Low temperature biodegradation of airport de-icing fluids

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Abstract The biodegradabilities of glycol- and acetate-based aircraft de-icing fluids on airport surfaces have been investigated at three temperatures between 0°C and 10°C. The aqueous solubilities of these substances can result in high BOD loadings in runoff and pose serious toxicity problems in receiving waters. The measured surface biodegradation rates for de-icing products based on ethylene/diethylene glycol (Konsin), propylene glycol (Kilfrost) and potassium acetate (Clearway) at 4°C were 0.082, 0.073 and 0.033 day⁻¹. The resulting reductions in the potential BOD loadings, of a single application of a typical mixture of these products, over a 5 day biodegradation period are predicted to be 32.9%, 30.2% and 21.4%, respectively at 8°C, 4°C and 1°C. For consecutive daily applications, the comparable cumulative reductions over 5 days are 20.8%, 18.9% and 13.3%. The subsequent savings in the amount of treatment required for airport runoff prior to safe discharge to receiving waters are discussed and hence the relevance of surface biodegradation processes to the design of stormwater treatment systems involving the wash-off of biodegradable pollutants following retention on urban surfaces.

Keywords Airport surfaces; biodegradation; de-icers; runoff; stormwater

Introduction During extreme cold weather conditions, the safe operation of airport activities is maintained through the appropriate use of de-icing and anti-icing agents. De-icing fluids are used to remove ice from impermeable surfaces during aircraft movements and, in the UK, are mainly formulated from ethylene and diethylene glycol mixtures or potassium acetate. Anti-icers are formulated to prevent the build-up of ice on aircraft surfaces and propylene glycol is widely used as the main active constituent. Despite the addition of polymeric thickening agents, there can be considerable losses of anti-icers to impermeable surfaces within the airport boundary. The high application rates of anti- and de-icers and their subsequent removal from the treated impervious surface (particularly by rain), can pose serious problems for receiving water quality in the absence of treatment facilities (Ellis et al., 1997). Glycols are completely miscible with water and can exert high biochemical oxygen demands degrading water quality in receiving water bodies (Evans, 1996). Potassium acetate based de-icers have been advocated as a lower polluting alternative for runways (O’Connor and Douglas, 1993) due to a lower biochemical oxygen demand (BOD) than glycol solutions of equivalent de-icing power.

A number of different approaches have been utilised to prevent or reduce the possible environmental contamination which may result from the use of de-icing fluids within airports. These include the transfer of stormwater runoff to wastewater treatment plants or the use of on-site treatment or recycling. Examples of on-site treatment generally involve biological degradation within systems such as constructed wetlands (Revitt et al., 2001), root zone soil environments (Bausmith and Neufeld, 1999), sand filter strips (Danielsberg et al., 1998), aerobic reactors (Sabeh and Narasiah, 1992; Safferman et al., 1998; Kent et al., 1999) or anaerobic reactors (Rusten et al., 1996; Schoenberg et al., 2001). Based on biodegradation studies of propylene glycol based fluids in sand columns, Bielefeldt et al.
(2002) have demonstrated the potential for propylene glycol to be degraded in either engineered biofilters or the natural subsurface regardless of electron acceptor availability. French et al. (2001) have also studied the behaviour of de-icers in the unsaturated zone immediately below an airport and field experiments indicated measurable biodegradation rates for propylene glycol and potassium acetate.

The biodegradation potential of glycol-based de-icing fluids, and to a lesser extent of acetate-based de-icing fluids, has clearly been established in a range of different media. However, there is also the possibility that de-icers and anti-icers retained on airport surfaces may undergo aerobic degradation, prior to their removal in runoff. This would result in lower BOD concentrations in discharged waters and hence influence the level of treatment which could be required before release to receiving waters is permitted. This paper describes an experimental approach to investigate the extent to which the biodegradation of glycol- and acetate-based de-icing fluids can occur at the low temperatures existing during winter conditions. The findings are used to estimate savings in treatment capacity which may be achieved whilst still ensuring that an acceptable discharge level exists. In addition to their direct relevance to airport runoff, the results also have implications for other stormwater treatment systems involving potentially biodegradable pollutants where surface retention may contribute significantly to the overall reduction of pollutant loadings.

**Experimental methods**

In order to assess the potential for the biodegradation of de-icers on an airport surface it was necessary to initially detect the presence of appropriate microorganisms followed by the determination of surface biodegradation rates. The determination of the microbial population (bacteria, actinomycete and fungi) populations has been described previously (Revitt et al., 2002) with the levels being considered sufficient to support a viable biodegradation process. The representative airport surfaces were kindly provided by Heathrow Airport Ltd, in the form of paving blocks (200 mm x 100 mm x 80 mm), which were removed from the aircraft standing areas during routine maintenance work in December 2000. The blocks were used in the experiments as quickly as possible and in the interim period they were stored undercover at ambient external temperatures.

The biodegradation rates on the surfaces were measured at temperatures of 1°C, 4°C and 8°C, which are considered to be representative of the range of temperatures encountered on airport surfaces during the application of de- and anti-icers. Each of the de- or anti-icer products (ethylene/diethylene glycol-based [trade name: Konsin], propylene glycol-based [trade name: Kilfrost] and potassium acetate-based [trade name: Clearway]) was investigated together with a control experiment (no de- or anti-icer), in separate experiments, at these temperatures. The experimental procedure for the investigation of surface biodegradation at each temperature involved the use of twelve paving blocks. For the control investigation, the upper surfaces of three blocks were each comprehensively sprayed with 300 mL of a nutrient solution (previously cooled to the required temperature) and the total washings (900 mL) were collected, combined, made up to a volume of 1 L and cooled to the test temperature. The objective of the spraying/washing process was to remove the surface attached microorganisms and surface associated soluble and particulate associated contaminants. The overall spraying/washing process was repeated using separate 20 mg/L concentrations of the supplied proprietary liquids of Konsin, Kilfrost and Clearway in the nutrient solution. All resulting solutions (1 L) were cooled to the test temperature and then fully aerated at this temperature.

After measuring the starting dissolved oxygen concentration of the four different solutions (control, Konsin, Kilfrost and Clearway) they were each transferred to three BOD bottles (273 L volume) and thoroughly sealed. The remaining solutions were placed in half-
filled BOD bottles to be used for topping-up purposes. The sixteen BOD bottles (containing microorganisms, surface contaminants, nutrients and control or de-icer) were incubated at the test temperature for periods of up to 14 days and dissolved oxygen measurements performed initially at short time intervals (1 day) and subsequently at longer time intervals (e.g. 4 days). Triplicate or duplicate dissolved oxygen readings were obtained for each different solution and the liquid lost from each BOD bottle, due to immersion of the dissolved oxygen probe, was compensated for by topping-up with the solution in the fourth BOD bottle.

**Results and discussion**

**Determination of surface biodegradation rates**

All monitored solutions demonstrated a progressive decrease in dissolved oxygen content with time, clearly indicating the potential for surface biodegradation to occur due to the presence of appropriate microbial populations. The existence of a dissolved oxygen decrease in the case of the control indicates the presence of biodegradable organic contaminants on the surface of the paving blocks. As the blocks were collected during the winter (December 2000) these contaminants could include tracers of applied de-icer as well as other general use airport products such as fuels, oils and detergents. However, the temporal decreases in dissolved oxygen for the de-icer solutions were always greater than for the control solutions with the differences becoming more enhanced over the time period of the experiment. The incubated solutions which developed anoxic conditions during the lifetime of the experiment were *Konsin* (after 7 days), *Kilfrost* (after 8 days) and *Clearway* (after 11 days) at 8°C. At 1°C and 4°C only *Konsin* reached zero oxygen levels after 12 days and 13 days, respectively.

The biodegradation rates for the three de-icing products at the different monitored temperatures are derived by plotting the dissolved oxygen concentrations (adjusted for the decreasing oxygen levels of the control solution) against the time of incubation. A typical plot of the experimental data is shown in Figure 1 for *Konsin* at 1°C. This figure also shows the derived equation for the best fit exponential curve and the associated correlation coefficient. The derived characteristics for the fitted exponential curves describing the biodegradation of each of the three de-icers at the three monitored temperatures are summarised in Table 1.

**Derivation of biodegradation rate**

The derived equation describing the exponential decay rate for *Konsin* at 1°C is of the form,

\[ y = 10.5 \, e^{-0.0563x} \]  

(Table 1; Figure 1).

**Table 1** Equations and correlation coefficients for the fitted exponential equations relating to the biodegradation of each de-icer at 1°C, 4°C and 8°C

<table>
<thead>
<tr>
<th>De-icer</th>
<th>Temperature (°C)</th>
<th>Equation</th>
<th>R² value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Konsin</td>
<td>1</td>
<td>( y = 10.5 , e^{-0.0563x} )</td>
<td>0.9757</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>( y = 10.1 , e^{-0.072x} )</td>
<td>0.8213</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>( y = 8.2 , e^{-0.0798x} )</td>
<td>0.8874</td>
</tr>
<tr>
<td>Kilfrost</td>
<td>1</td>
<td>( y = 10.0 , e^{-0.0403x} )</td>
<td>0.8443</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>( y = 10.2 , e^{-0.0645x} )</td>
<td>0.9801</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>( y = 8.2 , e^{-0.0713x} )</td>
<td>0.8859</td>
</tr>
<tr>
<td>Clearway</td>
<td>1</td>
<td>( y = 10.1 , e^{-0.0425x} )</td>
<td>0.9543</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>( y = 10.0 , e^{-0.0300x} )</td>
<td>0.9061</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>( y = 8.0 , e^{-0.0322x} )</td>
<td>0.9899</td>
</tr>
</tbody>
</table>
This corresponds to the theoretically predicted exponential decrease in dissolved oxygen (DO), which can be expressed as:

\[ e^{-kt} = \frac{C_t - C_u}{C_o - C_u} \]

where

- \( C_t \) = DO concentration after time, \( t \)
- \( C_o \) = initial DO concentration
- \( C_u \) = ultimate DO concentration

The initial dissolved oxygen concentration \( (C_o) \) in this instance was 10.5 mg/L.

The ultimate dissolved oxygen concentration \( (C_u) \) corresponds to the constant equilibrium value, which could be achieved after a prolonged biodegradation time. Consideration of the shape of the biodegradation curves and the minimum dissolved oxygen concentration at the end of each experiment indicates that a 90% reduction in the initial dissolved oxygen concentration is appropriate for the attainment of this value (i.e. in this case, \( C_u = 1.05 \text{ mg/L} \)).

The time to reach a \( C_u \) value of 1.05 mg/L can be calculated from

\[ C_u = 1.05 = 10.5 e^{-0.0563 \times t} \]

From which

\[ t = 40.9 \text{ days} \]

Applying this approach to the exponential equations in Table 1 indicates that the times to reach realistic \( C_u \) values vary from 28.8 days (for Konsin at 8°C) to 76.8 days (for Clearway at 4°C).

The dissolved oxygen concentration after any time \( (C_t) \) can be calculated by introducing the appropriate value of \( t \) into the derived equation. Using a value of \( t = 5 \) days,

\[ C_t = C_5 = 10.5 e^{-0.0563 \times 5} = 7.92 \text{ mg/L} \]
Applying the values $C_5 = 7.92 \text{ mg/L}$ and $C_u = 1.05 \text{ mg/L}$ gives:

$$e^{-5k} = \frac{C_5 - C_u}{C_o - C_u} = 0.723$$

$$k = 0.064 \text{ day}^{-1}$$

This is the experimentally determined biodegradation rate for *Konsin* at 1°C based on a $C_u$ value of 1.05 mg/L achieved after 40.9 days. The corresponding biodegradation rates of all de-icers at each temperature can be calculated similarly and the results are listed in Table 2.

Comparison of the determined biodegradation rates for the three de-icers indicates that *Konsin* has the highest potential for biodegradability at all three monitored temperatures. At 4°C and 8°C, *Kilfrost* has a slightly lower potential for biodegradability with *Clearway* being considerably less susceptible to microbiological decay under the applied test conditions. The higher biodegradation rates observed for the glycol-based de-icing fluids (*Konsin* and *Kilfrost*) are consistent with the previously determined aerobic removal of glycols from wastewaters despite the reported stability of diethylene glycol (Evans and David, 1974; Schoberl, 1985). The consistently higher values determined for *Konsin* compared to *Kilfrost* at equivalent temperatures indicate that propylene glycol, which is the main constituent of *Kilfrost*, is less biodegradable than the mixture of ethylene and diethylene glycols, which make up the major composition of *Konsin*. However, previous evidence suggests that the higher biodegradability of *Konsin* is due to the presence of ethylene glycol, which has been shown to be capable of providing the only source of carbon and energy for consortia of bacteria (Nikitin *et al*., 1999; McVicker *et al*., 1998). The biodegradability of propylene glycol in the presence of *Pseudomonas* and *Aerobacter* has been demonstrated by Raja *et al*. (1991) in experiments where 90% of the BOD due to a mixture of propylene oxide, propylene glycol and associated polyols was removed. Under ideal conditions, the aerobic biodegradation of glycols is reported to consist of two stages. The initial enzymatic conversion of glycols to carboxylic and hydroxycarboxylic acids is followed by further degradation to carbon dioxide and water. The observed lower biodegradation rates for *Clearway* are consistent with results reported by French *et al*. (2001) for the degradation of potassium acetate in the unsaturated soil layer beneath an airport in the winter season. The measured sub-surface biodegradation rate was 0.02 day$^{-1}$, which compares favourably with the measured rate for *Clearway* (0.033–0.048 day$^{-1}$) in this study for the surface process. French *et al*. (2001) also measured a microbial decay rate for propylene glycol in the sub-surface soil and the highest value (0.047 day$^{-1}$) is very similar to the surface biodegradation rate of *Kilfrost* at 1°C (0.045 day$^{-1}$).

The biodegradation rates for *Konsin* and *Kilfrost* show clear trends of decreasing biodegradation rate with decreasing temperature. However, this is not the case for *Clearway*, where the lower values do not demonstrate any clear temperature dependence. The effect of temperature on the biodegradation rates of ethylene and propylene glycols has

<table>
<thead>
<tr>
<th></th>
<th>1°C</th>
<th>4°C</th>
<th>8°C</th>
</tr>
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<tbody>
<tr>
<td>Konsin</td>
<td>0.064</td>
<td>0.082</td>
<td>0.091</td>
</tr>
<tr>
<td>Kilfrost</td>
<td>0.045</td>
<td>0.073</td>
<td>0.081</td>
</tr>
<tr>
<td>Clearway</td>
<td>0.048</td>
<td>0.033</td>
<td>0.036</td>
</tr>
</tbody>
</table>
been observed by previous workers although not within such a low and narrow temperature range. Colucci and Inniss (1996) found that the time period required by Pseudomonas fluorescens to completely utilise ethylene glycol, as a sole carbon source, increased from 20 to 55 days as the temperature was reduced from 25°C to 5°C. In the soil environment, the biodegradation rate of the same glycol was reduced by 2.44 times as the temperature dropped from 25°C to 10°C (McGahey and Bouwer, 1992). In this study, the surface biodegradation of ethylene glycol (represented by Konsin) decreased by a factor of 1.42 between 8°C and 1°C. In comparison, the propylene glycol (represented by Kilfrost) biodegradation rate decreased by a factor of 1.80 between the same temperatures. Experiments utilising high propylene glycol concentrations (1,000 mg/L) in different root zone environments produced between 2.2 and 4.2-fold decreases in mineralisation rates as the incubation temperature was lowered from 22°C to 7°C (Shupack and Anderson, 2000). Therefore, it is clear that the low temperature surface degradation process is less sensitive than has been found for other systems. This is further illustrated by the results from an aerobic bioreactor where glycols derived from de-icing fluids have been shown to degrade 5.8 times more slowly at 4°C compared to 10°C (Sabeh and Narasiah, 1992).

**Implications for surface biodegradation of de-icers**

Airports do not necessarily apply the same combinations of de- and anti-icing fluids or at identical application rates and the result will be airport specific surface compositions. In addition, the applications of the fluids vary for different airport areas with anti-icers (e.g. Kilfrost) being predominantly located on airport stands due to the immediate losses from aircraft surfaces whereas de-icers (e.g. Konsin and Clearway) are applied directly to taxi-ways and runways. There will also be continuous losses of applied anti-icers from the aircraft during taxi-ing and take-off. The consequences of these factors are that it is difficult to identify a uniform composition of the different de- and anti-icing fluids across the different airport impermeable surfaces which may contribute to runoff. Discussions with airport operators have suggested that typical surface compositions of de- and anti-icers for UK airports could be 71% Kilfrost, 12% Konsin and 17% Clearway. Using the respective BOD values for each of the neat liquids (Konsin, 0.590 kg/L; Kilfrost, 0.470 kg/L; Clearway, 0.142 kg/L) provides the relative contributions to surface biodegradable material as 77.9% from Kilfrost, 16.5% from Konsin and 5.6% from Clearway. These relative compositions are used in this paper to predict the variations in surface BOD levels over time at low temperatures.

The relationship between the derived biodegradation characteristics and the potential reduction in associated BOD, which has been used to calculate the losses of biodegradable material from de-icing fluid mixtures on airport surfaces due to the presence of microbial populations, is shown below:

\[
\text{BOD}_t = L_u (1 - e^{-kt})
\]

where \(\text{BOD}_t\) = remaining Biochemical Oxygen Demand after time \(t\) in days

\(L_u\) = ultimate oxygen demand

\(k\) = biodegradation rate (day\(^{-1}\))

\(t\) = time in days

The fraction of BOD remaining after time, \(t\), can be expressed by:

\[
\frac{\text{BOD}_t}{L_u} = 1 - e^{-kt}
\]
For Konsin at 4°C the determined biodegradation rate, $k = 0.082$ day\(^{-1}\), therefore over a period of 1 day ($t = 1$):

$$\frac{\text{BOD}_t}{L_u} = 1 - e^{-kt} = 1 - e^{-0.082 \times 1} = 1 - 0.9213 = 0.0787$$

The percentage decrease in BOD due to Konsin over a period of 1 day at 4°C would be 7.9%. Similar calculations for pure Kilfrost and pure Clearway predict BOD reductions at the same temperature of 7.0% and 3.2%, respectively. Under the same conditions the combined de-icing products in the proportions previously suggested would decrease by 7.0% in terms of the potential surface BOD contribution.

In practice it is unlikely that applied de-icing products would be washed off the receiving surface within such a short timescale as 1 day. However, a number of different temporal scenarios can be envisaged by which surface pollutant wash-off occurs following de- and anti-icing fluid applications. Experiences of the prevalent rainfall-runoff conditions at London Heathrow Airport suggest that a maximum surface duration of 5 days is appropriate. Based on this, the impacts of two different application/runoff relationships are investigated in this paper. In Scenario A, it is assumed that de- and anti-icing operations are carried out on Day 1 and there is then a period of 5 dry days during which surface biodegradation can take place before rainfall wash-off occurs. The consequences of this scenario with regard to potential losses of biodegradable material (calculated as BOD reductions) are shown in Figure 2. The maximum loss of the combined de- and anti-icing mixture is predicted to be 32.9% at 8°C decreasing to 30.2% and 21.4% at 4°C and 1°C, respectively. Thus, even at the lowest monitored temperature, marked reductions are possible in the amount of biodegradable material, which is potentially available for removal as airport runoff.

A more probable scenario (Scenario B) is that there are repeated daily applications of de- and anti-icing fluids over a 5 day cold weather period before rainfall produces a contaminated runoff event. The cumulative effects of the predicted biodegradable material losses are shown in Figure 2. The impacts on the amount of BOD potentially remaining on the surface are not substantially different at 8°C and 4°C (20.8% and 18.9% removals over 5 days) but at 1°C, the overall removal is considerably lower (13.3% over 5 days). However, this would still be significant in terms of the benefits with regard to the treatment potential of

![Figure 2](https://iwaponline.com/wst/article-pdf/48/9/103/423774/103.pdf)
the subsequent runoff prior to discharge to receiving waters. If this treatment were to be by
storage and aeration in a balancing reservoir, the advantages would be a lowering of the
reservoir capacity and/or a shortening of the required storage time. For example, the time
required for the reduction of the BOD of a representative de-icing mixture from 100 mg/L
to 20 mg/L by aeration alone at 8°C would be reduced from 20 to 17 days. Therefore, it is
possible that significant savings could be made in both engineering design costs, in con-
struction costs and in operational costs by considering the extent of surface biodegradation.
Although the situation described here is specific to airport surfaces and the application of
de-icers, the indicated reduction in required stormwater treatment is expected to apply to
other urban surfaces exposed to the deposition of biodegradable pollutants.

Conclusions
An experimental approach has shown that airport applied de- and anti-icing fluids have the
potential to undergo significant biodegradation during surface storage at temperatures as
low as 1°C. Glycol based de-icers demonstrate the highest measurable biodegradation rates
at all monitored temperatures and a simple modelling routine has shown that reductions in
the biodegradable material, available for incorporation in surface runoff, can be as high as
32.9% five days after a single application of a de- and anti-icer mixture. At lower tempera-
tures of 1°C and with consecutive daily applications, the BOD reductions are predicted to
be 13.3% over the same time period. It is acknowledged that different airports will have
their own preferences for the types of de- and anti-icing fluids applied resulting in different
surface compositions. However, the outlined modelling approach demonstrates a proce-
dure which it is proposed should be incorporated into the design of airport runoff treatment
systems in order to achieve important benefits relating to the size, cost and operation of
such systems.

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References
Colucci, M.S. and Inniss, W.E. (1996). Ethylene glycol utilization, cold and ethylene glycol shock and
decontamination of airport runoff. In: Proceedings of International Symposium on Deicing and
Institution of Civil Engineers – Transport, 117(3), 216–221.
control conditions. Water Research, 8, 97–100.
glycol and potassium acetate in the unsaturated zone. J. of Contaminant Hydrology, 49(1–2),
23–48.


