Transport and degradation of de-icing chemicals in the unsaturated zone – 15 years of research at Gardermoen

Av Helen. K. French

Helen K. French is Dr.scient and hydrogeologist/senior research scientist at Norwegian Institute for Agricultural and Environmental Research (Bioforsk)
e-mail: helen.french@bioforsk.no

Summary
The objective of several field, laboratory and modelling studies has been to quantify flow, transport and degradation of de-icing chemicals at Oslo airport, Gardermoen. Studies have revealed that chemicals have a spreading zone of 30 m from the runway and melt out from snow pack before the main snowmelt. The spatial variability of infiltration is high due to ice on the ground surface. As a rule of thumb 1 mm of infiltration gives 7 mm of vertical displacement in a coarse sandy soil. Soil heterogeneities cause highly variable plume distribution. Measured half lives of Propylene Glycol,
Formate and Acetate range from 2.6 – 54 days, 2.6 – 61 days, 2 - 34 days accordingly. Variation is explained by temperature and availability of nutrients. Manganese indicates anaerobic conditions during degradation. Future challenge is to control flow and infiltration to ensure sufficient retention times for degradation and return to reference state.

Introduction

In 1998 the new main airport of Norway, Oslo airport, was opened at Gardermoen. Large amounts of de-icing chemicals are required for safe airport operations in cold climates; hence the environmental effects of these chemicals were a major concern at Oslo airport, which is situated on Norway’s largest unconfined rain-fed aquifer. There have been numerous projects considering various aspects of the fate of de-icing chemicals from application on airplanes and runways to the surrounding environment (French et al., 2000). The Gardermoen project (1992-2001), funded by the Norwegian research council and the Norwegian aviation authorities, produced a large number of studies of the geology, transport mechanisms and degradation of de-icing chemicals from the area (Kitterød, 2001). Oslo airport, which has three hydrogeologists among their staff, have also performed their own studies and funded research projects focussed on de-icing chemicals in the unsaturated and saturated zones. In this paper I will highlight some of the results and conclusions of the research that has been performed over the last 15 years and outline some of the future challenges and gaps in our knowledge. When taking the broad perspective, the following aspects should be considered when describing the fate of de-icing chemicals at an airport: 1) The spreading of de-icing chemicals along the runway; 2) Infiltration of de-icing chemicals; 3) Transport patterns and velocities in the unsaturated zone; 4) Degradation rates in the unsaturated zone and 5) Changes in geo-chemistry. These aspects will be described and discussed separately with reference to more complete articles and reports which should be consulted for more in depth information. An overall discussion of conclusions in view of the overall fate of de-icing chemicals is given at the end.

The de-icing chemicals and site specific conditions

The main constituents of the commercial de-icing chemicals used on airplanes are Propylene Glycol (PG) and Potassium Format (KFo) on runways. Potassium Format has replaced the previously used Potassium Acetate (KAc). These de-icing chemicals are generally considered as easily degradable (Sabee & Narasiah, 1992; Laake & Effraimsen, 1992) and non-toxic. Both chemicals are completely degradable under aerobic and anaerobic conditions, the chemical oxygen demand is 1.68 g COD/g PG and 0.35 g COD/g Fo, both compounds have a low octanol-water coefficient, which implies that no or little adsorption is expected. The Gardermoen glacial-contact delta, approximately 40 km north of Oslo in south-eastern...
Norway, is an aquifer composed of sand with beds of gravel underlain by silty glaciomarine deposits (Jørgensen & Østmo, 1990, Tuttle, 1997). The unsaturated zone thickness varies between 5 to 15 m below the airport. The annual precipitation is approximately 800 mm and the evapotranspiration is about 400 mm. More than 50% of the groundwater recharge occurs during the snowmelt period (3-5 weeks) (Jørgensen & Østmo, 1990).

**Spread of de-icing chemicals along the runway**

During mechanical removal of snow from the runways and by the airborne drift of chemicals from the aeroplanes at take-off, the de-icing chemicals are mixed with snow. De-icing chemicals for runways is spread evenly over the entire runway. De-icing of airplanes takes place on de-icing platforms where most of the surplus chemicals are collected and sent to a waste water treatment system. It is estimated that approximately 10% of the consumed de-icing chemicals used on airplanes is dispersed on the runway or diffusively on the green areas along the run-ways. Hence, there is a variable concentration along the length of the runways. The spreading zone of the de-icing chemicals has been monitored by the airport and is approximately 30m wide (OSL, this will be further reported in the next issue of VANN). The width of the spreading zone is confirmed by georadar measurements which showed large attenuation due to higher salt concentrations in soil water within this zone (Hamran pers. comm.). The maximum concentrations of de-icing chemicals in the snow along the runways measured in 2006 was 2500 PG mg/l and 576 mg Fo/l in January, less than 50 mg/l was measured at the end of March, which was still prior to snowmelt (data from OSL). This indicates that most of the chemicals melt preferentially from the snow and may infiltrate the soil during the winter period, this effect was also shown experimentally in experiments in 1994 (French and van der Zee, 1999).

**Infiltration of de-icing chemicals**

Typically the winters at Gardermoen have stable temperatures below 0°C, and the bulk of the snow melts at the end of the winter season in March/April (The Norwegian Meteorological Institute). Collection of meltwater from snow lysimeters and visual observations on the surface revealed a large variability of meltwater below the snow cover, and ponding of meltwater in local depressions on the surface. Although the snowcover was flat, the collected meltwater between snow lysimeters varied from 0 to 270% of expected amounts of meltwater relative to stored water in snowcover above the snow lysimeters (French and van der Zee, 1999). Time lapse measurements of electrical resistivity in ground below the snow cover during snowmelt also revealed a highly variable infiltration pattern as illustrated in figure 1 (French and Binley, 2004). Both of these studies took place at Moreppen which is an experimental field site for studies of processes in the unsaturated zone (French et al., 1994, Aagaard et al., 1990).
While the Moreppen field station is fairly flat (topographical differences of about 0.5 m) the green areas of the airport have differences of several meters. After the airport was opened in 1998 small lakes of meltwater containing de-icing chemicals were formed in depressions. The Maximum ponding depth was 2.1 m, but was possibly higher during the first year of running the airport in 1998.

**Transport patterns and velocities in the unsaturated zone**

Both numerical and field experiments have been conducted in order to examine the flow and transport patterns in the unsaturated zone. Field experiments were conducted next to a lysimeter trench where soil water samples were taken from 30 to 40 points using Prenart suction cups installed at different depths from the surface (French et al., 1999; French et al., 2001; Søvik et al., 2002). Also cross-bore hole electrical resistivity surveys have been conducted (French et al., 2002). All studies revealed a highly irregular plume movement and the presence of preferential flowpaths influenced by soil heterogeneities and variability of infiltration conditions. Numerical studies (using the flow and transport model SUTRA, Voss, 1984) of flow patterns in a highly heterogeneous soil ($k_s=5e^{-11}$ $m^2$, $Ln k_s = 2.3$) were conducted in order to examine the importance of these heterogeneities, and revealed that in cases with little topographical difference the flow pattern is mainly influenced by the high level of soil heterogeneity (French et al., 1999). Due to larger topographical differences on the airport the variability of infiltration is believed to have stronger effect on the vertical flow velocities there.

*Figure 1. Variability of snowmelt infiltration monitored by time-lapse electrical resistivity measurements during the snowmelt of 2001 at Moreppen (French and Binley, 2004), dark parts show areas where most infiltration has taken place from 1st of April until 16th April.*
velocities of extreme infiltration events, up to 250 mm/day over 16 days following a steady state situation with 2.5 mm/day, was simulated with Tough 2 (Preuss, 1991). These simulations revealed velocities of up to 300 mm/day (Kitterød, 2008). All studies reveal that the vertical flow is highly dependent on the total amount of infiltration. Based on transport studies in the coarse sandy soil at Moreppen, a rough rule of thumb is that 1 mm of infiltration can give approximately 7 mm of vertical displacement of an inactive tracer (French, 1999). Another feature of the transport pattern is that there is an initially rapid transport of the centre of mass (approximately 1.5 m depth in 1994 and 1995, French et al., 2001) until all the melted snow has infiltrated. The depth will be a function of the total amount of infiltration during snowmelt. It is assumed that only a minor part evaporates during this period, which typically lasts for 3-5 weeks. During the following summer period (roughly June and July), precipitation is balanced by evapo-transpiration and water percolation to larger depth ceases. Field experiments in 1994, 1995, 1996 and 2001 showed that the vertical displacement of the centre of mass was negligible during the summer period. Measured and simulated vertical movement of the centre of mass of PG and Ac during a snowmelt period of 3 weeks followed by several months of no infiltration is shown in figure 2. During autumn conditions, percolation increases again and the plume starts to move downwards. Hence it is very important that the de-icing chemicals do not reach the groundwater during the snowmelt in order to allow for sufficient degradation time in the unsaturated zone. No retardation of PG or Ac was observed from field experiments. Column studies have supported this conclusion also for Formate and for the commercial products which also

Figure 2. Measured vertical displacement of PG (triangles) and Ac (squares), thick line is average of 10 simulations, and thin lines indicate 2 standard deviations on each side.
contain a swelling polymer and some other additives (Linjordet et al., 2008.). One realisation of simulated plume movement and degradation is shown in figure 3.

Degradation rates in the unsaturated zone
The measured overall loss of de-icing chemicals in experimental field studies during the snowmelt (French et al., 2001) fits well with first order degradation kinetics with an initial lag phase. This conclusion is supported by Sabeh and Narasiah (1992), McGahey and Bower (1992) who observed that propylene glycol (PG) and acetate (Ac−) (Stevenson and Katznelson, 1958), were degraded according to first order degradation kinetics. Acetate was degraded at a rate constant of 0.02 d−1 in 1994. The overall degradation rate of PG increased from 0.015 d−1 in 1994 to 0.047 d−1 in 1995. Although first order degradation normally describes systems with no bacterial growth, the natural system is more complex and field results may fit several kinetic models. We therefore conclude that the

Figure 3. Simulated PG plume movement in the unsaturated zone at Moreppen (French et al., 2001), assuming higher degradation rates near the surface, and a hydraulic conductivity of 5e−11 m2, and a variance of the LnKs=2.3 transformed to a scaling parameter used in the van Genuchten equation.
increased degradation rate is most likely explained by an increase in the microbial biomass after the previous application. Different degradation rates measured in the field and the laboratory are summarised in table 1. These rates also show the increased degradation rates due to added nutrients (N and P). Besides biomass and nutrients, temperature is another important factor for the efficiency of micro-organisms to degrade organic material. De-icing chemicals at airports infiltrate during the cold season, hence, they may bypass the zone of largest degradation activity as low temperatures limit microbial activity. As de-icing chemicals only infiltrate during snow melt, activation of dormant cells from previous applications and growth rates are important.

Changes in geo-chemistry
Champ et al. (1979) and Berner (1981) suggested describing the redox environment in terms of the presence or absence of indicative red-ox species such as Mn$^{2+}$ and Fe$^{2+}$. In the absence of oxygen, iron and manganese oxides can function as electron acceptors for oxidation processes (eg. Appelo and Postma, 1996). Increased concentration of the reduced form of these electron acceptors in soil water may indicate large degradation activity and more anoxic conditions. Several studies at the Moreppen field site (French et al, 2001), in column

<table>
<thead>
<tr>
<th>De-icing chemical</th>
<th>Half-life (days)</th>
<th>Location</th>
<th>Initial conc. (g/l)</th>
<th>Temperature °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylenglycol</td>
<td>15 - 45</td>
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<td>15-100</td>
<td>0-10</td>
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<tr>
<td>Propylenglycol</td>
<td>25 - 54</td>
<td>Lab.</td>
<td>15 -100</td>
<td>5</td>
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<td>8.5</td>
<td>6)</td>
</tr>
<tr>
<td>Anaerobic</td>
<td>18 - 34</td>
<td>Field</td>
<td>273</td>
<td>3-8 (0)</td>
<td>3)*</td>
</tr>
<tr>
<td>Formate</td>
<td>7</td>
<td>Lab.</td>
<td>273</td>
<td>20</td>
<td>4)</td>
</tr>
<tr>
<td>Formate</td>
<td>16 - 61</td>
<td>Lab.</td>
<td>0.5-1.50</td>
<td>5</td>
<td>2)</td>
</tr>
<tr>
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<td>0.5 - 4.5</td>
<td>Lab.</td>
<td>0.5-1.50</td>
<td>8-20</td>
<td>5)</td>
</tr>
<tr>
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<td>Lab.</td>
<td>273</td>
<td>8.5</td>
<td>6)</td>
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<tr>
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<td>8.5</td>
<td>6)</td>
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<tr>
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<td>Lab.</td>
<td>0.5 - 5</td>
<td>20</td>
<td>1)</td>
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<tr>
<td>Acetate and nutrients</td>
<td>2 - 5</td>
<td>Lab.</td>
<td>5</td>
<td>20</td>
<td>1)</td>
</tr>
</tbody>
</table>

1) French et al., 2002; 2) Linjordet et al., 2008; 3) Estimated based on Hellstén et al., 2005, K-formate was added over a longer period, highest half life estimated with shortest retention time; 4) Estimated from Roseth et al. 1998; 5) Oslo lufthavn, 2001, 6) Linjordet, 2005

Table 1. Half life of different de-icing chemicals in soil from Gardermoen

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experiments (Linjordet et al., 2008; Linjordet, 2008) and in groundwater from monitoring wells at the airport (OSL) indicate that manganese concentrations increase in soil water and groundwater during degradation activity in the unsaturated zone. An example of the increase in manganese observed in the unsaturated zone after application of 100 g PG/l in 1994 is shown in Figure 4. The main increase in manganese occurred some time after the peak concentration of PG in the profile. The same was found for KAc.

**Conclusion and future challenges**

All experimental and modelling results show that the soil has a good potential for degradation. The challenge from a management perspective is to be able to control the concentration of de-icing chemicals and amount of water that can infiltrate at any given location and be sure that it will give sufficient retention time for complete degradation before reaching the groundwater level. The monitoring of the infiltration and degradation process is also a challenge. A newly started EU project, SoilCAM (www.soilcam.eu) will be using Gardermoen as one of the field sites for testing optimisation of monitoring techniques by combining traditional soil and water sampling with geophysical techniques and flow and transport modelling. A third challenge is to ensure enough electron acceptors (such as Fe and Mn) are available for degradation under anaerobic conditions, and that the soil returns to its reference state before the next pulse of de-icing chemicals. In figure 5 the available iron and manganese sources at different depths at Moreppen and OSL are shown. The kinetics of manganese oxidation is not well

![Figure 4. Average concentration of Mn and normalised total mass of PG measured in soil water from 30 suction cups during the snowmelt of 1994 (French et al., 2001).](image-url)
described, but is important in order to know the time required to obtain the reference state after a contaminant plume has passed through the unsaturated zone.

References


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![Figure 5. Citrate-dionite solvable manganese (left) and iron (right) measured in soil at different depths (x-axis) at OSL and Moreppen (French and Søvik, 2007)](image)
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