MIGRATION OF ALTERNATIVE DE-ICING CHEMICALS IN SHALLOW AQUIFERS

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1. Abstract

The main harmful impacts the de-icers have on ground water quality are leaching of heavy metals from soils, corrosion of water supply systems, chemical residues, and oxygen loss in water caused by organic de-icers. The migration of organic de-icers in the shallow aquifers typical in Finland is not well known and we should find solutions to minimize the negative impacts the de-icing have on ground water quality. The objective the project MIDAS (**Mi**gration of Alternative **D**e-icing Chemicals in **A**quifer**s**) is to find de-icers which have the least harmful impacts on groundwater quality. Migration of sodium chloride as a tracer and five alternative de-icers in aquifers are being studied. The alternative de-icers are calcium chloride, magnesium chloride, calsium-magnesium-acetate, potassium acetate and potassium formiate. The research consists of *in vitro study* and field research that will follow. The results will be use to choose a de-icer from existing chemicals and for the development of new less harmful de-icers. The information will be use mainly in Scandinavia and North America where the hydrogeological conditions are similar to those in Finland.

2. Introduction

In Finland, the Environment Protection Act forbids even endangering the quality of ground water. However, de-icing can´t be stopped completely on a legal basis and we have to find solutions to minimize the negative effects of de-icing without endangering traffic safety. Salting has polluted ground water in Finland and in several other countries. Approximately 70 % of the Finnish people drink ground water. However, of the 2226 important ground water areas at least 528 are traversed by roads that need winter salting. Comparative public information on de-icers has not been available. Especially the migration of organic de-icers in the shallow aquifers typical in Finland is not well known. The objective of the MIDAS project is to get more information on the effects de-icers have on ground water quality and to find de-icers which have the least harmful impacts on ground water quality and soil. The main harmful impacts de-icers have on ground water quality are leaching of heavy metals from soils, chemical residues, and oxygen loss in water caused by organic chemicals. The damage to cars and bridges caused by corrosion could also be decreased by using organic de-icers. High chloride concentration in ground water induces corrosion in water pipes.

3. Materials and Methods

The migration of sodium chloride (as a tracer) and five alternative de-icers in Finnish aquifers are studied. The research consists of the on-going *in vitro study* (1998-2001) (Figure 1) and the subsequent field research (2001-2003) (Figure 2). In our *in vitro study* the migration and decomposition of different de-icers calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), potassium formiate (KFo), potassium acetate (KAc), calsium magnesium acetate (CMA) are compared by filtering de-icer solutions through 1.0 meter and 3.5 meter (Figure 3.a, 3.b) high sand and sandy gravel filters with and without topsoil horizon. The chemical characteristics (temperature, conductivity, pH, alkalinity, O_2, CO_2, acetate, formiate, chloride, Br^-, F^-, total N, NO_3-N, total P, PO_4-P, SO_4, TOC, BOD_7, COD_{Cr}) and metal concentrations of the filtrates are analysed.

The ground water area for the field research will be chosen based on *in vitro study* and geological criteria. The area will be similar than the aquifers on roads and airport areas. Transport of the de-icer will be monitored by analysing ground water quality regularly and simulated by mathematical modelling.

IN VITRO – STUDY	**1998** **I-VI**	**VII-XII**	**1999** **I-VI**	**VII-XII**	**2000** **I-VI**	**VII-XII**	**2001** **I-VI**	**VII-XII**
Infiltration tests in soil filters								
I NaCl, $CaCl_2$, $MgCl_2$								
II CMA, KFo, $CaCl_2$, NaCl	→	→	→					
-final reporting of the infiltration tests				→	→	→	→	
Further infiltration tests								
III NaCl, CaCl, CMA, KFo, H_2O				→	→			
-selection of the most promising de-icing chemical for further infiltration tests and preparation					→	→		
of the more detailed research plan for field research						→		
Further infiltration tests for the most promising de-icing chemicals								
IV KFo and KAc								
-geotechnical tests for gravel						→		
-leaching tests for gravel soil material (metals and biotests)						→	→	
-preparation of filters					→			
-further infiltration tests in gravel/sand filters						→	→	
-final reporting of the in vitro-study							→	→

Figure 1. Timetable of *In Vitro Study*.

FIELD RESEARCH	**2001** **I-VI**	**VII-XII**	**2002** **I-VI**	**VII-XII**	**2003** **I-VI**	**VII-XII**	**2004** **I-VI**	**XII-VII**
-preparation of the detailed field study programme			→					
-selection of field study area		→						
-in situ field studies			→	→	→			
-monitoring of ground water quality				→	→	→		
-in situ infiltration tests and laboratory analyses			→	→	→			
-mathematical transport modelling			→	→	→	→		

Figure 2. Timetable of The Field Research.

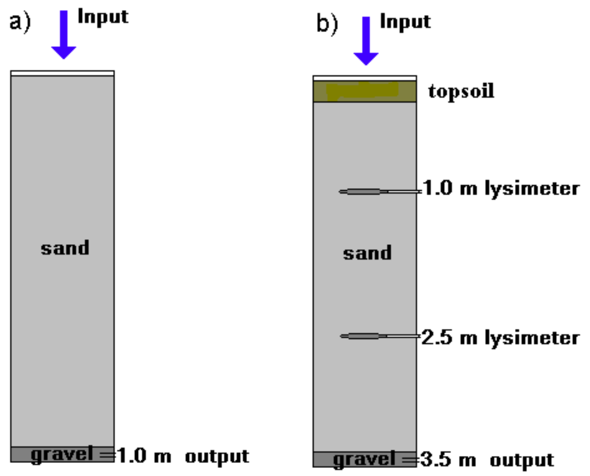

Figure 3.a) 1.0 Meter and b) 3.5 Meter High Sandfilters.

4. Results and Discussion

The organic de-icers acetate and formiate biodegraded by microbes. The biological and chemical oxygen demand increased by the organic de-icers. Organics de-icers increased and chlorides decreased pH and alkalinity of the water. Organics de-icers also decreased the amount of nutrients (NO_3-N and PO_4-P) in the filtrates. The concentration of acetate (CMA), formiate (KFo) and chlorides (NaCl, $CaCl_2$) were 700 mg/l in the feeding solutions. After five weeks infiltration, in 1.0 m high sand filters, total biodegradation of acetate was about 70 % and formiate about 82 %. Concentration of chlorides were after five weeks almost the same as in the feeding solutions (Table 1).

Table 1. Concentrations of Anions in the Filtrates from 1.0 Meter High Filters.

duration of infiltration	concentrations of anions in the filtrates (mg/l)			
days	acetate of CMA	formiate of KFo	Cl of NaCl	Cl of $CaCl_2$
5	410	420	280	500
12	140	320	-	-
19	110	0	620	700
26	130	0	-	-
33	180	0	-	-
40	290	43	660	710

After a period of five months infiltration, in 3.5 m high sand filters, formiate of KFo was found in the filtrates only within the first weeks. After the same time, acetate of KAc was found only in filtrates of 1.0 meter and 2.5 meter depth, not in the filtrates of 3.5 meters depth (Table 2). The contents of acetate was about 300 mg/l and formiate 270 mg/l in the feeding solutions.

Table 2. Concentration of Anions in the Filtrates from 3.5 Meter High Sand Filters with Topsoil.

concentrations of acetate and formiate in the filtrates after five months infiltration (mg/l)		
depht of filters (m)	acetate of KAc	formiate of KFo
1.0	110	0
2.5	32	0
3.5	0	0

After five months filtration formiate was found only in the sandy gravel filter without topsoil in the filtrates from 1.0 meter and 2.5 meter deth (Table 3).

Table 3. Concentration of Formiate in the Filtrates of 3.5 Meter High Filters.

concentrations of formiate (KFo) in the filtrates after five months infiltration (mg/l)			
depth of filters (m)	sandy gravel filter without topsoil	sandy gravel filter with topsoil	sand filter with topsoil
1.0	80	0	0
2.5	59	0	0
3.5	45	0	0

After the first weeks, the formiate had started to biodegrade faster than the acetate had. The organic topsoil in the columns proved a very important factor in the degradation of the formiate (Table 3). As a result of the laboratory test, the formiate may biodegraded at a faster rate than the acetate at low temperatures (T 3-6 ^{o}C) and the residue of the formiate in the ground water of shallow aquifers may be less obviously. The formiate also needs less oxygen to degrade than the acetate does and so it will also degrade in the ground water where there is less dissolved oxygen available. The possibility of leaching of heavy metals from the contamined horizons along the roads by de-icers has not yet been researched. If the formiate biodegrade in the soil before leaching into the ground water, it will cause less changes to the quality of the water than the chlorides, because chloride does not biodegrade. However, the biodegradation of the formiate during winter and spring may be different at the field study scale from that recorded *in vitro study*. As far as we are able to determine, KFo may be a potential alternative de-icer to the NaCl.