not monitored and might be a limiting factor, however this cannot be confirmed.

It is seen that the performance is increasing when adding the nutrients nitrogen and phosphorous. Adding nutrients to the filter media should be considered when designing the filter for the application of treating stormwater from airport. It might also be necessary to add nutrients after a certain period of time. Costs and monitoring of nutrients should be considered when designing the filter, however this is not investigated in this thesis.

#### **6.10.4 Bacteria in column test**

Soil from the area at Valgrinda, NTNU was mixed with the synthetic stormwater. There are bacteria in the soil, however the bacteria fed into the filter with the synthetic stormwater will be lower than a grown bacteria culture pre-fed in the filter. In the study performed by Bielefeldt et al. (2002), a bacteria culture that can specifically degrade propylene glycol was taken from the Denver International Airport. It was grown before it was mixed with the media and entered in the columns, in a column study of sand and gravel. As seen from the ATP measurements in the column experiment conducted for this thesis, the ATP is considered low. This might be a reason for the relatively lower degradation (50%) compared to the study of Bielefeldt et al. (2002) (98%). However, if the filter is installed for a field application, the bacteria will most probably be more natural, compared to the Bielefeldt et al. (2002) study. Conditions might be more similar to what was used in this thesis. However, it might be possible to pre-seed the media with bacteria to some extent to improve the degradation in the Filtralite media.

As seen in for all the ATP measurements Figure 6-13 and Figure 6-20, it is clearly seen that concentration was observed to decrease with depth. This is in line with literature, where it is stated that ATP concentrations usually decrease with depth (Vandevivere and Baveye, 1992). In an active, acclimated drinking water biofilter the ATP typically ranges from  $10^2$  to  $10^3$  ng ATP/cm<sup>3</sup> media. Some studies show a typical ATP concentration of 600 ng ATP/cm<sup>3</sup> media for the top 15 cm of the filter (Pharand et al., 2014).

When transferring the measured values for the ATP to the comparable study by Pharand et al. (2014), it is observed that values obtained in the experiment are low. As an example, ATP in the tank after ~16 days was found to 0.22 ng ATP/cm<sup>3</sup>, which is much lower than the average 600 ng ATP/cm<sup>3</sup> media reported by Pharand et al. (2014). However, the comparison values are from drinking water biofilter. As results show low ATP in the media, it is still shown degradation of chemicals in the media.

#### **6.10.5 Temperature in biofilter**

Temperature in the biofilter at the inflow was measured to ~ 10°C in the three first phases with the small feed tank. The temperature in the end of the columns was 20°C due to the heat exchange with the room where the columns were stored. Temperatures are low in the winter

and in early spring, but will rise in the summer, where degradation of de-icing chemicals will continue if the stormwater has not passed through the filter or soil and into the groundwater. A temperature around 10°C is therefore considered realistic for the experiment.

The degradation is shown at the top of the filter, and is dependent on temperature. The temperature is increasing with depth, however the degradation in the filter dependent on the temperature change is neglected.

Considering the future climate change with warmer temperatures in the summers, it can also be evaluated if the degradation in the soil will be higher during the summers than what is the fact in the column tests. As previously mentioned, the degradation will continue in the summer when temperatures are high and favourable for chemicals degradation (French et al., 2001). Another concern is that the amount of de-icing chemicals might be too high compared to the available nutrients and oxygen in the soil. It is therefore interesting to investigate and optimize a biofilter.

#### **6.10.6 Flow**

The flow was supposed to be constant during the experiment to look at the pressure change for the media, however the flow decreased significantly for both columns. This was especially observed for column 1 at the first three parts of the experiment (low flow). This is increasing the EBCT of the stormwater in the filter, hence also the relative result obtained. If it is assumed that the flow is linearly decreasing with time, and reaching approximately 0 ml/min after a day, the average flow through the filter will be half of the start flow. If the flow is adjusted to 7 ml/min, the average will be around 4 ml/min. This leads to a flow of around 0.5 m/day in the columns. In turn this flow for 30 days represents the flow for a year for a real application, when considering the precipitation pattern found at Værnes Airport, Trondheim.

The flow was again adjusted for the fourth part of the experiment. Pumps were installed for suction to keep the flow constant at 40 ml/day. With this flow, one year for the real application is simulated with 3 days of column test operation. As seen from the measurements, the pressure is reduced when increasing the flow. This is most probable due to

the suspended solids that block the pores. If the application from section 7.2.3 is used, a strip of grass will most probably make most of the particles settle, before entering the filter.

Although the filter show an estimated lifetime of 2 years for the solution proposed, it is important to consider locally adaptation to the climate where the biofilter is implemented. Yearly precipitation patterns varies through the country, hence the expected lifetime of this filter calculated for the Trondheim region will vary from what can be calculated for Oslo region. As well, the lifetime depends on the size of the catchment as well as the size of the infiltration facility.

#### **6.10.7 Flow comparison in the two filters**

The two filters in general operated similarly, which is expected due the similarities between the filter media. As stated, the only difference is the grain size. Column 2 with Filtralite NC 1.5-2.5 showed a larger capacity of infiltrating the water, which is logical since the fraction is highest. Column 1 with Filtralite NC 0.8-1.6 showed in general slightly better removal. This might be due to the longer contact time between the stormwater and the media due to the decrease of flow every day during the first three phases. This indicates that Filtralite NC 1.5-2.5 has better infiltration capacity, which is important when designing the filter. Trend for the flow is shown in Figure 6-23, as data points collected after the flow decrease that occurred naturally during the night. Both outlets were adjusted to 7 ml/min every morning.

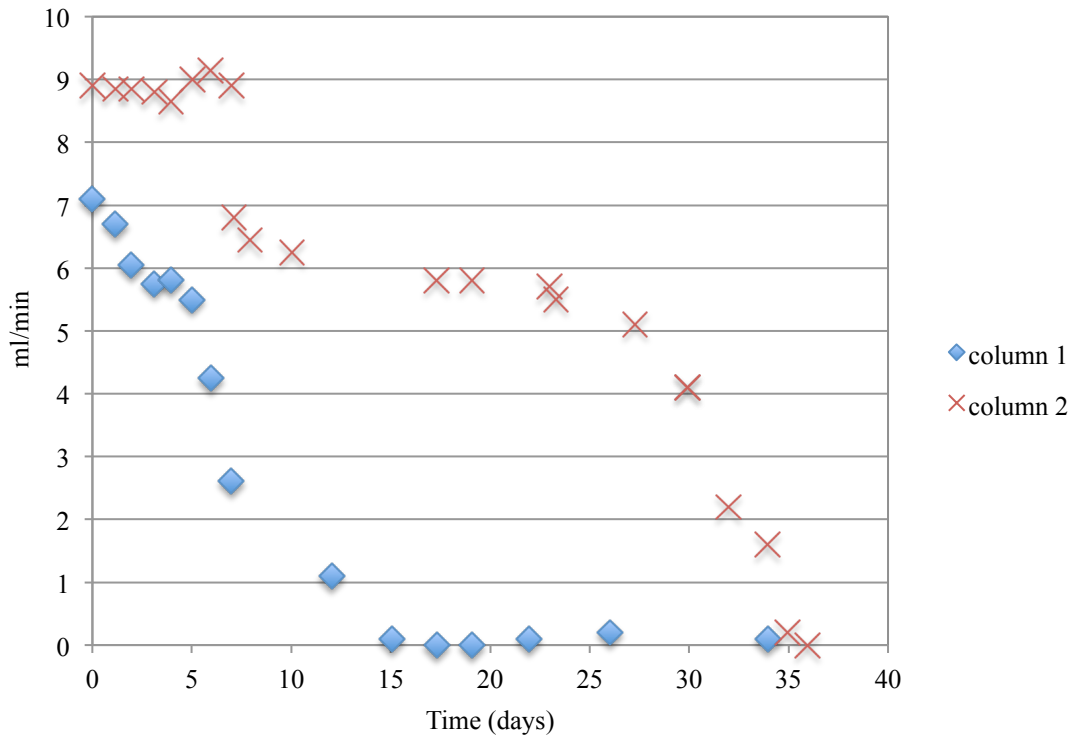


Figure 6-23: Trend, flow

### 6.10.8 Time and depth of clogging

As seen from the pressure monitoring, clogging will occur on top of the filter. As mentioned, the suspended solids and the bacteria are the reasons for clogging, and are contributing to pressure loss in the columns. The column study by Bielefeldt et al. (2002) found a high pressure loss where the biomass concentration was high. The results obtained in the study is thus in line with literature. The data represents that changes will occur to the top of the filter. This is also in line with the DOC removal from the first phase of the experiment. There was only seen a significant change at the top of the filter, in this case the first ~15 cm. This means that the filter depth does not necessary need to be very deep.

Clogging is also occurring due to particle settlement in the filter. Most of the particles coming from overland flow, will probably settle on the strip between the runway and the filter. A negative pressure indicates that the filter is clogged and should be changed. As observed from the pressure monitoring, both filters clog after 43 days of column study. Synthetic stormwater for the first three phases contained about 50 mg SS/l, and the fourth phase 25 mg SS/l. Considering the volume through the columns, total amount of sediments

into the filter is thus approximately 1.5 kg SS/l for both columns. As reported in literature, clogging will occur with accumulation of 1.2-5 kg/m<sup>2</sup> of sediment per filter area. Hence, the time of the clogging is logical based on the amount of SS added. In an attempt of backwashing the media to investigate the recovery, it was clearly visual that there was a compact layer on top of the filter, which indicates the filter cake. Unfortunately backwashing was impossible due to leaking in the columns due to the high pressure when backwashing, as well as low capacity of the pumps.

It has been considered that the sediment load might have been high, however necessary due to the need of bacteria addition via sediments in the stormwater.

#### **6.10.9 Preferred filter media**

As seen, the two filter media perform similarly, as expected. Filtralite NC 1.5-2.5 has a higher filtration capacity, and almost the same removal efficiency as the Filtralite NC 0.8-1.6 media. Filtralite NC 1.5-2.5 has a larger filtration capacity, compared to the Filtralite NC 0.8-1.6. Filtralite NC 0.8-1.6 shows a slightly better and more stable removal capacity through the whole experiment, probably due to the relatively longer contact time due to the decrease in flow through the experiment. However, a deeper filter of a Filtralite NC 1.5-2.5 media might be able to show the same removal as the Filtralite NC 0.8-1.6. In addition, column 1 clogs faster than column 2. Hence Filtralite NC 1.5-2.5 is considered as the preferred media of these two, however more investigations should be done to verify this statement.

Unfortunately, sand filters were not tested in this thesis to be able to compare the Filtralite media. In wastewater and drinking water treatment, Filtralite media has shown to have a much larger capacity compared to a sand filter. This is due to the large surface area of the media, which leads to longer periods between backwashes. For an application of stormwater treatment, this could mean longer lifetime of a Filtralite media compared to a sand filter. Larger surface area theoretically means a larger biofilm area, which in turn will result in a higher degradation rate, compared to a sand filter.



## **7 Application of results**

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There are various options for a set up with a biofilter. The best option for a system is dependent of where the surface water is coming from, if it is from a road or an airport, as well as the local precipitation pattern. The runways and taxiways at airports are flat, therefore it can be difficult to implement a swale, due to the need for a certain longitudinal slope. At airports, ponding of water is prohibited, due to potential wildlife attraction (WSDOT, 2008). This means that the option implemented needs the hydraulic capacity to handle the runoff, as well as the capacity to treat the water.

### **7.1 Strips**

Strips are surfaces where the water flows in a thin sheet flow. They are often vegetated with turf grasses (Water Environment Federation, 2012). Strips are often used upstream filters to pre-treat the flow. The primary purpose of a filter strip is to remove sediments and other pollutants coming directly from the pavement (WSDOT, 2008). Requirements for filter strips are that the water flows in a sheet flow, to prevent channelization of water and erosion. For this reason, filter strips are not a good solution in steep slopes, but due to the flat topography at airports, a filter strip can be considered as a good option.

If the filters are installed with a strip of grass in front, it is very likely that the suspended solids from the pavement will be trapped before entering the filter. Related to the column experiment performed in this thesis, it might lead to a higher lifetime of the filter than observed, due to lower amounts of sediments infiltrating to the filter.

### **7.2 Biofiltration set up**

#### **7.2.1 Media in biofiltration system**

A biofiltration system can consist of monolayer, dual layer or mixed layer. The focus in this thesis is Filtralite media of different fractions, which can be mixed, or mixed with other types of media like sand. Filtralite NC 0.8-1.6 and Filtralite 1.5-2.5 were tested as monolayer media, and they show interesting results for the application.

As the adsorption experiments done in this thesis shows, there is little to no adsorption onto the Filtralite media in general. This finding was done by Persson et al. (2002) as well. This results in the assumption that all the degradation in the filter is due to biodegradation and adsorption is neglected.

Persson et al. (2006) found that a combination of Filtralite NC 0.8-1.6 and GAC can be used in an application where the Filtralite is the carrier medium and the GAC is adsorbing some of the chemicals. Filtralite can be the carrier medium where the biological degradation will occur, and degradation can continue during summer when temperatures are high. Persson et al. (2006) found that GAC could be added for robustness to the removal process.

Andersen (2016) found that a layer of GAC on top of the filter showed some adsorption of de-icing chemicals onto the GAC. As found from the batch experiment, the adsorption is not significant. It was shown greater clogging tendencies in the columns tested with a GAC layer on top, in the study by Andersen (2016). Clogging is decreasing the capacity and lifetime of the filter. The biofiltration capacity in Filtralite is larger than the adsorption capacity of GAC, hence it is not recommended with GAC for this application.

As seen from the experimental data, maximum removal after nutrient addition shows around 50% removal for both media. Compared to the study by Bielefeldt et al. (2002), 98% removal of propylene glycol was found in sand filter. However, the sandy media was mixed with a grown bacterial culture prior to the experiment start in the experiment by Bielefeldt et al. (2002). The removal of de-icing chemicals in the experiments conducted in this thesis has mimicked natural conditions compared to the study of Bielefeldt et al. (2002). Therefore, a removal rate of 50% for the Filtralite media tested does not necessarily give a lower performance than a sand filter, if the same conditions are applied. Filtralite media is in general performing better than sand filters with longer operational time between backwashes for drinking- and wastewater treatment.

Filtralite NC 1.5-2.5 has better infiltration capacity compared to Filtralite NC 0.8-1.6. The degradation of de-icing chemicals can be considered similar for both media. The preferred media for the application is therefore Filtralite NC 1.5-2.5 of the two media tested. There are more fractions to be tested at a later stage in the work package in the Klima2050 project,

therefore it is a possibility that another fraction of Filtralite media will perform better than the ones investigated in this experiment.

Pressure monitoring of the filter shows that the filter clogged around the first 15 cm of the filter for both media. As well as the ANOVA analysis states, the filter is removing most of the chemicals after port one, which is the sampling port around 15 cm depth. This also illustrates that the filter does not need to be very deep. However, the degradation will most probably continue in the filter during the summer, when temperatures are higher than during the melt period. To be able to retain the water in the filter, it needs to have a certain depth to hold the stormwater. If a drain is installed, it needs to be calculated how much chemicals is degraded in the filter, and what concentration the filtered stormwater has when the drained water is reaching a receiving water

### **7.2.2 Biofilter at airport**

The runway on Værnes airport is 45 m wide, taxiways are 23 m wide and both have 7.5 m shoulders on each side. For the runway, the total width will be 60 m, and for taxiways, the width will be 38 m. As an example, a filter can be located at the edges of the runways and taxiways. If a filter of one meter width is placed on both sides along the runway, the drainage area into the filter will be 30 times the filter area of one meter, defining the hydraulic loading rate and degradation potential. The taxiways and runways are designed with a crown point along the centerline, which will lead the stormwater to both sides of the runway. A filter on both sides of the runway or taxiway can therefore be considered, and both sides will take approximately the same amount of stormwater.

### **7.2.3 Filter with underdrain**

An underdrain for the filter can be installed, if the filter and soil does not have the capacity to infiltrate the desired volume of water. The drained water thus have to have a sufficiently low chemicals concentration if the drain is leading into the nature. As an example, standard media filter drain (MFD) has four basic components: a gravel no-vegetation zone, a grass strip, the FD mix bed and a conveyance system for flows leaving the MFD mix (WSDOT, 2008). An example section is shown in Figure 7-1.

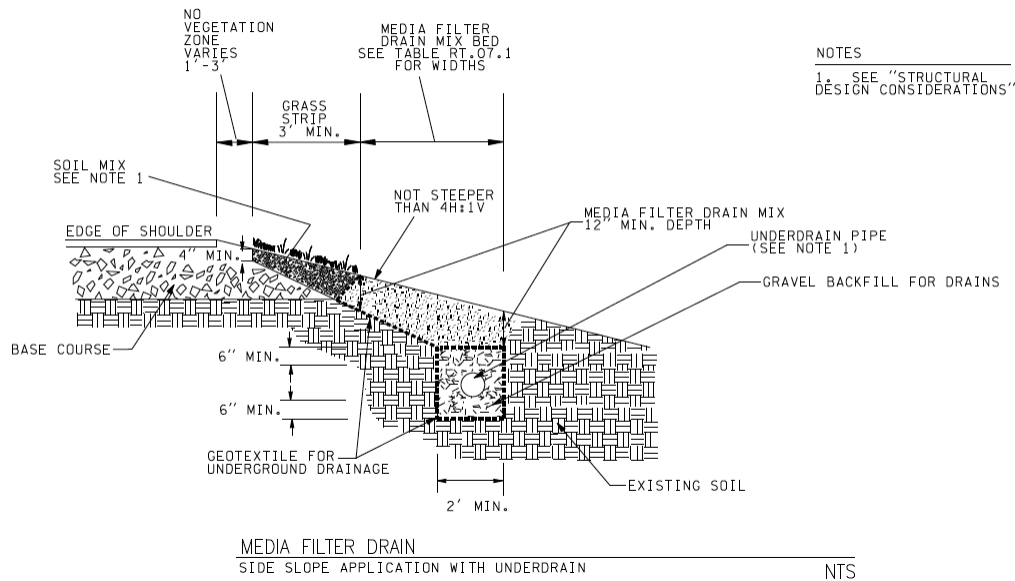


Figure 7-1: Example of media filter drain (WSDOT, 2008)

## 7.2.4 Boxes application

A filter can be installed as boxes or bags with filter media. For an application like this, the bags or boxes can easily be changed when maintenance is needed. The width of the filter is flexible and can be calculated based on the amount of water that needs to be handled from the designing precipitation event, as well as the necessary degradation capacity dependent on the removal rate in the filter. The boxes or bags can be placed after the grass strip, and can be flushed with the existing soil.

## 7.2.5 Erosion protection

The filter media consists of smaller grains that can be transported with wind and weather. A grass layer is commonly used to protect the filter from erosion from heavy rainfalls and extreme weather. A grass layer requires a 10 cm of soil on top of the filter to grow. Maintenance of the filter is needed, and the filter is replaced after a certain period. When the filter is changed, the topsoil needs to be removed. This operation needs to be considered. If grass is chosen as the erosion protection, the vegetation needs to be chosen dependent on local conditions.

Another option to a grass layer is to use a geo-textile layer at the top, which will secure the filter from weather. It is also possible to have a larger media like rocks as erosion protection. These options are easier to handle when the filter needs to be maintained.

### **7.2.6 Operation and maintenance**

In some filtration systems there are possibilities to backwash the filter, but in applications like these examples, the filter needs to be changed. Usually it is sufficient to change the upper few centimetres of the filter. This depends if the filter is a monolayer filter, dual layer filter or mixed. If an application with boxes is installed, the boxes can be replaced during maintenance. How often the filter needs to be changed or maintained depends on the properties of the filter as well as the properties of the stormwater.

As observed from the pressure monitoring in the filter (section 6.9.1), clogging occurs in the upper 15 cm. The lifetime for the filter, if installed as a one-meter filter at the side of the runway, is approximately 2 years for both Filtralite NC 0.8-1.6 and Filtralite NC 1.5-2.5.

As previously mentioned, the stormwater for the column test contained suspended solids. For a real application, a grass strip between the filter and the runway will probably settle most of the suspended solids before entering the filter. This will lead to a longer lifetime of the filter, because observations show that clogging is both due to bacteria growth as well as sediments trapped in the filter.

For a long time the surface water treatment applications have had a focus on being maintenance free. In the recent years, this focus has changed, due to that all applications needs maintenance. However, it is important to consider the maintenance cost and complexity of changing the filter when deciding which system to choose.

### **7.2.7 Limitations**

As mentioned, ponding water should be avoided due to the possible attraction of wildlife. The groundwater also needs to be taken into consideration. When implementing the filter, one has to be sure that the media filter and underdrain will not be saturated by ground water (WSDOT, 2008).



## 8 Conclusion

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Adsorption and biodegradation on de-icing chemicals have been examined by batch experiments and column experiment.

Batch experiments of adsorption of propylene glycol (PG) and potassium formate (PF) onto GAC resulted in Linear isotherm and pseudo-second-order kinetics as best-fit models in both cases. Evaluating the Freundlich isotherm, adsorption is favourable if  $n > 1$ . Results show  $n$  values close to 1 (PG 1.13 and PF 1.15), which indicate that de-icing chemicals are relatively weak for adsorption onto GAC. However, literature states that GAC in general has shown to be effective for removal of many pollutants. Propylene glycol can be classified as semi-polar molecule, which might be an explanation for the relatively low adsorption found. When evaluating extra robustness possibilities of a biodegradation system with a layer of GAC, conclusions show that a GAC layer is not recommended due to the drawbacks of increased clogging when implemented. No adsorption onto Filtralite NC 0-2 and Filtralite NC 0.8-1.6 was found, which is in line with observations from literature.

For the column experiment Filtralite NC 0.8-1.6 was tested in column 1, and Filtralite 1.5-2.5 was tested in column 2. Due to no adsorption onto Filtralite media shown in batch experiments, the degradation in the columns was considered biological degradation. Initial measurements of degradation in both columns were found to be relatively low (column 1: 20% removal, column 2: 15% removal at upper 15 cm). An ANOVA analysis shows a significant difference between the feed tank and the first sampling valve (upper 15 cm of the filter) in both columns. Clogging occurred at the top ~15 cm in both columns, probably both due to particle settlement and bacteria growth. This indicates that the filter does not necessarily need to be very deep.

After stabilising the initial conditions, nutrients were added. After phosphorous and nitrogen addition (C:N:P ratio 24:7:1), degradation was found to average 50% removal for both columns at all depths. Filtration coefficients were evaluated with Iwasaki model, and found to decrease with depth for both columns. Filtration coefficients increased after nutrient addition. Adenosine triphosphate (ATP) measurements were considered low, which compared to other studies, resulted in relatively low degradation in both columns. ATP was observed to

decrease with depth during the whole experiment, which is in line with literature. Pressure observations resulted in a lifetime of 2 years for both columns. Clogging occurred slightly earlier for column 1 compared to column 2, which might be linked to the media size. Sediment load was as shown relatively high for the experiment, which caused clogging after a relatively short period.

Compared to literature, the degradation in the columns was considered low. A study with a pre-grown bacteria culture in a sand filter, achieved a removal rate of 99% of propylene glycol. However, the bacteria culture used in the study strongly influence the degradation, and this does not necessarily mean that the degradation found in the column study in this thesis is low.

In conclusion, results show degradation in the filter, and theoretically, Filtralite media will perform better than sand filter, due to the high surface area in the media. Further investigations therefore need to be done, in order to optimize the biofilter to treat the stormwater from airports.



## 9 Further work

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As seen from the results, compared to other similar studies, the degradation is not considered very high. One option is to investigate the media performance with a grown bacteria culture for biofiltration, in a similar column study as performed for this thesis. As previously mentioned, it is a risk of low oxygen in the filter, which should be monitored. If this is done, it should be compared to a sand filter media or natural soil.

To improve the adsorption onto Filtralite, the properties of the media might be changed for better adsorption capacity. The affinity, which is the tendency of a molecule to associate with another, can be improved in order to increase the adsorption capacity of the media.

There are also more fractions of Filtralite media of larger grain size that might be tested. So far, Filtralite NC 0-2, NC 0.8-1.6 and NC 1.5-2.5 have been tested by Andersen (2016) and in this study. A study of Filtralite media compared to a sand filter with the same conditions would be of interest as well.

If Filtralite media show good removal and the best fraction can be determined, the goal is to install a pilot plant either at an airport or roadside to test the conditions full scale. All the column tests in the project, both by Andersen (2016) and myself, have been conducted with constant water pressure and wet conditions for the filters at all times. It is important to further investigate the dry-wet conditions, and how this affects the biodegradation.



## 10 References

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# Appendix

# **Appendix A**

**ANOVA analysis and t-test**



# One-Way ANOVA: TANK; sample port C1.1; sample port C1.2; sample port C1.3; outlet c1

---

## Method

Null hypothesis  $H_0$ : All means are equal  
Alternative hypothesis  $H_1$ : At least one mean is different

*Equal variances were assumed for the analysis.*

## Factor Information

Factor	Levels	Values
Factor	5	TANK; sample port C1.1; sample port C1.2; sample port C1.3; outlet c1

## Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	4	44,7782	11,1946	13,10	<0,0001
Error	45	38,4609	0,8547		
Total	49	83,2391			

## Model Summary

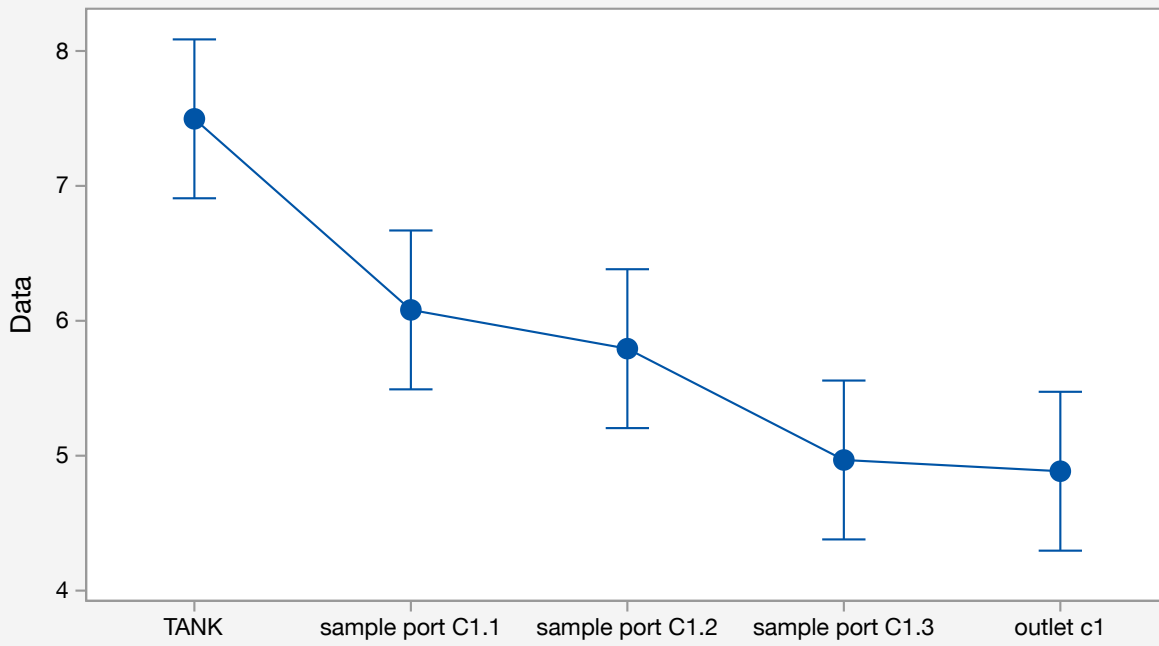
S	R-sq	R-sq(adj)	R-sq(pred)
0,924492	53,79%	49,69%	42,96%

## Means

Factor	N	Mean	StDev	95% CI
TANK	10	7,4970	0,8880	(6,9082; 8,0859)
sample port C1.1	10	6,0807	0,6915	(5,4919; 6,6695)
sample port C1.2	10	5,7934	0,7156	(5,2046; 6,3823)
sample port C1.3	10	4,9683	1,4226	(4,3795; 5,5571)
outlet c1	10	4,8849	0,6863	(4,2961; 5,4738)

*Pooled StDev = 0,924492*

Interval Plot of TANK; sample port C1.1; sample port C1.2; sample ...  
95% CI for the Mean



*The pooled standard deviation was used to calculate the intervals.*

# One-Way ANOVA: TANK\_1; sample port c2.1; sample port c2.2; sample port c2.3; outlet c2

---

## Method

Null hypothesis  $H_0$ : All means are equal  
Alternative hypothesis  $H_1$ : At least one mean is different

*Equal variances were assumed for the analysis.*

## Factor Information

Factor	Levels	Values
Factor	5	TANK_1; sample port c2.1; sample port c2.2; sample port c2.3; outlet c2

## Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	4	22,1663	5,54159	10,09	<0,0001
Error	45	24,7083	0,54907		
Total	49	46,8746			

## Model Summary

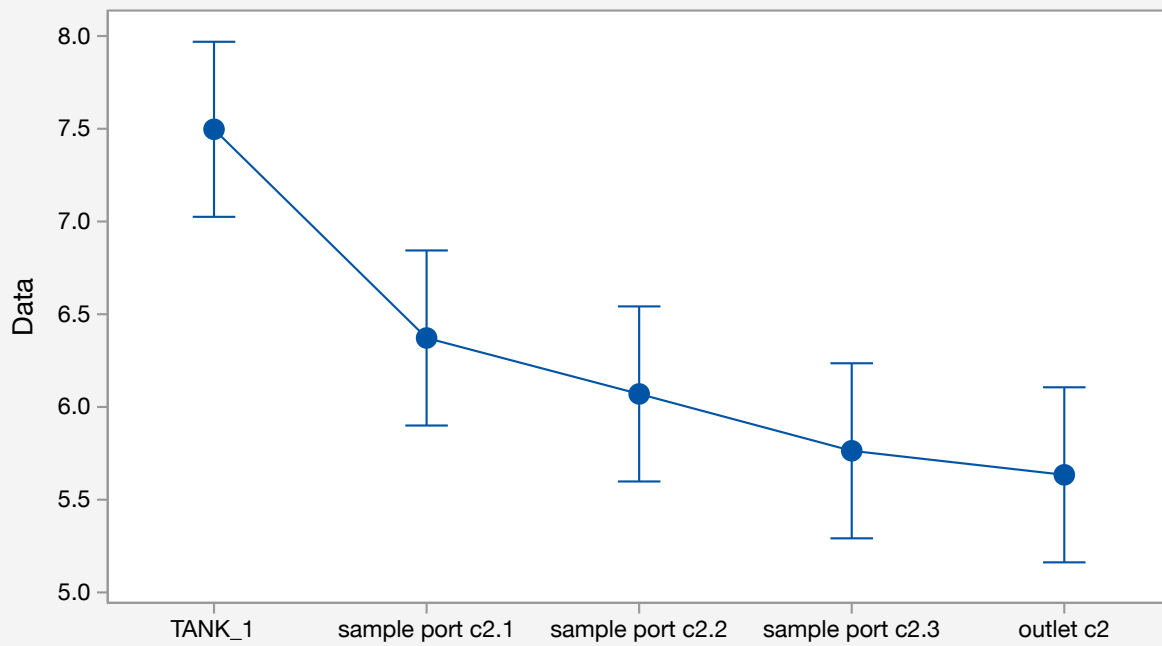
S	R-sq	R-sq(adj)	R-sq(pred)
0,740995	47,29%	42,60%	34,92%

## Means

Factor	N	Mean	StDev	95% CI
TANK_1	10	7,4970	0,8880	(7,0251; 7,9690)
sample port c2.1	10	6,3719	0,6012	(5,8999; 6,8438)
sample port c2.2	10	6,0702	0,8353	(5,5983; 6,5422)
sample port c2.3	10	5,7636	0,6342	(5,2917; 6,2356)
outlet c2	10	5,6341	0,7039	(5,1622; 6,1061)

*Pooled StDev = 0,740995*

Interval Plot of TANK\_1; sample port c2.1; sample port c2.2; sample ...  
95% CI for the Mean



*The pooled standard deviation was used to calculate the intervals.*

## 2-Sample t: TANK; sample port C1.1

---

### Method

$\mu_1$ : mean of TANK

$\mu_2$ : mean of sample port C1.1

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
TANK	10	7,4970	0,8880	0,2808
sample port C1.1	10	6,0807	0,6915	0,2187

### Estimation for Difference

Difference	95% CI for Difference
1,4163	(0,6619; 2,1708)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
3,98	16	0,0011

## 2-Sample t: TANK; sample port C1.2

---

### Method

$\mu_1$ : mean of TANK

$\mu_2$ : mean of sample port C1.2

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
TANK	10	7,4970	0,8880	0,2808
sample port C1.2	10	5,7934	0,7156	0,2263

### Estimation for Difference

Difference	95% CI for Difference
1,7036	(0,9427; 2,4645)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
4,72	17	0,0002

## 2-Sample t: TANK; sample port C1.3

---

### Method

$\mu_1$ : mean of TANK

$\mu_2$ : mean of sample port C1.3

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
TANK	10	7,4970	0,8880	0,2808
sample port C1.3	10	4,9683	1,4226	0,4499

### Estimation for Difference

Difference	95% CI for Difference
2,5288	(1,3984; 3,6591)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
4,77	15	0,0002

## 2-Sample t: TANK; outlet c1

---

### Method

$\mu_1$ : mean of TANK

$\mu_2$ : mean of outlet c1

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
TANK	10	7,4970	0,8880	0,2808
outlet c1	10	4,8849	0,6863	0,2170

### Estimation for Difference

Difference	95% CI for Difference
2,6121	(1,8598; 3,3644)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
7,36	16	<0,0001



## 2-Sample t: sample port C1.1; sample port C1.2

---

### Method

$\mu_1$ : mean of sample port C1.1

$\mu_2$ : mean of sample port C1.2

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
sample port C1.1	10	6,0807	0,6915	0,2187
sample port C1.2	10	5,7934	0,7156	0,2263

### Estimation for Difference

Difference	95% CI for Difference
0,2873	(-0,3766; 0,9512)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
0,91	17	0,3741

## 2-Sample t: sample port C1.1; sample port C1.3

---

### Method

$\mu_1$ : mean of sample port C1.1

$\mu_2$ : mean of sample port C1.3

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
sample port C1.1	10	6,0807	0,6915	0,2187
sample port C1.3	10	4,9683	1,4226	0,4499

### Estimation for Difference

Difference	95% CI for Difference
1,1124	(0,0318; 2,1930)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
2,22	13	0,0445

## 2-Sample t: sample port C1.1; outlet c1

---

### Method

$\mu_1$ : mean of sample port C1.1

$\mu_2$ : mean of outlet c1

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
sample port C1.1	10	6,0807	0,6915	0,2187
outlet c1	10	4,8849	0,6863	0,2170

### Estimation for Difference

Difference	95% CI for Difference
1,1958	(0,5458; 1,8458)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
3,88	17	0,0012

## 2-Sample t: sample port C1.2; sample port C1.3

---

### Method

$\mu_1$ : mean of sample port C1.2

$\mu_2$ : mean of sample port C1.3

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
sample port C1.2	10	5,7934	0,7156	0,2263
sample port C1.3	10	4,9683	1,4226	0,4499

### Estimation for Difference

Difference	95% CI for Difference
0,8252	(-0,2627; 1,9130)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
1,64	13	0,1253

## 2-Sample t: sample port C1.2; outlet c1

---

### Method

$\mu_1$ : mean of sample port C1.2

$\mu_2$ : mean of outlet c1

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
sample port C1.2	10	5,7934	0,7156	0,2263
outlet c1	10	4,8849	0,6863	0,2170

### Estimation for Difference

Difference	95% CI for Difference
0,9085	(0,2470; 1,5700)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
2,90	17	0,0100

## 2-Sample t: sample port C1.3; outlet c1

---

### Method

$\mu_1$ : mean of sample port C1.3

$\mu_2$ : mean of outlet c1

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
sample port C1.3	10	4,9683	1,4226	0,4499
outlet c1	10	4,8849	0,6863	0,2170

### Estimation for Difference

Difference	95% CI for Difference
0,0834	(-1,0049; 1,1716)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
0,17	12	0,8702

## 2-Sample t: TANK\_1; sample port c2.1

---

### Method

$\mu_1$ : mean of TANK\_1

$\mu_2$ : mean of sample port c2.1

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
TANK_1	10	7,4970	0,8880	0,2808
sample port c2.1	10	6,3719	0,6012	0,1901

### Estimation for Difference

Difference	95% CI for Difference
1,1252	(0,4023; 1,8480)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
3,32	15	0,0047

## 2-Sample t: TANK\_1; sample port c2.2

---

### Method

$\mu_1$ : mean of TANK\_1

$\mu_2$ : mean of sample port c2.2

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
TANK_1	10	7,4970	0,8880	0,2808
sample port c2.2	10	6,0702	0,8353	0,2642

### Estimation for Difference

Difference	95% CI for Difference
1,4268	(0,6134; 2,2402)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
3,70	17	0,0018



## 2-Sample t: TANK\_1; sample port c2.3

---

### Method

$\mu_1$ : mean of TANK\_1

$\mu_2$ : mean of sample port c2.3

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
TANK_1	10	7,4970	0,8880	0,2808
sample port c2.3	10	5,7636	0,6342	0,2006

### Estimation for Difference

Difference	95% CI for Difference
1,7334	(1,0019; 2,4649)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
5,02	16	0,0001

## 2-Sample t: TANK\_1; outlet c2

---

### Method

$\mu_1$ : mean of TANK\_1

$\mu_2$ : mean of outlet c2

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
TANK_1	10	7,4970	0,8880	0,2808
outlet c2	10	5,6341	0,7039	0,2226

### Estimation for Difference

Difference	95% CI for Difference
1,8629	(1,1069; 2,6189)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
5,20	17	<0,0001

## 2-Sample t: sample port c2.1; sample port c2.2

---

### Method

$\mu_1$ : mean of sample port c2.1

$\mu_2$ : mean of sample port c2.2

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
sample port c2.1	10	6,3719	0,6012	0,1901
sample port c2.2	10	6,0702	0,8353	0,2642

### Estimation for Difference

Difference	95% CI for Difference
0,3017	(-0,3883; 0,9916)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
0,93	16	0,3677

## 2-Sample t: sample port c2.1; sample port c2.3

---

### Method

$\mu_1$ : mean of sample port c2.1

$\mu_2$ : mean of sample port c2.3

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
sample port c2.1	10	6,3719	0,6012	0,1901
sample port c2.3	10	5,7636	0,6342	0,2006

### Estimation for Difference

Difference	95% CI for Difference
0,6083	(0,0252; 1,1913)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
2,20	17	0,0418

## 2-Sample t: sample port c2.1; outlet c2

---

### Method

$\mu_1$ : mean of sample port c2.1

$\mu_2$ : mean of outlet c2

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
sample port c2.1	10	6,3719	0,6012	0,1901
outlet c2	10	5,6341	0,7039	0,2226

### Estimation for Difference

Difference	95% CI for Difference
0,7378	(0,1202; 1,3554)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
2,52	17	0,0220

## 2-Sample t: sample port c2.2; sample port c2.3

---

### Method

$\mu_1$ : mean of sample port c2.2

$\mu_2$ : mean of sample port c2.3

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
sample port c2.2	10	6,0702	0,8353	0,2642
sample port c2.3	10	5,7636	0,6342	0,2006

### Estimation for Difference

Difference	95% CI for Difference
0,3066	(-0,3965; 1,0097)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
0,92	16	0,3690

## 2-Sample t: sample port c2.2; outlet c2

---

### Method

$\mu_1$ : mean of sample port c2.2

$\mu_2$ : mean of outlet c2

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
sample port c2.2	10	6,0702	0,8353	0,2642
outlet c2	10	5,6341	0,7039	0,2226

### Estimation for Difference

Difference	95% CI for Difference
0,4361	(-0,2927; 1,1649)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
1,26	17	0,2238

## 2-Sample t: sample port c2.3; outlet c2

---

### Method

$\mu_1$ : mean of sample port c2.3

$\mu_2$ : mean of outlet c2

Difference:  $\mu_1 - \mu_2$

*Equal variances are not assumed for this analysis.*

### Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
sample port c2.3	10	5,7636	0,6342	0,2006
outlet c2	10	5,6341	0,7039	0,2226

### Estimation for Difference

Difference	95% CI for Difference
0,1295	(-0,5026; 0,7616)

### Test

Null hypothesis  $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis  $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
0,43	17	0,6710



## **Appendix B**

**Analysis of soil at Værnes Airport, Trondheim (Norway) by Eurofins**

SINTEF UTVIKLING AS  
Kløbuvn 153  
7465 Trondheim  
Attn: **Gema Sakti Raspati**

**Eurofins Environment Testing Norway  
AS (Moss)**  
F. reg. 965 141 618 MVA  
Møllebakken 50  
NO-1538 Moss

Tlf: +47 69 00 52 00  
Fax: +47 69 27 23 40

**AR-15-MM-021589-01**



**EUNOMO-00129397**

Prøvemottak: 30.11.2015  
Temperatur:  
Analyseperiode: 30.11.2015-07.12.2015  
Referanse: KLIMA2050

## ANALYSERAPPORT

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Tegnforklaring:

\* Ikke omfattet av akkrediteringen      LOQ: Kvantifiseringsgrense      MU: Måleusikkerhet  
<: Mindre enn      >: Større enn      nd: Ikke påvist

Opplysninger om måleusikkerhet fås ved henvendelse til laboratoriet.

Rapporten må ikke gjengis, unntatt i sin helhet, uten laboratoriets skriftlige godkjenning. Resultatene gjelder kun for de(n) undersøkte prøven(e).



Prøvenr.:	<b>439-2015-11300030</b>	Prøvetakingsdato:	20.11.2015
Prøvetype:	Jord	Prøvetaker:	Oppdragsgiver
Prøvemerkning:	1 - Soil Værnes	Analysestartdato:	30.11.2015
Analyse	Resultat	Enhet	LOQ MU Metode
a) Arsen (As)	3.5	mg/kg TS	0.5 30% NS EN ISO 17294-2
a) Bly (Pb)	6.1	mg/kg TS	0.5 40% NS EN ISO 17294-2
a) Kadmium (Cd)	0.15	mg/kg TS	0.01 25% NS EN ISO 17294-2
a) Kobber (Cu)	82	mg/kg TS	0.5 30% NS EN ISO 11885
a) Krom (Cr)	20	mg/kg TS	0.3 30% NS EN ISO 11885
a) Kvikksølv (Hg)	0.002	mg/kg TS	0.001 20% NS-EN ISO 12846
a) Nikkel (Ni)	17	mg/kg TS	0.5 30% NS EN ISO 11885
a) Sink (Zn)	44	mg/kg TS	2 25% NS EN ISO 11885
a) Tørrstoff	89.0	%	0.1 5% EN 12880
<b>a) Totale hydrocarboner (THC)</b>			
a) THC >C5-C8	<5.0	mg/kg TS	5 ISO/DIS 16703-Mod
a) THC >C8-C10	<5.0	mg/kg TS	5 ISO/DIS 16703-Mod
a) THC >C10-C12	<5.0	mg/kg TS	5 ISO/DIS 16703-Mod
a) THC >C12-C16	<5.0	mg/kg TS	5 ISO/DIS 16703-Mod
a) THC >C16-C35	340	mg/kg TS	20 25% ISO/DIS 16703-Mod
a) Sum THC (>C5-C35)	340	mg/kg TS	25% ISO/DIS 16703-Mod
<b>a) PAH 16 EPA</b>			
a) Naftalen	<0.010	mg/kg TS	0.01 ISO/DIS 16703-Mod
a) Acenaftalen	<0.010	mg/kg TS	0.01 ISO/DIS 16703-Mod
a) Acenaften	<0.010	mg/kg TS	0.01 ISO/DIS 16703-Mod
a) Fluoren	<0.010	mg/kg TS	0.01 ISO/DIS 16703-Mod
a) Fenantren	<0.010	mg/kg TS	0.01 ISO/DIS 16703-Mod
a) Antracen	<0.010	mg/kg TS	0.01 ISO/DIS 16703-Mod
a) Fluoranten	0.019	mg/kg TS	0.01 40% ISO/DIS 16703-Mod
a) Pyren	0.055	mg/kg TS	0.01 25% ISO/DIS 16703-Mod
a) Benzo[a]antracen	0.013	mg/kg TS	0.01 40% ISO/DIS 16703-Mod
a) Krysen/Trifenylen	0.17	mg/kg TS	0.01 35% ISO/DIS 16703-Mod
a) Benzo[b]fluoranten	0.085	mg/kg TS	0.01 25% ISO/DIS 16703-Mod
a) Benzo[k]fluoranten	0.019	mg/kg TS	0.01 40% ISO/DIS 16703-Mod
a) Benzo[a]pyren	0.050	mg/kg TS	0.01 35% ISO/DIS 16703-Mod
a) Indeno[1,2,3-cd]pyren	0.031	mg/kg TS	0.01 40% ISO/DIS 16703-Mod
a) Dibenzo[a,h]antracen	0.020	mg/kg TS	0.01 40% ISO/DIS 16703-Mod
a) Benzo[ghi]perylen	0.059	mg/kg TS	0.01 40% ISO/DIS 16703-Mod
a) Sum PAH(16) EPA	0.52	mg/kg TS	30% ISO/DIS 16703-Mod

**Utførende laboratorium/ Underleverandør:**

a) ISO/IEC 17025 SWEDAC 1125, Eurofins Environment Sweden AB (Lidköping), Box 887, Sjöhagsg. 3, SE-53119, Lidköping

**Kopi til:**

Kamal Azrague (Kamal.Azrague@sintef.no)

**Tegnforklaring:**

 \* Ikke omfattet av akkrediteringen LOQ: Kvantifiseringsgrense MU: Måleusikkerhet  
 <: Mindre enn >: Større enn nd: Ikke påvist

Opplysninger om måleusikkerhet fås ved henvendelse til laboratoriet.

Rapporten må ikke gjengis, unntatt i sin helhet, uten laboratoriets skriftlige godkjenning. Resultatene gjelder kun for de(n) undersøkte prøven(e).



Moss 07.12.2015

*Kjetil Sjaastad*

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Kjetil Sjaastad

Laboratorie Tekniker

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Tegnforklaring:

\* Ikke omfattet av akkrediteringen      LOQ: Kvantifiseringsgrense      MU: Måleusikkerhet  
<: Mindre enn      >: Større enn      nd: Ikke påvist

Opplysninger om måleusikkerhet fås ved henvendelse til laboratoriet.

Rapporten må ikke gjengis, unntatt i sin helhet, uten laboratoriets skriftlige godkjenning. Resultatene gjelder kun for de(n) undersøkte prøven(e).