Article

Effect of Grain Size and Nutrient Feeding on the Treatment Potential of Biofilters for Treatment of De-Icing Chemicals

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Abstract: Biofilter application for treatment of stormwater containing de-icing chemicals commonly applied in airports, propylene glycol and potassium formate, was investigated. Lab-scale adsorption tests using filter media made of crushed clay (Filtralite) and granular activated carbon showed that adsorption was unsuitable for removal of propylene glycol and potassium formate. Column filtration experiment testing two different crushed clay size ranges was conducted. The results showed that DOC removal was dependent on a number of factors. This study investigated the impact of filter depth, nutrients addition, and filtration rate. DOC removal suggested that DOC degradation occurred on the top filter layer. It was shown that the most active separation occurred in the first ~20 cm of filter depth. This was confirmed by results from water quality analysis (i.e. DOC removal and ATP measurement) and calculations based on a filtration performance analysis (Iwasaki model) and filter hydraulic evaluation (Lindquist diagram). It was shown that for the highest C:N:P ratio tested (molar ratio of 24:7:1), 50-60% DOC removal was achieved. Addition of nutrients was found important and determining the biofilter performance.

Keywords: stormwater; biofilter; de-icing chemicals; nutrients; filtration performance

1. Introduction

Air travels during winter months are made safer owing to de-icing practice in place. In most cases, low molecular weight alcohols are used for de-icing the airplanes, whereas for the runways alcoholic compounds are often combined other non-corrosive deicers. Consequently, the run-off water from airplanes and runways contains high concentrations of the aforementioned chemicals. These chemicals infiltrate to the soil or release into water bodies around the airports when the snow melts. Even though the de-icing chemicals are readily biodegradable, the degradation requires a high oxygen demand and this may affect the natural state of the soil [1, 2].

For airports in Norway, propylene glycol (PG, C₃H₈O₂) is the main component of aircraft de-icing fluids and potassium formate (PF, HCO₂K) is used for de-icing of runways and taxiways (Figure 1). Studies were conducted investigating infiltration of such chemicals into groundwater during the development of Gardermoen Airport in Oslo. At low concentrations, these chemicals are readily biodegradable over a wide range of temperature, but exhibit inhibitory behavior at higher concentrations i.e. in the order of a few grams/kg [3]. In addition, French et al. [4] showed that the rate of biodegradation of de-icing chemicals is limited not only due to low temperatures, but also due to their limited residence time in the unsaturated zone for the soil bacteria to perform biodegradation. Residence time plays a major role especially if biodegradation rates are low.
Notwithstanding to that, climate change poses real threats in coming years. In cold regions like Norway, winter temperatures are expected to increase. This means that temperatures will 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 [1].

![Chemical structures of de-icing chemicals, (a) propylene glycol and (b) potassium formate.](image)

Moreover, airport operators worldwide are under scrutiny to cope with the regulations focusing on the environmental impacts of de-icing practices. Particularly for airports in Europe, Water Framework Directive (2000/60/EC) and Soil Directive (2004/35/EC) have put de-icing practices under the microscope. Many major international airports are operating management systems to handle these chemicals. A wide range of practices is currently in place ranging from sophisticated recycling units to simple aerated lagoons. The focus of managing de-icing chemicals containing water has been put on source reduction, containment, stormwater treatment, and/or safe disposal [5, 6].

Among many treatment alternatives mentioned above, this study has focused exclusively on a biofiltration system for de-icing chemicals containing stormwater. Biofiltration system is considered a promising method for reducing both dissolved and particulate pollutants that improves water quality improvement and flow retention [7-10]. The main objectives of this study have been application of a biofiltration system for treatment of de-icing chemicals containing stormwater and investigation of factors affecting the performance of such a biofiltration system especially when biological activity within the filter is established.

2. Materials and Methods

2.1. De-icing chemicals

PG and PF solutions obtained from Værnes Airport in Trondheim were used as the chemicals for the tests. PG was obtained in a concentrated form with a density of 1.04 g/cm³. PF solution was delivered in a diluted form consisting of 50:50 water-to-PF ratio that gives the solution a density of 1.33-1.37 g/cm³. Average concentrations of PG and PF during winter 2013-2014 as monitored in the runoff water from Trondheim Airport Værnes were around 20 mg/L and 13 mg/L, respectively. These concentrations were used for the column filtration tests.

2.2. De-icing chemicals

Commercially available filter media Filtralite (Leca) of different sizes were used in the experiments. Filtralite is produced from incineration process of expanded clay material at 1200 ºC that makes the density of the material very low (1100 kg/m³) and highly porous. Despite differences in size and, consequently, specific physical properties (e.g. specific surface area, shape factor, uniformity coefficient), the different Filtralite media should display similar physico-chemical properties (e.g. surface charge, hydrophobicity/hydrophilicity). Table 1 summarizes the media commercial names, size ranges, effective diameters ($D_{50}$ correspond to 10% passing weight from sieving test), and the type of tests they were assigned to.

| Table 1. Filtralite media used in the study with corresponding test | Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 20 March 2018 | doi:10.20944/preprints201803.0181.v1 | Peer-reviewed version available at Water 2018, 10, 620; doi:10.3390/w10050620 | 2 of 13 |
### Media name

<table>
<thead>
<tr>
<th>Media name</th>
<th>Nominal size range [mm]</th>
<th>$D_{eff}$ [mm]</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC 0-2</td>
<td>0 – 2</td>
<td>0.11</td>
<td>Adsorption test</td>
</tr>
<tr>
<td>NC 0.8-1.6</td>
<td>0.8 – 1.6</td>
<td>0.96</td>
<td>Filtration and adsorption test</td>
</tr>
<tr>
<td>NC 1.5-2.5</td>
<td>1.5 – 2.5</td>
<td>1.75</td>
<td>Filtration test</td>
</tr>
</tbody>
</table>

#### 2.3. Adsorption studies

Adsorption of de-icing chemicals onto granular activated carbon (GAC), Filtralite NC 0-2 and Filtralite NC 0.8-1.6 was studied in a batch experiment. The Filtralite media were presoaked in distilled water to ensure wettability as specified by the manufacturer. The experiment was carried out in 1 L beakers with continuous mixing (Kemira Kemwater Flocculator 2000). The dry weight of media was 2 g media for each beaker. Different concentrations of de-icing chemicals were prepared by diluting PG and PF with Milli-Q water. For both PG and PF, the corresponding dissolved organic carbon (DOC) concentrations were ranging from 0.6 – 24 mg C/L.

#### 2.4. Filtration test

Two parallel sets of 120 mm inner diameter, 180 cm tall plexi-glass columns filled with a total of ~160 cm media bed were used (Figure 2). Column 1 and 2 were filled with Filtralite NC 0.8-1.6 and NC 1.5-2.5, respectively. Each column was equipped with valves to allow sampling at different depths. Pressure along the filters depths were continuously monitored and recorded by installing pressure transducers (ABB 51T series) along several filter depths, a logger (Agilent 34970a), and a computer.

Fresh synthetic stormwater (diluted PG and PF solutions in distilled water) was prepared daily to avoid biodegradation in the feedwater container. The concentrations of PG and PF in the feed was kept constant at 20 mg/L and 13 mg/L following the monitored average concentration in stormwater runoff at Værnes Airport (Trondheim, Norway). The corresponding inlet DOC concentration was between 6 and 7 mg C/L. Nutrients were added at later stages of the test in form of inorganic salts of monopotassium phosphate (KH₂PO₄) and ammonium nitrate (NH₄NO₃). Suspended solid (real sediment taken along the airport runway and de-icing area) was added to mimic the actual condition at ~50 mg/L (turbidity of 6-13 NTU), and to seed the filter with indigenous microbes naturally adapted to the de-icing chemicals. The feedwater temperature was cooled to ~10°C by a cooling element (Grant GD100).

The column study was divided into four phases based on adjustment applied owing to the observed filtration performance. Phase 1 (C:N:P molar ratio 6500:750:1) relates to acclimatization step of the filters in which biological activity was established. The filters were fed with water containing only de-icing chemicals. Phases 2 and 3 investigate the effect of nutrients addition (N and P) represented by specific C:N:P molar ratios (100:10:1 and 24:7:1, respectively). The flow was kept constant at 7 ml/min by peristaltic pumps (Masterflex LS). This flow was calculated from the average rainfall at Værnes Airport in year 2015 obtained from The Norwegian Meteorological Institute (www.met.no) and the corresponding ratio of filter bed to drainage area of 3.33%. Consequently, the empty bed contact time (EBCT) was calculated about ~34 h. The flow was also monitored regularly by weight-based measurement (Mettler Toledo PB8001-L). Phase 4 investigates the accelerated filter fouling test with higher filtration rate (40 ml/min) to simulate clogging of the filters.
2.5. Filtration performance analysis

The Iwasaki model that describes the decrease in concentration of a substance within the filter depth was used to evaluate the filtration performance. The decrease in concentration is described as a function of the input concentration and the filtration coefficient [11]:

\[
\frac{C}{L} = -\lambda C,
\]

Where:
- \( C \) is the concentration of suspension [mass/volume]
- \( L \) is the media depth [length]
- \( \lambda \) is the filter coefficient [length\(^{-1}\)]

2.6. Water quality analysis

Samples from inlet, outlet, and along the filter depth were drawn regularly. DOC, adenosine triphosphate (ATP), turbidity, phosphorous, and nitrogen were monitored to assess the filtration performance. DOC was measured using Teledyne-Tekmar Apollo 9000. ATP was measured by total cell count technique using luciferase enzyme with a luminometer (Hygiena PI102). Turbidity is measured using Hach 2100N Turbidimeter. Total phosphorus and nitrogen are measured spectrophotometrically using Hach test tubes and a spectrophotometer (DR3900).

3. Results

3.1. Lab-scale adsorption test

Little to no adsorption of PG and PF was observed on Filtralite NC 0-2 as seen from the nearly constant values of DOC. Figure 3 shows a typical DOC profile during adsorption tests. The fluctuations shown in the figure are within the standard deviation of the DOC measurement. Indeed, affinity for adsorption is dependent on the hydrophilic nature of the adsorbed species [12]. PG is a
semi-polar hydrophilic chemical with dielectric constants (ε) of 32. A solvent might be classified as semi-polar if its ε-value lies between 20 and 50 [13]. PF is a salt with high solubility in water and, hence, is found in water in its dissociated form. This explains the relatively low adsorption onto Filtralite observed in the batch experiment. Adsorption onto GAC, although better than that of Filtralite, was shown unsatisfactory. As seen from the figure, the concentrations after more than 24 hours were still comparable to the initial concentration. Thus, adsorption alone may not be sufficient for effective removal of the de-icing chemicals targeted in this study.

Persson et al. [14] investigated removal of geosmin and 2-methylisoborneol (MIB) by biofiltration with filters of Filtralite NC 0.8-1.6 compared to granular activated carbon (GAC). Good removal of the chemicals was achieved by both filters during biofiltration when concentrations were low. The properties of the target compounds used in the abovementioned study are of course different than the de-icing chemicals. However, the study also underlined 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 mainly due to biodegradation and, consequently, was temperature dependent. It is indeed shown by the results on this study that adsorption plays a minor role in removal of de-icing chemicals, and thus investigation of biodegradation process on the media in a biofilter setup capable of degrading de-icing chemicals is of paramount importance.
3.2. Column filtration test – the effect of nutrients on biofilter performance

The treatment performance of the biofilters was assessed by comparing the inlet and outlet DOC levels of Columns 1 and 2 (Figure 4). The DOC values are normalized to the initial concentrations to highlight the trend better. Phases 1 to 4 represent the experimental conditions tested as describe in the methodology section. The low DOC concentrations on the first days of operation may be attributed to the fact that the media was soaked with distilled water before use. Owing to long EBCT (~34 h), dilution may have occurred at the beginning of filtration test before the intended concentration of DOC was achieved throughout the filter volume. After ~5 days of operation, a steady decrease of DOC can be observed.

![Figure 4. Normalized DOC profile at the inlet and outlet of the filters at different phases.](image)

It was observed that the DOC concentrations, and consequently DOC removal levels, vary as a function of filter depth. Figure 5 presents the average % DOC removal by the column at different phases of the experiment. During Phase 1 the removal rates along the filter depth were ranging from ~20-40% and ~10-25% for Column 1 and Column 2, respectively. It is unlikely that adsorption onto filter media plays a major role in the removal of the de-icing chemicals as evident from the adsorption test. However, since suspended materials were added to the feed water and the likelihood of adsorption of de-icing chemicals onto suspended materials exist, consequently, steric exclusion may contribute to the removal process. In such a case, grain size of the filter media is important. However, one can observe that there is minor difference of DOC concentrations leaching from both columns. Thus, steric exclusion may not play a significant role either, at least at this early stage when accumulation of suspended materials filter depth is still low.

Availability of nutrients is a major factor in establishing a fully functional biofilter. The amount of naturally available nutrients may not be sufficient and be a limiting factor for an engineered biofilter [15]. The impact of nutrients addition is pronounce in this study as seen from the increase of DOC removal after addition of N and P (specific C:N:P molar ratios of 100:10:1 and 24:7:1 for Phases 2 and 3, respectively). Indeed, given the rich carbon content in de-icing chemicals, N and P may be the limiting factors for the microbes for biological carbon degradation. In Phase 2, the average % DOC removal along the filter depth were slightly improved ranging from ~30-40% and ~25-40% for Column 1 and Column 2, respectively. Only when the specific molar ratio was increased again in Phase 3, the filters were able to achieve 50-60% of DOC removal depending on the depth of the filter. The optimal nutrients ratio would be treatment goal specific. However, there is no specific regulation imposed by the authorities in Norway against the acceptable level of de-icing chemicals that may be
safely released to the environment. On the other hand, artificial nutrient addition may pose other issues to the environment if this is practiced in an uncontrolled manner [16, 17].

Figure 5. Level of DOC at different sampling points (i.e. filter depths) in (a) Column 1 and (b) Column 2 at different phases of experiment.

The impact of higher filtration rate on the separation performance studied in Phase 4 suggests that there was a slight decrease of DOC removal compared to that of Phase 3. Given the same amount of nutrients ratio as in Phase 3, the average % DOC removal in Phase 4 is ranging from 40-50%. Lower retention time in the filter can be seen as an explanation for this phenomenon. A higher flow means higher availability of the nutrients. However, this may become a shock-loading for the already established biology in the filters. Even though the biological activity may increase, it may take a while before the biological community adapts to the change of condition. The decrease of biofilter performance due to increase inflow was also reported by Hatt et al. [10]. A higher flow may also promote microorganism wash-out due to sloughing effect of interstitial water along the pore channels of a filter [18]. This in return will decrease the viable microorganisms contributing to the biological degradation process.

3.3. Separation behavior along the filter depth

Judging the filtration performance by solely looking at the DOC removal levels in Figure 5 can be misleading since the thickness of filter media in which separation takes place is neglected in the calculation. Iwasaki model evaluates the filtration performance by taking into account different filtration layers along the filter depth and characterizes these layers according to the amount of...
separation that takes place at different filter depths. Figure 6 presents the calculated filtration coefficient (\(\lambda\)) for the two columns based on DOC concentration removed. As seen in the figure, for both filters \(\lambda\) is highest in the first predetermined filter layer (i.e. 14 cm) and acquires similar values in the following layers.

![Filtration coefficient graph](image)

**Figure 6.** Filtration coefficients (\(\lambda\)) of (a) Column 1 and (b) Column 2 as a function of filter depth at different phases of the experiment.

This means separation occurs on the top layer of the filter columns while the extra depth has little to no contribution in the degradation of DOC. This is an important characteristic of the biofilter performance that has to be taken into account in the design and operation of a biofilter. \(\lambda\) also suggests the maximum separation (i.e. degradation) capacity of the biofilter to which additional length would not benefit the process. Moreover, the impact of nutrients addition as discussed in the previous section is also confirmed. As seen from Figure 6, \(\lambda\) increases as nutrients are added to the feedwater. This can be a tradeoff one has to incur in order to optimize the biofilter performance. The impact of an increased filtration rate in Phase 4 is also represented by the lower \(\lambda\) values for both filters. Interestingly, the top filter layer was still the most active separation layer event though the possibility of the microorganism carry-over to the lower layer exists. Comparing the \(\lambda\) values between the two filter media, the effect filter media grain size on the separation performance seems of little significance.

### 3.4. Biological activity in the filter media

Biological activity along the filter depths was investigated using ATP as a measure of viable cells. Figure 7 presents the values of ATP as a function of filter depth. The figure is consistent with the discussion in the preceding section. As seen in the figure, as C:N:P ratio increases, the ATP values
become larger. The figure also confirms the higher ATP values at the top filter layer. The fact that the ATP values of both filter columns in Phases 1-3 are comparable is rather intriguing. One would argue that smaller filter grains would provide a larger surface area for microorganism attachment and, thus, results in more densely packed active layer. However, this premise is not necessarily true from the observation of this study as seen from the similar DOC removal percentage and the ATP values.

Figure 7 also suggests that there is a growth limitation in increasing depth confirming that extra bed depth would not be beneficial for the type of application studied. Oxygen can be a limiting factor as filter depth increases and, thus, microorganisms are indeed more viable in the top layer of the filters. The ATP values presented here are, however, much lower than those found in wastewater application e.g. as reported by Hong [19] and Bourke et al. [20]. This is completely logic given the type of application of biofilter considered in this study, i.e. no intensive aeration that promote growth of microorganisms.

The ATP values in Phase 4 were indeed highest. As discussed previously, DOC removal was actually lower than that of Phase 3 even though the nutrient availability should be higher in higher filtration rate. Thus, the higher ATP values may be explained by a possible carry-over of microorganisms to the lower filter layers and also the resulting growth of the microorganisms.

3.5. Hydraulic performance of the filters

Material buildup inside the porous structure due to solid retention and growth of biofilm leads to reduction of filtration capacity of the biofilters. Figure 8 shows the progression of headloss throughout the filter depth during the phases of the experiment represented by the Lindquist
diagram. The diagram shows the deviation from a theoretical line (hydrostatic pressure) in which no headloss occurs.

![Diagram showing headloss development](image)

**Figure 8.** Headloss development at different phases of filtration test for (a) Column 1 and (b) Column 2.

As expected, Column 1 that consists of a smaller media exhibits higher headloss compared to Column 2. The initial clean water resistance (headloss) that corresponds to headloss in the media if tap water flows through the column is, however, very small (< 5 cm) for both filter media. After the filters are fed with feedwater containing particles and de-icing chemicals, the lines start to deviate from the hydrostatic line indicating increase of headloss due to particle retention and, in later stages, growth of active biofilm onto the media surface as will discussed in the following sections.

Lindquist diagram also indicates the depth in which the activities of such separation and biofilm growth occurs. Interestingly, for both filters these activities occur on the top layer, i.e. the first ~20 cm of filter depth as indicated by the lines confirming the trends shown by λ and ATP values. The headloss below this point is more or less stable i.e. indicated by similar deviation from the ideal hydrostatic pressure line. The diagram also indicates that separation occurs along the filter depth (i.e. depth filtration) like in the case of rapid sand filters rather than surface filtration that predominantly occurs in slow sand filters. This finding is interesting and suggests that the separation performance may be independent of the effective size of the filter media i.e. the size of the media affects only the filtration hydraulic.
Figure 9. Fouling rates of (a) Column 1 and (b) Column 2 calculated from Lindquist diagram.

Figure 9 depicts fouling rate of the two filter columns calculated from the Lindquist diagram. Values in x-axis correspond to the assigned filter depth equipped with pressure sensors. As seen from the figure, each phase of the experiment resulted in different fouling rates. However, the trend is consistent with those of DOC removal and $\lambda$ and confirming the depth of the active layer in the filters that contributes to DOC degradation.

As expected, Column 1 with smaller filter media exhibits higher fouling rate compared to the larger ones in Column 2. Column 1 was clogged at the end of the experiment period while Column 2 could still maintain a degree of flow after ~45 days of experiment. Even though the operation time of the filters were rather short, one must concede that this type of test can be seen as an accelerated filtration performance test in which constant amount of solids, nutrients, and target compounds were supplied and the flow was adjusted. In reality, one must consider also many factors that were not covered in this study and may pose operational challenges to such a biofilter such as intermittent flow, freezing condition, first flush, etc.

4. Conclusions

The treatment potential of biofilters for treatment of water containing de-icing chemicals was assessed. Lab-scale adsorption tests using filter media made of crushed clay (Filtralite) and granular activated carbon showed that adsorption was unsuitable for removal of de-icing chemicals (propylene glycol and potassium formate) considered in this study.
Column filtration experiment testing two different crushed clay size ranges was conducted to assess de-icing chemicals removal by biodegradation. The results showed that DOC removal was dependent on a number of factors. This study investigated the impact of filter depth, nutrients addition, and filtration rate.

DOC removal suggested that DOC degradation occurred on the top filter layer and, hence, additional filter depth would be unnecessary. It was shown that the most active separation occurred in the first ~20 cm of filter depth. This was confirmed by results from water quality analysis (i.e. DOC removal and ATP measurement) and calculations based on a filtration performance analysis (Iwasaki model) and filter hydraulic evaluation (Lindquist diagram). It was shown that for the highest C:N:P ratio tested (molar ratio of 24:7:1), 50-60% DOC removal was achieved. Addition of nutrients was found important and determining the biofilter performance.

The filtration test conducted in this study can be seen as an accelerated filtration performance test in which constant amount of solids, nutrients, and target compounds were supplied and the filtration rate was adjusted. Other factors that could be of importance for the design and operation of a biofilter treating de-icing chemicals, e.g. intermittent flow, freezing condition, first flush, were not covered in this study.

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References


