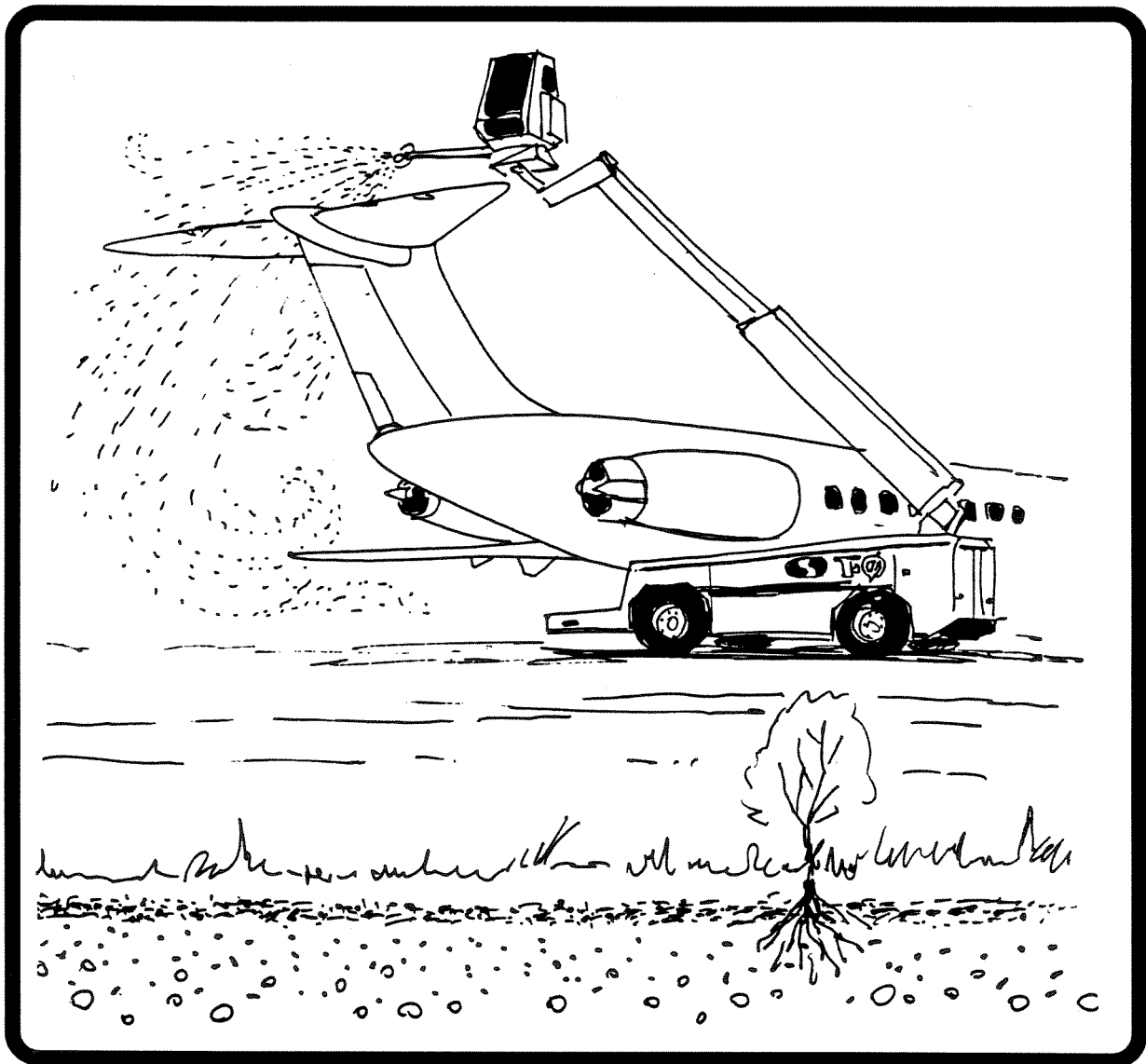



NEW OSLO AIRPORT GARDERMOEN

# Biodegradation of the de-icing fluids Kilfrost DF and Clearway 1 in a soil profile

O-91114



CIVIL AVIATION  
ADMINISTRATION, NORWAY

Norwegian Institute for Water Research  NIVA

# NIVA - REPORT

Norwegian Institute for Water Research  NIVA

Report No.:	Sub-No.:
O-91114	4
Serial No.:	Limited distrib.:
2797	

<b>Main Office</b> P.O. Box 69, Korsvoll N-0808 Oslo 8 Norway Phone (47 2) 18 51 00 Telefax (47 2) 18 52 00	<b>Regional Office, Sørlandet</b> Televeien 1 N-4890 Grimstad Norway Phone (47 41) 43 033 Telefax (47 41) 44 513	<b>Regional Office, Østlandet</b> Rute 866 N-2312 Ottestad Norway Phone (47 65) 76 752 Telefax (47 65) 76 653	<b>Regional Office, Vestlandet</b> Thornøhlensgt 55 N-5008 Bergen Norway Phone (47 5) 32 56 40 Telefax (47 5) 32 88 33	<b>Akvaplan-NIVA A/S</b> Søndre Tollbugate 3 N-9000 Tromsø Norway Phone (47 83) 85 280 Telefax (47 83) 80 509
--	---	--	---	--

Report Title: <b>Biodegradation of the de-icing fluids Kilfrost DF and Clearway 1 in a soil profile</b>	Date: 7. oktober	Printed: NIVA 1992
	Topic group: Ecotoxicology	
Author(s): Morten Laake Harry Efraimssen	Geographical area: Akershus, Norway	
	Pages: 33	Edition: 1

Contractor: Civil Aviation Administration, Norway	Contractors ref. (or NTNf-No.): Contract no. 43208.284.3
--	---

Abstract: <p>The fate of the de-icing fluids Kilfrost DF (propylene glycol) and Clearway 1 (K-acetate) has been studied in soil lysimeters incubated in the laboratory. Experiments were carried out by 2-4 °C and 12-14 °C and the water quality of percolated water followed for 284 days. The results show that both chemicals are biodegraded efficiently when oxygen is available by a load of 20-50 mg/l measured as DOC, both at high and low temperature regimes and by a hydraulic retention time of 20 days in the 0-1 m depth interval. By higher loads anoxic conditions can develop. The biodegradation of acetate was inhibited by anoxic conditions, while propylene glycol was only partially degraded, possibly to intermediate products. When measures are taken to aerate and fertilize the topsoil the capacity for biodegradation is likely to increase somewhat.</p>
---

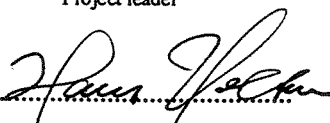
4 keywords, Norwegian

1. Avisingsvæsker
2. Propylenglykol
3. Acetat
4. Flyplasser


4 keywords, English

1. De-icing chemicals
2. Propylene glycol
3. Acetate
4. Airfields

Project leader

  
.....  
Hans Holtan

For the Administration

  
.....  
Rainer G. Lichtenthaler

ISBN-82-577-2181-6

Norwegian Institute for Water Research

**O-91114**

**Biodegradation of the de-icing fluids Kilfrost DF  
and Clearway 1 in a soil profile**

**Final Report  
English**

Oslo 7. October 1992

Morten Laake  
Harry Efraimssen

# Contents

Preface .....	3
1. INTRODUCTION .....	4
1.1. Background of the investigation .....	4
1.2. De-icing chemicals .....	4
1.3. Environmental properties .....	5
2. TEST CONDITIONS .....	7
2.1. Experimental set-up.....	7
2.2. Collection and preparing of soil for the experiment .....	7
2.3. Grain size analysis of the sand.....	7
2.4. BOD dilution water .....	8
2.5. Incubating and dosing of test water .....	9
2.6. Water balance over the lysimeters .....	10
2.7. Determination of hydraulic retention time in the lysimeters .....	11
3. RESULTS AND DISCUSSION .....	13
3.1. The development of the acidity of the effluents .....	13
3.2. The development of electrolytic conductivity of the effluents .....	14
3.3. The release of potassium from the soil columns.....	16
3.4. The content of iron and manganese in the effluents.....	16
3.5. Dissolved organic carbon in the effluents .....	19
3.5.1. Degradation by low temperature.....	19
3.5.2. Degradation by higher temperature.....	20
3.5.3. Steady-state level of DOC as function of the load.....	21
3.6. The washout of inorganic carbon from the soil columns .....	23
3.7. The washout of nutrients (N and P) from the soil columns.....	23
3.8. The redox-potential of the soil columns by the end.....	26
3.9. Organic dry matter in the soil columns by the end .....	27
3.10. Microbial biomass in the soil columns by the end.....	28
4. DISCUSSION .....	29
5. CONCLUSIONS .....	32
6. LITERATURE REFERENCES .....	33

## Preface

The project was initiated by Avioplan A/S in May 1991 and is part of the pre-study study of the new national airport at Gardermoen conducted by the Luftfartsverket (Civil Aviation Administration, Norway). NIVA delivered its proposal for a test program dated 3. June and on this background technical preparations and in July trial tests were started. The project was discussed again on 8. August, a issued by Luftfartsverket (contract no.43208.248.1), signed on 26. August and terminated by 15. October, 1991.

Based on a progress report dated 30.10.91 it was extended the contract until the end of May 1992, in order to test the effect of high chemical loads and high water flow in periods of snow-melting and to follow how the system regenerates.

The project included from the start degradation studies of de-icing agents for use on aeroplanes (Kilfrost) and runways (Clearway 1) both in soil lysimeters and in activated sludge pilot units. The later part was continued as a separate project in 1992 and has been reported separately (Biological treatment of a de-icing fluid, NIVA Report 0-92036).

Research manager of biotechnology, Morten Laake, has been responsible for planning the experiments and writing this report. The experiments were conducted and the results prepared by laboratory manager Harry Efraimsen with essential support from research assistant Liv Bente Skancke. In the planning process research manager of ecotoxicology, S. Torsten Källqvist, took part. Project leader and the NIVA contact person towards Luftfartsverket was senior scientist Hans Holtan.

NIVA looks forward to a possible extension of this - in a Norwegian context - outstanding project, which will expand our knowledge of degradation of chemicals by microbes in soil and ground water and of methods to attack such pollution problems.

**Morten Laake**

# 1. INTRODUCTION

## 1.1. Background of the investigation

One of the largest polluting activities on an airspace is the use of chemicals to remove ice and snow from airplanes and runways. On the airplanes is today used mono-propylene glycol (Kilfrost DF) which is added anticorrosion and other additives in small amounts. On the runway a potassium acetat product named Clearway 1 is being used in Norway. Both agents are generally easy degradable in standardized biodegradation tests.

To avoid water pollution - ground water as well as surface water - it is essential to have knowledge of the self-cleaning capacity of the recipient, the risk of releasing chemicals into the water and the technical treatment processes available for protecting the local environment. The aim of this project was primary to enlighten how the de-icing agents Kilfrost and Clearway 1 are degraded under the temperature and load conditions which will be of actuality at Gardermoen. These questions are essential in the Luftfartsverket (LV) study of a new main airport on this location.

The Norwegian institute of water research (NIVA) was commissioned by the LV to perform experiments in laboratory scale to procure data for the degradation of Kilfrost and Clearway 1 in the top soil layer and in the soil above the water table (unsaturated zone).

The degradation study in soil was executed as a lysimeter experiment with soil profiles incubated in the laboratory. The extent of degradation was studied at actual loading rates of chemicals and precipitation and by temperatures in soil coinciding with situations in the autumn/spring (2-4 ° C) and summer (12-14 ° C).

## 1.2. De-icing chemicals

The available literature that give direct information about physical and chemical characteristics, degradation and effects of de-icing chemicals is not very extensive. To our knowledge there has not earlier been carried out any corresponding research on biodegradation in soil and unsaturated ground .

A summary of chemical and physical data on various de-icing chemicals was recently made by Breedveld and Laake (1992a). Among the glycol-based products which are in commercial use as de-icing agents, is propylene glycol (1,2-propane diol) the most commonly used for de-icing of airplanes. The substance is also used as monomer in the production of polymers (poly-ester, poly-propylene glycols) and is also used for several other technical features.



**1,2-propene diol** (mono-propylene glycol)

Propylene glycol (syn. mono-propylene glycol) is a transparent fluid by room temperature, easily dissoluble in water with a weak alkaline reaction, and has a very low vapour pressure. It thereby evaporates very slowly from water, soil or other surfaces. The tendency of accumulation in organisms and adsorption to organic material is low, which is indicated by a low n-octanol/water distribution coefficient;  $\log P_{ow} = -1.41$ .

Propylene glycol is active ingredient in "Kilfrost DF Aircraft De-icing Fluid", Kilfrost Ltd, UK. They inform that it contains a 80% solution of propylene glycol in water whit 1-2% additives, most of which probably is phosphonate as corrosion inhibitor. It also likely contains detergents and preserving agents. The solution is sprayed on airplanes as a 50% solution of propylene glycol in hot water (about 90 °C).

Potassium acetate is the active ingredient in a de-icing fluid for runways, Clearway 1, from BP Chemicals. It is a transparent liquid, usually used as a 10% solution in water. It is an effective pH-buffer which in water will adjust pH to 8,4-8.8. Other additives are for us unknown. In the last few years the product has replaced urea-based products on Norwegian airports.

### 1.3. Environmental properties

The Kilfrost DF glycol shows a medium to high, but variable toxicity to algae and crawfish in tests executed by NIVA. For mammals the agent exhibits medium to low toxic (Verschueren 1983). Acetate present in Clearway is low toxic, but might in strong solutions have a restraining effect on the activity of microbes. Both chemicals needs a lot of oxygen for complete degradation to carbon dioxide and water, and the environmental effects will primary arise from oxygen consumption of the materials. Theoretical oxygen demand can be calculated as follows:

$\text{CH}_3\text{COOH}$                       1.60mg COD/mg dry weight      160 g COD/l (10%solution)

$\text{CH}_3\text{CHOHCH}_2\text{OH}$       1.77mg COD/mg dry weight      885 g COD/l (50%solution)

Acetate is actually a good substrate for the growth of bacteria, both under aerobic and anaerobic conditions, and can under anaerobic conditions also be split into carbondioxide and methane.

Factors which affect the degradation of chemicals in unsaturated ground has recently been discussed in detail by Breedveld and Laake (1992 b). In few words one can state that type of soil, temperature, supply of oxygen, dampness, pH in the soil and the supply of nutrient salts (N and P) are vital factors influencing the extent of biodegradation by microbes in the unsaturated zone. It is obvious that a number of these factors also depend on one another.

For anaerobic degradation to take place when the oxygen is consumed, the availability of alternative electron acceptors for anaerobic respiration will be of most importance. Actual alternatives are nitrate, nitrite, sulphate, thio-sulphate and sulphate. Production of methane by respiration of carbon dioxide (methanogenesis) is primarily depending on that a strong reducing environment already is established by the other mechanisms.

In standardized tests both mono-propylene glycol and potassium acetate are degraded effectively already within 3 days and completely within a 28 days test period (Verschueren, 1983). Acetate can after coenzyme-activation become directly incorporated into the energy metabolism of the microorganisms. Propylene glycol is supposed to be degraded in steps via the intermediates lactic acid and pyruvic acid, which then after being activated is incorporated into the metabolism. In mammals propylene glycol is metabolized by the same mechanism, but is also secreted unchanged through the urine (Yu and Sawchuk, 1987).

In conjunction with a discussion of waste treatment efforts at Stanstead Airport, U.K., it is referred to experiments with propylene glycol carried out in England (Gay et.Al, 1987). A pilot experiment carried out by 30-35 °C has shown that mono-propylene glycol is biologically degradable under

anaerobic conditions in the methane process. The end product is 70% methane in the gas phase, and as intermediate products propionic acid and acetate are formed in liquid phase. The process must be neutralized by addition of base to avoid inhibition due to the formation of acids.

Under aerobic conditions a complete degradation of propylene glycol can take place in biological sewage treatment processes. As recently shown by Mørkved, Laake and Aasgaard (1992) the activated sludge process is effective down to a temperature of 2.0 °C. Also at aerobic conditions there was a need for neutralisation by adding of base in the process. Growth of filamentous bacteria can cause operating problems and thick, foamy layers may also appear. By joint treatment of mono-propylene glycol with acetate (75% Kilfrost, 25% Clearway) and with addition of nitrogen these problems did not occur, however.

Investigations carried out in Canada, where glycol was tested at relatively low concentrations (280 mg/l BOD) together with municipal sewage in the proportion 2:1, show that about 93-95% degradation was reached even by as low temperature as +2 °C (Jank, Guo and Cairns, 1974).

It is in fact not possible to deduct data of relevance to the processes taking place in soil profiles from degradation tests carried out in small, homogeneous volumes or from pilot tests with biological reactors, except that mono-propylene glycol and potassium acetate are biologically degradable products. Both aerobic and anaerobic processes can occur supposed that the conditions are right, and this has to be tested in model experiments which are as similar as possible to the conditions within the future airfield area at Gardermoen.



## 2. TEST CONDITIONS

### 2.1. Experimental set-up

The lysimeters which were used for the experiments, were made by stainless steel, with an inner diameter of 20 cm. and a length of 80 cm. In the bottom of each tube a perforated support-plate with openings of 8 x 8 mm was welded on. On this support plate of stainless steel a steel grid with openings of 1 x 1 mm was placed to keep the soil in place. All the tubes were washed in warm water and then washed with acetone on the whole inner surface. Finally they were rinsed in distilled water and let dry before use.

### 2.2. Collection and preparing of soil for the experiment

On the 10. July 1991 soil mass was collected from an area with grass vegetation just north of the runway at the present Gardermoen Airfield. A cut was made in the ground down to about 80 cm. depth. The profile can be described as typical for soil at moors with a dominance of finegraded sand. It consisted of a inhomogenous, sandy layer of turf about 5 cm. thick, with  $5.4 \pm 2.4\%$  of organic matter (varying from about 3 to 9%). An underlying rusty brown sand layer (iron-deposit layer) was about 10 cm. thick with a fairly dense root system from the gras vegetation, and contained 2-3% of organic matter.

Deeper down in the profile (about 15-80 cm. depth) there were two separate layers, of which the top one contained a lot of capillary roots from the gras vegetation. This sand layer was about 30 cm thick, had a light brown colour and contained about 1% of organic matter. The bottom sand layer was light gray and coarser than the overlaying layer, contained about 0.6% of organic matter and was nearly free of roots.

After transport to the laboratory the three types of sand were mixed separately to obtain homogeneous masses. All the soil columns were packed with 35 cm of the bottom sand layer. Then 30 cm of the light brown sand layer was added and loosely packed. On top of this was filled about 10 cm of the top sand layer, before an undisturbed layer of turf was put on. The composition of the profiles in the columns correspond to the natural profile as far as practically possible. At the same time it was important that all the columns should be as equal as possible.

### 2.3. Grain size analysis of the sand

A suitable portion of each sand layer was wet-sieved by means of a Fritsch sieving machine. Differentiation was made of the grain sizes from larger than 1 mm and down to 0.025 mm. Each fraction was dried by 105 °C to stable dry weight. Thereafter were all the sand fractions heated at 520 °C in 1-2 hours to burn off the organic matter. Table 1 shows the differentiation in the various size fractions by weight in percent.

Only the top 15 cm sand layer (including the turf layer) contained measurable quantities of organic matter. It contributed about 4,2% of the total dry weight. The sieving showed that most of the sand was present in the 0.063 to 0.25 mm fraction, which is typical for fine sand. More than 70% of the

sand in the top layer had particles in this size fraction, while of the next layer more than 90% was within the same limits. The bottom layer had more than 80% within these limits and about 17% was larger than 0.25mm. The grain size analysis confirm the visual observation that the bottom sand layer was coarser than the others.

Particle grade	Soil profile, 5-15 cm below turf				Soil profile, 15-40 cm below turf				Soil profile, 40-75 cm below turf			
	Dry-wt. g	Org. dry-wt. g	% inorg. dry-wt.	% org. dry-wt.	Dry-wt. g	Org. dry-wt. g	% inorg. dry-wt.	% org. dry-wt.	Dry-wt. g	Org. dry-wt. g	% inorg. dry-wt.	% org. dry-wt.
>1 mm	2.62	0.45	0.44	2.03	0.37	0.37	0.35	0	0.13	0.13	0.13	0
- 0,5 mm	3.23	2.95	2.87	0.26	0.13	0.13	0.12	0	1.16	1.16	1.21	0
- 0,25 mm	25.08	23.72	23.11	1.27	4.94	4.94	4.7	0	14.89	14.83	15.51	0
- 0,125 mm	54.63	53.94	52.58	0.64	70.22	70.22	66.72	0	60.14	59.93	62.62	0
- 0,063 mm	20.3	20.05	19.54	0	28.25	28.25	26.84	0	18.72	18.7	19.54	0
- 0,025 mm	1.55	1.5	1.46	0	1.33	1.33	1.26	0	0.96	0.95	0.99	0
SUM	107.41	102.61	100	4.2	105.24	105.24	99.99	0	96	95.7	100	0

**Table 1.** Size-grading and organic content of the soil profile for the 3 soil layers used.

## 2.4. BOD dilution water

For best to imitate the content of dissolved salts in natural surface water, but without any dissolved humic materials, it was necessary to compose a defined diluting water (BOD-water). Distilled water was added dissolved salts in a concentration which is typical for surface water, but with an extra addition of nitrogen and phosphorus. For these two elements a concentration was chosen which is commonly used in algal biotests. The concentrations of the added elements and which salts that were used are shown in Table 2.

Extra addition of nitrogen and phosphorus were considered important to avoid limitation of biodegradation of carbonaceous substrate. To be on the safe side, the amount of N and P added were multiplied by 10 after 234 days, whence the amount of carbon then exceeded 200 mg/l in all the columns.

Element	mg/L	mg/L #	Salt
Mg	0.5	0.5	MgSO <sub>4</sub>
Ca	4	4	CaCl <sub>2</sub>
K	0.3	0.3	KCl
Na	1.0	1.0	NaHCO <sub>3</sub>
P	0.05	0.5	KH <sub>2</sub> PO <sub>4</sub>
N	0.5	5	NH <sub>4</sub> Cl

**Table 2.** BOD-water used as reference water and as diluting water by lysimeter experiments.  
# increased values of N and P after 234 days.

## 2.5. Incubating and dosing of test water

The 4 soil columns were placed in a thermostated room at 2-4 °C and 4 columns at 12-14 °C, and were given the following treatment:

- Column 1, - by each temperature was used as control and fed water (BOD-water) with inorganic salts corresponding to natural surface water (see Table 2).
- Column 2, - pure propylene glycol (p.a. quality) dissolved in the same BOD-water.
- Column 3, - Kilfrost DF, dissolved in BOD-water.
- Column 4, - Clearway 1, dissolved in BOD-water.

Pure BOD-water was added at a flow rate of 630 ml/day in the beginning (7 days), then reduced to 315 ml/day in the following, altogether 19 days before the dosing of the test chemicals started. This was done to "wash out" loosened materials after the mechanical treatment which was necessary for mixing and packing the sand layers uniformly in the lysimetres. After this stabilizing of the soil columns the dosing of test chemicals were started.

The flow rate was from the start adjusted to 315 ml/day which correspond to about 10 mm rainfall per day. The test solution was added over a period of 12 hours, with a corresponding brake. After 56 days the dosing was increased to 630 ml/day, corresponding to 20 mm rainfall per day, which was added continuously. The doses of the chemicals Kilfrost, Clearway and pure propylene glycol were normalized by their content of dissolved organic carbon (DOC) found by analysing diluted solutions of the chemicals. The DOC-content of the three test chemicals according to this analysis are shown in Table 3

Test substance	% DOC analysed	% DOC calculated
Propylene glycol, p.a.	49	47
Kilfrost DF	22	38
Clearway 1	13.5	12

**Table 3.** Analysed and calculated content of dissolved organic carbon (DOC) in the products.

The analysed DOCs are in good agreement with the theoretical carbon content for pure propylene glycol and for Clearway 1, which is said to be a solution of about 50% potassium acetate. The content of DOC in Kilfrost is however only about half of the amount expected in a solution of 80% propylene glycol, which is the concentration the producer declare.

The dosing was from the start 20 mg/l DOC, which correspond to 41 mg/l of propylene glycol, 91 mg/l Kilfrost and 148 mg/l Clearway. The loading was gradually increased during the test by changing the concentration in the test solution in steps. The concentration of DOC in the effluent was decisive as to when the change in the test solution was made. Changes in the concentrations of the test solutions during the test and changes in the water dosing is shown in Table 4.

Days	Propylen glycol		Kilfrost DF		Clearway 1		Water, ml/day	
	2-4°C	12-14°C	2-4 °C	12-14°C	2-4 °C	12-14 °C	2-4 °C	12-14 °C
0	0	0	0	0	0	0	315	315
18	20	20	20	20	20	20		
38	20	50	20	50	20	50		
41	50	50	50	50	50	50		
56	50	100	50	100	50	50	630	630
80	100	100	100	100	100	200		
141	100	100	100	100	100	0		
154	100	200	100	200	100	0		
198	100	300	100	300	100	0		
201	0	300	0	300	0	0		
234	200	300	200	300	0	300		
245	200	400 #	200	400	200	300		
270	0	400	0	400	0	300	0	
282		0		0		0		0

**Table 4.** Dosing of chemicals (mg/l DOC) and water during the test.  
# added Kilfrost in the last phase of the test. **O** abrupt dosing of test medium.

## 2.6. Water balance over the lysimeters

The amounts of water added to the lysimeters were controlled and adjusted 1-2 times a week by means of measuring cylinders and a stop watch. The effluent was collected and the volume noted by use of the measuring cylinder. Based on these measurements a calculation of the loss of water by evaporation at the two temperature domains was carried out. The mean amounts of water in and out from the lysimetres per day through the first 3 months of the test is shown in Table 5 for 2-4 °C and in Table 6 for 12-14 °C. The results are representative for the whole test period.

2-4 °C		Control		Prop. glycol		Kilfrost DF		Clearway 1	
Dosing period	Day	Lys.1 (ml)		Lys. 2 (ml)		Lys. 3 (ml)		Lys. 4 (ml)	
		In	Out	In	Out	In	Out	In	Out
12.-31.07.91	0-19	310	311	302	280	302	272	317	307
01.-22.08	41	315	316	324	297	317	286	317	316
22.08.- 6.09	56	302	299	317	301	310	294	288	288
06.09-30.09	80	633	590	633	614	633	624	605	576
30.09-10.10.	90	550	550	630	630	650	650	580	580
Average loss of water		2,1 %		3,8 %		3,9 %		1,9 %	

**Table 5.** Water balance over the lysimeters (lys.) incubated at 2-4 °C.

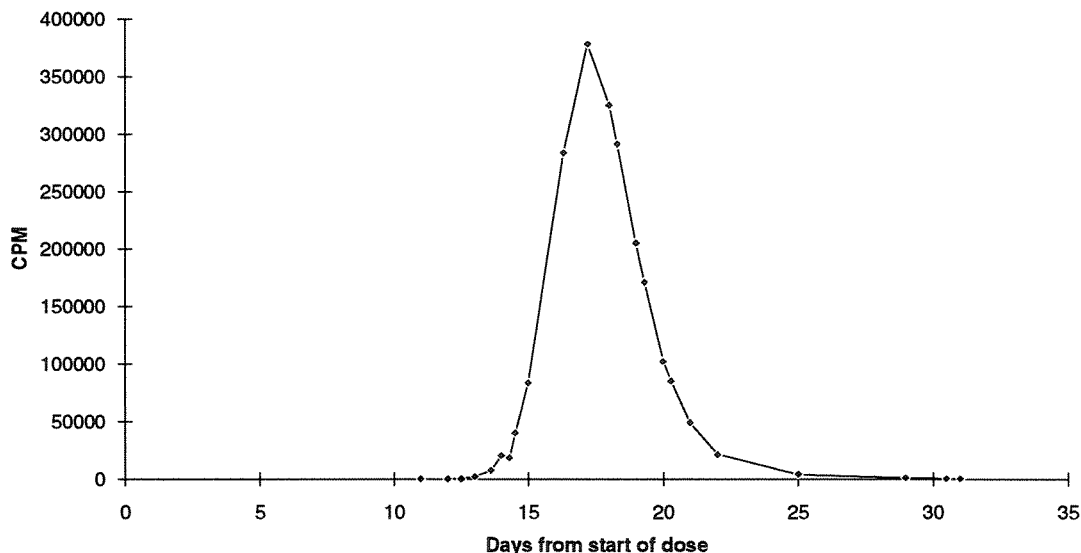
12 - 14 °C		Control		Prop. glycol		Kilfrost DF		Clearway 1	
Dosing period	Day	Lys. 1 (ml)		Lys. 2 (ml)		Lys. 3 (ml)		Lys. 4 (ml)	
		In	Out	In	Out	In	Out	In	Out
12.-31.07.91	0-19	331	304	336	305	324	285	331	290
01.-22.08	41	317	293	331	297	317	281	310	285
22.08.- 6.09	56	302	261	324	290	317	275	310	280
06.09-30.09	80	547	520	648	594	634	558	648	576
30.09-10.10.	90	619	560	619	590	605	503	634	582
Average loss of water		8,4 %		8 %		13,4 %		10 %	

**Table 6.** Water balance over the lysimeters incubated at 12-14 °C.

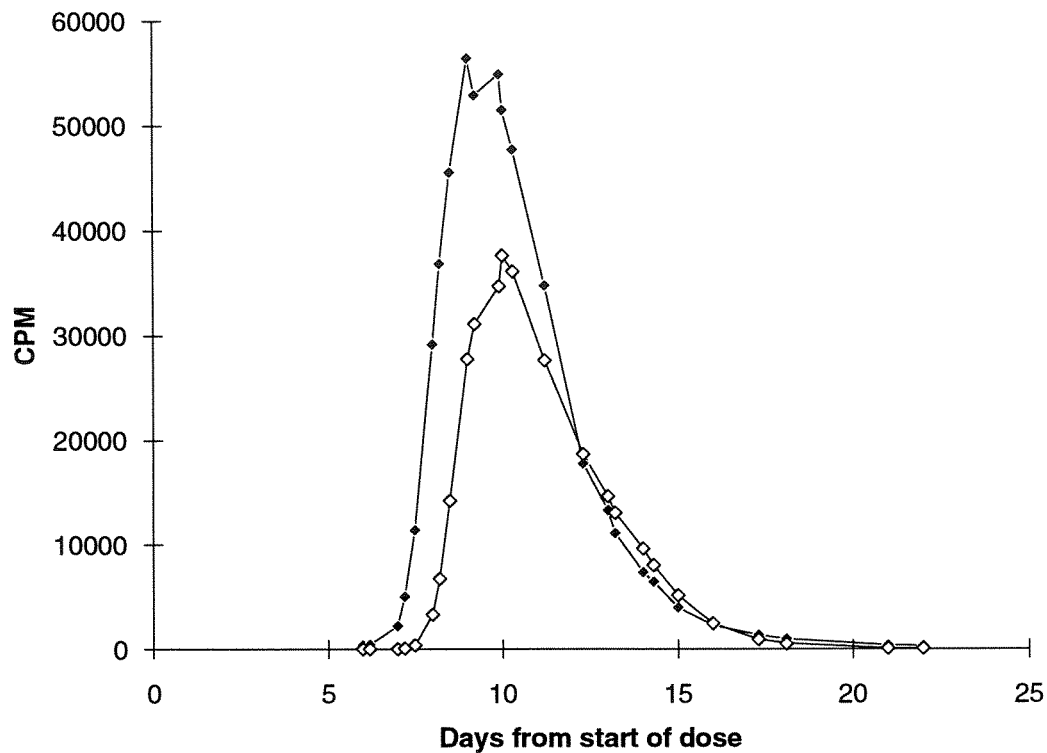
The loss of water by evaporation was significantly different at the two temperature regimes. By 2-4 °C the loss was 2-4%, meanwhile by 12-14 °C the loss amounted to 8-10%. The difference in loss between the columns by the same temperature is low and vary unsystematically, which indicate that the chemicals added had no effect on the evaporation of water from the surface.

## 2.7. Determination of hydraulic retention time in the lysimeters

The retention time of the test water was examined by means of tritium marked BOD-water. BOD-water added 1  $\mu\text{Ci/l}$   $\text{H}_2\text{O}$  was added in the control column by 2-4 °C. The dosing continued for 12 hours, with a water flow of 315 ml/day. The effluent was by intervals collected during one hour and 5 ml transferred to a scintillation glasses for determination of radioactivity by liquid scintillation counting. The results show that the mean retention time of the water in the soil column was 17 days by the lowest hydraulic loading, as shown in Figure 1.



**Figure 1.** Determination of the retention time for the test water in the lysimeters by a dosing of 315 ml/d.



**Figure 2.** Determination of the retention time for the test water in the lysimeters by a dosing of 630 ml/d.

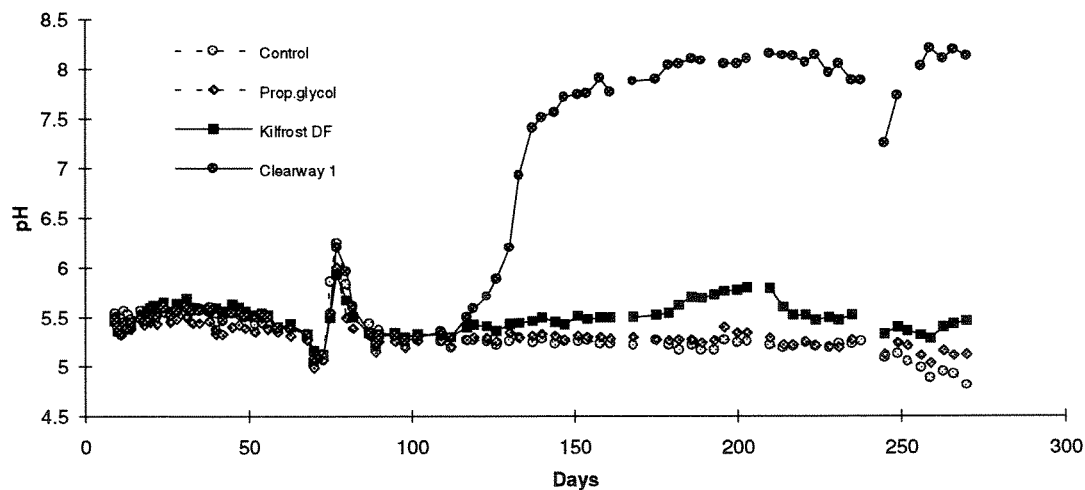
A corresponding measurement was also carried out in the control columns at a water flow of 630 ml/day by both temperature domains. The concentration of tritium was reduced to 0.2  $\mu\text{Ci/l}$  in the BOD-water, while the first experiment showed that this would be sufficient. The retention time for the water at a dosing of 630 ml/day is shown in Figure 2. The retention times were slightly different in the two lysimeters, which was due to a slight difference in the water supply rate. The mean retention time was 9-10 days.

### 3. RESULTS AND DISCUSSION

The dosing of BOD-water has been proceeding for 282 days, and the adding of test-chemicals has then been going on for just over 260 days. The experiment has continued without brake and the development has been followed by measuring the chosen parameters. In the following paragraphs the results shall be presented and discussed.

#### 3.1. The development of the acidity of the effluents

The acidity of the effluents were followed by regular measurements of pH. The results for lysimeters incubated at 2-4 °C are shown in Figure 3.

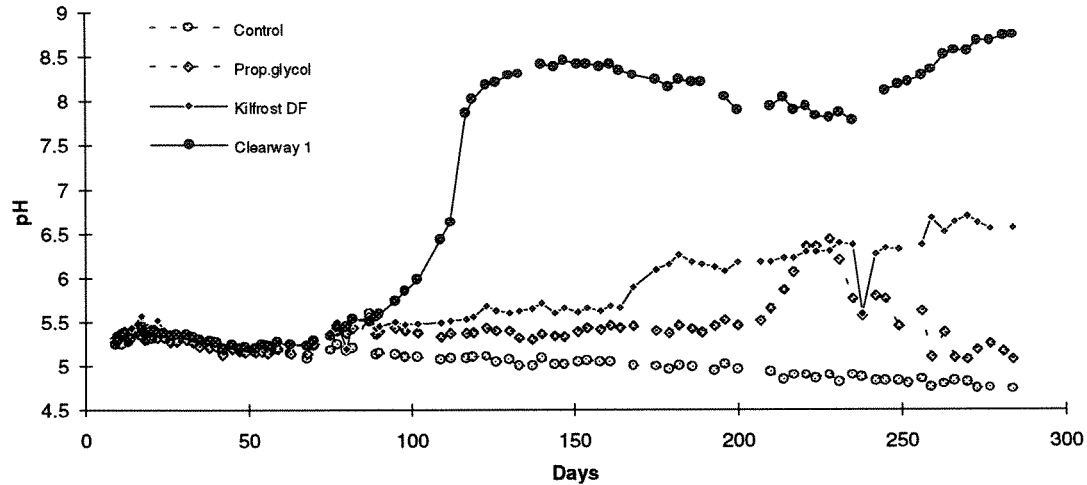


**Figure 3.** The development of pH in the lysimeters incubated at 2-4 °C

At 2-4 °C a stable and homogeneous development of pH was measured in all effluents until after 70 days. Then there was a temporary pH-decrease and a following increase, which can be due to the change in the water flow. Towards 90 days the pH-values decreased again to the stable level as was registered before this temporary fluctuation arose in the effluent from all the columns. No analytical data exists which with certainty can explain this, since data for most of the other cations other than  $H^+$  are missing. Most reasonably, however, this phenomenon is due to a dislocation of the zone of absorption of cations and release of  $H^+$  downwards in the column by the increased water flow and is not supposed to be due to changes in microbial activity.

A long-term differentiation of pH took place in the columns loaded with propylene glycol and Kilfrost, slightly in the direction of neutral pH for Kilfrost, while propylene glycol alone stayed on the acid side. This may have been due to the additives. By increased loading an abrupt and strong alkaline reaction took place in the column with Clearway. The pH-rise in the Clearway-columns can either be due to a change to anaerobic cleavage of acetate to methane and carbon dioxide, or more likely that potassium-acetate penetrated all the way through the column. In a water solution of Clearway the pH is buffered to 8-9 by those concentrations which were used in the experiment.

The results from the measurements of pH for the lysimeters incubated by 12-14 °C are shown in Figure 4. The pH in the effluent from these columns showed for all a weak acidification in the first 70 days of the test period. The increase of chemicals to 100 mg/l DOC and water flow to 630 ml/day after 56 days were reflected as a small pH-increase in the effluent.



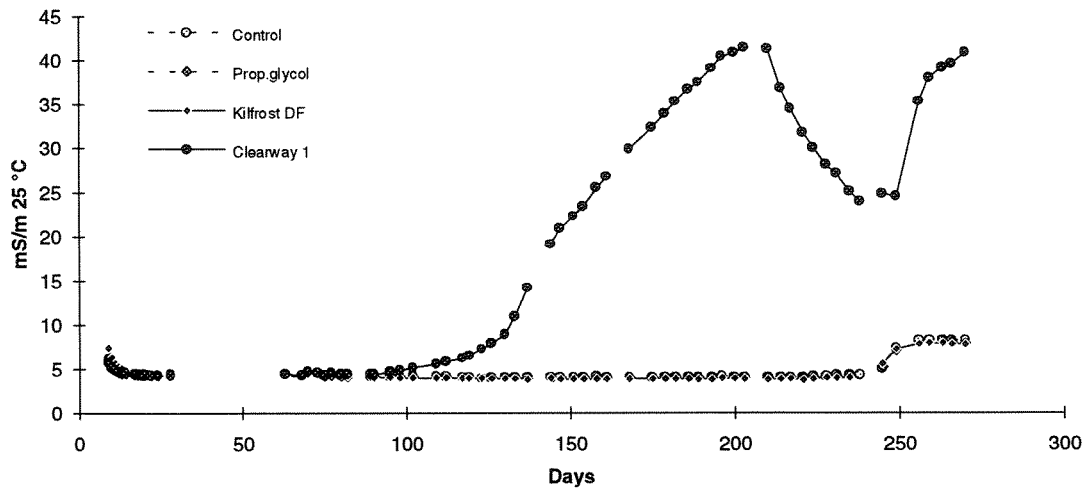
**Figure 4.** The development of pH in the lysimeters incubated at 12-14 °C

After 90 days the pH at 12-14 °C increased strongly in the effluent from the columns, which - as for 2-4 °C - can be due to a rapid change to anaerobic digestion of acetate, or that potassium acetate went unchanged through. The acidity of the effluent from the columns with propylene glycol and Kilfrost DF developed more clearly towards an increased difference compared to the control at this temperature. The effluent from the control showed a weak acidification during the whole test period.

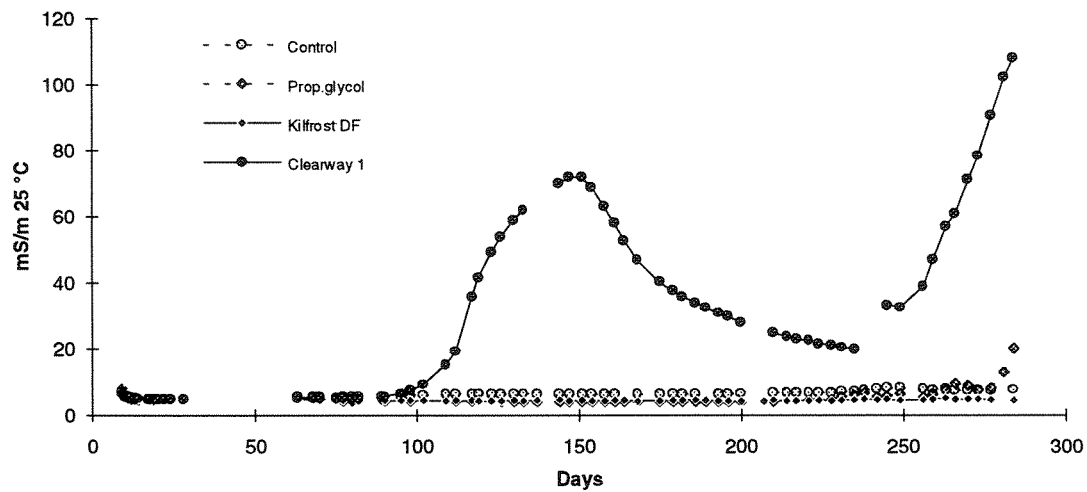
### 3.2. The development of electrolytic conductivity of the effluents

Figure 5 and 6 shows the effluent conductivity with time. By exception of a marked, but small increase at 12-14 °C in the column with propylene glycol towards the end, which corresponds with measurable values for iron and a strong increase of organic carbon, it was only in the Clearway columns where dramatic changes occurred. By the higher temperature the conductivity increased simultaneously with a change to alkaline pH. When Clearway was removed from the added water a gradually reduction in the conductivity was registered, with a time delay that corresponds with the retention time for water in the lysimeters.





**Figure 5.** The development of electrolytic conductivity in the effluent at 2-4 °C



**Figure 6.** The development of electrolytic conductivity in the effluent at 12-14 °C

### 3.3. The release of potassium from the soil columns

Clearway consists of the potassium salt of acetic acid (potassium acetate), which exist in dissociated form at the actual pH values. The washing out of potassium from the columns is shown in Figure 7. The results show that - simultaneously with the increase in pH and conductivity - a marked increase of potassium took place in the water from columns with Clearway.

Only a few measurements were made because this parameter was not included in the test program, but penetration of potassium seems to follow the conductivity. The increase of conductivity can be explained as being due to a wash-out of potassium and partly acetate. In the aerobic phase earlier in the experiment absorption of potassium is likely to have taken place in the soil matrix. This matter deserve further studies.

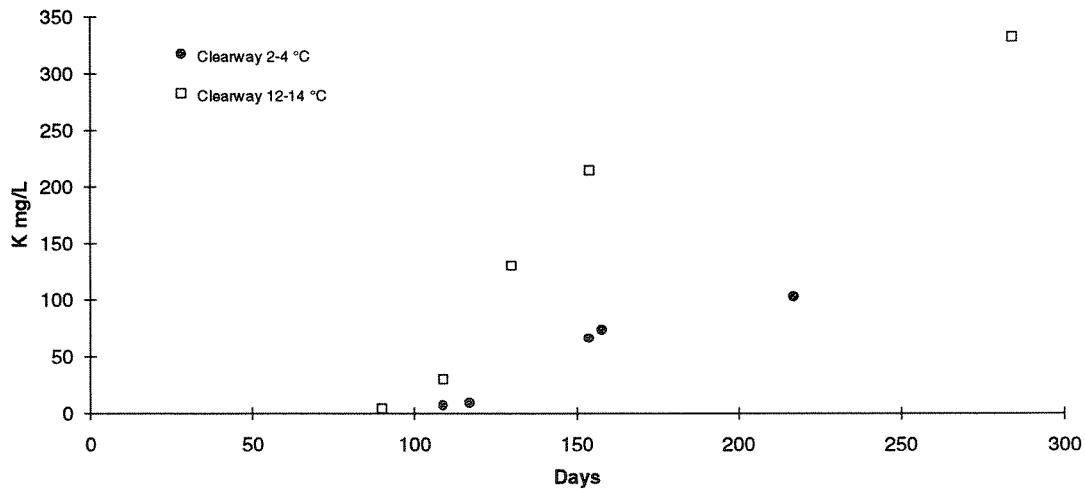


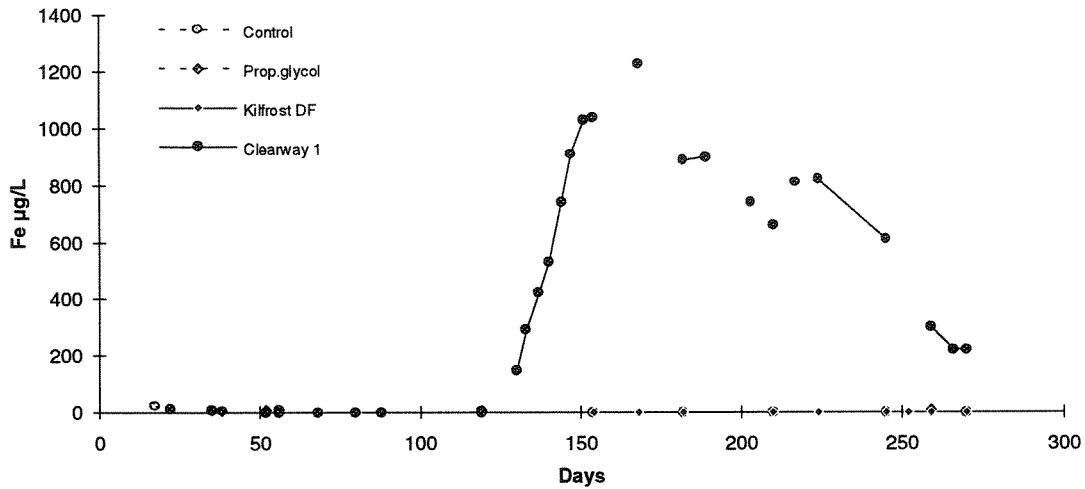
Figure 7. The release of potassium with the effluent from the soil columns

### 3.4. The content of iron and manganese in the effluents

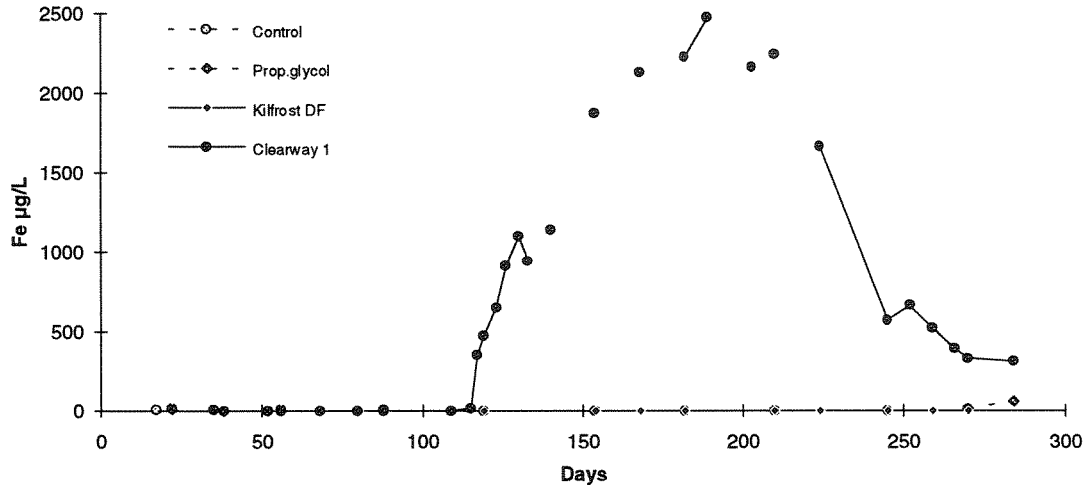
The level of iron in the effluent was at the beginning influenced by the mechanical mixing of soils before the reconstruction of the soil columns. After a period of 40 to 50 days the values were down to - and sometime lower than - the detection limit of 5 µg/l. This situation was stable until the pH-values increased and the effluent got a rusty, brown appearance (Clearway 1, only). This is a clear indication of a change to an anoxic environment and that iron from deposits in the soil was mobilised, particularly at the higher temperature. But the values then decreased gradually even though the Clearway concentration was kept at the same level, probably due to depletion of iron in the soil matrix..

The results of the analysis are shown in figure 8 and 9 for the experiments by 2-4 and 12-14 °C, respectively. They show that by the low temperature regime a change to anoxic conditions took place after 130 days, where the loading of Clearway had been 100 mg/l DOC the last 50 days

(Table 4), and after 116 days by high temperature, where the addition was 200 mg/l DOC during the last 36 days.



**Figure 8.** The iron content of the effluent from lysimeters incubated at 2-4 °C.



**Figure 9.** The iron content of the effluent from lysimeters incubated at 12-14 °C.

The content of manganese in the effluent was measured regularly only for 153 days, but was low throughout the whole experiment and showed a downward trend with time. The results are shown in Figure 10 for 2-4 °C and Figure 11 for 12-14 °C, respectively. On the average the Control columns showed the highest values, especially at high temperature. Larger biological activity might have caused an increased re-absorption in the biomass by the highest temperature.

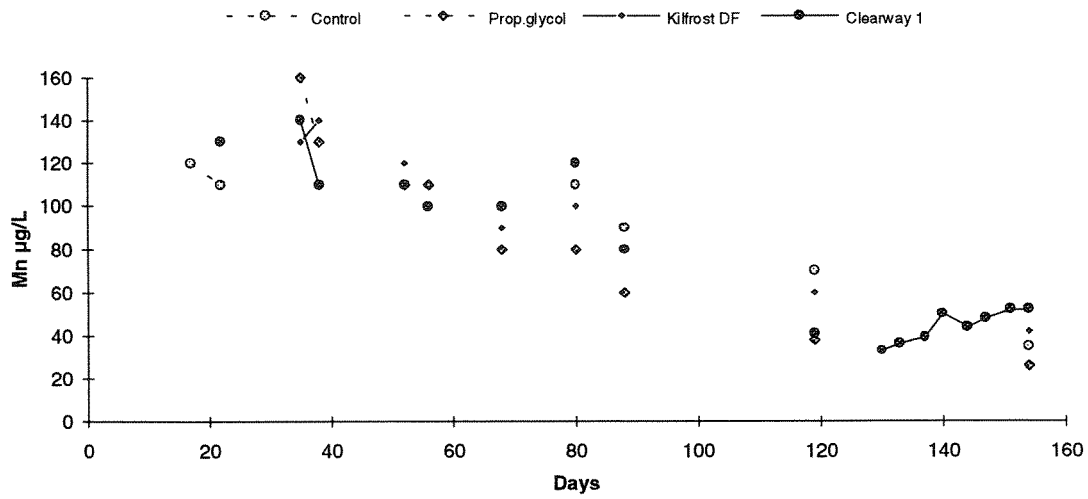


Figure 10. The manganese concentrations of effluents from lysimeters incubated at 2-4 °C.

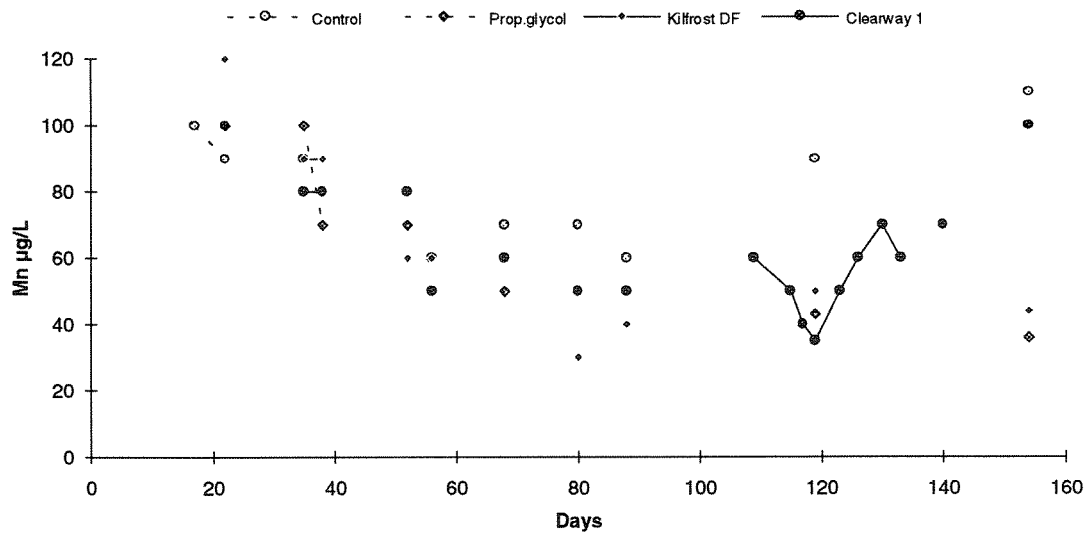


Figure 11. The manganese concentrations of effluents from lysimeters incubated at 12-14 °C.

The analysis results for iron and manganese in conjunction shows that there was no any abrupt changes in the redox conditions in the columns until 122 days. The release of iron would be expected to increase strongly also in the columns with propylene glycol if anaerobic conditions had developed due to overloading with oxygen-consuming materials, similar to what happened in the column with acetate at this point.

### 3.5. Dissolved organic carbon in the effluents

#### 3.5.1. Degradation by low temperature

The content of dissolved organic carbon (DOC) in the effluent can be used as basis of a further description of biodegradation in the individual lysimeters. The results from the columns incubated at 2-4 °C are shown in Figure 12.

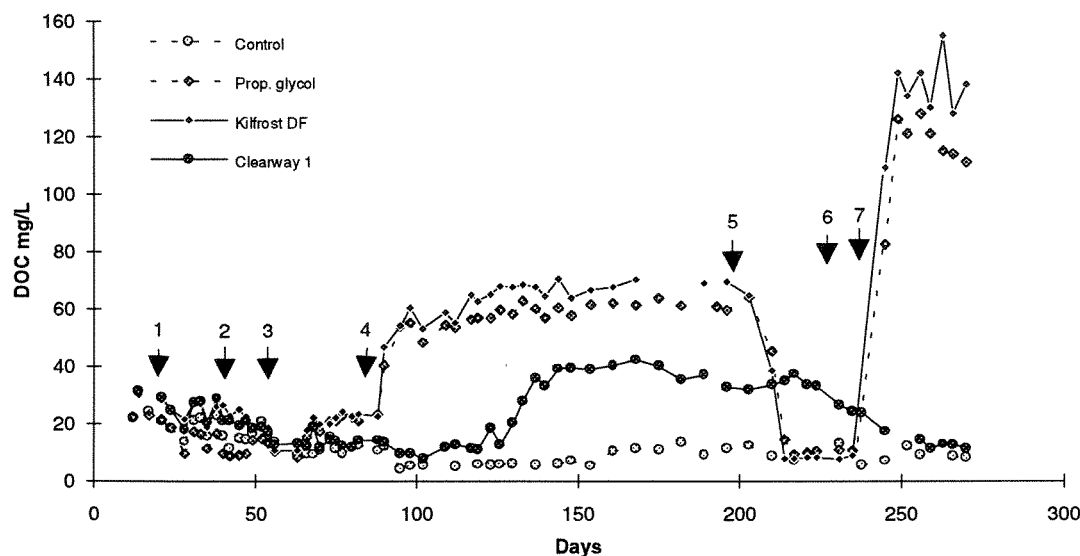


Figure 12. DOC in the effluent from the lysimeters incubated at 2-4 °C.

- Notes:
- 1 Started dosing of 20 mg/l DOC test-chemical, by a water flow of 315 ml/day.
  - 2 Increased the dose to 50 mg/l DOC
  - 3 Increased the water flow to 630 ml/day
  - 4 Increased the dosing to 100 mg/l DOC
  - 5 Stopped the dosing of test chemical, continued with pure BOD-water
  - 6 New dosing of Propylene glycol and Kilfrost at 200 mg/l DOC  
New concentrations of N (5 mg/l) and P (0.5 mg/l) in BOD-water
  - 7 New dosing of Clearway 1 with 200 mg/l DOC

The background level of carbon in the effluent from the Control columns and in columns with chemicals added stayed surprisingly stable in the test period up to 63 days. A trend towards lower levels with time occurred, however, during the period of 315 ml/day of water added, and which can be attributed to the restabilizing process after filling of the lysimeters.

The effluent from the columns added pure propylene glycol and Kilfrost were on background levels until the dosing was increased to 50 mg/l DOC at the same time as the water-flow was increased to 630 ml/day. By later increments to 100 mg/l DOC by 80 days and 200 mg/l DOC by 234 days the level in the effluent increased almost in proportion, with Kilfrost 5-10% above pure propylene glycol.

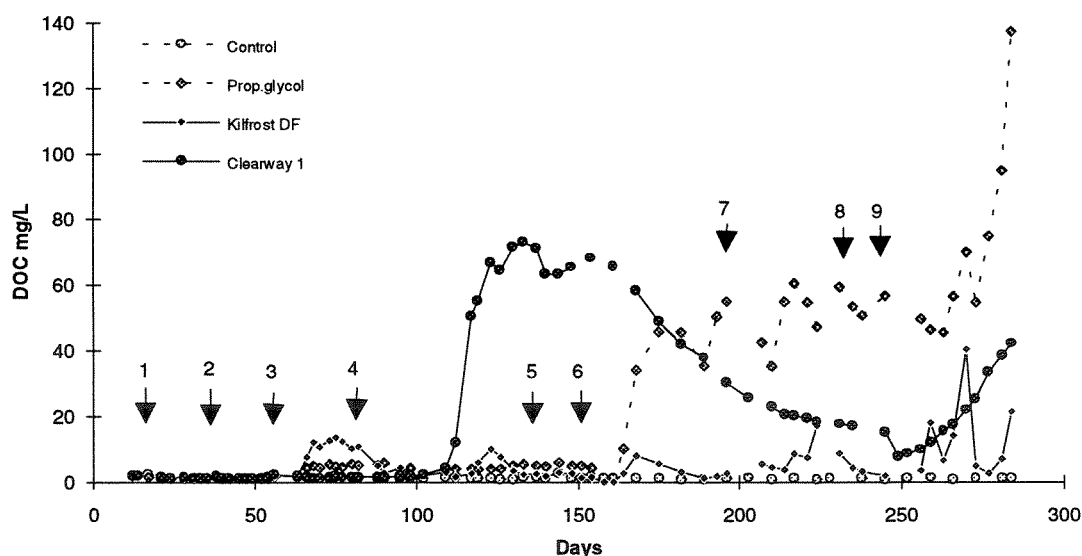
The DOC in the effluent with Clearway 1 was at the same level as for the Control column, also after the water-flow was increased and DOC in the inflow was up to 100 mg/l. But after about 50 days the DOC in the effluent increased gradually until a steady-state level of 35-40 mg/l was

reached. By abrupt dosing after 201 days a slow reduction down to background level took place after another 50 days, which corresponds to about 5 times the hydraulic retention time (10-11 days).

Biological degradation of both Kilfrost and Clearway 1 can be assumed to have been almost complete by 2-4 °C at a hydraulic retention time in the soil column of 17 days and by up to 50 mg/l DOC in the supplied water. By shorter retention times the capacities were exceeded.

### 3.5.2. Degradation by higher temperature

The content of DOC in water from the columns incubated at 12-14 °C is shown in figure 13. During the period with 20 and 50 mg/l DOC in the inflow very low concentrations were measured in the effluent from all the columns, generally less than 2 mg/l DOC. This shows that both mobilised carbon reserves in the soil and supplied chemicals were totally degraded when the hydraulic retention time was kept at 17 days.



**Figure 13.** DOC in the effluent from lysimeters incubated at 12-14 °C.

- Notes:**
- 1 Started dosing of test chemicals with 20 mg/l DOC. Water-flow 315 ml/day.
  - 2 Increased the dosing to 50 mg/l DOC
  - 3 Increased the dosing to 100 mg/l DOC. Increased the water-flow to 630 ml/day
  - 4 Increased the dosing of Clearway till 200 ml/day
  - 5 Stopped the dosing of Clearway , continued with BOD-water
  - 6 Increased the dosing of Propylene glycol and Kilfrost to 200 mg/l
  - 7 Increased the dosing of Propylene glycol and Kilfrost to 300 mg/l
  - 8 New dosing of Clearway started at 300 mg/l DOC level
  - 9 Increased the dosing of Kilfrost to 400 mg/l DOC  
Changed from Propylene glycol to Kilfrost at 400mg/l DOC  
in the column with propylene glycol

When the retention time was reduced by 56 days and the concentrations increased to 100 mg/l DOC for propylene glycol and Kilfrost, a temporary increase in effluent DOC took place. But after new 50 days the system adjusted to this loading. The biomass already established was not at once

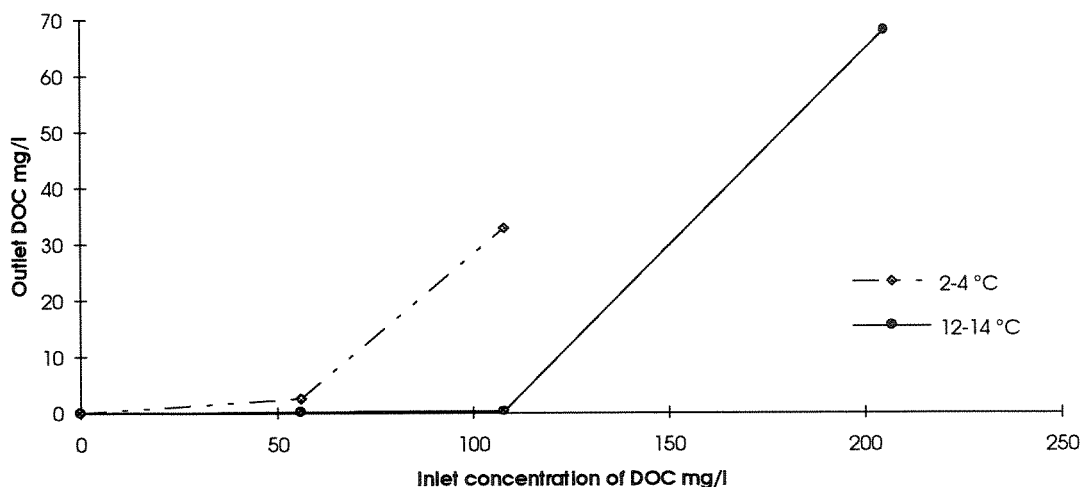
able to digest the increased loading, but the growth of active biomass then increased the capacity. A corresponding development occurred after a new increase to 100 mg/l DOC, but by 200 and later by 300 mg/l this happened only for the column with Kilfrost. The column with pure propylene glycol showed a high level and large instability of DOC in the effluent, but still without signs of anoxic conditions.

In the last experiment carried out with the lysimeters, both columns fed with propylene glycol were added Kilfrost DF after 245 days at 400 mg/l DOC-level. In the column which earlier received pure propylene glycol, the DOC in the effluent increased rapidly after about 265 days, and a beginning release of iron indicate that anoxic conditions were developing. On the other hand, the Kilfrost column again adapted itself, but with signs of instability. The self-cleaning capacity of the soil was violated at 200-400 mg/l DOC for the propylene glycol products by a retention time of 10-11 days at the higher temperature.

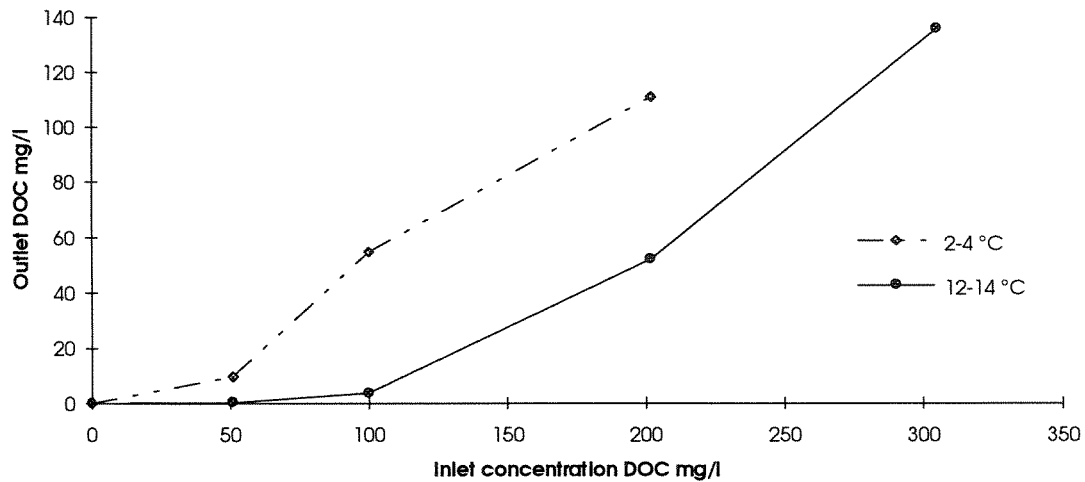
For acetate present in Clearway the maximum capacity was reached at a concentration of 200 mg/l DOC and at 10-11 days retention time, where anoxic conditions developed. The ability of the soil to regenerate was then tested by dosing clean BOD-water from day 141. First by 250 days the DOC-level in the effluent was almost at background level. The process of regeneration took about 10 times the hydraulic retention time. By new dosing of Clearway at concentration of 300 mg/l DOC the level in the effluent increased again but slower than after 110 days. The regeneration of the soil may have caused a marginal increase in the capacity of biodegradation.

### 3.5.3. Steady-state level of DOC as function of the load

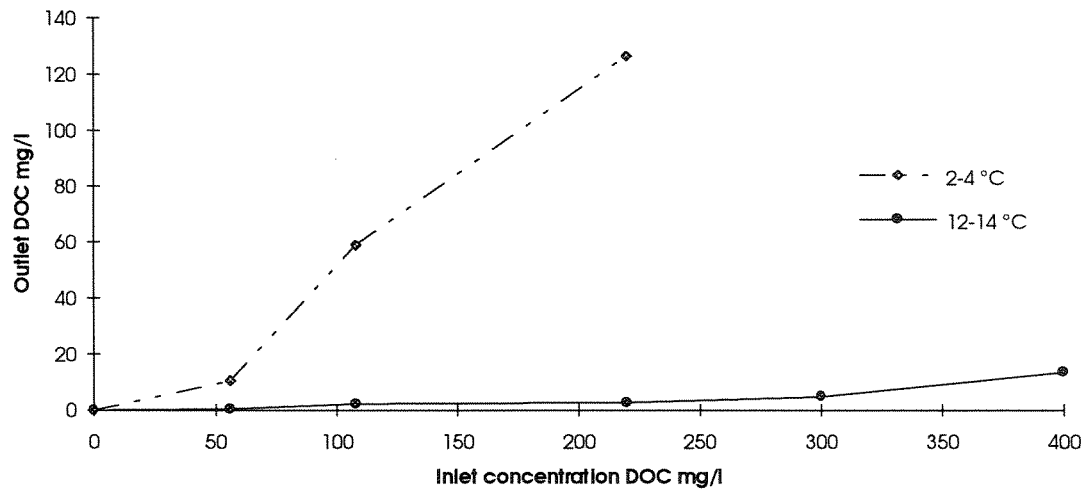
For each step-up of concentrations of chemicals in the added water, a steady-state effluent concentration was attempted before a new step-up was initiated. As the time-dependent DOC-plots show, this was to a large extent successful, although the time allowed for this was very limited. The average DOC-levels in the outlet which were approached at each steady-state have been calculated and plotted versus inlet concentrations, as shown in Figures 14, 15 and 16.



**Figure 14.** Steady-state level of DOC from Clearway 1 in the effluent as function of loading



**Figure 15.** Steady-state level of DOC from propylene glycol in the effluent as function of loading



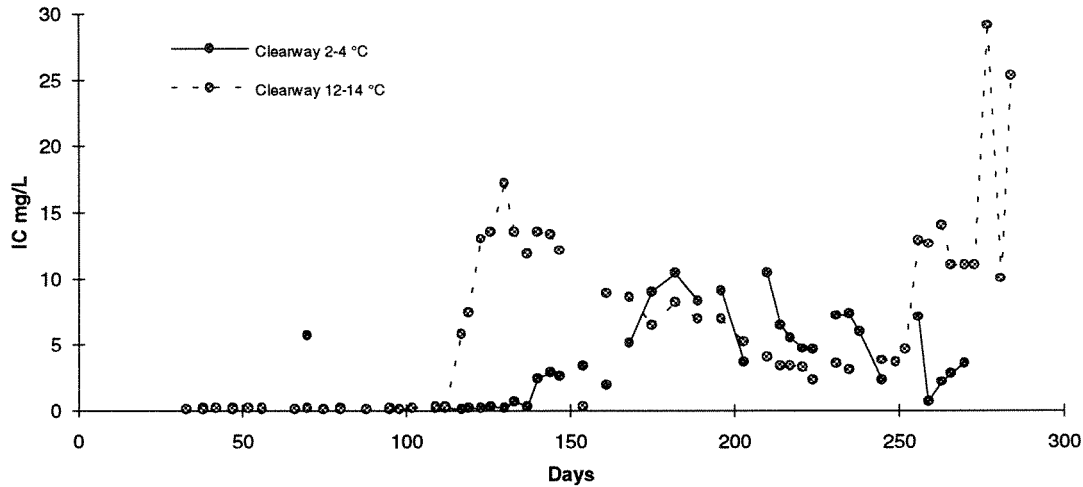
**Figure 16.** Steady-state level of DOC from Kilfrost DF in the effluent as function of loading

From these figures the maximum capacity of biodegradation referred to for the various treatments become more evident. A temperature increase from 2-4 °C to 12-14 °C generally increase the maximum capacity with a factor of 2, which is in the range of the commonly accepted temperature constant of biological reactions ( $Q_{10}$ ) of 2-3. The maximum load accepted under the prevailing temperatures and other conditions can be deduced from the intercepts with the X-axis.



### 3.6. The washout of inorganic carbon from the soil columns

Inorganic carbon (IC) cover dissolved carbonate- and bicarbonate ions, and eventual undissociated carbonic acid. IC was analyzed simultaneously with organic carbon (DOC), but is burdened with greater uncertainty due to the sampling procedure used. The results for Clearway 1 are shown in Figure 17.

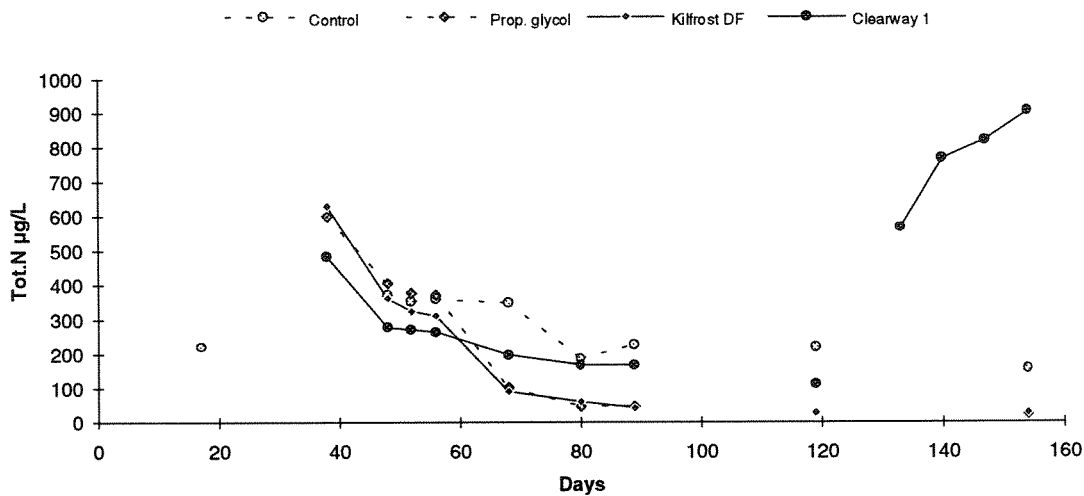


**Figure 17.** The elution of inorganic carbon from the lysimeters with Clearway.

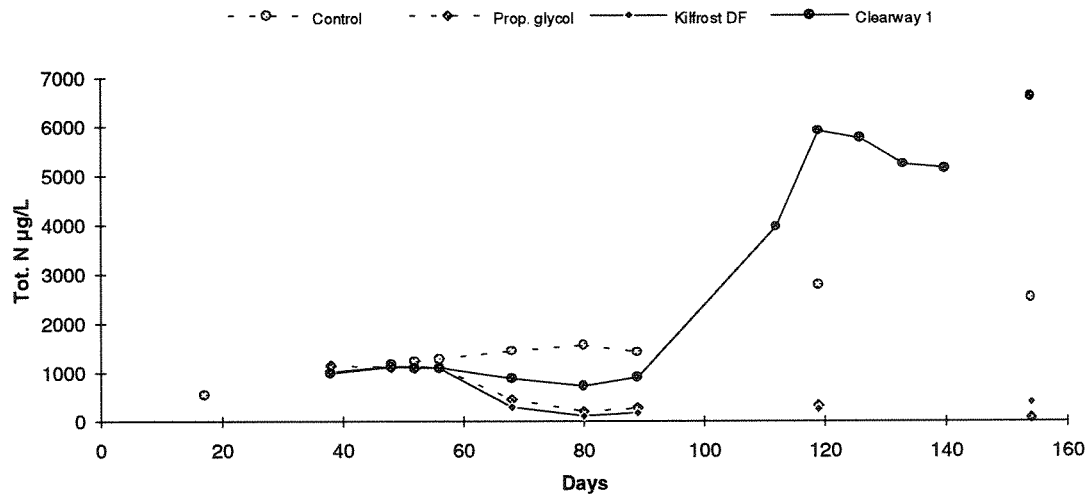
In the lysimeters loaded with Clearway 1 a notable release of carbonates coincided with the increase of pH and penetration of DOC from the columns. The carbonate amounts to 20-25% of the DOC-levels. Due to the higher pH at this stage the carbon dioxide produced from biodegradation will be partly dissolved in the effluent as carbonates. This may explain the apparent release of carbonates and also partly explain the increased conductivity.

### 3.7. The washout of nutrients (N and P) from the soil columns

The effluent from the lysimetres were analysed with respect to total nitrogen (TOT-N) and total phosphorus (TOT-P) until 154 days after the start in order to control that measurable concentrations prevailed and a as an indication of available nutrients for biodegradation. The results are given in Figure 18 and 19 for nitrogen and Figure 20 and 21 for phosphorus.



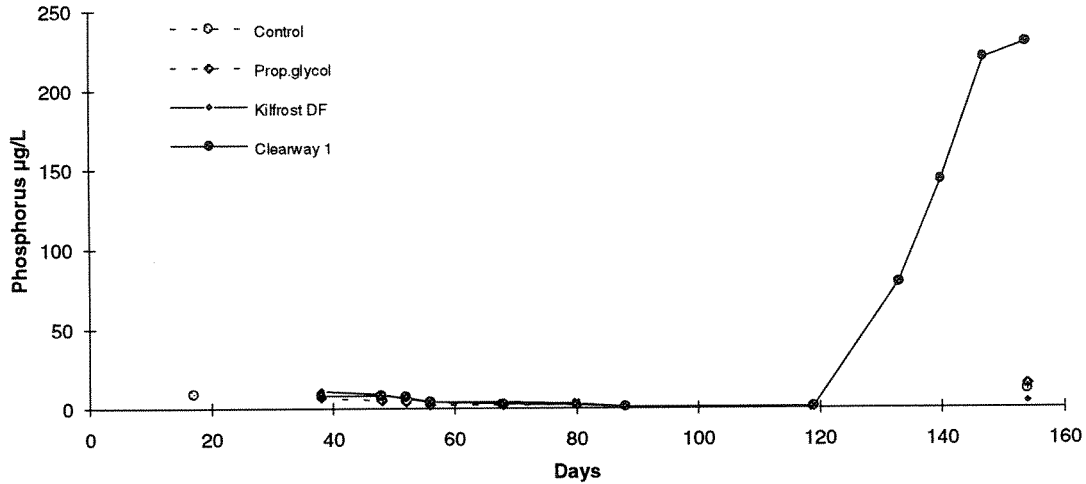
**Figure 18.** The level of TOT-N in the effluent from the lysimeters at 2-4 °C.



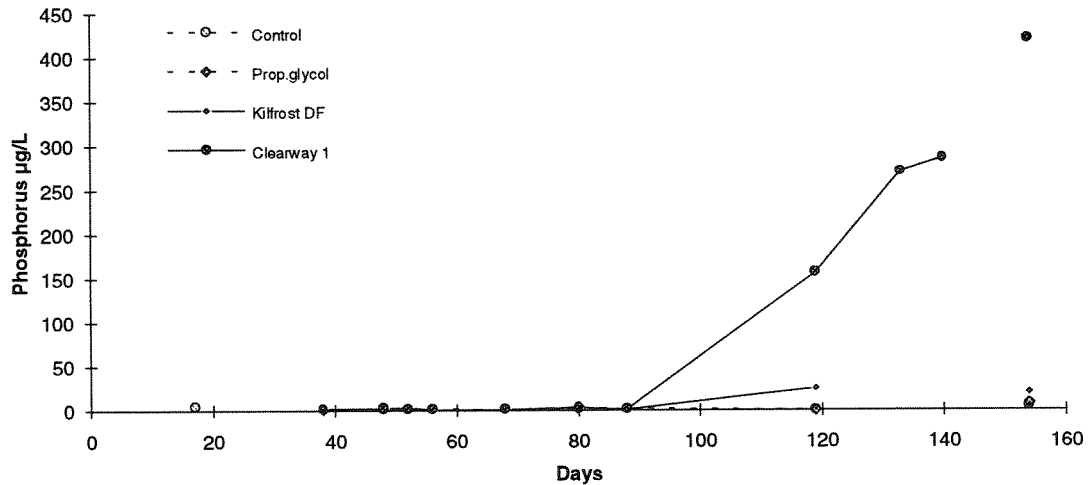
**Figure 19.** The level of TOT-N in the effluent from the lysimeters at 12-14 °C

Nitrogen was dosed as ammonium at a level of 500 µg/l. The results indicate both resorption of ammonium and release of nitrogenous substances from soil. The aerobic decomposition of propylene glycol and Kilfrost pushed the level in the effluent down to 100-200 µg/l after 80 days by both temperature regimes, and later a further decrease was observed. In this period the low levels observed may have influenced the rates of biodegradation. By 100 mg/l DOC a balanced supply of fixed nitrogen was available for aerobic decomposition. When increased to 200 mg/l DOC and higher, more N was added and should be available in surplus amounts.

By decomposition of Clearway a surplus of fixed nitrogen prevailed throughout the experiment. When anoxic conditions developed a notable release of fixed nitrogen took place, probably as ammonium, which by 12-14 °C exceeded the added amount 10 times.



**Figure 20.** The level of TOT-P in the effluent from the lysimeters at 2-4°C.



**Figure 21.** The level of TOT-P in the effluent from the lysimeters at 12-14°C.

The phosphorous values were very low but measurable in all the lysimeters, but increased slightly after 146 days. When anoxic conditions developed in the Clearway-columns a release of phosphorous was evident, simultaneously with iron. Phosphorus is effectively tied up in Fe-(III)-hydroxides under oxic conditions, but by reduction to Fe-(II) the complexes are dissolved and phosphorous released. From the figures it is not likely that the phosphorous availability has limited biodegradation of the test chemicals.

### 3.8. The redox-potential of the soil columns by the end

By the end of the experiments the redox potential of the columns were measured with a platinum electrode introduction into the sand columns as the soil was removed for analysis. The results are given in Figure 22 and 23. The results confirm other observations which show that the Clearway columns were anoxic ( $E_h < +150\text{mV}$ ), below 10 cm depth by the high and 25 cm by the low temperature, respectively.

The columns with Kilfrost show a clear indication of oxygen depletion in the upper 15 cm layer compared to the control, while columns with pure propylene glycol were comparable to the Control in the upper layer. This might be due to a significantly lower rate of biodegradation of the pure glycol than the formulated product. By 12-14 °C a tendency to anoxic conditions developed towards the bottom of the column, as indicated previously by the rising DOC-values towards the end of the experiment.

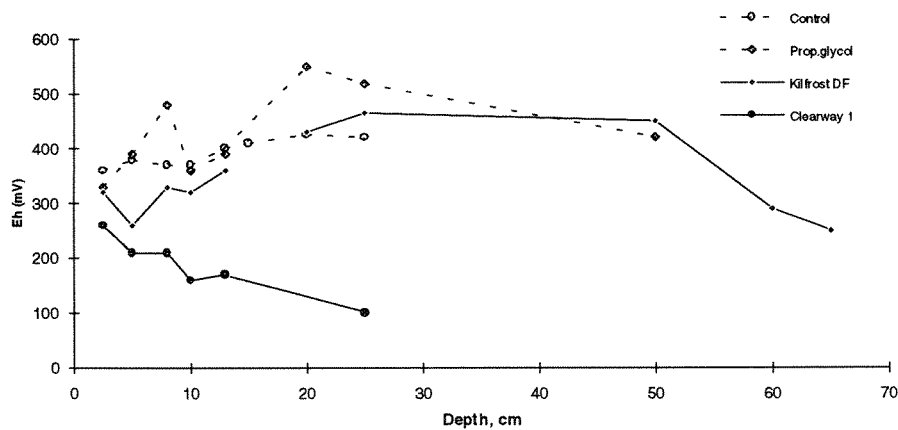


Figure 22. The redox potential as function of depth in the lysimeters incubated at 2-4 °C

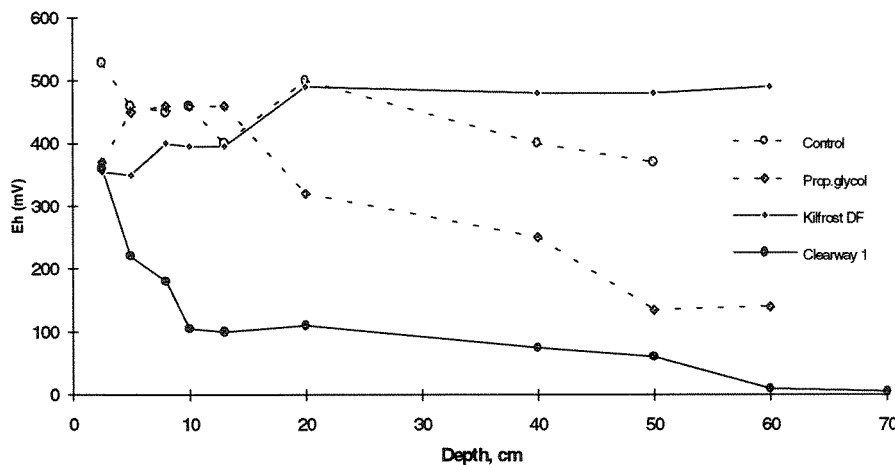


Figure 23. The redox potential as function of depth in the lysimeters incubated at 12-14 °C

### 3.9. Organic dry matter in the soil columns by the end

The organic dry matter, determined by loss of dry weight by heating to 550 °C, was analysed on samples taken from fixed intervals in the columns, as shown in Figure 24 and 25. As mentioned before, the arbitrary variations prevail in the upper layers and further down only slight differences in between the lysimeters are evident. Any measurable accumulation of organic matter from the added chemicals has not occurred. Possible remaining amounts of chemicals can constitute 1% as organic dry-weight down to 10 cm without giving any measurable increase, when compared to the natural variation and background levels.

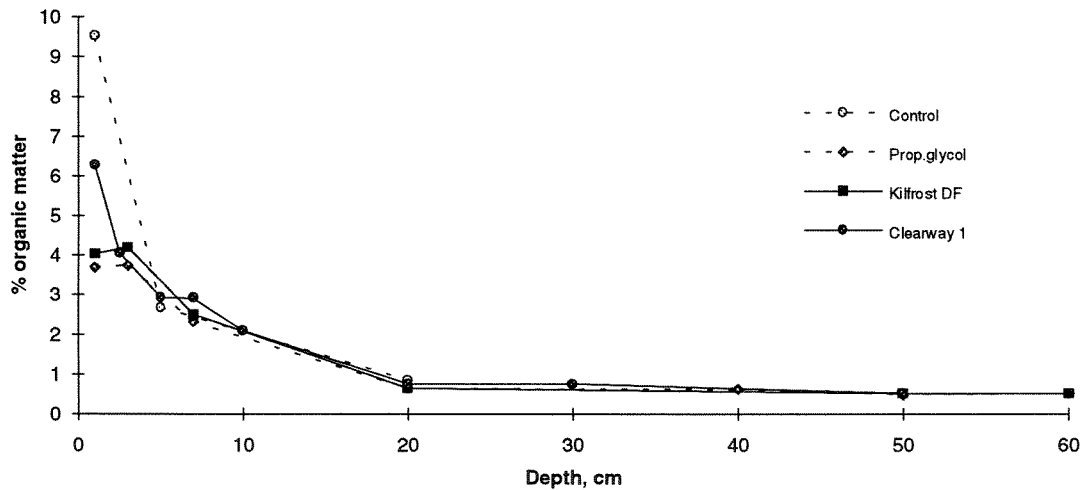


Figure 24. Organic dry weight in various depths in soil after treatment (2-4 °C)

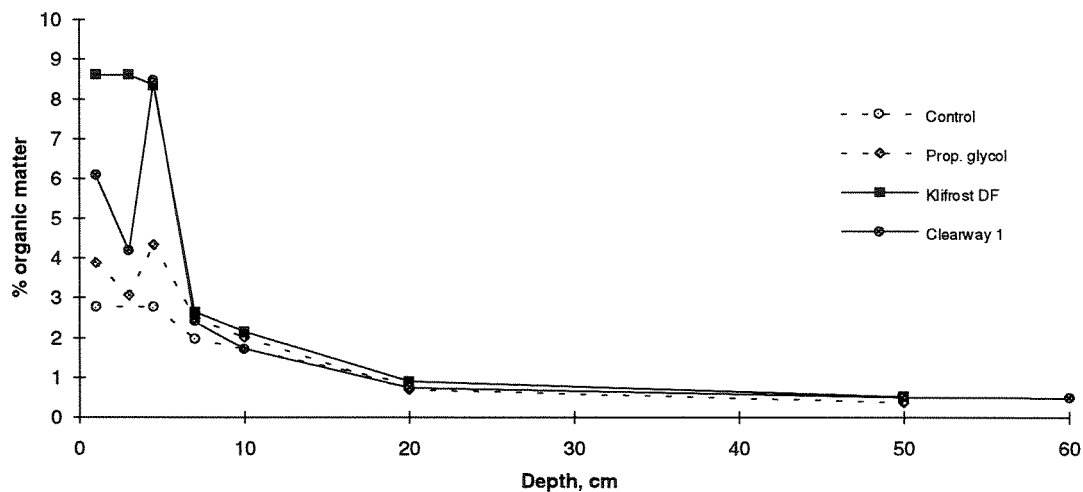
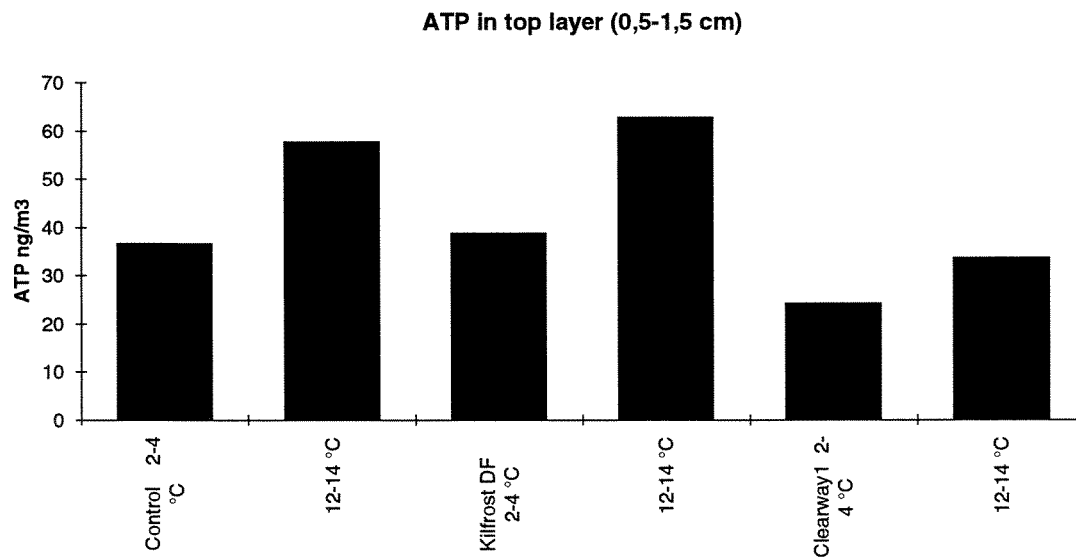


Figure 25. Organic dryweight at various depths in soil after treatment (12-14 °C)

### 3.10. Microbial biomass in the soil columns by the end

Microbial biomass in the soil was determined indirectly by the extraction and analysis of adenosine tri-phosphate (ATP) from microbial cells at 1, 7, 20 and 50 cm depth in the soil columns. ATP is present in stable concentrations in all viable cells. Analysis of selected samples indicated that more than 95% of the biomass was established in the upper 10 cm of the soil, and that no effects of the various treatments can be detected at lower levels, apart from a slight increase in all treatments compared to the control.

The results from the 0.5-1.5 cm level are given in Figure 26. These show that the predominant effect by all treatments is a stimulation with increasing temperature. At 2-4 °C there is an apparent 25-35% reduction of biomass compared to 12-14 °C. Clearway 1 may exhibit a slight inhibitory effect on aerobic biomass in the upper levels of the soil columns.



**Figure 26.** Microbial biomass (ATP) in the topsoil (0.5-1.5 cm) of treated lysimeters

## 4. DISCUSSION

The experimental set-up was chosen from the need of realism with respect to soil type and profile on the one hand, and controlled experimental conditions within a realisable budget on the other hand. Lysimeters constructed in the laboratory and of the actual size is a well recognized method which has been used, i.e., in many investigations of pesticide biodegradation. Homogeneity with respect to layers of sand were achieved in all units, but the uppermost rhizosphere-containing soil was not homogenized and did show some deviations in organic dry-weight in between columns. On average and across the whole surface, however, there is reason to believe that the columns were not significantly different from each other.

The BOD dilution water was comparable to Norwegian surface water from the Oslo area in terms of ionic strength, and there is no reason to believe that softer or somewhat harder water could have influenced retention or decomposition of the de-icing chemicals. The load was in times lower than pre-regulated levels due to growth of bacteria in the tubes, but this was frequently removed manually. The water balance showed a loss due to evaporation below 10%, but this is so low that it has not been corrected for in the concentrations measured in the penetrating water.

By the use of tritiated water as a tracer the hydraulic retention times and wet volumes of the soil columns were accurately determined, arriving at 5.8 l water volume by a retention time of 9.25 days (630 ml/day added), respectively 5.5 l volume by 17.5 days (315 ml/day added). From this a direct relationship of precipitation and retention time in the upper 1 m unsaturated zone was found, while the retention volume was not affected significantly within this interval. Following dry periods under field conditions and when the ground is frozen, the water-binding capacity will certainly be affected, but the figures given may represent the typical autumn and spring situations.

Clearway 1 (K-acetate) is completely biodegraded as long as oxygen is available in the topsoil, but when the porewater is stripped for oxygen the decomposition evidently stops. Because the substance is easily degradable the consumption of oxygen is very intensive in the upper layers. A tendency to a formation of bacterial slimes may have worsened the conditions for oxygen diffusion from the air above, a phenomenon which was not observed on the soil columns amended with the glycol products.

The lack of evidence of any anaerobic decomposition of acetate was surprising, but must be ascribed to the lack of nitrate and nitrite for denitrification. Methanogenesis could not occur due to the fairly high redox potential. A moderate use of fertilizers, i.e., ammonium nitrate or similar, might induce rapid denitrification and efficient biodegradation of the acetate. There are also other alternatives which should be investigated, with the aim also to avoid polluting the ground water with nitrogenous ions.

Penetration of acetate caused changes in pH and the release of carbonates with the water, probably also mobilisation of potassium ions absorbed when acetate was decomposed, while iron has been released due to changes in the redox-conditions. The soil profile has a large but finite capacity for ion exchange, which will influence the concentrations measured in the effluent, as well as the retention capacity, both in the long and short term. The goal of these experiments have not been to study interactions with soil minerals in detail, which will require more detailed chemical as well as mineralogical analysis and has to be done by participation of geological expertise.

Mono-propylene glycol is decomposed aerobically in the upper part of the soil, but at low temperatures the degradation evidently becomes incomplete already at a concentration of 50 mg/l

DOC in water. The degradation products are unknown, but most likely there was a conversion to lactic acid, pyruvic acid and possibly other organic acids, which together with the remaining glycol are released from the soil columns when their retention times in the upper 15-20 cm becomes too short for the soil microbes to deal with this load. pH is only moderately changed since mono-propylene glycol is a weak buffer and the degradation products have  $pK_a$  -values around 4-6.

The redox measurements do not indicate that oxygen levels were extremely low, but it could have been low enough to stop further oxydation of the intermediates. Anaerobic decomposition probably did not take place. Analysis of the effluent water samples by, i.e., gas chromatography/mass spectrometry should be carried out in order to identify what products are formed by the partial decomposition of mono-propylene glycol in soil, because it is not very likely that these will be absorbed or degraded before being transported down to the ground-water table.

Second to oxygen, certainly the most important factor influencing the extent of biodegradation in the top-soil, it is evident that temperature did play a significant role in determining both degradation rate and fate of the de-icing chemicals in soil. At low temperatures the amount of active biomass became less, as shown by the ATP analyses. Theoretically the diversity of the microbiota is also reduced at temperatures as low as 2-4 °C, since several metabolic types of bacteria can not grow. This effect was most clearly demonstrated by the fact that carbon released from the soil matrix initially was washed out from the soil columns at 2-4 °C, while at 12-14 °C nothing was released, assumably due to a complete biodegradation. For the biodegradation specifically of acetate and mono-propylene glycol, however, the effect of temperature is most likely a reduction of rate. Theoretically the rate of biodegradation will increase by a factor ( $Q_{10}$ ) of 2-3 per 10 °C increase of temperature within the actual range, given a constant biomass. An additional effect may be due to the observed biomass increase.

Both test chemicals are purely carbonaceous energy substrates, while the build-up and maintenance of microbial biomass also requires the coincident supply of fixed nitrogen (as ammonia, nitrates or amines) and phosphorous (as easily available phosphates). Other mineral nutrients are presumably available in surplus quantities. As determined by Mørkved, Laake and Aasgaard (1992) a balanced C/N-ratio for aerobic biodegradation of mono-propylene glycol is approximately 120:10 on a weight basis, while the demand for P commonly is less than 1/10th of the N-requirement. The figures for decomposition of acetate are within the same range. Fertilizing the top-soil will be necessary to assure a sufficient rate of self-purification concerning these chemicals.

The increased decomposition of Kilfrost DF compared to the pure mono-propylene glycol, which was observed at 12-14 °C, can probably be explained from additional amounts of phosphorous and nitrogen present in Kilfrost. The nitrogen content is in any case too low to cover the needs, but even trace amounts may exhibit a stimulation effect, as any presence of other organic substrates that give the micro-organisms a more diverse diet will do. The amount of phosphorous is, however, significantly higher than in the pure chemical, and the observed increased decomposition rate observed may be explained as an effect of an increased availability of phosphorous.

Following the overloading of the soil columns with Clearway 1, the regeneration process was surprisingly slow, which can be due to bad conditions for oxygen diffusion, as mentioned earlier. A similar long concentration tail of DOC in the eluated water was not observed with mono-propylene glycol or Kilfrost after the dosing was stopped for a period of time, rather a reduction of DOC levels right down to the baseline. The redox profiles confirm that anoxic conditions did not develop in these soil columns. The diffusivity of oxygen was probably better in the top-soil, since no formation of bacterial slimes was observed.



The slime formation observed on the Clearway 1 columns was probably caused by the growth of slime-forming bacteria, which are known to thrive on acetate as a growth substrate. It may function as a protective measure against toxic effects of high substrate concentrations, extreme pH conditions, and similar circumstances. As the ATP figures show, the biomass was in fact lower than in the control. This formation of slimes can be counteracted by the use of calcium-containing fertilizers, the use of other chemicals in combination with acetate, aeration of the top-soil, etc., which should be investigated and further evaluated. However, it can be concluded that good diffusivity for oxygen is a pre-requisite for efficient biodegradation and rapid regeneration of the soil following a peak load, i.e., during snowmelt situations.

Lysimeter experiments carried out in the laboratory can hardly replace field experiments, and further investigations and evaluations should be carried out in conjunction with model studies of the geological and hydrological processes taking place in the unsaturated zone. Hereby the effects of peak loads caused by snowmelt can also be studied and the overall influence of climatic factors and soil chemistry be further clarified.

## 5. CONCLUSIONS

1. The de-icing fluid Kilfrost DF is biodegraded almost completely in sandy soil columns at a concentration of 20-50 mg/l DOC in the percolation water, both at 2-4 °C and 12-14 °C. It is mandatory that the retention time is sufficient in the upper layers of soil, in other words that the hydraulic load is moderate, and that mineral nutrients (N and P) not are limiting to the process.
2. The analytical data for higher concentrations of Kilfrost and in combination with low temperature indicate that both factors result in a lower extent of biodegradation. The result may be penetration of mono-propylene glycol to depths in the soil profile were a microbial biomass can not be developed and sustained. The carrying capacity per ground area should be determined from the extent of biodegradation in the upper 15 cm of soil, where the active zone was found.
3. Additives present in the Kilfrost DF product probably had a short-lived and moderately negative effect on the decomposition of mono-propylene glycol. This effect can be of importance when the load of de-icing fluid on the soil column approach its carrying capacity and if the additives accumulate in soil over time. However, the long-term effect seemed to be positive due to stimulative properties also being present, primarily phosphorous. By overloading with Kilfrost the decomposition capacity of the soil was rapidly regenerated.
4. Clearway 1 seems to be completely decomposed at concentrations up to 100 mg/l DOC when the hydraulic load was moderate and the temperature in the high range. At low temperatures the capacity for biodegradation was gradually reduced with time at this concentration, while 50 mg/l was decomposed even at low temperatures. Higher loads can not be tolerated for an extended period of time (weeks), because anoxic conditions may then develop and decomposition become inhibited. The regeneration of the biodegradation capacity of the soil following an overload with Clearway 1 may take a long time (months).
5. For both chemicals the hydraulic retention time should be at least 20 days in the upper 1 m of the soil profile, equivalent to a maximum daily precipitation of 10 mm per day. Concentrations in water should not exceed 50 mg/l measured as DOC to assure a more or less complete biodegradation of de-icing chemicals during spring and autumn situations in a typical soil profile from the Gardermoen area. By introducing a good routine for amending the exposed top-soil with fertilizers these limits may be moved towards a larger carrying capacity of the soil.
6. Provided that the optimal arrangements are made for the the recollection of the run-off water and for the stimulation of biodegradation of chemicals spilled on the airfield grounds, there is good reason to believe that the ground-water reservoirs will be efficiently protected against contamination by potassium acetate and mono-propylene glycol present in the de-icing fluids used on aircrafts and runways.

## 6. LITERATURE REFERENCES

Breedveld, G., and M. Laake (1992a). Contaminants which will be studied in the project. Pp. 10. Ch. 7, In: J.-O. Englund and T. Moseid (eds.): Research Programme. The environment of the subsurface, Part I: The Gardermoen Project, 1992-94. Preliminary report: Literature Review and Project Catalogue, March 1992. The Norwegian Committee for Hydrology (NHK), Oslo.

Breedveld, G., and M. Laake (1992b): Biodegradation of organic pollutants in soil and groundwater. Pp. 12. Ch. 15, In: J.-O. Englund and T. Moseid (eds.): Research Programme. The environment of the subsurface, Part I: The Gardermoen Project, 1992-94. Preliminary report: Literature Review and Project Catalogue, March 1992. The Norwegian Committee for Hydrology (NHK), Oslo.

Gay, J., R. Jeffcoate, P.J. Dunn and J.E. Hawkins (1987): Stormwater contamination at airports and remedial options - with particular reference to Stansted. Inaugural Meeting, Inst. East Anglian Branch, 9. July, 1987.

Jank, B.E., H.M. Guo and V.W. Cairns (1973): Activated sludge treatment of airport wastewater containing de-icing fluids. *Water Res.* **8**:875-880.

Mørkved, K., M. Laake and G.F. Aasgaard (1992): Biological treatment of a de-icing fluid. NIVA-report, O-92036, Oslo. Pp. 30.

Verschueren, K. (1983): Handbook of environmental data on organic chemicals, 2.nd ed.. Van Nostrand Reinhold, New York. Pp. 1310.

Yu, D.K., and R.J. Sawchuk (1987): Pharmacokinetics of propylene glycol in the rabbit. *J. Pharmacokin. Biopharm.* **15**(5):453-471.

---

Norwegian Institute for Water Research  NIVA

P.O.Box 69, Korsvoll N-0808 Oslo, Norway  
Phone (+47 2) 18 51 00, Fax (+47 2)18 52 00  
ISBN-82-577-2181-6