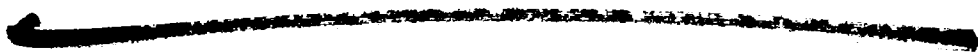


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De-icing Chemicals: Priorities for Environmental Quality Standards Development

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**DE-ICING CHEMICALS: PRIORITIES FOR ENVIRONMENTAL QUALITY
STANDARDS DEVELOPMENT**

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R&D Technical Report P31

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Statement of Use

This report reviews the available environmental data on de-icing chemicals commonly used within the UK. It prioritises the chemicals for EQS development and will be of value to Agency staff in assessing the potential effects of these substances on water quality.

Dissemination status

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EXECUTIVE SUMMARY

WRc has been contracted by the Environment Agency to review the possible environmental impacts of de-icing chemicals used in the UK and, where necessary, prioritise substances for the development of Environmental Quality Standards. The major de-icing chemicals in the UK are glycols, urea and acetate compounds, used for aircraft and airfield de-icing, antifreeze in engine cooling systems, and other miscellaneous uses.

The review comprises of an assessment of the impact on the aquatic environment of de-icing chemicals in relation to their usage, likelihood of entry into aquatic systems, fate and behaviour, toxicity, and bioaccumulation in aquatic organisms.

The de-icing chemicals used in the UK were all found to be of low aquatic toxicity although urea de-icers rapidly degrade to form ammonia which is of high toxicity. In addition, de-icing chemicals were found to rapidly degrade in aquatic systems, with the main degradation process being aerobic biodegradation. The largest use of de-icing chemicals in the UK is the use of glycols in vehicle cooling systems and car engines, however, impact on the aquatic environment from this use is likely to be low as they are used in sealed units and wastes are discharged to sewer, although incorrect disposal practices can lead to adverse effects on the environment. The use of glycol and urea de-icing chemicals on external surfaces such as at airports or on roads is likely to have the greatest impact on the environment because of their high biochemical oxygen demands and high solubility in water. Glycols can be considered as having the highest priority as urea is rapidly degraded to ammonia for which an EQS has been derived. Acetate-based de-icing chemicals should also be considered for EQS development as they are used at airports and on road surfaces and their use has vastly increased in the last few years, a trend which is likely to continue in future years.

The use of urea-based de-icing chemicals at UK airports has rapidly decreased in recent years, a trend which is likely to continue due to its ability to form ammonia. Thus it is not thought necessary to consider urea when prioritising de-icing chemicals for EQS development. In addition, EQSs have already been developed for the main constituents of rock salt and thus this has also not been considered for the purposes of this review.

KEY WORDS

Prioritisation, Environmental Quality Standards, EQS, de-icing chemicals, glycols, urea, acetate compounds, aquatic toxicity, biochemical oxygen demand.

1. INTRODUCTION

WRc has been contracted by the Environment Agency to review the de-icing chemicals used in the UK in order to prioritise substances for EQS development. The major de-icing chemicals in the UK are glycols, urea and acetate compounds, and these are used for aircraft and airfield de-icing, antifreeze in engine cooling systems, and other miscellaneous uses. Although the largest amount of de-icing chemicals used in the UK is in vehicle cooling systems, the main risk to the environment comes from use at airports as due to their high water solubility they may enter the aquatic environment via normal runoff.

Sections 2-4 review the available literature on the types of de-icing chemical, their main uses, likely environmental concentrations and their impacts on the aquatic environment. In Section 5 the types of de-icing chemicals are discussed individually, reviewing the available data on their fate and behaviour in the aquatic environment and their toxicity to aquatic organisms. Based on information on the usage, fate and behaviour, biochemical oxygen demand and aquatic toxicity, Section 6 identifies those chemicals of most concern and suggests priorities for further investigation and EQS development. Conclusions are presented in Section 7. Toxicity data for de-icing chemicals are presented in Tables A1-A5 of Appendix A.

2. SELECTION OF DE-ICING CHEMICALS FOR REVIEW

This section briefly reviews the different types of de-icing chemicals and discusses their properties which are of relevance to possible environmental impacts. The major types of de-icing chemical in the UK are products based on the following:

- glycols (ethylene glycol, diethylene glycol and propylene glycol)
- urea
- acetate salts (potassium acetate, sodium acetate and calcium magnesium acetate)
- formate compounds (sodium formate and potassium formate)
- rock salt (sodium chloride)

At the request of the Environment Agency, rock salt, which is commonly used on roads throughout the UK in winter has only been briefly considered in Section 5.8 because its constituents, sodium and chloride are both covered by Environmental Quality Standards derived for the Environment Agency and SNIFFER (Gardiner and Smith 1992). In addition, a brief summary has been provided concerning the impurities found in rock salt. However, the main body of this review focuses on urea, glycols, acetates and formate compounds.

In the UK, the major uses of de-icing chemicals are for:

- aircraft de-icing
- runway and taxiway de-icing at airports
- antifreeze in engine cooling systems
- other miscellaneous uses (e.g. de-icing of freight containers, industrial coolants, de-icing of surfaces at industrial plants)
- antifreeze in cooling engine systems
- other miscellaneous uses.

The major manufacturers and users of de-icing chemicals in the UK were approached for the following information:

- de-icing chemicals produced/used
- their constituents

- volumes used in the UK and application
- aquatic fate and behaviour
- aquatic toxicity.

The data received from these sources have been incorporated into this review in the relevant sections.

The use of de-icing chemicals is temperature dependent and is confined to periods of low temperature, largely the winter months. Glycol and urea de-icing chemicals are highly water soluble and, consequently, may occur in airport runoff. However, runoff water from airports has a complex nature, often containing de-icing chemicals, detergents, oil and fuel, grit and organic matter, and because of this, it is difficult to accurately determine the impact of de-icing chemicals from this source, although de-icers are likely to contribute to the overall impact.

De-icing chemicals can potentially have adverse effects on the environment throughout the year from other uses such as from industrial cooling plants, for example if such as leakage or incorrect disposal practices occur.

The de-icing chemicals used in vehicle cooling systems may be replaced when a vehicle is serviced (i.e. throughout the year), and the waste chemicals are likely to largely be discharged to sewers and will undergo treatment before they reach the receiving water. However, discharges to surface waters could occur due to poor disposal practises from garages and home servicing, and these may have an impact on the aquatic environment.

3. USE OF DE-ICING CHEMICALS IN THE UK

The major uses of de-icing chemicals in the UK are listed in Section 2 and are discussed in more detail below in Sections 3.1-3.4.

Although data for recent years is not available, it was estimated (DoE 1988) that in the late 1980s typically 12 000 tonnes of glycol were purchased annually for antifreeze or de-icing activities in the UK. Of this, approximately 4750 tonnes were used for airfield and aircraft de-icing, 7200 tonnes were used for antifreeze in engine cooling systems and 50 tonnes were used for other purposes. Clearly the largest usage of de-icing chemicals in the UK is antifreeze in engines. However, it is their use at airports which is of greatest environmental concern due to localised application, concentrated winter use and high water solubility, and the fact that entry into the aquatic environment occurs in the runoff from airports, which may or may not have received treatment.

Most de-icing chemicals exert their effect by converting the ice into a de-icer-water solution which has a freezing point below that of water. If applied as an anti-icer before freezing weather conditions, then the formation of ice is prevented.

3.1 The use of de-icing chemicals at airports

De-icing chemicals serve two functions at airports, and accordingly this section has been split into two. Section 3.1.1 concerns their use on runways, taxiways and other sections of airfields, while Section 3.1.2 concerns their use on aircraft.

In general, the amount of de-icer used at airports is dependent on local conditions, such as weather patterns and the size of area/number of aircraft to be treated. The amount of glycol-based de-icing agents used at BAA airports in the mid-1980s is given in Table 3.1, unfortunately a comprehensive list of more recent figures are not available. However, up-to-date usage figures have been obtained from Gatwick airport on the types and amounts of de-icing chemicals applied, and this is presented in Table 3.2. As can be seen from the data in Table 3.2, the amount of neat product used each year varies considerably according to the weather conditions, and therefore any trends such as a decline in the use of one type of de-icing chemicals will be very difficult to assess. The amount used also depends on the latitude of the airport, with airports in the north of the UK generally requiring more de-icer than airports in the south.

Glycols, urea, formates and acetates can either be used for preventing ice formation (anti-icing) or for clearing ice (de-icing), although the application rates tend to be slightly lower for anti-icing practices.

Table 3.1 Reported use of glycol-based de-icing agents at BAA airports (in litres)

Airport	Application ¹	Use in 1984/85	Use in 1985/86	Use in 1986/87	Amount in storage
Aberdeen	runways	151 000	-	-	200 000
	aircraft	13 069	-	-	
Edinburgh	runways	45 317	73 365	93 870	109 104
	aircraft	25 017	23 830	-	
Gatwick	runways	151 922	185 659	95 161	95 000
	aircraft	-	-	-	
Glasgow	runways	-	148 500	137 350	90 920
	aircraft	-	72 812	85 903	
Heathrow	runways	177 657	7 500	123 878	100 012
	aircraft	224 263	428 974	146 617	
Prestwick	runways	-	-	-	18 184
	aircraft	-	-	-	
Stansted	runways	60 948	7 405	106 085	45 000
	aircraft	33 611	-	37 422	

Note:

¹ de-icer fluids for runway application are approximately 90% (w/w) glycol and those used for aircraft application are approximately 50% (w/w) glycol

Table 3.2 Summary of the use of neat de-icing chemicals at Gatwick Airport (Pers. comm., R. Yarr, Gatwick Airport Ltd, 1995)

Chemical (Company)	Amount in litres used per month (as neat product)												Total
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	
Winter 1990-1991													
Konsin	0.00	0.00	8 800.00	12 300.00	103 450.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	124 550.00
Kilfrost	0.00	1 725.00	128 917.00	37 212.00	382 772.00	2 985.00	545.00	545.00	545.00	545.00	545.00	545.00	554 166.00
Total	0.00	1 725.00	137 727.00	49 512.00	486 222.00	2 985.00	545.00	545.00	545.00	545.00	545.00	545.00	678 716.00
Winter 1991-1992													
Konsin	0.00	2 500.00	30 050.00	3 700.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	36 250.00
Kilfrost	26 016.00	28 423.00	57 353.00	42 762.00	19 662.00	12 275.00	1 000.00	1 000.00	1 000.00	1 000.00	1 000.00	1 000.00	187 491.00
Total	26 016.00	30 923.00	87 403.00	46 462.00	19 662.00	12 275.00	1 000.00	1 000.00	1 000.00	1 000.00	1 000.00	1 000.00	223 741.00
Winter 1992-1993													
Kilfrost (Nordic Aero)	0.00	1 494.00	10 405.00	0.00	0.00	900.00	0.00	0.00	0.00	0.00	0.00	0.00	12 799.00
Kilfrost (Servisair)	12 900.00	2 216.00	7 375.00	5 369.00	1 921.00	3 389.00	0.00	0.00	0.00	0.00	0.00	0.00	33 170.00
Clearway 1 (GAL MT)	0.00	0.00	13 900	1 500.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	15 400.00
Total	12 900.00	3 710.00	31 680.00	6 869.00	1 921.00	4 289.00	0.00	0.00	0.00	0.00	0.00	0.00	61 369.00

Chemical (Company)	Amount in litres used per month (as neat product)										Total	
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul		
Winter 1994-1995												
Kilfrost (Nordic Aero)	1 860.60	0.00	25 527.80	11 370.75	7 124.25	36 294.00	NY ^(a)					82 177.65
Kilfrost (British Airways)	0.00	0.00	12 397.75	15 942.25	2 567.75	24 844.45	2 254.50					58 006.00
Clearway 1 (GAL MT)	0.00	0.00	19 750.00	17 500.00	1 500.00	6 150.00	0.00					44 900.00
Total	1 860.00	0.00	57 675.55	44 813.00	11 192.00	67 288.70	2 254.50					185 084.35

Notes:

^a NY -Data was collected up until 25 April 1995, and to this date, no Kilfrost had been used by Nordic Aero.

At Newcastle International Airport a new de-icer based on acetate called Safegrip was used during the 1994/5 winter. This was being tested at Newcastle in response to pressure from Regulatory Authorities to minimise the use of urea and glycols. Table 3.3 shows the use of Safegrip at Newcastle.

Table 3.3 Use of Safegrip (neat product) at Newcastle International Airport (A. Groves, Assistant Planner, Newcastle International Airport, Pers. Comm. 1995)

Month	Amount Used (litres)	Month	Amount Used (litres)
October 1994	299	February 1995	8 075
November 1994	0	March 1995	38 293
December 1994	49 589	April 1995	7 201
January 1995	103 169		

Table 3.4 shows examples of the composition of some de-icing chemicals used at airports. It can be seen that some de-icing chemicals contain a mixture of more than one glycol and that a mixture of glycol and urea may be present in one formulation. No further details of the composition of de-icing formulations could be located. A new group of de-icing chemicals have appeared on the market in recent years which are based on potassium and sodium acetates. The first to be developed was Clearway 1 by BP Ltd in 1987. BP Chemicals Ltd now have a range of Clearway compounds available, including liquid and solid formulations and although the Clearway products are the most frequently used acetate de-icers in the UK, a number of other formulations are now available. BAA are also testing Clearway products and assisting BP in product development (P. Dunn, Environment Manager, BAA, Pers. Comm. 1996).

3.1.1 Aircraft

Aircraft de-icing chemicals used in the UK are all based on glycols. Urea, formate and acetate compounds are not suitable for this purpose, and so far a suitable alternative to glycols has not been developed. It was estimated in the late 1980s (DoE 1988), sales for aircraft de-icing in the UK were in the order of 1000-1500 tonnes per annum, more recent tonnage data could not be located.

Table 3.4 Composition of a number of de-icing chemicals

Name	Use	Major components	Manufacturer
Kilfrost	aircraft de-icer	propylene glycol	Kilfrost Ltd
Konsin	runway de-icer	monoethylene glycol (30-60%) diethylene glycol (40-70%)	ICI
Clearway 2S	runways de-icer (solid)	sodium acetate	BP Ltd
Clearway 1	runway de-icer (liquid)	potassium acetate	BP Ltd
Safewing MP I	aircraft de-icer (Type I)	glycol (80%) water (19%) surfactants and additives	Hoechst
Safewing MP II	aircraft de-icer (Type II)	glycol (50%) water (49%) surfactants and additives	Hoechst
Safeway KA	runway de-icer (liquid)	potassium acetate (50%) water (49%) additives	Hoechst
Safeway SD	runway de-icer (solid)	potassium acetate (>99%) additives	Hoechst

Due to advanced aerodynamics, modern aircraft are very sensitive to the effects of ice on the wing surface which may result in non-laminar flow, increasing the pressure over the wing, and reducing lift. De-icing of aircraft is usually carried out by mobile dispensers which spray the de-icing solution (often heated to 90 °C) onto ice-sensitive surfaces. The solution forms a film over the surface which gives protection from ice for up to 8 hours after spraying. The concentration of the de-icing agent used varies according to the climatic conditions. In a severe UK winter the product may be applied neat, whereas in a relatively mild winter, a 50% aqueous solution may be used (R. Yarr, Gatwick Airport, Pers. Comm., 1995).

At Gatwick Airport, the main de-icer used on aircraft is a product called Kilfrost, and since 1990 between 46 000 and 554 000 litres of neat product have been used annually (Table 3.2). The large variation between years is due to the severity of the winter (R Yarr, Gatwick Airport Ltd, Pers. Comm., 1995).

Many independent carriers at commercial sites carry out the de-icing of their own aircraft. De-icing is at the discretion of the pilot and usually occurs within an hour of take-off with volumes of up to 1000 litres necessary to de-ice one large aircraft (R. Yarr, Gatwick Airport, Pers. Comm., 1995). The residual fluid rolls off onto the runway during take-off and if not collected, will enter the watercourse dissolved in runoff water.

There are two types of glycol-based de-icing agents used for aircraft application recommended by the Association of European Airlines, and these are known as AEA Type I and AEA Type II. AEA Type I fluids contain approximately 80-90% glycol and are of low viscosity so that they will not remain on the aircraft after take-off. AEA Type II fluids contain a minimum of 50% glycols, and usually contain a thickening agent to enhance adsorption to the aircraft giving protection against refreezing for up to 8 hours. AEA Type I de-icing chemicals runoff on the runways before and during take-off whereas AEA Type II chemicals shear off during flight. Therefore, AEA type I de-icers have a much greater potential for entering local watercourses or entering the airport runoff treatment systems than AEA Type II de-icers. AEA Type II fluids are the only type used in the UK as the climate is not suitable for AEA Type I fluids.

An alternative to the use of chemicals for aircraft de-icing is hot water de-icing. Some airports in Europe and America are successfully using only hot-water prior to a spray of anti-icing agent (Gay *et al.* 1987). This is an effective way of reducing the use of de-icing chemicals, but has obvious drawbacks, most importantly the refreezing of water on contact with the aircraft. In the UK the climate is not suitable for hot water de-icing of aircraft (P. Dunn, Environment Manager, BAA, Pers. Comm. 1996).

3.1.2 Runways and taxiways

The traditional chemical used for runway de-icing was granular urea, which was adopted on a large scale about three decades ago. Urea was selected because it did not corrode aircraft parts, stain paints or affect the plastic of aircraft windows, and because large quantities were available at a low price. Glycol formulations can also be used for runway de-icing, although some de-icers such as granular rock salt and calcium magnesium acetate are not suitable because of their corrosive nature to aircraft. However, glycol formulations generally have high oxygen demands on rivers and urea is converted to the highly toxic ammonia. The problems associated with the use of urea and glycols have given rise to the development of new alternatives based on potassium and sodium acetate or potassium and sodium formate. The first to become commercially available was Clearway 1 in the late 1980s marketed by BP Chemicals Ltd. Other acetate compounds are now available (e.g. Safeway developed by Hoechst), although the various Clearway formulations remain the market leaders. Formate de-icing chemicals are an even more recent development than those based on acetates, and have been trialled successfully at a number of airports, although are not yet widely available on a commercial basis.

It was estimated in the late 1980s (DoE 1988), that sales of glycol-based de-icing chemicals were in the order of 3000-4000 tonnes per year for runway de-icing at UK airfields. Annual sales, however, do not necessarily reflect usage rates since products are stored and may not be used on the year of purchase. The data provided by Gatwick Airport (Table 3.2) and DoE

(1988) appears to indicate that 2 or 3 times more de-icing chemical is used on aircraft than on runways, however, while this ratio is typical for Gatwick airport, it will vary from airport to airport.

Urea de-icing chemicals have been found to corrode electrical cables under runways (G. Stephen, Gatwick Airport Ltd, Pers. Comm. 1995). BAA airports including Gatwick, Heathrow and Stansted withdrew the use of urea in the late 1980s because of the concern of Thames Water Authority (predecessor of the Environment Agency - Thames Region) regarding the impact of urea on the aquatic environment when it hydrolyses to ammonia (which is toxic to fish and impairs water quality). Runway de-icers containing urea were replaced with Konsin in the late 1980s. Konsin was used at Heathrow until 1992, when it was decided that Clearway 1 should undergo trials largely as a result of pressure to move away from glycol-based de-icers. In the winter of 1994-95, 44 900 litres of Clearway 1 were used by Gatwick airport (R Yarr, Gatwick Airport Ltd, Pers. Comm., 1995). However, at Heathrow, operational experience has cast doubts on the effectiveness of some acetate compounds, especially under severe snow conditions, when greater quantities of acetate have been used in order to achieve the same results as the previously used glycol based de-icer. For this reason it was decided that Heathrow airport should, in the short term, revert to the use of glycol de-icers, pending development and testing of new acetate and formate formulations (P. Dunn, Environment Manager, BAA, Pers. Comm. 1996).

The use of urea based de-icing chemicals was phased out at Newcastle International Airport in 1991 in a programme agreed with the Environment Agency to reduce ammonia levels in the Ouseburn catchment, and an acetate compound called Safegrip is now being used (see Table 3.3). However, acetate compounds are usually applied as solutions in water (usually as 50% aqueous solutions), and so there is some fear that the water may cause problems with refreezing. To combat the potential refreezing problems, BP Chemicals Ltd are now marketing a solid formulation of Clearway called BP Clearway 2S based on sodium acetate which contains double the amount of active ingredient and Hoechst have introduced Safeway SD, a solid de-icer containing >99% sodium acetate. While these solid formulations may eliminate refreezing problems, because they contain a higher percentage of active ingredient, they are much more costly. At Newcastle, spreading rates for acetate compounds of 15 g m^{-3} are used in mild winters, although this can be increased up to 50 g m^{-3} in severe winters (Mr Douglas Reed, Newcastle International Airport, Pers. Comm., 1995).

At Aberdeen airport, 'Konsin' (a glycol-based de-icing chemical) is used during the winter period for de-icing the runways. In January 1993, they took the decision to halt the use of urea-based de-icing chemicals.. The use of the acetate-based Clearway 1 is currently being investigated at Aberdeen, although it is estimated that approximately three times the volume is needed, making it an expensive alternative to glycol-based chemicals. Recent data available for Edinburgh Airport show that until the winter of 1993/94 a urea based de-icer was used for de-icing runways. However, this has now been replaced with the glycol-based 'Konsin'. In the winter of 1993/94, 37 608 gallons of Konsin were used and this had increased to 57 000 in the winter 1994/95 (Pers. Comm., Edinburgh Airport, 1995). The data in Table 3.3 suggest that between 17 100 and 22 800 gallons of monoethylene glycol and 34 200 and 39 900 gallons of

diethylene glycol were used at this airport for aircraft de-icing in 1994. In summary, it appears that glycols are used at a number of airports in preference to urea, and that acetate compounds may assume greater importance in the future through a combination of improved efficacy and regulatory pressure.

Hydro Chemicals Ltd have developed a new fluid for de-icing runways based on potassium formate called Aviform L50. It has been successfully tested at Oslo airport during the 1995 winter. The product works by breaking the bond between the surface and the ice making it easier for the ice to be removed by mechanical means. It is easy to apply, of low toxicity, has a low BOD and is biodegradable. In addition, initial results indicate that its de-icing characteristics are comparable or better than glycols and acetates (correspondence between Environment Agency and Hydro Chemicals Ltd, September 1995).

Minor de-icing is also carried out on passenger loading bridges and others bridges at airports to keep them free of ice and safe for operation.

3.2 Antifreeze for vehicle cooling systems

The largest use of glycols in the UK is as antifreeze in vehicle and engine cooling systems, and the amount used annually in the late 1980s was reported to be 7200-8000 tonnes (DoE 1988). Whilst the use of de-icing chemicals at airports is restricted to the winter, that used in vehicle antifreeze may be discharged throughout the year during the vehicles service. The majority of discharge will be to the foul sewer and receive treatment, and due to the rapid biodegradation of glycols during sewage treatment it is unlikely that they will enter the aquatic environment (see Section 5.2.2). However, discharge to surface water drains does occur due to poor disposal practices by garages and from home-servicing, and this will not pass through sewage treatment works.

3.3 Usage on public highways

Rock salt (sodium chloride) remains, undoubtedly, the major de-icing agent used on roads throughout the UK. In water it rapidly dissociates to sodium and chloride ions, which have been covered previously in an Environmental Quality Standard report prepared by WRc for the Environment Agency and SNIFFER (Gardiner and Smith 1992). Thus the Environment Agency have requested that this report should concentrate on the other de-icing chemicals. However, a brief summary of the fate and behaviour and the aquatic toxicity of rock salt has been reported in Section 5.8.

The transport departments of some county councils have been contacted to determine the quantity of salt spread on roads, which roads are targeted and where they buy their salt. Berkshire County Council apply approximately 7-8000 tonnes of salt to their roads in a mild winter. The amounts used are dependent on the temperature during the winter period, and in an extreme winter 15-20 000 tonnes may be used. Buckinghamshire County Council stock about 25 000 tonnes of salt each year, but the amount used is weather dependent. A list of

priority salting routes exist within each County. These include the most frequently used roads, and up to half of the county's road network may receive some salting during an average winter. In an average winter, 8000 tonnes are spread on the roads of Oxfordshire.

In an average winter, North Yorkshire County Council use 50-70 000 tonnes and a stock of 100 000 tonnes is kept in storage. Spreading rates on roads vary between 10 g m^{-2} in mild winter up to 40 g m^{-2} in a severe winter, and these values are fairly typical of rates throughout the UK. Roadside piles of rock salt have been reported to cause elevated levels of chloride in nearby watercourses, although no data on actual concentrations were provided, however, chloride could not be detected 100 m downstream of the piles. Weather forecasts from the Metropolitan Office in Bracknell and 10 remote sensing stations are used to predict weather conditions, and rock salt is spread in light of these. Other de-icing chemicals have not been tested in this region as rock salt costs <£20 a tonne and other chemicals would cost in the order of 5 times this (Robert Burns, North Yorkshire County Council, Highways Department, Pers. Comm., 1995).

For the last 10 years or so, urea has been used on the elevated section of the M62 in winter to keep it ice-free as the chloride in rock salt was found to affect the concrete road surface. Originally, the urea spreading was carried out by the county council who applied it liberally regardless of the weather forecast. Recently a private contractor has carried out the spreading and weather forecasts have been used to try to reduce the amount of urea used. This has resulted in a reduction in annual use from 2000 tonnes to 400-500 tonnes. High urea levels in the River Thames (a tributary of the River Trent) have been reported, although the concentration is not available. Urea is not thought to have a major impact on this river as it is already highly polluted from sewage effluent and does not support fish. Because of the presence of the sewage effluent high numbers of bacteria are present which accelerate degradation of the urea. Elevated urea levels have been reported as far downstream as Nottingham, 40 miles away (Mr Dolby, Environment Agency - Severn Trent Region, Pers. Comm., 1995).

The Environment Agency has produced guidance notes on pollution prevention measures for salt stores as well as for stocks of urea and acetates.

3.4 Other uses of de-icing chemicals

Other uses of glycol based de-icing chemicals include keeping bridges ice-free, de-icing freight containers during storage in depots, keeping emergency areas such as hospital forecourts ice-free, de-icing surfaces at industrial plants, and as coolants in industrial cooling systems and large deep freeze installations. However, the market for these uses is very small in comparison to its uses at airport and in vehicles, and has been estimated to be less than 50 tonnes per year (DoE 1988).

Urea is used on the Landrover test track at Solihull to keep it ice-free. No further details are known on the amounts of urea used or if any detrimental effects to the quality of nearby watercourses have arisen from this use (Mr Dolby, Environment Agency - Severn Trent Region, Pers. Comm., 1995).

3.5 Corrosion inhibitors in de-icing chemicals

A number of corrosion inhibitors are used in antifreeze and de-icing products. They only account for a small percentage of total product (<2-5%), but could potentially have harmful effects on the aquatic environment. A report on corrosion inhibitors is currently being produced by the Environment Agency.

A number of corrosion inhibitors are used in the automobile industry, which are listed below, these can either be used on their own or in combination with others.

Corrosion inhibitors in antifreeze include:

Borate salts	Sodium salts (including the nitrite, nitrate and silicate)
Borax	Tolyazole
Carboxylic acid salts	Nitrate salts
Metasilicate salts	Triethanolamine
Polytriazole	

Corrosion inhibitors in runway de-icing agents may also be used individually or in combination and include:

Benzotriazole	Sodium benzoate
Potassium phosphate	Sodium nitrite

A separate report reviewing corrosion inhibitors is currently being prepared by WRc for the Environment Agency (July 1996).

4. ENTRY INTO THE AQUATIC ENVIRONMENT

Glycols, urea and some acetate compounds (e.g. potassium acetate) are highly soluble in water and they have low octanol-water partition coefficients, indicating that they are not strongly bound to soil and will enter the watercourse dissolved in the runoff. Consequently, maximum potential for entry into the aquatic environment is after rainfall. The amount of de-icer used, and the number of months its use is necessary depends partially on the latitude of the airport. For example, winter conditions prevail at Aberdeen for much longer than in the south of England, and hence, whereas de-icers are often only necessary at Gatwick between December and March each year, at Aberdeen the use period is likely to extend between October and May. Thus, in Scottish rivers, pollution from the use of de-icing chemicals may, depending on local weather patterns, continue thorough until June and have a more long-lasting effect on the water quality. However, in general, the larger the airport, the more de-icer is necessary, and therefore the potential for impact from airports such as Gatwick and Heathrow is much greater than from much smaller airports.

4.1 Prediction of surface water contamination at airports

De-icer loads in surface water are dependent on the following:

- number of aircraft departures per day
- number of night-time versus day-time flights
- proportion of day-time flights which are short turnarounds
- amount of de-icers applied per aircraft and type used
- climatic conditions (i.e. day and night temperatures, amount of rainfall)
- runway surface (porous asphalt versus concrete)
- central collection systems for runoff de-icers and recycling facilities.

Computer models have been developed to predict runoff, taking into account the above factors and meteorological data collated over the last 10 years. These have been trialled and well tested at Stansted, Gatwick, Heathrow and Aberdeen airports, among others.

4.2 Concentrations of de-icing chemicals in the aquatic environment

Glycols and urea have been frequently reported downstream of UK airports, and the data are summarised below in Section 4.2.1 and 4.2.2, respectively. Data could not be located on the concentrations of potassium and sodium acetates in UK waters.

4.2.1 Glycol-based de-icing chemicals

There are many recorded cases of glycol concentrations in excess of 100 mg l⁻¹ in the site drainage of airports in the UK. Highest concentrations in receiving waters are largely likely to occur with maximum use, and may be in excess of 1000 mg l⁻¹. Between 40-100% of the de-icers applied to an aircraft or runway will end up in runoff and will enter either surface waters or the airport sewer system (DoE 1988).

Downstream of RAF Wootton Bassett (Anglian Region), a glycol concentration of 1 mg l⁻¹ was reported in the River Stour. Intermittent growths of sewage fungus have been reported in the river as a result of contamination by airport runoff and, after this incident, Anglian water considered the closure of a nearby abstraction point. No further details have been provided on this incident.

Problems of sewage fungus attributed to glycol use were reported downstream of both Birmingham International and East Midlands airports (in tributaries of the Rivers Soar and Thame, respectively). However, balancing tanks have now been installed which have eliminated these problems. No further details have been provided on this (Mr Dolby, Environment Agency- Severn Trent Region, Pers. Comm., 1995).

An increased BOD has also been reported in the Cowage Brook (Wessex Region) as a result of the use of glycols at RAF Lyneham, no details have been provided on the BOD value recorded (DoE 1988).

There are few other reports of glycols in surface waters. The highest reported concentration of ethylene glycol in receiving waters in Canada is 13 200 mg l⁻¹, measured in the drainage ditch carrying runoff from Dorval Airport in 1974 (CCREM 1994). Since 1974, glycol pollution has decreased due to a change in the de-icing chemicals used and increased efficiency of use, and typical concentrations in the range 4.5-552 mg l⁻¹ have been reported. At other Canadian International airports (Halifax, Mirabel and Pearson) reported ethylene glycol concentrations in receiving waters ranged from <10-643 mg l⁻¹. No data could be located on the concentrations of diethylene glycol and propylene glycol in Canadian surface waters (CCREM 1994).

Data on levels in groundwater are limited to those collected at Ottawa International Airport in 1985 and 1986, with 415 mg l⁻¹ being the maximum reported ethylene glycol concentration. The maximum diethylene glycol concentration was 188 mg l⁻¹. Propylene glycol concentrations have not been found to be greater than 10 mg l⁻¹ (CCREM 1994).

4.2.2 Urea-based de-icing chemicals

In the aquatic environment urea rapidly degrades to ammonia. Ammonia has been reported at concentrations of 1-173 mg l⁻¹ in rivers downstream of airports, and these have been associated with fish kills. The use of a urea-based de-icing chemical at RAF Church Fenton (North East Region) was found to cause a high fish mortality and ammonia concentrations in the receiving river of upto 40 mg l⁻¹ were reported (DoE 1988).

Turnbull and Bevan (1995) carried out routine monitoring of the Ouseburn catchment downstream from Newcastle International airport. In the winter of 1991/92, 91 tonnes of granular urea were used. This resulted in a maximum concentration of 173.4 mg l⁻¹ ammonia reported (on 26 February 1992) in the airport tributary, and a maximum concentration further downstream of 36.79 mg l⁻¹.

In the mid-1980s, there was a pollution incident concerning the discharge of storm-water from Gatwick airport to the River Mole. High ammonia levels in excess of 100 mg l⁻¹ were reported resulting in fish mortality, and this is possibly a result of urea use at Gatwick airport, although the exact source cannot be identified (G. Stephen, Gatwick Airport Ltd, Pers. Comm., 1995).

RAF Lyneham is known to discharge urea into Cowage Brook (Wessex Region) and ammonia concentrations of 15-20 mg l⁻¹ have been observed in the Brook as a result of urea hydrolysis. An increased BOD has also been reported as a result of the use of glycols (DoE 1988).

The use of urea for de-icing at a group of airfields which discharge into the River Ouse have caused problems for drinking water abstraction downstream. Ammonia concentrations in excess of 1 mg l⁻¹ have been reported, and these interfere with the chlorination process at drinking water treatment works.

A trial was carried out in the early 1970s at selected RAF airfields using urea as a de-icer (Capon and Nicholson 1974). During the winter of 1972/3, between the months of November to April, 12 separate applications of urea amounting to 68 tonnes were applied to the runways at RAF Brize Norton. The maximum concentrations of urea detected in Shill Brook at Bampton and in the River Thames at Newbridge were 75 and 4.3 mg l⁻¹, respectively.

4.3 The reduction of aquatic concentrations

There are a number of methods by which concentrations of de-icing chemicals can be reduced in the aquatic environment. The most widely employed are a reduction in the amount used, collection and recycling, and treatment prior to discharge. The various options are discussed below.

4.3.1 Treatment of de-icing chemicals at airports

Because the runoff from airports can contain numerous pollutants (oils, detergents, suspended solids, organic matter, gravel etc.), there is increasing pressure for the collection of runoff and for it to undergo some form of treatment before discharge to rivers. For example, at Birmingham International Airport runoff passes through oil interceptors and settlement lagoons before being discharged into the River Blythe. Runoff from Heathrow and Gatwick airports enters lagoons before being discharged into local rivers. However, in smaller airports, runoff may be discharged into drainage ditches and not undergo any treatment. For example, the East Midlands airport and the aerodrome at Dunsfield (Southern Region) both discharge their runoff into minor ditches and streams which has caused problems of eutrophication, and prolific algal and fungal growths. However, because of the complex nature of airport runoff, these algal growths cannot be attributed solely to de-icing chemicals.

At Aberdeen airport a provisional £9.5 million is being invested in a new airport drainage system consisting of a storage lagoon and a system for sea disposal, in order to meet water quality demands imposed on them. The building of the new system was due to begin in May 1995. Their effluent quality is monitored by the Scottish Environmental Protection Agency (SEPA) who have detected sewage fungus just below the outlet of an airport due to the increased biochemical oxygen demand (BOD). The sewage fungus is thought to be caused by the use of de-icing chemicals as maximum growth of the algae coincides with maximum use of de-icers during the winter. The BOD of the receiving water is not known (Mike Davidson, SEPA, Pers. Comm., 1995). Also, in the 1980's, salmon in the River Don became anaemic and de-icers were originally implicated as the cause of this although more recent data suggest that resin acids were responsible, although the exact reason has not been confirmed (Mike Davidson, SEPA, Pers. Comm., 1995).

Both aerobic and anaerobic biological treatment processes have been reported to remove glycols effectively from wastewaters over a wide range of concentrations. The low temperature of storm water in the winter is not conducive to efficient aerobic treatment in isolation (e.g. the balancing ponds at Gatwick froze over during the winter of 1986-7). In full-scale trials of the treatment of glycols in admixture (75-200 mg l⁻¹) with sewage, the glycol was effectively removed at all concentrations and nitrification was not inhibited (Gay *et al.* 1987).

The most popular treatment method seems to be by pumping runoff into a lagoon which can then be discharged to sewer or aerated and discharged directly to the river. New lagoons have been built at Gatwick and Manchester airports. At Gatwick airport the new lagoon, which can hold 200 000 m³ of water, cost of £4.5 million. It was completed in 1995, and was fully operational and highly successful by April 1996 (P. Dunn, Environment Manager, BAA, Pers. Comm. 1996). It is intended that the large majority of runoff from the aprons and taxiways will enter this lagoon. The runoff is aerated in order to stimulate degradation of glycols and other substances. The collected runoff will then be pumped to Crawley sewage treatment works before discharge to the River Mole. In addition, the use of reeds for the treatment of runoff are currently being tested at Gatwick.

In the 1980s, Manchester airport, the most rapidly expanding airport in the UK, was experiencing problems due to excess BOD in local watercourses, some of which were Sites of Special Scientific Interest (SSSIs). To solve the problem, a new collection and containment system was installed, which became fully operational in the winter of 1995. The runways are divided into catchment areas, each of which has its own balancing tank. These all drain into a central balancing tank, and the collected runoff is pumped to a local sewage treatment works. Storm flows are still discharged directly into local rivers. The use of urea based de-icing chemicals was phased out in the early 1990s, and Konsin is currently being used and acetate compounds are undergoing trials. A stringent consent has been set for the airport because of the SSSIs, and last winter, these sites had improved in quality from a Class 4 to a Class 1 (John Capper, Environment Agency, North East Region, Pers. Comm., 1996).

4.3.2 Recycling and other methods of reducing impact

There are a number of alternative methods to treatment to reduce the amount of de-icing chemical reaching the aquatic environment. These include decreasing the quantity of chemicals used, and the collection of the de-icing chemical for re-use, although the latter does not occur in the UK.

Glycol recycling has been tested at a number of airports in the world, and has generally, not been found to be totally successful because of the high costs incurred and the impracticability of operation.

Glycol recycling can be achieved by (typically) vacuum distillation. Centralised de-icing facilities have been installed in a number of airports in Europe and Canada including Mirabel in Canada, Charles De Gaulle in France, and Kallax in Sweden. They were designed to collect used fluid and process it to provide a clean fluid of the required concentration for use. One of the main problems has been congestion from aircraft which have to pass through the system before take-off (Gay *et al.* 1987). In addition, they do not eliminate the problem of surface water contamination as a significant proportion of de-icing chemical use at airports is on the runways and taxiways which is not addressed in a centralised de-icing system. A further difficulty arises from the widely differing sizes of aircraft which would all need to pass through the facility.

Because of the problems experienced at other airports, it is unlikely that centralised de-icing facilities will be installed at airports in the UK. At Gatwick it was decided against because of the congestion it would cause and as approximately 5 de-icing facilities would be necessary - one at either end of the runway (aeroplanes take-off from both ends according to the direction of the wind), a back-up and a separate system for turbo engines (R. Yarr, Gatwick Airport Ltd, Pers. Comm., 1995).

At Heathrow, centralised de-icing facilities including a system similar to that installed at Charles De Gaulle airport in France have been considered as one of many options for glycol reduction. However, dedicated facilities are large and demanding of area which would be a problem at this space-constrained airport. All methods considered so far are likely to reduce the aircraft departure rate, and the provision of a centralised facility is not being pursued (B. Tew, Airfield Operations Manager, Heathrow Airport Limited, Pers Comm., 1996).

Because of spray drift and engine blast which account for the loss of upto 40% of the de-icing chemical applied, it will never be possible to collect all the used glycol. In addition, recycling of used AEA Type II fluid (the type suitable for use in the UK) is not possible with current technology.

If glycol recycling is to be carried out successfully, the following are necessary:

- the glycols must be in a concentrated form, and therefore it is not suitable for runway de-icer which are diluted in runoff water.
- the glycols must be collected immediately following use.

In general, glycol recycling has not been highly successful, and new developments in technology are required before recycling can be carried out at more airports.

At Newcastle International Airport the amount of glycols entering the Ouseburn catchment downstream of the airport is monitored by the Environment Agency, with sampling carried out every 4 weeks. Currently runoff water from the airport enters directly into the river and does not undergo any treatment processes. However, in order to minimise pollution, after de-icing chemicals have been applied the excess liquid is sucked up using a mobile vehicle and the wastewater is disposed of through a waste handling firm. An alternative method is to reduce the amount of chemical used, but of course, this must not lead to a public safety risk.

At airports the use of de-icing chemicals is generally more efficient than it has been in the past, and this is, in part, due to the introduction of computerised weather forecasting systems to predict local weather conditions. De-icing operations are only carried out when the temperature is forecast to remain at or below 1 °C. In addition, at Heathrow and other BAA airports, temperature probes have been mounted onto the runway to accurately record temperature (P. Dunn, Environment Manager, BAA, Pers. Comm. 1996).

As has been previously mentioned, glycol reduction may also be achieved through the de-icing of aircraft using hot water which has been trialled at some airports in Europe and America.

5. THE FATE AND TOXICITY OF DE-ICING CHEMICALS

The release of de-icing chemicals into surface waters can pose an environmental hazard which is largely as a result of biodegradation which dramatically reduces dissolved oxygen concentrations.

However, the impact of de-icing chemicals in the winter, when use is at its greatest, is limited by a number of factors. These are listed below:

- the temperature of the waterbody in the winter is less than in summer. Therefore the standard 5 day BOD test which is carried out at 20 °C, may over-estimate the oxygen demands of de-icing chemicals at ambient temperatures;
- river flows, and therefore dilution, are generally at a maximum in winter;
- metabolic activity of flora and fauna is generally slower in winter and therefore they are less sensitive to water quality;
- the concentration of dissolved oxygen in the waterbody will generally be higher in the winter than in the summer because of the low oxygen demand of organisms, lower water temperatures and possibly greater water turbulence;
- input of de-icing chemicals into waterbodies as runoff varies according to the amount of rain and therefore maximum discharge will occur in episodes coinciding with higher flows.

The fate and toxicity of corrosion inhibitors has not been considered in this report as they are being reviewed in a separate report for the Environment Agency.

5.1 The biochemical oxygen demand (BOD) of de-icing chemicals

When organic wastes such as glycols and urea enter a watercourse, micro-organisms rapidly increase in number to take advantage of the increased food supply and during the breakdown process they use the oxygen dissolved in the surface water. The amount of oxygen required to degrade a compound is termed its BOD (biochemical oxygen demand) and is typically measured in laboratory tests over 5 days at 20 °C. The higher the BOD of a compound, the more oxygen is required for its degradation.

As the BOD of a river rises the concentration of dissolved oxygen (DO) present is likely to be increasingly reduced. The effects of low dissolved oxygen have been discussed in the WRc EQS report for dissolved oxygen (Stiff *et al.* 1992). This report suggests that freshwater life are likely to be affected at dissolved oxygen concentrations of <6 mg l⁻¹, while the absolute minimum DO for survival of any life stage of freshwater fish is 2 mg l⁻¹ (although this level will not permit the survival of the population as a whole). In the EC Freshwater Fish Directive (CEC 1978) mandatory values of 9 and 7 mg l⁻¹ DO have been proposed as 50%-iles for the protection of fish in designated salmonid and cyprinid fisheries, respectively.

The BOD of an unpolluted river is typically $<5 \text{ mg l}^{-1}$ and when a pollution incident involving a rise of BOD occurs, the degradation of material will continue to have an effect on the water quality and dissolved oxygen concentrations until the breakdown process is complete or there is sufficient additional dilution to reduce the BOD to $<5 \text{ mg l}^{-1}$ (NRA 1992). The BODs of ethylene, diethylene and propylene glycols are 800 000, 300 000 and 1 000 000 mg l^{-1} , respectively and in order to maintain a BOD of $<5 \text{ mg l}^{-1}$ and hence avoid a significant deterioration in water quality dilutions of 160 000-, 60 000- and 200 000-fold are necessary. If a continuous discharge occurs at a rate above the capacity of the water to degrade the glycols, a large community of micro-organisms - known as sewage fungus - will often develop on the bed of a watercourse, sometimes for a distance of several kilometres (NRA 1992). Sewage fungus has been observed downstream of a number of airports in the UK (see Section 4.2).

Depending on the quantities of glycol compounds involved, the discharge of de-icing chemicals into rivers may pose a serious pollution risk involving the death of organisms as a result of severe oxygen depletion.

Acetate and formate compounds have a low BOD (>0.5), and if these chemicals enter a waterbody, oxygen levels are unlikely to fall to levels low enough to be harmful to aquatic life.

5.2 Glycols (ethylene glycol, diethylene glycol and propylene glycol)

Because of the similarity of ethylene glycol (EG), diethylene glycol (DG) and propylene glycol (PG) in terms of aquatic fate, toxicity and potential for bioaccumulation, all three glycols used in de-icing chemical formulations have been covered together in this section. Data on the toxicity of EG, DG and PG to aquatic organisms are presented in Tables A1-A3 in Appendix A, respectively.

5.2.1 Abiotic degradation of glycols

The important physico-chemical properties EG, DG and PG are shown in Table 5.1. From this, it can be seen that they are of high water solubility (completely miscible) and have low octanol-water partition coefficients ($\text{Log Kow} = -0.3/-1.41$ to -1.93) indicating that they will not sorb to sediments or bioaccumulate in aquatic systems. They have a very low vapour pressure and are thus, unlikely to be volatilized to any significant extent. EG and PG are resistant to hydrolysis in the aquatic environment, but hydrolysis is likely to be a significant degradation process for diethylene glycol (DoE 1992). Kaplan *et al.* (1982) reported that approximately 75% of the DG in a sample of sterile, distilled water was degraded in 25 days. However, in relation to biodegradation, abiotic removal processes for all three glycols are likely to be insignificant.

Table 5.1 Physical and chemical properties of the various de-icing chemicals (see bottom of table for notes)

Chemical name	Structure	Molecular weight	Melting point (°C)	Boiling point (°C)	Water solubility (mg l ⁻¹)	Vapour pressure ^(a)	Henry's Law Constant ^(b)	Log Kow ^(c)
Ethylene glycol C ₂ H ₆ O ₂	<pre> H H H - O - C - C - O - H H H </pre>	62.1	-17 to -12.6	198	miscible	0.05	6x10 ⁻⁸	-1.93
Diethylene glycol C ₄ H ₁₀ O ₃	<pre> H H H H H - O - C - C - O - C - C - O - H H H H H </pre>	106.12	-6.5	244-245	miscible	<0.01	1.2x10 ⁻¹³	-1.98
Propylene glycol C ₃ H ₈ O ₂	<pre> H H H H - O - C - C - C - O - H H H H </pre>	76.09	-59	188.2	miscible	0.2	1.31x10 ⁻¹⁰	-1.41/-0.3
Isopropanol C ₃ H ₈ O	<pre> H H H H - C - C - C - O - H H H H </pre>	60.1	-86 to -89	82.4	miscible	32	8.07x10 ⁻⁶	0.05
Potassium acetate C ₂ H ₃ KO ₂	<pre> K O - H O = C - C - H H </pre>	98.14	292	ND	2530 (at 20 °C) 4920 (at 62 °C)	ND	-	-

Chemical name	Structure	Molecular weight	Melting point (°C)	Boiling point (°C)	Water solubility (mg l ⁻¹)	Vapour pressure ^(a)	Henry's Law Constant ^(b)	Log Kow ^(c)
Sodium acetate C ₂ H ₃ NaO ₂		82.03	58	123	1190 (at 0 °C) 1701.5 (at 100 °C)	ND	-	-
Calcium magnesium acetate ^d		ND	ND	ND	ND	ND	ND	ND
Sodium formate NaCHO ₂		68.01	253	ND	972 (at 20 °C) 1600 (at 100 °C)	ND	ND	ND

Chemical name	Structure	Molecular weight	Melting point (°C)	Boiling point (°C)	Water solubility (mg l ⁻¹)	Vapour pressure ^(a)	Henry's Law Constant ^(b)	Log Kow ^(c)
Potassium formate KCHO ₂	$\begin{array}{c} \text{O} - \text{H} \\ \\ \text{K} - \text{C} \\ \\ \text{O} \end{array}$	84.12	167.5	ND	331 (at 18 °C) 657 (at 80 °C)	ND	ND	ND

Notes:

- a Vapour pressure measured in mm Hg at 20 °C
- b Henry's Law measured in atm m³ mol⁻¹
- c Log Kow is the octanol-water partition coefficient
- d Mixture of calcium acetate (CH₃COO)₂Ca and magnesium acetate (CH₃COO)₂Mg

References:

Data taken from number of standard Chemical Handbooks including Merck Index (1989), Verschueren (1983), Howard *et al.* (1990), Howard *et al.* (1993)

5.2.2 Biodegradation of glycols

Biodegradation is the most important degradation process of glycol de-icing compounds. At temperatures greater than 5-7 °C, glycol based de-icing chemicals are rapidly biodegraded in the aquatic environment. Below this temperature, the degradation rate is much reduced.

The biodegradation of glycols has been extensively studied in wastewater, sewage sludge and the aquatic environment, both in aerobic and anaerobic conditions. Ethylene glycol and propylene glycol have been demonstrated to be readily biodegradable in the biochemical oxygen demand (BOD) test. The biodegradation of diethylene glycol has been found to depend on the source and acclimation of micro-organisms, for example, Dwyer and Tiedje (1983) reported that acclimated micro-organisms were able to metabolise 100% of the initial DG concentration in 5 days. In comparison, during the same period, non-acclimated bacteria only decomposed 21% of the DG.

Klecka *et al.* (1993) studied the degradation of 5 de-icing agents in a soil (sandy loam) and found that biodegradation was found to be a significant degradation process in the soil environment. EG, DG and PG were all found to be readily degraded in soil at 8 and 25 °C, regardless of whether the compounds were present singly or as a mixture, although the degradation rate was approximately 3.4 times faster at the higher temperature. In addition, biodegradation was reported even at concentrations as high as 1000 mg kg⁻¹ glycols. After 14 days incubation at 25 °C the levels of EG, PG and DG were reduced by 67, 87 and 90%, respectively, and average biodegradation rates were 66.3, 83.5 and 93.3 mg kg⁻¹ per day, respectively. These results indicate that even at high concentrations glycols are not toxic to micro-organisms and degradation in the aquatic environment will be rapid.

Klecka *et al.* (1993) suggested that the aerobic degradation pathway of these glycols is likely to be by sequential oxidation of the terminal alcohol group via an aldehyde to a carboxylic acid. During their study, the authors noticed the production of high levels of carbon dioxide at 8 and 25 °C suggesting that complete mineralisation had occurred. Biodegradation of EG was also reported at temperatures of -2 °C, although reaction rates were remarkably reduced. Reaction rates of 2.3-4.5 mg kg⁻¹ per day were observed at this temperature. However, the CCREM (1994) observed that DG did not degrade below 8 °C.

Glycols also degrade anaerobically although the degradation rate is slower than that reported in aerobic environments, with complete degradation occurring within a couple of weeks (Dwyer and Tjedie 1983, Battersby and Wilson 1989). CCREM (1994) report that anaerobic bacteria can degrade glycols sequentially to acetaldehyde, ethanol, acetate and, in the presence of methanogenic bacteria, methane.

Kaplan *et al.* (1982) reported that the complete degradation of PG under anaerobic conditions required 9 days, but under aerobic conditions and at the same temperature, the same concentration of PG only required 4 days for complete degradation. Battersby and Wilson (1989) observed that anaerobic degradation of EG was completed in 1-2 weeks.

While glycols are rapidly degraded in laboratory studies (usually >10 °C), very little data are available to determine their persistence in much colder, winter conditions. In British winters, if temperatures are consistently low, glycols may persist for a couple of months in the aquatic environment, but they will be rapidly biodegraded in spring when the warmer weather arrives, or downstream if they meet an effluent from a sewage treatment works.

5.2.3 Bioaccumulation in aquatic organisms

Because of the high water solubility and low octanol-water partition coefficient of all three glycols it is unlikely that significant bioaccumulation will occur in aquatic organisms. The only data available are for ethylene glycol for which BCFs of 10 and 190 (both as wet weight) have been reported for the golden orfe (*Leuciscus idus*) and the green alga (*Chlorella fusca*) exposed to 0.05 mg l⁻¹ for 1 and 3 days, respectively (Freitag *et al.* 1985).

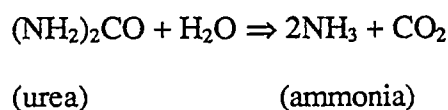
5.2.4 Aquatic toxicity of glycols

Glycols can be one of the major contributors to oxygen depletion in aquatic systems downstream of airports, and therefore, to ensure that aquatic life is protected in these areas, it is important to consider the oxygen levels in receiving waters in conjunction with glycol concentrations.

A representative sample of reliable toxicity data for EG, DG and PG, including the most sensitive species are summarised in Tables A1-A3 of Appendix A, from which it is clear that all three glycols are of low acute toxicity to aquatic organisms, with the majority of effect concentrations greater than 1000 mg l⁻¹. Much of the data are reported as 'greater than' concentrations, i.e. the measured end-point (usually EC50 or LC50) was not reached even at the highest test concentration, and so, should not necessarily be interpreted as a toxic concentration.

5.3 Urea-based de-icers

The main threat of urea-based de-icers to the aquatic environment results from their breakdown to ammonia which is highly toxic to aquatic organisms (Seager *et al.* 1988). In addition, the presence of ammonia may eventually lead to the formation of nitrates in the water which can stimulate the growth of algal blooms and cause eutrophication. In water, urea undergoes the following degradation process:



5.3.1 Aquatic fate and behaviour of urea

The relevant physical and chemical properties of urea are given in Table 5.1. These indicate that it is highly soluble in water (780 000 mg l⁻¹ at 5 °C), and is unlikely to bioaccumulate in aquatic organism or adsorb on the sediments and suspended solids because of its low octanol-water partition coefficient (log Kow = -2.97/-2.26).

In the aquatic environment, urea is readily biodegraded to ammonia. The rate of degradation increases with increasing bacterial activity and increasing temperature, and negligible breakdown is likely to occur below 8 °C. The rate of degradation has been found to increase in streams from November to April as favourable bacteria become established. There are over 200 species of bacteria capable of degrading urea, of which, *Micrococcus ureae*, *Proteus vulgaris* and *Bacillus pasteurii* are the most important. The resulting total aqueous ammonia consists of two principal forms, un-ionised ammonia (NH₃) and ionised ammonium (NH₄⁺). At 20 °C urea is completely degraded within 4-6 days.

5.3.2 Aquatic toxicity of urea

Urea is relatively non-toxic to aquatic organisms as shown in the summary of available toxicity data in Table A4, however, ammonia is highly toxic to freshwater life. The toxicity of ammonia is discussed in the ammonia EQS (Seager *et al.* 1988) in which reported acute LC50s are 0.068-2.2 mg NH₃-N l⁻¹ and 0.31-6.6 mg NH₃-N l⁻¹ as unionised ammonia for freshwater fish and invertebrates, respectively. The EQS values for ammonia are as follows:

	EQS (mg NH ₃ -N l ⁻¹)		Note
Protection of freshwater fish			
EC Designated salmonid and cyprinid water	0.021	U	
Non-EC designated waters	0.78	T	AA
	0.015	U	
Protection of saltwater fish and shellfish	0.021	U	AA

U un-ionised ammonia
 T total ammonia
 AA concentration expressed as an annual average

Ammonia toxicity is primarily due to un-ionised ammonia, and has been found to be highest at low levels of dissolved oxygen (Turnbull and Bevan 1995). Therefore, if glycols are used in conjunction with urea at airports, deoxygenation resulting from glycol degradation could increase the sensitivity of organisms to ammonia.

In a study in the Ouseburn catchment downstream of Newcastle International Airport, higher levels of ammonia have been reported than found upstream of the airport, and this was associated with a less diverse macro-invertebrate fauna and a larger bacterial population, although there are no data on which species were affected. The airport has responded by changing to a de-icing chemical based on potassium or sodium acetate.

In British winters, when urea concentrations are likely to be at a maximum in receiving waters, hydrolysis to ammonia is likely to occur at a reduced rate due to colder temperatures which may cause a build up of urea in static or slow moving waterbodies, and for this reason urea toxicity may assume a greater importance.

The majority of the available acute toxicity data for urea lies in the range 2500->10 000 mg l⁻¹, indicating very low toxicity. However, some of the data report toxic effects at much lower concentrations, and this may be a result of the hydrolysis of urea to ammonia during the exposure period. For example, Pandey and Shukla (1983) report an LC50 of 5 mg l⁻¹ to the giant gourami (*Colisa fasciata*). In contrast to this, Gillette *et al.* (1952) did not observe mortalities to creek chub (*Semotilus atromaculatus*) exposed for 24 hours to 16 000 mg l⁻¹ urea.

5.4 Calcium magnesium acetate

In the 1970's the Federal Highways Administration in the United States developed calcium magnesium acetate (CMA) as a de-icing salt for road use as an alternative to rock salt. It is a mixture of calcium acetate and magnesium acetate, although no details could be located regarding the proportion of the two salts in CMA, or about its physico-chemical properties.

CMA is less toxic to aquatic life than rock salt, less damaging to roadside vegetation, less corrosive (but still capable of causing some corrosion to vehicles) and yet just as effective. However, although it may be a suitable alternative for road de-icing/anti-icing, its corrosive nature renders it unsuitable for use on runways. It is generally believed that CMA has little or no impact on the general water quality (J Eastwood, Environment Agency - Thames Region, Pers. Comm., 1995).

5.4.1 Environmental fate and behaviour of calcium magnesium acetate

CMA is biodegradable in soils and does not affect soil compaction (unlike sodium chloride which increases soil compaction thus decreasing permeability). It has a poor mobility in soils and is therefore unlikely to reach groundwater. The calcium and magnesium ions may potentially increase the hardness of the receiving water, although no further details are available (Fritzsche 1992).

CMA has the potential for decreasing oxygen potential at concentrations above 100 mg l⁻¹ in closed systems. In the aquatic environment degradation is rapid, with degradation occurring in 5 days at 20 °C, 10 days at 10 °C (Fritzsche 1992), although, it is not known whether this refers to partial or complete degradation.

5.4.2 Aquatic toxicity of calcium magnesium acetate

Very little data are available on the toxicity of calcium magnesium acetate to aquatic organisms. It is of lower toxicity to aquatic life than conventional rock salt, with no reported effects on the food chain (zooplankton, waterflea, bluegill sunfish and fathead minnow) at concentrations of 1000 mg l⁻¹. Only a minimal effect on trout eggs was noted at concentrations of 5000 mg l⁻¹ (Fritzche 1992), although no further details were available.

5.5 Potassium and sodium acetates

Acetate de-icing chemicals were introduced in 1987 with Clearway 1, manufactured by BP Ltd, being the first to become commercially available. There are now a number of Clearway formulations available, as both a liquid and a solid, for use on public highways and airport runways/taxiways.

Acetates have not been found to be corrosive like urea and rock salt, and they are effective down to -11 °C, compared with about -5 °C for urea and -8 to -10 °C for rock salt. However, acetates have the disadvantage of being far more expensive than urea or glycol based de-icers, and some problems have been encountered due to refreezing after application.

5.5.1 Environmental fate and behaviour of potassium and sodium acetates

The oxygen demand of acetate de-icing compounds in the aquatic environment are low, with BODs of 0.295-0.325 g O₂ l⁻¹ for Clearway 1 (based on potassium acetate), and 0.406 g O₂ l⁻¹ for Clearway 2S (based on sodium acetate) quoted in the Clearway de-icers handbook produced by BP Chemicals (date not known). These low BODs indicate that both Clearway 1 and 2S have the potential to fully degrade in the aquatic environment, without causing problems resulting from oxygen depletion from the water column. Both chemicals are highly soluble in water, and are of high density (1300 kg m⁻³ for potassium acetate and 750 kg m⁻³ for sodium acetate). The freezing point of Clearway 1 is less than -60 °C, which suggests that, in theory, this compound should provide ideal protection against refreezing in the UK. However, some refreezing problems have been experienced largely as Clearway 1 has the ability to rapidly uptake water, thus lowering its efficiency.

5.5.2 Aquatic toxicity of acetates

De-icing chemicals based on metal acetates are of low toxicity to aquatic organisms. No mortalities were reported to rainbow trout (*Oncorhynchus mykiss*) after 48 hours exposure to 1000 mg l⁻¹ of either potassium acetate or sodium acetate (Data supplied by BP Chemicals Ltd in Turnbull and Bevan 1995). Further data on this study have not been provided.

5.6 Isopropanol

Isopropanol is used in some antifreeze compositions (Howard *et al.* 1990), although its use has declined over the years and is now rare. However, no other information regarding the use of isopropanol for this purpose could be located.

5.6.1 Aquatic fate and behaviour of isopropanol

The relevant physical and chemical properties of isopropanol have been summarised in Table 5.1. Isopropanol has a moderate vapour pressure (32 mm Hg at 20 °C) and therefore volatilisation is likely to be a significant loss process from both aquatic and terrestrial ecosystems. The estimated half-life of isopropanol in water is 5.4 days. It is also likely to be rapidly degraded as is shown by its rapid biodegradation at sewage treatment works, however, no data could be located on the biodegradation of isopropanol in natural surface waters. Concentrations of 3, 7 and 10 mg l⁻¹ with filtered sewage seed in freshwater resulted in 28% decrease in BOD after 5 days and a 78% decrease after 20 days. Isopropanol has also been found to be biodegraded in anaerobic conditions during sludge treatment (54 °C, thermophilic reactor) (Howard *et al.* 1990). Following a 30 day acclimation period, a sewage feed concentration of 500 mg l⁻¹ was 50% oxidised by activated sludge bacteria following 1 day exposure at 20 °C (Verschuere 1983).

No information could be located on the adsorption of isopropanol in soils or sediment, or its bioaccumulation potential in aquatic organisms. However, due to its low octanol water partition coefficient (log K_{ow} = 0.05) and its high water solubility (completely miscible with water), neither process is likely to be important in the aquatic environment (Howard *et al.* 1990).

5.6.2 Aquatic toxicity of isopropanol

The available toxicity data for isopropanol is summarised in Table A5. The majority of acute effects data lies in the range 1150-11 830 mg l⁻¹, indicating low toxicity to aquatic organisms. Wolverson *et al.* (1970) reported that the LC₅₀ for the mosquitofish (*Gambusia affinis*) was above the highest concentration tested of 1400 mg l⁻¹. Although Veith *et al.* (1983) report a 96 hour LC₅₀ of 10 mg l⁻¹ for the fathead minnow (*Pimephales promelas*), other data for this species indicate much lower toxicity, with 96 hour LC₅₀s of 10 400-11 130 mg l⁻¹. For invertebrates, the lowest acute effect concentration is a 96 hour LC₅₀ to the marine shrimp (*Crangon crangon*) of 1150 mg l⁻¹ (Blackman 1974). Data for the algal species (*Chilomonas paramecium*) indicate that a slight reduction in cell count (≥5%) has been reported at concentrations of 104 mg l⁻¹, however, this reduction is not significantly different enough from control growth to justify concern.

5.7 Rock salt

At the request of the Environment Agency, the de-icing chemical rock salt, which is commonly used on roads throughout the UK in winter has only been briefly considered in this section as it is largely composed of sodium and chloride for which EQSs have been derived (Gardiner and Smith 1992). A brief summary of the properties and effects of rock salt impurities and anti-caking agents has also been included.

5.7.1 Aquatic fate and behaviour of rock salt

In water rock salt rapidly dissociates releasing sodium and chloride into the water. Concentrations of chloride in groundwater and rivers have been reported as high as 20 and 465 mg l⁻¹, respectively. Rock salt used for highway de-icing also contains small quantities of magnesium, iodine and an anti-caking agent (sodium hexacyanoferrate or potassium ferrocyanide). The anti-caking agent is likely to be fairly unreactive in the aquatic environment and would only dissociate to form cyanide in extremely acidic waters (Pers Comm. S Blake, Senior Chemist, WRc).

Magnesium and iodine are both present as natural mineral elements and are largely insoluble in water, although magnesium does react slowly with water to form the hydroxide (Merck Index 1989).

Rock salt is renowned for its damage to roadside vegetation and corrosion of metal structures. Alternatives include calcium chloride and calcium magnesium acetate (see Section 5.4), both of which are of lower aquatic toxicity than rock salt, and the latter is approximately 10 times less corrosive than chloride salts.

5.7.2 Aquatic toxicity of rock salt (and its impurities)

The toxicity of these are discussed in greater detail in the EQS report prepared by WRc for the Environment Agency and SNIFFER (Gardiner and Smith 1992). Mineral impurities in rock salt such as magnesium and iodine and the anticaking agent are unlikely to be highly toxic due to their low solubility in water.

5.8 Formate-based de-icers

A new group of de-icing chemicals based on sodium or potassium formate have appeared in the last few years, and results of trials in Canada and Norway appear very promising. It is not thought that they have been used in the UK to date.

Sodium formate is currently undergoing trials at Halifax International Airport in Canada on its suitability as a runway de-icer. In general, sodium formate has been found to have little or no impact on water quality. However, in water it could dissociate giving rise to high concentrations of sodium, although this was difficult to establish in Canada because of the high background sodium concentrations in the river (mainly as a result of road salting using sodium chloride). Formate was not detected in the majority of water samples (J Eastwood,

Environment Agency - Thames Region, Pers. Comm., 1995), which may suggest that formate is not an important or persistent contaminant, or just that suitable analytical techniques were not used.

A further de-icer based on potassium formate called Aviform L50 was tested last winter (1995/6) in Norway at Fornebu airport, Oslo, and is suitable for use on runways (correspondence between Environment Agency and Hydro Chemicals Ltd, September 1995).

5.8.1 Aquatic fate and behaviour of formate de-icers

In water formates will dissociate to form the metal ion (Na^+ or K^+) and formate. Aviform L50 is readily biodegradable in water, with >60% degradation in 10 days (correspondence between Environment Agency and Hydro Chemicals, September 1995) although no data could be located on its degradation products.

5.8.2 Aquatic toxicity of formate de-icers

Canadian trials found no effect on the phytoplankton, periphyton or macroinvertebrate abundance in streams receiving sodium formate in drainage water collected from the runway (J Eastwood, Environment Agency - Thames Region, Pers. Comm., 1995).

Aviform L50 has been found to be of low toxicity to aquatic organisms, although only limited toxicity data are available. The 48 and 96h LC50s to the waterflea (*D. magna*) and the rainbow trout (*O. mykiss*) of 540 and >1000 mg l⁻¹, respectively. The EC50 (growth inhibition) to algae (species unknown) was >1000 mg l⁻¹ after 72-h (Correspondence between Environment Agency and Hydro Chemicals, September 1995).

5.9 De-icing chemical formulations

A limited amount of data exists for glycol-based de-icing chemical formulations and this has been summarised below.

5.9.1 Fate and behaviour of de-icing chemical formulations

Data are available on the biodegradation of two glycol-based de-icing formulations, Kilfrost ABC and Kilfrost KF 313 (DoE 1988). From the data below Kilfrost ABC appears to be degraded readily in the environment, although the data indicate that Kilfrost KF 313 may be more resistant to degradation. Data summarising their biodegradation is presented in Table 5.2, for comparison data from the same study has been given for ethylene glycol, diethylene glycol and propylene glycol.

Table 5.2 Biodegradability of two de-icing formulations and glycols undertaken by Northumbrian water (from DoE 1988)

	% reduction in glycol concentration		% reduction in BOD
	after 4 days	after 10 days	after 10 days
Ethylene glycol	46.6	90.3	>95
Diethylene glycol	0	28.7	-
Propylene glycol	>94.5	>94.5	>95
Kilfrost ABC	>94	>94	>95
Kilfrost KF 313	19.6	55	-

As has been mentioned in Section 5.2.2, temperature has been observed to have a significant effect on the rate of degradation of de-icing chemicals. Degradation of a 10 mg l⁻¹ mixture of Kilfrost and Konsin at 17 °C had a BOD of 77% (of the ThOD) indicating rapid biodegradation, whereas biodegradation at 4 °C was not seen to occur (DoE 1988).

Carpenter (1990) noted that a variety of AEA Type I and Type II de-icing fluids were readily degraded in BOD tests seeded with secondary effluent from a municipal wastewater treatment plant. Similar results were obtained when river water was used as the source of inoculum.

From these data it can be seen that glycol-based de-icing chemicals are rapidly degraded, although de-icing chemicals containing a large proportion of diethylene glycol may be more resistant to degradation.

5.9.2 Aquatic toxicity of de-icing chemical formulations

The only formulation for which toxicity data exists is for glycol-based Konsin, and this data has been summarised in Table 5.3. From this data it can be seen that Konsin is of low toxicity to the species tested. However, all these tests have been carried out with fish and no data are available for invertebrates or algal/macrophyte species.

The only data for bioaccumulation of de-icing formulations is for Konsin, provided by the manufacturers (Ellis and Everard (UK) Ltd), who claim that this chemical has a low bioaccumulation potential.

Table 5.3 Toxicity of Konsin to freshwater fish (from DoE 1988)

Species	Exposure and end-point	Formulation	Effect Conc'n (mg l ⁻¹)	Data source
Harlequin fish (<i>Rasbora heteromorpha</i>)	24-h LC50	50% Konsin	1400	DoE 1988
Brown trout (<i>Salmo trutta</i>)	96-h LC50	Konsin	>1000	Ellis and Everard (UK) Ltd
Goldfish (<i>Carassius auratus</i>)	24-h LC50	Konsin	>5000	Ellis and Everard (UK) Ltd

6. ASSESSMENT OF HAZARD TO THE AQUATIC ENVIRONMENT

6.1 Prioritisation schemes for the classification of substances

A number of prioritisation schemes have been developed and these vary according to the purpose for which they have been developed and the organisation involved in the development. They all share the common aim of classifying substances in terms of their potential harm. The central question common to such classification schemes are:

- What volume or amount of chemical is used?
- How persistent is the chemical?
- What harm does the chemical cause to living organisms?

The prioritisation schemes tend to classify chemicals into one of the following groups (cited in Hedgecott 1993):

- Those with no or low likelihood of environmental hazard
- Those with a high likelihood of environmental hazard
- Those with uncertain likelihood of environmental hazard and require further study.

WRc has developed a computerised prioritisation scheme for the DoE for the selection of candidate List I substances that are potentially hazardous to aquatic life (Hedgecott and Cooper 1991). This scheme follows the decision tree method in which chemicals are assigned to a final priority category (i.e. high, medium or low) but the order of priority within each category is not defined. The argument in support of this approach is that the amount and quality of data currently available, and our present understanding of chemical hazard, are so inadequate that a 'broad brush' approach is the most appropriate (Hedgecott and Cooper 1991). The categorisation of values as 'high' 'medium' or 'low' avoids problems experienced with other prioritisation schemes where the various parameters are scored and then combined.

6.2 Prioritisation of de-icing chemicals for EQS development

Table 6.1 details the initial criteria for the prioritisation of chemicals. From comparison between Table 6.1 and Table 6.2 (important characteristics of de-icing chemicals in relation to hazard) it is clear that in assessing the potential risk of de-icing chemicals to the aquatic environment two areas need consideration, i) the likelihood of entry into the aquatic environment and ii) the biochemical oxygen demand (BOD). The toxicity, bioaccumulation and persistence of the chemicals can effectively be discounted because, as can be seen in Table 6.2, these are all likely to be of low hazard.

Table 6.1 Criteria for prioritisation of chemicals

Hazard	Priority band	Effect	Range
BOD	High Medium Low	oxygen demand	>500 mg l ⁻¹ 10-500 mg l ⁻¹ <10 mg l ⁻¹
Risk of contamination to aquatic systems	High	According to use	Usage on roads and at airports (near to water)
	Low		Sealed cooling systems, deep freezers, industrial coolants.
Aquatic toxicity	High	Lowest toxic concentration	<1 mg l ⁻¹
	Medium		1-100 mg l ⁻¹
	Low		>100 mg l ⁻¹
Bioaccumulation	High	BCF	>1500
	Medium		110-1500
	Low		<110
Bioaccumulation	High	Log Kow	>4.5
	Medium		3.0-4.5
	Low		<3.0
Persistence in water	High	Half-life	>100 days
	Medium		10-100 days
	Low		<10 days

Table 6.2 Summary of the important characteristics of de-icing chemicals

Substance	Persistence	Toxicity	BOD	Bioaccumulation
Ethylene glycol	L 34% biodegradation after 5 days 100% degradation after 20 days	L 326-45 500 mg l ⁻¹	H 800 000 mg l ⁻¹	L 10-190 (wet weight) Log Kow = -1.93
Diethylene glycol	L half-lives = 3.5>20 days	L 3 065-84 100 mg l ⁻¹	H 300 000 mg l ⁻¹	L Log Kow = -1.98
Propylene glycol	L half-lives = 2.5-9 days	L >1 000-797 000 mg l ⁻¹	H 1 000 000 mg l ⁻¹	L Log Kow = -1.41/-0.3
Urea	L Negligible below 8 °C Rapidly degrades to ammonia at higher temperatures	L (urea) H (ammonia) 5-30 000 mg l ⁻¹	H (speculation only) No data	L Log Kow = -2.97/-2.26
Isopropanol	L half-life = 5.4 days	L 10-11 130 mg l ⁻¹	H (speculation only) No data	L Log Kow = 0.05
Potassium acetate	No data	L No mortalities to fish at 1000 mg l ⁻¹	L 0.295-0.325 g l ⁻¹	No data
Sodium acetate	No data	L No mortalities to fish at 1000 mg l ⁻¹	L 0.406 g l ⁻¹	No data
Calcium magnesium acetate	L (based on soil data) readily biodegradable in soils	L No effect on food chain at 1000 mg l ⁻¹ , minimal effect on fish eggs at 5000 mg l ⁻¹	Lower than glycols	No data
Potassium/sodium formate	L readily biodegradable (>60% degradation in 10 days)	L 540 - >1000 mg l ⁻¹	L 0.0278 g O ₂ g ⁻¹	ND

Notes:

L Low hazard
M Medium hazard
H High hazard

Using the data presented in Table 6.2, the Hedgecott and Cooper (1991) prioritisation scheme was adapted to evaluate the hazard of de-icing chemicals according to likelihood of entry into the aquatic environment and BOD.

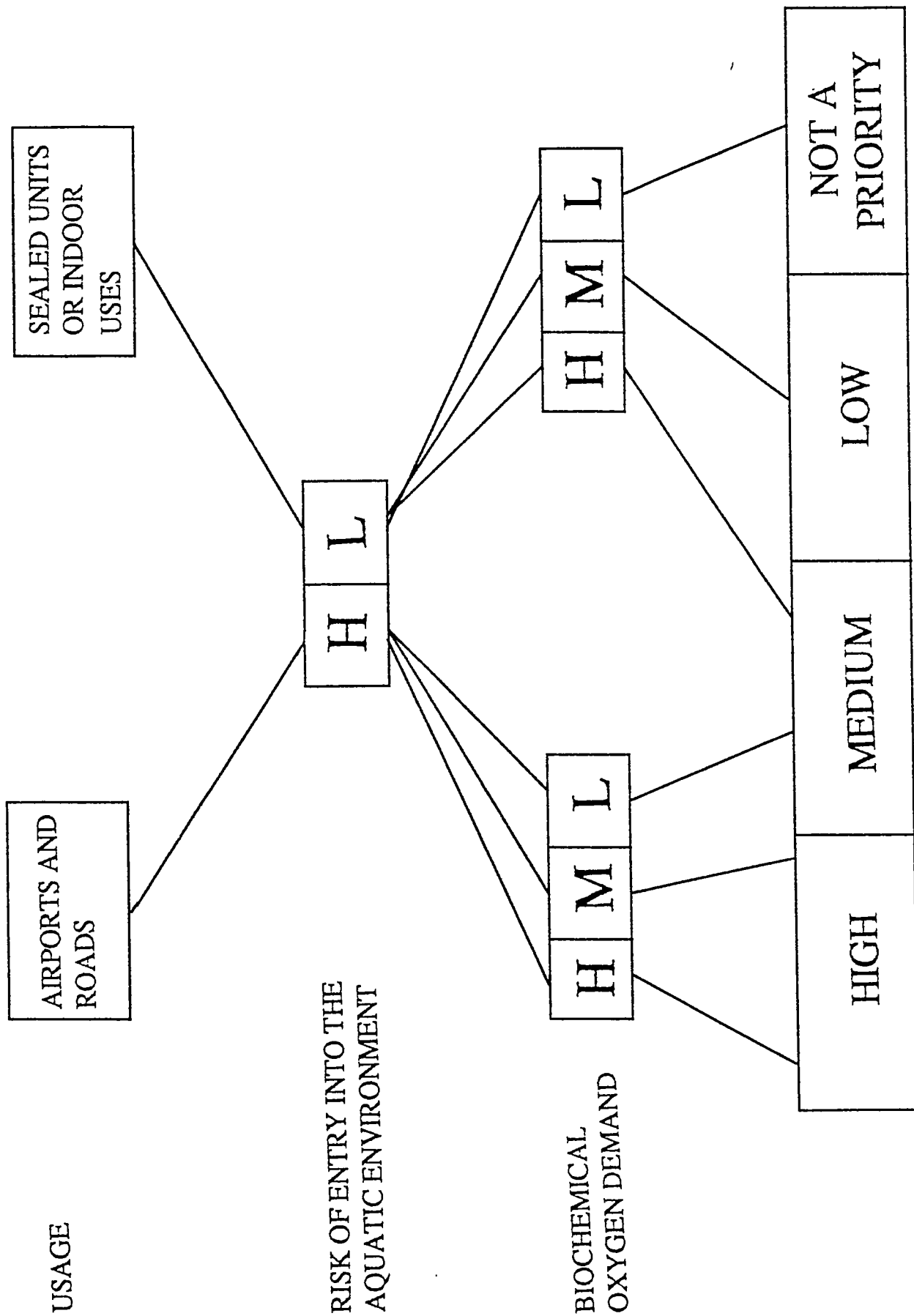
The use of production data to evaluate the likelihood of entry into the aquatic environment would be misleading and a more general approach based on type of use was considered more appropriate. Low likelihood of entry can be assumed for glycols used in car engines, vehicle cooling systems, freezers, or those used in which are used in enclosed units or an enclosed environment and discharged directly to sewer. High likelihood of entry can be assumed for glycols, urea and acetate compounds which are used at airports or on roads surfaces where they are likely to become dissolved in runoff water which may or may not be collected before it reaches the aquatic environment. It is likely that in the future, the usage of acetate and formate de-icers will be the most important growth area and these chemicals could represent a hazard to the aquatic environment in the future. In addition, the use of urea-based de-icers is likely to decrease significantly.

This final prioritisation is thus based on the BOD of the de-icing chemical and its likelihood of entry into the aquatic environment. The criteria used to prioritise BOD values were based on data for untreated sewage effluent and a number of farm wastes (Environment Agency 1992) and also with consultation from a number of experts within WRc (Stuart Hedgecott - Group Manager, Ecotoxicology, Paul Whitehouse - Senior Ecotoxicologist, Simon Blake - Senior Chemist).

6.3 Discussion and short list of priority substances

The main chemicals used as de-icing chemicals in the UK are based on glycols (ethylene glycol, diethylene glycol or propylene glycol), urea, and rock salt. The use of acetate compounds has grown rapidly in recent years, and, depending on the results of more extensive trials, it is likely that formates will follow a similar trend. Rock salt has not been reported in detail in this review as EQSs have already been derived for its main constituents (Na^+ and Cl^-). The largest use of de-icing chemicals in the UK is in vehicle cooling systems, however, glycols used for this purpose are unlikely to enter the aquatic environment because they are contained in sealed units and disposal is largely to sewers, although some may be discharged to surface water drains as a result of bad disposal practices. The greatest impact on the aquatic environment from de-icing chemicals in the UK is likely to occur as a result of their use at airports and this has been reflected in the prioritisation scheme (see Table 6.1 and Figure 6.1). The use of glycols, acetates, formates and urea on roads and at airports is seasonal and runoff into nearby rivers and watercourses is a potential possibility because of their use in the open environment and the fact that they are highly water soluble.

Figure 6.1 Prioritisation scheme for de-icing chemicals



At airports de-icing chemicals are used for de-icing aircraft, and the de-icing of runways, taxiways and aprons. The only formulations currently suitable for aircraft de-icing are based on glycols, and hence for the foreseeable future until suitable alternatives are identified, glycols will continue to be used at all UK airports. However, formulations containing urea, glycols or acetate compounds are all suitable as runway de-icers. The runway de-icer is selected according to a number of factors including cost, location, severity of winter, size of airport, traditional usage, availability of different type of de-icer and pressure from regulatory authorities. Until the mid to late 1980's urea was the most widely used chemical for runway de-icing because of its low cost and ease of application to runways. However, its use is now being phased out in the UK due to the high toxicity of its degradation product, ammonia.

The effects on the aquatic environment of de-icing chemicals used at airports are difficult to accurately determine as the runoff from airports may contain many chemicals including oils, metals, gravel, organic matter, debris and others. However, the use of de-icing chemicals is often associated with a seasonal decline in water quality, for example, in small watercourses immediately downstream of Aberdeen airport, the decline in water quality can be directly attributed to de-icing chemicals as the quality of the water declines as the amount of de-icing chemical used increases.

According to the classification scheme for the Groundwater Directive (CEC 1980), glycols, urea, isopropanol and the acetate compounds can be classified as being of low persistence in the environment, and are therefore unlikely to enter groundwater.

In a number of streams in the UK downstream of airports sewage fungus growth has been reported, and in response to this most airports are now under great pressure from regulatory bodies to reduce the amount of runoff reaching rivers. Therefore, the majority of the larger airports in the UK have installed runoff collection systems, and control operations currently used in the UK include lagoons, reed beds, or discharge to sewers. Biological treatment, at temperatures high enough to cause rapid degradation (i.e. $>10^{\circ}\text{C}$), appears to be the most practical treatment method. A reduction in the amount of de-icing chemical used can be achieved by more efficient practise such as the use of weather monitoring systems to predict when spraying is necessary. Some airports have tried to recycle glycols, but recycling is largely impracticable and expensive, based on current technologies.

Ethylene glycol, diethylene glycol and propylene glycol are all of low toxicity to aquatic organisms, with acute toxicity usually occurring at concentrations $>1000\text{ mg l}^{-1}$, and are of low persistence in the aquatic environment, with the majority of half-lives reported as >10 days. From the very limited data available they would also not appear to be a hazard in terms of bioaccumulation. However, all three chemicals have a very high biochemical oxygen demand, with BODs (a measure of the amount of oxygen used up during the degradation of a substance) of $300\ 000\text{--}1\ 000\ 000\text{ mg l}^{-1}$. The BODs of glycols are well in excess of those of organic farm wastes which are known to have caused serious pollution incidents such as fish kills as a result of severe oxygen depletion. Although there have been no incidences of mortality of aquatic organisms as a result of oxygen depletion caused by glycol degradation, the growth of sewage fungus, which has been reported downstream of a number of airports in the UK, is a clear sign of reduced oxygen levels. Potential problems concerning the use of glycols are highest at large airports and at airports in Scotland and the North of England, where the period of use is longer than in the warmer south.

Oxygen depletion is likely to be most severe in spring when the temperature is slightly warmer and biodegradation will be stimulated. Although the effects of reduced oxygen in the river are only likely to occur for a few months a year, it may have a sufficient impact to prevent sensitive species from dwelling there, and could therefore have a permanent effect on the diversity of aquatic life present. In addition, glycols, urea and acetates are highly soluble in water and their use in open situations such as on runways and roads means that they are likely to enter the aquatic environment in runoff water unless some form of collection system is put in place to prevent this.

Urea is also of low toxicity, with effects occurring at concentrations in excess of 100 mg l^{-1} , although its BOD may be high, especially if it is degraded to form nitrate. Urea is persistent in waters below $5 \text{ }^{\circ}\text{C}$, but at higher temperatures hydrolysis occurs rapidly to form ammonia which is highly toxic to aquatic organisms. It is generally accepted that the toxicity of ammonia is due to the un-ionised NH_3 molecule, and acute effects to aquatic organisms have been reported in the range $0.068\text{-}6.6 \text{ mg l}^{-1}$ (Seager *et al.* 1988). The EQSs for ammonia should ensure the protection of aquatic life (Seager *et al.* 1988).

Few data exist for the relatively new acetate-based de-icing chemicals, although they appear to be readily biodegradable, of low toxicity and have a very low BOD. The largest manufacturer of acetate compounds in the UK is BP Chemicals Ltd who market a number of formulations based on potassium and sodium acetate known as Clearway. The market for de-icing chemicals based on acetate compounds is rapidly expanding due to regulatory pressure limiting the use of glycols and urea. In addition to the high cost of acetate compounds, a further disadvantage is their high water content which may give rise to refreezing problems if excess water is not drained away. A new formulation of Clearway (Clearway 2S) is now available as a solid which is less susceptible to refreezing because of its lower water content. Acetate compounds are suitable for use as road de-icers, but this is unlikely because of their high cost in relation to rock salt.

More recently, compounds for runway de-icing based on sodium and potassium formate have been developed. These were trialled in Canada and Norway during the winter of 1995/6. They are of low toxicity to aquatic organisms, readily biodegradable, easy to apply and have a low BOD. They appear not to have any of the problems associated with the use of glycols, urea or acetates. However, further trials are necessary before a full assessment can be made, and if these are successful, use may become widespread in the UK in the future.

Rock salt is not suitable for use in airports because of its corrosive nature. However, it is used extensively throughout the UK for the de-icing of roads, largely because it is easily available and about a fifth of the price of suitable alternatives. Roadside piles of rock salt have been reported to cause elevated levels of chloride in nearby watercourses, although concentrations rapidly decline to below the limit of detection. The impurities and anti-caking agent in rock salt are fairly unreactive and unlikely to give rise to problems. A suitable alternative could be calcium magnesium acetate, which is less corrosive than rock salt (although still considered too corrosive to be used at airports) and less damaging to roadside vegetation. From the limited data available, it is also likely to be less toxic to aquatic organisms than rock salt, although further toxicity data are necessary to confirm this.

From the conclusions made above, the de-icing chemicals can be listed in order of priority for EQS development or further investigation as shown in Table 6.3. Urea is not considered a priority for EQS development as it is of low toxicity to aquatic organisms, it rapidly degrades to form ammonia for which EQSs have already been proposed, and its use is being phased out of UK airports. It may be appropriate, however, to consider its use in catchments sensitive to eutrophication.

Rock salt is also not considered as a priority because EQSs have been derived for its main constituents.

Table 6.3 Prioritisation of de-icing chemicals for EQS development

Prioritisation ranking	Chemical	Reasons for prioritisation
1	Glycol de-icing chemicals	<ol style="list-style-type: none"> 1. Extremely high BOD. 2. Widespread use and high water solubility, therefore high risk of entry into aquatic environment. 3. Use for aircraft de-icing is likely to continue due to lack of suitable alternatives.
2	Potassium acetate and sodium acetate de-icing chemicals	<ol style="list-style-type: none"> 1. Used at airports and on roads and therefore, may have high risk of entry into aquatic environment. 2. Fate and behaviour in environment need further investigation. 3. Rapid increase in usage in last few years which is predicted to continue.
3	Potassium and sodium formate	<ol style="list-style-type: none"> 1. Suitable for use at airports (and on road surfaces) 2. Fate and behaviour need further investigation 3. If results of current trials are successful may be used widely in the future.

Prioritisation ranking	Chemical	Reasons for prioritisation
4	Calcium magnesium acetate de-icing chemicals	<ol style="list-style-type: none">1. Used on roads and therefore, may have high risk of entry into aquatic environment.2. Fate and behaviour in environment not known, although unlikely to have significant impact on aquatic systems.3. BOD not known, but unlikely to be high4. Not widely used in UK yet, may increase in future as an alternative to rock salt.

7. CONCLUSIONS

1. The largest use of de-icing chemicals in the UK is in vehicle engines and cooling systems, although their potential impact on the aquatic environment from these uses is probably low due to enclosed usage and disposal should be to sewers. Discharge to surface waters will only occur as a result of poor disposal practices which may have detrimental effects on the aquatic environment. The use of de-icing chemicals at airports is likely to have a greater impact on the aquatic environment as use is seasonal (i.e. concentrated into winter months), large quantities are used, and their method of use will result in dissolved residues in runoff.
2. The majority of de-icing chemicals currently used at airports in the UK are based on ethylene glycol, diethylene glycol, propylene glycol, urea, or sodium or potassium acetate. On road surfaces the only de-icing chemical used in any significant amount in the UK is rock salt. Suitable alternatives do exist, but are many times more expensive, and therefore are not widely used. In the future, the use of calcium magnesium acetate and formates may become more widespread on roads and at airports, respectively.
3. Glycols are of low toxicity to aquatic organisms. The main concern with glycol-based de-icing chemicals is their very high biochemical oxygen demand (BOD), which may have serious effects on the aquatic environment as a result of oxygen depletion.
4. The main concern with urea-based de-icing chemicals is their rapid hydrolysis to ammonia. Ammonia is of high toxicity to aquatic organisms in comparison to urea (which can be classed as being of low toxicity). Ultimately, ammonia may be converted to nitrates which may cause eutrophication in waterbodies.
5. In laboratory studies, glycol and urea have been found to rapidly biodegrade in the aquatic environment, with half-lives in the order of days. However, in winter conditions in the UK, when most de-icing chemical is likely to enter waterbodies, biodegradation is negligible and therefore these compounds may persist in the environment for a number of months until the warmer conditions of spring arrive. In addition, the high BOD of glycols may exacerbate urea/ammonia toxicity.
6. New de-icing chemicals based on acetates and formates have been developed as suitable alternatives for runway de-icing. These appear to be of low aquatic toxicity, are biodegradable and have a much lower BOD than glycol compounds. Acetates have been successfully trialled at a number of airports in the UK and have not given rise to any deterioration in water quality similar to those reported from the use of glycols and urea. However, some problems have occurred due to difficulty in even application, and refreezing of the chemicals once applied to the runways. Even more recently, some compounds based on sodium or potassium formate have been developed. These appear to eliminate all the problems encountered when using glycols, urea or acetates, however, further research is necessary to determine their suitability for widespread use. Formates have not yet undergone testing in the UK, but have been successfully trialled in Norway and Canada.

7. Further research and development is necessary to identify suitable alternatives to glycols for aircraft de-icing, and to improve existing acetate/formate formulations to enable widespread use on runways.
8. The concentrations of glycols and urea reaching the aquatic environment must be minimised. This can be achieved by treating airport wastewater (therefore encouraging the biodegradation of de-icing chemicals), or by reducing the amounts of de-icing chemicals used by recycling, or by the use of alternate compounds for runway de-icing.

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APPENDIX A AQUATIC TOXICITY OF DE-ICING CHEMICALS

Table A1 Toxicity of ethylene glycol to freshwater life

Species	Life stage	Test type	Analysis	Temp (°C)	Hardness (mg CaCO ₃ l ⁻¹)	pH	Exposure time	Concn (mg l ⁻¹)	Effect	Ref
ALGAE										
<i>Scenedesmus quadricauda</i> (Green alga)	ND	S	N	27	ND	7.0	ND	>10000	Toxicity threshold for mortality	1
<i>Selenastrum capricornutum</i> (Green alga)	ND	ND	ND	ND	ND	ND	336-h	18200	EC50 (reduced population growth)	2
<i>Anacystis aeruginosa</i> (Blue-green alga)	ND	S	N	27	ND	7.0	ND	2000	Toxicity threshold for mortality	1
INVERTEBRATES										
<i>Daphnia magna</i> (Water flea)	ND	S	N	ND	ND	ND	48-h	>10000	LC50	3
<i>Daphnia magna</i> (Water flea)	neonate	S	N	20.15-20.86	ND	8.0-8.6	48-h	41100	LC50	4
<i>Daphnia magna</i> (Water flea)	neonate	S	N	24.06-24.84	ND	8.13-8.63	48-h	45500	LC50	4
<i>Ceriodaphnia dubia</i> (Water flea)	neonate	S	N	20.35-20.88	ND	8.05-8.66	48-h	22600	LC50	4

Species	Life stage	Test type	Analysis	Temp (°C)	Hardness (mg CaCO ₃ l ⁻¹)	pH	Exposure time	Concn (mg l ⁻¹)	Effect	Ref
<i>Ceriodaphnia dubia</i> (Water flea)	neonate	S	N	24.1-24.7	ND	8.20-8.58	48-h	13900	LC50	4
<i>Ceriodaphnia dubia</i> (Water flea)	neonate	S	N	24.1-24.7	ND	8.20-8.50	48-h	10000	LC50	4
FISH										
<i>Carassius auratus</i> (Goldfish)	3.3g weight	S	A	20	ND	7.0	24-h	>5000	LC50	5
<i>Oncorhynchus mykiss</i> (Fathead minnow)	ND	ND	ND	ND	ND	ND	48-h	54500	LC50	2
<i>Pimephales promelas</i> (Fathead minnow)	ND	S	N	ND	ND	ND	96-h	>10000	LC50	3
<i>Pimephales promelas</i> (Fathead minnow)	juvenile 30-35 days old	S	N	21 to 23	96-125	7.2-7.5	96-h	49000	LC50	6
<i>Pimephales promelas</i> (Fathead minnow)	ND	ND	ND	ND	ND	ND	24-h	83400	LC50	2
<i>Oryzias latipes</i> (Medaka)	ND	S	N	10	ND	ND	48-h	>1000	LC50	7
<i>Oryzias latipes</i> (Medaka)	ND	S	N	20	ND	ND	48-h	>1000	LC50	7

Species	Life stage	Test type	Analysis	Temp (°C)	Hardness (mg CaCO ₃ l ⁻¹)	pH	Exposure time	Concn (mg l ⁻¹)	Effect	Ref
<i>Oryzias latipes</i> (Medaka)	ND	S	N	30	ND	ND	48-h	>1000	LC50	7
AMPHIBIANS										
<i>Xenopus laevis</i> (Clawed toad)	3-4 weeks old	S	N	20	ND	ND	48-h	326	LC50	8

Notes:

- ND No data
- S Static test conditions
- N Nominal test concentrations
- A Analysed test concentrations
- d Days
- h Hours

References:

1. Bringmann and Kuhn (1978a)
2. Ward *et al.* (1992)
3. Conway *et al.* (1983)
4. Cowgill *et al.* (1985)
5. Iridic *et al.* (1979)
6. Mayes *et al.* (1983)
7. Tsuji *et al.* (1986)
8. De Zwart and Slooff (1987)

Table A2 Toxicity of diethylene glycol to aquatic organisms

Species	Life stage	Test type	Analysis	Temp (°C)	Hardness (mg CaCO ₃ l ⁻¹)	pH	Exposure time	Concn (mg l ⁻¹)	Effect	Ref
ALGAE										
<i>Scenedesmus quadricauda</i> (Green alga)	ND	S	N	27	ND	7.0	ND	2700	Toxicity threshold for mortality	1
<i>Scenedesmus capricornutum</i> (Green alga)	ND	ND	ND	ND	ND	ND	336-h	37000	EC50 (reduction of population growth)	2
<i>Anacystis aeruginosa</i> (Blue-green alga)	ND	S	N	27	ND	7.0	ND	1700	Toxicity threshold for mortality	1
INVERTEBRATES										
<i>Daphnia magna</i> (Water flea)	24-h	S	N	20-22	'soft'	7.6-7.7	24-h	>10000	LC50	3
<i>Daphnia magna</i> (Water flea)	ND	S	N	ND	ND	ND	24-h	>10000	EC50 (effect not reported)	4
<i>Artemia salina</i> (Brine shrimp)	nauplii	S	N	24	ND	ND	24-h	>10000	LC50	5
FISH										
<i>Oncorhynchus mykiss</i> (Rainbow trout)	ND	ND	ND	ND	ND	ND	96-h	84100	LC50	2

Species	Life stage	Test type	Analysis	Temp (°C)	Hardness (mg CaCO ₃ l ⁻¹)	pH	Exposure time	Concn (mg l ⁻¹)	Effect	Ref
<i>Pimephales promelas</i> (Fathead minnow)	ND	ND	ND	ND	ND	ND	96-h	52800	LC50	2
<i>Gambusia affinis</i> (Mosquito fish)	Adult	S	N	23-25	ND	7.9-8.5	96-h	32000	LC50	6
<i>Carassius auratus</i> (Goldfish)	3.3	S	A	20	ND	7.0	24-h	>5000	LC50	7
AMPHIBIANS										
<i>Xenopus laevis</i> (Clawed toad)	3-4 weeks	S	N	20	ND	ND	48-h	3065	LC50	8

Notes:

ND No data
S Static test conditions
F-T Flow-through test conditions
N Nominal test concentrations
A Analysed test concentrations
d Days
h Hours

References:

1. Bringmann and Kuhn (1978a)
2. Bringmann and Kuhn (1980)
3. Bringmann and Kuhn (1982)
4. Price *et al.* (1974)
5. Wallen *et al.* (1957)
6. Bridie *et al.* (1979)
7. De Zwart and Slooff (1987)

Table A3 Toxicity of propylene glycol to aquatic organisms

Species	Life stage	Test type	Analysis	Temp (°C)	Hardness (mg CaCO ₃ l ⁻¹)	pH	Exposure time	Concn (mg l ⁻¹)	Effect	Ref
ALGAE										
<i>Scenedesmus capricornutum</i> (Green alga)	ND	ND	ND	ND	ND	ND	ND	<5200-34100	EC50 (for population growth) (using 1,2-PE) ^(a)	1
INVERTEBRATES										
<i>Artemia salina</i> (Brine shrimp)	nauplii	S	N	24	ND	ND	24-h	>10000	LC50	2
<i>Daphnia magna</i> (Water flea)	ND	S	N	ND	ND	ND	24-h	>10000	EC50 (effect not recorded)	3
<i>Daphnia magna</i> (Water flea)	ND	ND	ND	ND	ND	ND	48-h	43500	LC50 (using 1,2-PE) ^(a)	1
<i>Daphnia magna</i> (Water flea)	ND	ND	ND	ND	ND	ND	48-h	>10000	EC50 (immobilisation) (using 1,2-PE) ^(a)	4
<i>Daphnia magna</i> (Water flea)	ND	ND	ND	ND	ND	ND	48-h	7417	EC50 (immobilisation) (using 1,2-PE) ^(a)	4
FISH										
<i>Oncorhynchus mykiss</i> (Rainbow trout)	ND	ND	ND	ND	ND	ND	24-h	79700	LC50 (using 1,2-PE) ^(a)	1

Species	Life stage	Test type	Analysis	Temp (°C)	Hardness (mg CaCO ₃ l ⁻¹)	pH	Exposure time	Concn (mg l ⁻¹)	Effect	Ref
<i>Carassius auratus</i> (Goldfish)	3.3g	S	A	20	ND	7.0	24-h	>5000	LC50	5
<i>Oryzias latipes</i> (Medaka)	ND	S	N	10	ND	ND	48-h	>1000	LC50	6
<i>Oryzias latipes</i> (Medaka)	ND	S	N	20	ND	ND	48-h	>1000	LC50	6
<i>Oryzias latipes</i> (Medaka)	ND	S	N	30	ND	ND	48-h	>1000	LC50	6

Notes:

ND No data

S Static test conditions

N Nominal test concentrations

A Analysed test concentrations

a isomer of propylene glycol used, if it is not indicated it is not known which isomer was used

References:

1. Ward *et al.* (1992)
2. Bringmann and Kuhn (1982)
3. Bridie *et al.* (1979)
4. Price *et al.* (1974)
5. Kuhn *et al.* (1989)
6. Tsuji *et al.* (1986)

Table A4 Toxicity of urea to aquatic organisms

Species	Life stage	Test type	Analysis	Temp (°C)	Hardness (mg CaCO ₃ l ⁻¹)	pH	Exposure time	Concn (mg l ⁻¹)	Effect	Ref
ALGAE										
<i>Chilomonas paramecium</i> (Cryptomonad)	ND	ND	N	20	ND	6.9	48-h	2683	>= 5% decrease in cell count	1
<i>Scenedesmus quadricauda</i> (Green alga)	ND	S	N	27	ND	ND	8-d	>10000	decrease in cell multiplication	3
<i>Anacystis aeruginosa</i> (Blue-green alga)	ND	S	N	27	ND	ND	8-d	47	decrease in cell multiplication	3
PROTOZOA										
<i>Entosiphon sulcatum</i> (Flagellate euglenoid)	Initial culture turbidity	S	N	25	ND	ND	72-h	29	>5% decrease in population growth	2
INVERTEBRATES										
<i>Daphnia magna</i> (Water flea)	24-h	ND	N	20-22	70	7.6-7.7	24-h	>10000	LC50	4
FISH										
<i>Semotilus atromaculatus</i> (Creek chub)	8-10 cm	S	N	15-21	98	8.3	24-h	16000	LC0	5

Species	Life stage	Test type	Analysis	Temp (°C)	Hardness (mg CaCO ₃ l ⁻¹)	pH	Exposure time	Concn (mg l ⁻¹)	Effect	Ref
<i>Semotilus atromaculatus</i> (Creek chub)	8-10 cm	S	N	15-21	98	8.3	24-h	30000	LC100	5
<i>Cirrhinus mrigala</i> (Hawk fish)	fingerlings	S	N	ND	ND	ND	84-d	10	lethal	6
<i>Colisa facitata</i> (Giant gourami)	fingerlings	SS	N	18.6	ND	7.2	96-h	5	LC50	7
<i>Colisa facitata</i> (Giant gourami)	Males only	ND	N	ND	ND	ND	30-d	2500	significant alteration of testicular histology	8
<i>Poecilia reticulata</i> (Guppy)	239 mg weight	ND	N	18.5-23.5	85-90	8.1-8.4	48-h	22295	LC50	9

Notes:

- ND No data
- S Static test conditions
- SS Semi-static test conditions
- N Nominal test concentrations
- d Days
- h Hours

References:

1. Bringmann *et al.* (1980)
2. Bringmann and Kuhn (1980)
3. Bringmann and Kuhn (1978a)
4. Bringmann and Kuhn (1977)
5. Gillette *et al.* (1952)
6. Srivastwa and Srivastava (1977)
7. Pandey and Shukla (1983)
8. Shukla and Pandey (1984)
9. Chouhan and Pandey (1987)

Table A5 Toxicity of isopropanol to aquatic organisms

Species	Life stage	Test type	Analysis	Temp (°C)	Hardness (mg CaCO ₃ l ⁻¹)	pH	Exposure time	Concn (mg l ⁻¹)	Effect	Ref
ALGAE										
<i>Chilomonas paramecium</i> (Cryptomonad)	ND	ND	N	20	ND	6.9	48-h	104	>= 5% decrease in cell count	1
<i>Scenedesmus quadricauda</i> (Green alga)	initial culture turbidity	S	N	27	ND	ND	7-d	1800	>= 3% decrease in extinction value	2
INVERTEBRATES										
<i>Arietia salina</i> (Brine shrimp)	nauplii	S	N	24	ND	ND	24-h	>10000	LC50	3
<i>Crangon crangon</i> (Common shrimp)	ND	SS	N	ND	ND	ND	96-h	1150	LC50	4
<i>Daphnia magna</i> (Water flea)	24-h	S	N	20-22	70	7.6-7.7	24-h	>10000	LC50	5
FISH										
<i>Gambusia affinis</i> (Mosquito fish)	96-h	S	N	22	ND	ND	96-h	>1400	LC50	6
<i>Lepomis macrochirus</i> (Bluegill sunfish)	96-h	S	N	22	ND	ND	96-h	>1400	LC50	6

Species	Life stage	Test type	Analysis	Temp (°C)	Hardness (mg CaCO ₃ l ⁻¹)	pH	Exposure time	Concn (mg l ⁻¹)	Effect	Ref
<i>Lepomis macrochirus</i> (Bluegill sunfish)	fingerlings	S	N	19.5-20.5	ND	ND	96-h	>10000	LC0	7
<i>Carassius auratus</i> (Goldfish)	3.3g	S	A	20	ND	7.0	24-h	>5000	LC50	8
<i>Pimephales promelas</i> (Fathead minnow)	4-8 weeks old	S	N	18-22	ND	ND	96-h	11130	LC50	9
<i>Pimephales promelas</i> (Fathead minnow)	0.12 g	FT	A	25	56.3	7.5	96-h	10	LC50	10
<i>Pimephales promelas</i> (Fathead minnow)	0.103g (29-d)	FT	A	24.6	52.5	7.1	96-h	10400	LC50	11

Notes:

- ND No data
- S Static test conditions
- SS Semi-static test conditions
- FT Flow through test conditions
- N Nominal test concentrations
- A Analysed test concentrations
- d Days
- h Hours

References:

1. Bringmann *et al.* (1980)
2. Bringmann and Kuhn (1980)
3. Price *et al.* (1974)
4. Blackman (1974)
5. Bringmann and Kuhn (1977)
6. Wolvetton *et al.* (1970)
7. Buzzeil *et al.* (1968)
8. Bridie *et al.* (1979)
9. Matteson *et al.* (1976)
10. Veith *et al.* (1983)
11. Brooke *et al.* (1984)

