National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

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Colophon

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Abstract

A method to rank the relative environmental hazard of coolants leaking directly into groundwater

Some coolants are hazardous when leaking into groundwater
This report ranks the relative environmental hazards of coolants from Borehole Thermal Energy Storage (BTES) systems, if these liquids were to leak into groundwater. Some coolants contain persistent and toxic chemicals which can pollute groundwater for many decades. The use of coolants with unknown, probably hazardous, constituents can form a risk for groundwater quality.

Most coolants contain unknown chemicals
Only a few producers were willing to inform the RIVM about the constituents of their coolants. The relative environmental hazard of coolants can be calculated from the maximum allowable concentration in the groundwater and their concentration in the coolants. 1 liter of coolant can pollute several cubic meters of groundwater, depending on the composition of the coolant. Environmentally friendly coolants can only pollute a few cubic meters groundwater per liter leaked coolant and will be degraded in the long run.

Only a few environmentally friendly coolants are already identified
Tap water, a potassium carbonate solution or monopropylene glycol can be suitable coolants and are tested as the top three coolants in a ranking of environmental effects. In peat areas the anaerobic and acid conditions in groundwater will strongly inhibit biodegradation of organic substances like monopropylene glycol. Potassium carbonate is therefore a better choice for peat areas. There are huge differences in the environmental hazards of coolants. More environmentally friendly coolants will probably be identified when sufficient information from the producers will become available.

Keywords:
groundwater, contamination, heat exchange, risk assessment

Rapport in het kort

Een methode om het milieurisico van koelvloeistoffen voor grondwater te rangschikken

Weglekkende koelvloeistoffen kunnen bedreiging voor grondwater vormen
Bij gesloten warmte-koude-opslagsystemen (WKO) zitten de warmtewisselaars in de ondergrond. Bij lekkages in de warmtewisselaar zal koelvloeistof lekken naar het grondwater en de ondergrond. Sommige koelvloeistoffen bevatten chemicaliën die langzaam afbreken en het grondwater tientallen jaren kunnen verontreinigen. Het RIVM heeft daarom op een rij gezet in welke mate verschillende soorten koelvloeistoffen een risico kunnen vormen voor de grondwaterkwaliteit.

Meeste koelvloeistoffen bevatten onbekende chemicaliën
Slechts enkele producenten van koelvloeistoffen waren bereid om het RIVM te informeren over de samenstelling van hun producten. De mate waarin koelvloeistoffen gevaarlijk zijn voor het milieu kan worden berekend door de concentratie van een stof in het koelmiddel, te delen door de maximaal toelaatbare concentratie van die stof in het grondwater. Afhankelijk van de samenstelling van het koelmiddel kan een liter koelvloeistof meer of minder kubieke meters grondwater verontreinigen. Relatief milieuvriendelijke koelvloeistoffen kunnen slechts een beperkt aantal kubieke meters grondwater verontreinigen per liter gelekt koelmiddel en worden op termijn afgebroken. Indien van meer koelvloeistoffen de samenstellingsgegevens ter beschikking komen, dan kunnen we het relatieve milieueffect daarvan berekenen.

Slechts enkele milieuvriendelijke koelvloeistoffen geïdentificeerd
Kraanwater, een kaliumcarbonaatoplossing of, in mindere mate, monopropyleenglycol zijn bruikbaar als koelvloeistoffen en komen als de beste drie koelvloeistoffen naar voren in de rangschikking naar milieueffect. Het bodemtype bepaalt in welke mate ze worden afgebroken. In veengebieden bijvoorbeeld wordt de biologische afbraak van organische verbindingen als monopropyleenglycol sterk geremd door de zure en zuurstofloze omstandigheden. Voor deze gebieden is kaliumcarbonaat daarom een betere keuze.
Meer milieuvriendelijke koelvloeistoffen zullen vermoedelijk worden geïdentificeerd wanneer voldoende informatie van de producenten beschikbaar komt.

Trefwoorden:
grondwater, verontreiniging, warmtewisselaar, risicobeoordeling

Contents

1 Introduction

1.1 The risk of coolants in BTES systems

Coolants are fluids that have long been used to cool engines and appliances, and one might raise a question about our sudden interest in a specific use of coolants. When coolants are used indoors or outdoors, accidental spills are normally discovered and cleaned up very quickly. An uncontrolled outdoor spill will reach the soil and the upper groundwater, where there is ample opportunity for biodegradation of the product (1). However, whether or not a spill has the chance to properly degrade, is dependent on the size of the spill. Massive spills can overwhelm the biodegradation capacity and exhaust the amount of available oxygen.
Borehole Thermal Energy Storage (BTES) systems have two properties that make the use of coolants more problematic:

- Leakage might occur directly into deeper groundwater without the possibility of biodegradation in the soil and the upper groundwater.
- The scale of the leakage can be relatively large.

1.2 The small risk of leakage is not negligible

The new Dutch measure (Algemene Maatregel van Bestuur) on soil energy systems, that will be implemented in 2013, prescribes a leakage detection system for larger BTES systems (2). For smaller exchangers a pressure drop due to leakage can shut down the system and alarm the user. Therefore, some people have argued that a large-scale leakage will never occur. However, leakage in underground systems is not easy or cheap to repair and therefore users might not take appropriate measures. For example, FlevOnice had an artificial skating rink with a capacity of 400,000 L coolant. When the firm was bankrupted, it appeared that over time 150,000 L coolant had leaked away (http://www.omroepflevoland.nl/nieuws/nieuwsbericht?NewsID=93273). FlevOnice was not a BTES system, but leakage of BTES systems in the Netherlands have occurred. At this stage, all systems are relatively new, but after a few decades this will not be the case anymore. The repair or replacement of BTES systems at great depths will be costly and therefore the systems are designed to work for many decades. Obviously, the old systems will be more prone to leakage than new ones.

1.3 Aircraft de-icing and benzotriazoles

BTES systems are a relatively new technique and therefore there is not much experience in the consequences of leakage on groundwater quality. There is, however, another sector which has ample experience in the leakage of coolants to groundwater. De-icing of aircrafts with de-icing fluids which are very similar to BTES coolants has resulted in major groundwater pollution (3). Propylene glycol is the major component of these fluids, but a proprietary mix of surfactants, buffers dyes and corrosion inhibitors, that make up to 2% of the fluid, is also added. Although the corrosion inhibitors tolyltriazole and benzotriazole are only minor components, they cause a major part of the toxicity (4). The degradation of propylene glycol in soil and groundwater requires sufficient oxygen and this degradation is inhibited by the tolyltriazole present in the fluid (4). Propylene glycol is very mobile in groundwater and its degradation slows down at greater depths (5). At an abandoned airport, the propylene glycol was degraded, but benzotriazole and methylbenzotriazoles were persistent in groundwater and sediment (6).
Benzotriazole and methylbenzotriazoles are very mobile and commonly occur in rivers and lakes (7). The average concentration of benzotriazole and also

methylbenzotriazoles in European rivers was around 0.5 µg/litre (8). Methylbenzotriazole is persistent and toxic during anaerobic wastewater treatment (9, 10). Benzotriazoles are mobile in groundwater and methylbenzotriazoles are not easily removed by active carbon filters during drinking water production (11). Methylbenzotriazoles and benzotriazole are metal complexing chemicals and are widely used as anti-corrosive agents in cooling and hydraulic fluids, anti-freezing fluids, aircraft de-icing fluids, dishwashing liquids for silver perfection, anti-fogging constituents, ultraviolet stabilizers and as chemical intermediates (12).

1.4 Composition of coolants

Several attempts were made to get the information on the composition of commercially available coolants in the Netherlands. A dozen different international producers were approached by email to deliver this information. At the closing ceremony of the 'Meer met Bodemenergie' conference in April 2012 a presentation was given with a request for information about the composition of commercially available coolants. The same question was also posted on the LinkedIn groups of 'Koude- en Warmteopslag en Geothermie Benelux' and 'Warmte/koude opslag Nederland'. The coolant producing firms were promised complete confidentiality. In addition, the RIVM promised to only publish a positive white list, with recommended coolants and not a blacklist with forbidden coolants. It was, therefore, made clear that delivering data could not have any negative effect on the sales of the firms' coolants. Nevertheless, the reactions were rather reserved and the firms expressed worries about the criteria that would be used. The same confidentiality problem was also reported in a Swiss study (13).

1.5 The purpose of this report

This report presents a method to rank the relative environmental hazard of coolants used in BTES systems. This method enables the producers of coolants to select more environmentally friendly coolants for the use in BTES systems.

2 Methods

2.1 Protection of groundwater against pollution

The European groundwater directive (14) requires member states to derive groundwater threshold values from toxicity data. These values set a maximum permissible concentration of pollutants in groundwater. Alternatively, the Annual Average Environmental Quality Standard of surface water (15) can also be used. The Maximum Permissible Concentrations (MTR in Dutch) are legal values limiting the amount of pollutants in the environment. The MTReco is a Maximum Permissible Concentration which aims to protect the environment. For naturally occurring compounds, like potassium, other specific groundwater quality criteria can also be used.

2.2 Degradation is not yet taken into account

Environmental pollutants in groundwater can be degraded when the conditions are favourable (16) . But even the aerobic degradation of a readily biodegradable substance like acetate is highly variable in groundwater (1). Both propylene glycol and ethylene glycol can be degraded under aerobic and a number of anaerobic conditions (17). Under anaerobic conditions, these glycols are degraded by fermentation forming aldehydes, alcohols and acids (17). In acid and anaerobic peat soils, the biodegradation of most organic compounds is extremely slow (18). Due to the high local variability, the biodegradation is not yet taken into account in the general ranking of the hazard of coolants.

2.3 Method for calculation of hazard

One can calculate the relative hazard (M) of 1 g of a chemical emitted into groundwater.

M = 1,000 / MTR

MTR in µg/litre groundwater
M in cubic meter groundwater/gram of chemical

The factor 1,000 comes from the conversion from cubic metre per gram into litres per µg:

$$M\left(\frac{m^3}{g}\right)=\frac{1}{MTR}\left(\frac{L}{\mu g}\right)\times 10^{-3}\left(\frac{m^3}{L}\right)\times 10^{6}\left(\frac{\mu g}{g}\right)=\frac{1000}{MTR}\left(\frac{m^3}{g}\right)$$

When the concentration of a chemical in the coolant is X gram/litre coolant, one can calculate the relative hazard (ML) of the coolant:

ML = X*M
with M in m^3/g and
X in g/litre coolant

Therefore ML is expressed in cubic metre groundwater per litre coolant.

3 Results

3.1 The used chemicals and environmental quality standards

Pure tap water can be used as a coolant but it has the disadvantage that it is prone to freezing. Therefore, other chemicals are generally added to water in order to lower the freezing point. The inventory yielded seven chemicals which might be regularly used in coolants. Table 1 shows these chemicals. The Maximum Permissible Concentrations (MTR in Dutch) are legal values limiting the amount of pollutants in the environment.
Only for propylene glycol an MTR value for surface water can be found on the RIVM website (http://www.rivm.nl/rvs/Normen). This value amounts 330 μg/litre and can also be used for groundwater.
The quality criterion for potassium is 12 mg potassium /litre groundwater (19). This makes the MTR for potassium from potassium carbonate equal to this value, because carbonate is a very common groundwater component which is converted to carbon dioxide under acidic conditions.

3.2 Ecotoxicological hazard

When a BTES system leaks coolants, the primary compartment involved will be groundwater. In this report only the ecotoxicological risks of coolants to groundwater will be considered, although it is of course possible that groundwater is also used for drinking water for humans or animals. In an urban situation in the Netherlands, this will not occur often. RIVM has developed methods to calculate ad hoc MTR values. These are MTR values calculated using a very simple preliminary approach and restrictive safety factors (20).

Table 1: The EC50 or LC50 of chemicals used in coolants calculated using ECOSAR from USEPA.

	Chemical	CAS nr	Fish mg/l	Daphnid mg/l	Algae mg/l
1	Potassium carbonate	584-08-7			
2	Monopropylene glycol	57-55-6			
3	Monoethylene glycol	107-21-1	38,110	16,104	3,536
4	Natrium 2-ethylhexanoate	19766-89-3	163	101	109
5	Sodium propionate	137-40-6	11,521	5,737	2,483
6	Potassium formate	590-29-4	6,129	2,773	807
7	Methyl benzotriazole	13351-73-0	33	78	7

Table 2: The relative environmental hazard for groundwater M in cubic metre polluted groundwater per gram chemical.

	Chemical	Safety Factor	MTR µg/litre	M m^3/g
1	Potassium carbonate		12,000	0.083
2	Monopropylene glycol		330	3
3	Monoethylene glycol	10,000	354*	3
4	Natrium 2-ethylhexanoate	10,000	10*	99
5	Sodium propionate	10,000	248*	4
6	Potassium formate	10,000	81*	12
7	Methyl benzotriazole	100,000	0.07*	14,712

*ad hoc MTReco calculated using Table 1

Only for the first two compounds in Table 1 proper MTR values are available. For the remainder the ECOSAR v1.11 program from the USEPA (http://www.epa.gov/oppt/newchems/tools/21ecosar.htm) was used to calculate the EC50 values for green algae or the LC50 values for fish and Daphnids. The minimal EC50 or LC50 value was divided by a safety factor of 10,000 to calculate the ad hoc MTReco (20). Since the EC50 is expressed in milligrams/litre and the MTReco in micrograms/litre the lowest EC50 value in Table 1 was divided by 10,000/1,000 = 10 to get the MTReco values of the chemicals 3-6 in Table 2. Except for methyl benzotriazole, which is not a simple chemical exhibiting baseline toxicity. In this case a Safety Factor of 100,000 must be used according to the guideline (20). The final column in Table 2 shows the relative hazard M of the chemicals expressed in cubic meter groundwater polluted by 1 g of chemical.

3.3 Example calculations for the impact of a spill

The application of the relative hazard M can be exemplified by a typical BTES system containing thousand litres of coolant which is hypothesized to leak 100 L. The amount of groundwater that can be polluted by 100 L coolant is largely dependent on the composition of the coolant. In the following list the amount of groundwater that can be polluted by 100 L of coolant is calculated:

1. TYFO-Spezial-Wärmepumpensole ohne Buntmetall-Korrosionsschutz from Tyforop Chemie Gmbh contains slightly less than 30% potassium carbonate. This amounts to 30 kg K_2CO_3, containing 16.8 kg potassium. According to Table 2, an amount of 1 kg potassium can pollute 83 m³ of groundwater. Therefore this 100 L coolant can pollute 1,394 m³ of groundwater.
2. Monopropylene glycol is often used at a 50% solution, which contains approximately 50 kg per 100 L. According to Table 2, this can pollute 150,000 m³ of groundwater.
3. In addition, a coolant can also contain a corrosion inhibitor like methyl benzotriazole. When this is present in a concentration of 1%, it contains 1 kg per 100 L. This can pollute 14,712,000 m³ of groundwater.

It is clear that the composition of a coolant has a major influence on the impact of a coolant spill in groundwater.

4 Discussion

4.1 Recommended coolants

A potassium carbonate solution can only pollute a limited amount of groundwater upon leakage. Note that tap water can also be used as a coolant and is much more environmentally friendly, because Dutch tap water is often derived from groundwater and generally does not contain added chemicals. The disadvantage of tap water is the possibility of freezing, which might damage the installation. Proper measures can be taken to avoid freezing in BTES systems. In addition, a monopropylene glycol solution can only pollute a moderate amount of groundwater upon leakage. In peat soils, which are generally acidic and anaerobic, the degradation of organic substances like monopropylene glycol will be strongly inhibited (18) and therefore organic coolants might not be the preferred choice for peat soils. The potassium carbonate solution might be better suited for these soils, since the strong buffering capacity of peat at low pH will rapidly convert the carbonate into carbon dioxide. Potassium is a cation normally present in groundwater (21) and will pose little risk upon dilution.

4.2 Corrosion inhibitors

The persistence in groundwater and toxicity of benzotriazoles were already indicated in a previous report (22). The low ad hoc MTReco value derived in Table 1 confirms these findings. Nevertheless, corrosion inhibitors like benzotriazoles are commonly used in coolants to prevent corrosion. Corrosion by itself can also dissolve iron and other metals in the coolant. Corrosion prevention might increase the lifetime of the installation, which is more sustainable.
It is a political decision to weigh the environmental risks against the economic benefits of corrosion inhibitors. The ecotoxicological hazard of coolants, in BTES systems for groundwater, has only very recently become an issue. At this early stage of knowledge development, there is much room for improvement in the assessment of the environmental risks. There might be corrosion inhibitors on the market which are much less environmentally hazardous. Although the persistence of the benzotriazoles in the environment is well-documented, the toxicity is less well-known. The very low ad hoc MTReco for methyl benzotriazole is based on theoretical calculations using a safety factor of 100,000. Actual toxicity data might prove methyl benzotriazole less hazardous.

4.3 Cooperation

The ecological risk assessment of groundwater thermal heat exchange systems requires a broad multidisciplinary approach. The environmental risks of the leakage of coolants form just one aspect of the complete assessment. Cooperation with other partners is necessary to perform the risk assessment.

5 Conclusions

The use of coolants with unknown additives in groundwater heat exchange systems can create environmental problems in the future. Some coolants are more environmentally friendly while others are clearly hazardous for groundwater.
Dutch tap water, being similar to groundwater without additions, is a very environmentally friendly coolant although it can easily freeze. A potassium carbonate solution is commercially available as a coolant with only minor environmental hazards. Also, a propylene glycol solution is commercially available and will not have major environmental hazards upon leaking in most groundwater systems.

Recommendations
The use of coolants with unknown additives in groundwater heat exchange systems can be discouraged in the future.
When the chemical composition of a coolant is revealed to the RIVM, a confidential hazard ranking can be performed.
Cooperation with Swiss researchers and with the Dutch Watercycle Research Institute will be very important in the future for a balanced ecological risk assessment of groundwater thermal heat exchange systems.

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