Does road salt affect groundwater in Denmark?

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Chloride (Cl) from dissolved salt is a major threat to groundwater quality in many regions of the world. In arid regions near present-day coastlines, where old seawater occurs in deeper sediments and where road salt is frequently used, Cl can be a significant pollutant (European Environmental Agency 2009). European Union member states have recently reported that next to nitrogen, Cl is the most commonly found pollutant and is often responsible for groundwater bodies being at risk or having a poor ecological status (European Commission 2010).

Intrusion of salty groundwater and infiltration by seawater near coastlines are well-known phenomena in Danish aquifers (Ødum & Christensen 1936; Bonnesen *et al.* 2009). Saltwater in aquifers may also come from human pollution such as landfills, road salt storage facilities, roads and agricultural activities (Panno *et al.* 2006). Since the 1970s, de-icing salt applied to roads has been recognised as a significant source of contamination that may deteriorate aquifers that are used as drinking water resources by increasing their Cl concentration and by harming stream and lake ecosystems (Jackson & Jabbogy 2005). Recent studies have suggested that the decade-long usage of road salt is becoming a rising threat to groundwater quality (Bester *et al.* 2006). Salt contamination from roads is therefore particularly problematic to aquifers already at risk (Lundmark & Olofsson 2007). The present paper explores the impact of road salt on groundwater quality in Denmark by means of a combination of chemical indicator analysis, temporal and spatial Cl analysis and numerical groundwater modelling.

The vulnerability of aquifers to road salt depends on the amount of salt applied per kilometre road, the degree of urbanisation and the percentage of salt lost to the subsurface. Based on a literature review, the estimated percentage of road salt lost to the groundwater is 10–20% of applied de-icing salt in Danish urban areas (Kristiansen *et al.* 2009). The average amount of road salt used during the winter in Denmark has risen since the late 1990s, but varies with weather conditions (Fig. 1). In comparison, Fig. 1 also shows that the atmospheric NaCl deposition for the entire Danish surface area is about 280 gigagrams (Gg) per year, which is tentatively estimated based on actual bulk deposition measurements (T. Ellerman, personal communication 2011). Thus, the total amount of applied road salt and the total atmospheric salt deposition in Denmark are of the same order of magnitude. However, the local surface load of road salt and atmospheric salt deposition vary widely across Denmark.

The Danish road salt project

This paper addresses the results from a recent assessment performed under the Danish groundwater mapping project in order to evaluate the impact and risk of road salt to the quality of Danish groundwater resources (Kristiansen *et al.* 2009). The project used groundwater quality data from the national database Jupiter. The data were downloaded in October 2008 and included approximately 140 000 analyses from approximately 24 000 groundwater sampling points corresponding to about one sample per 2 km^2. The oldest data are from 1890, the most recent from 2007. Data on the historical consumption of road salt were drawn from the Danish Road Directorate and involved municipalities.

Three different methods were used: (1) Evaluation of indicators to separate chloride sources in groundwater chemistry, (2) analysis of the distribution and variation of Cl in time and space, and (3) development of a numerical groundwater risk assessment tool in the hydrological modelling system MIKE SHE.

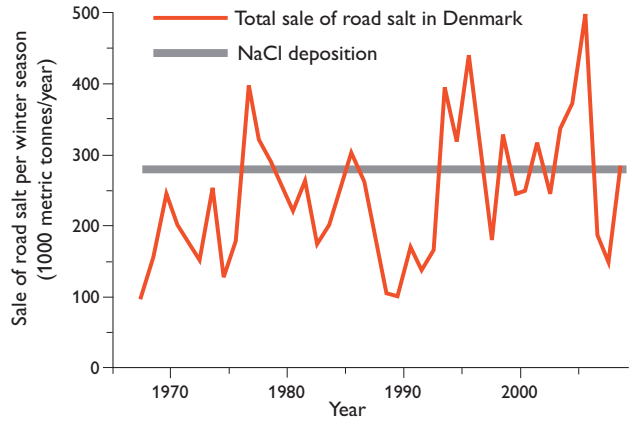

Fig. 1. Sale of road salt for highway use in Denmark from 1965/1966 to 2008/2009 in 1000 metric tonnes (Gg) per winter season based on data from the Danish Road Directorate. Atmospheric NaCl deposition in Gg per year is a tentative estimate for the entire Danish surface area based on bulk deposition measurements by T. Ellerman, University of Aarhus, 2011.

Chloride source indicators

Geochemical tools with mass ratios of especially the halides have proved useful for identifying different groundwater Cl sources (Davies *et al.* 1998). Groundwater salt origins were identified by a graphical technique that distinguishes between multiple sources (Panno *et al.* 2006). This approach discriminates sea salt from, for instance, vacuum salt used as road salt. An average of 40% of Danish de-icing salt is vacuum salt. Both Cl and Br form stable anions in water, which are usually not affected by sediment–water reactions. In addition, NaBr is less soluble than NaCl. As a consequence of the production process, vacuum salt has a Cl/Br mass ratio >1000. Sedimentary rock salt, and hence road salt coming from this source, has Cl/Br mass ratios similar to rain, as well as residual and infiltrating waters with a Cl/Br mass ratio <400 (Davis *et al.* 1998). Based on a literature review and own data analyses, we find that Cl/Br ratios are appropriate to detect the origin of dissolved Cl sources in Danish groundwater (Kristiansen *et al.* 2009).

The chemical indicator analysis shows that the potential impact of road salt on groundwater can be traced using a combination of Cl/Br mass and Na/Cl molecular ratios in groundwater where the Na/Cl ratio is affected by the exchange of sodium between the solid and liquid phases and the Cl/Br ratio is affected by the above-mentioned dissolution processes.

Groundwater chloride sources

Firstly, a prevalence of Br-poor groundwater (Cl/Br mass ratios >1000) was found in upper groundwater (<80 m below surface), which indicates that anthropogenic Cl sources (e.g. vacuum salt from roads, atmospheric deposition, or animal manure from farming) have a general impact on groundwater quality. Secondly, groundwater with reversed ionic exchange (Na/Cl molecular ratio <0.75) was also preferentially found in upper groundwater, which indicates infiltration of NaCl containing water into more fresh sediment. Thirdly, most

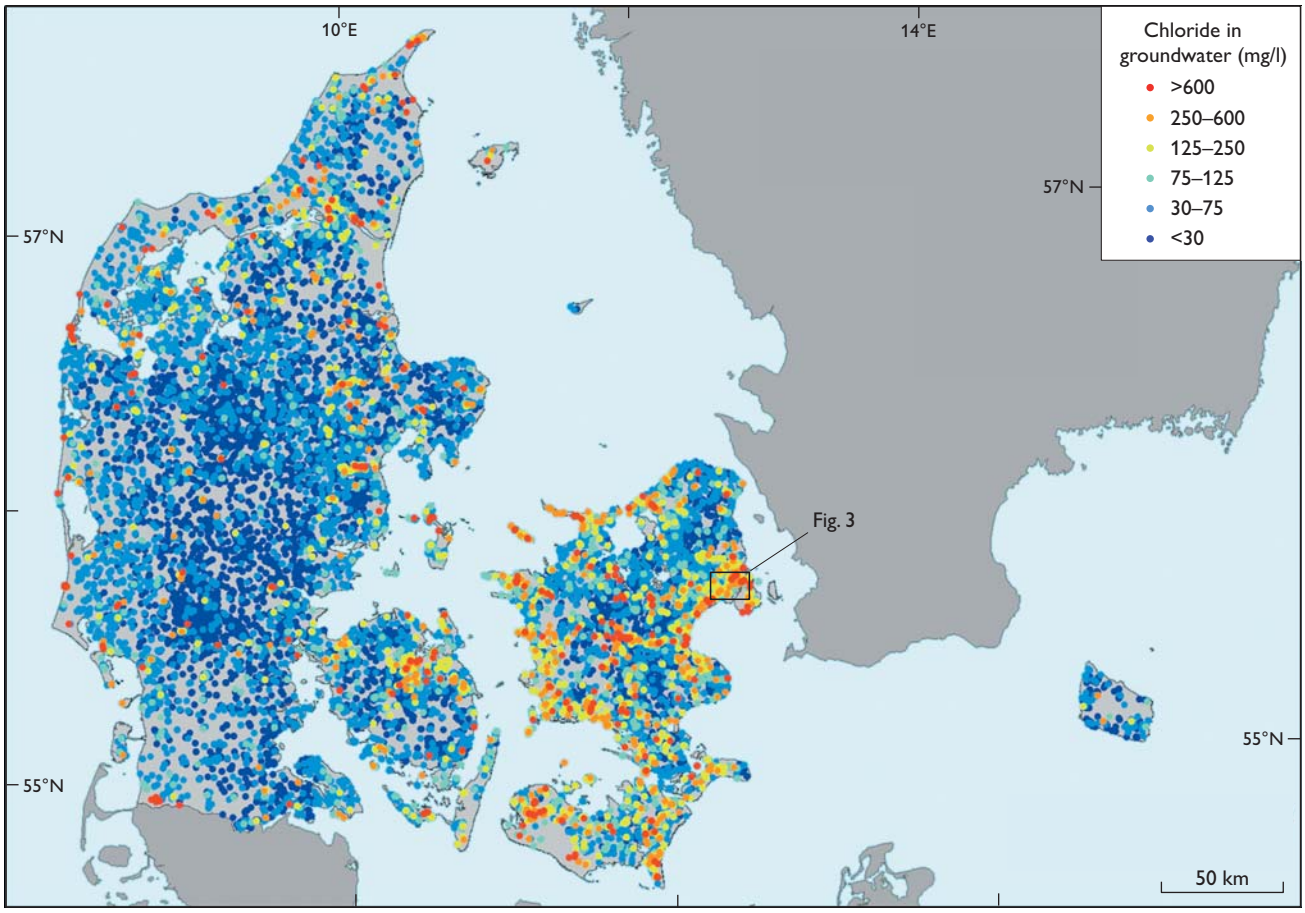

Fig. 2. Geographical distribution of the latest analysed chloride concentration in *c.* 24 000 Danish groundwater sampling points. The highest measured chloride concentration in wells with more than one measuring point is shown. Data were downloaded from the national database Jupiter in October 2008.

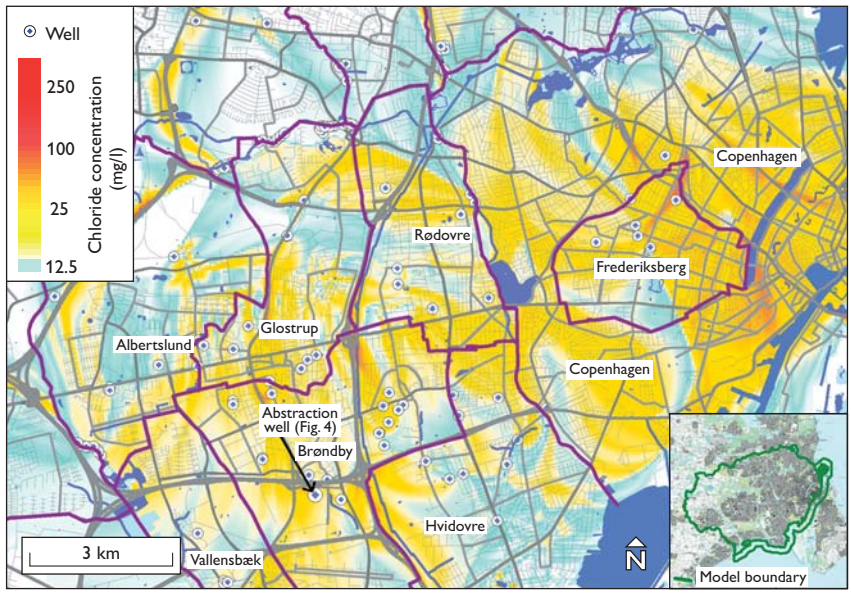

Fig. 3. Modelling results of chloride concentrations in the primary aquifer due to leaching of road salt estimated for a steady-state situation in 2060 in the greater Copenhagen area. The loss of historically used road salt is put to 15% and all factors are kept constant from 2008 to 2060. The background concentration of chloride is not included. For location see Fig. 2.

of the groundwater with high Cl concentrations was found in the upper groundwater with a gradual decrease from the surface to about 80 m below surface. These three different analyses support that the upper groundwater is affected by Cl sources at the soil surface. However, the analyses could not identify which specific type of Cl source at the surface influences groundwater quality.

In addition, the analyses showed that the deeper groundwater (>90 m below surface) often had Cl/Br mass ratios <550; moreover, a gradual increase in Cl concentrations with depth indicated that the primary Cl source in deeper Danish aquifers should be found in the underlying groundwater with much higher Cl concentrations.

Chloride distribution in Danish groundwater

The Cl concentration classes used in Fig. 2 are based on statistical analysis of the distribution of all the Cl analyses from Danish groundwater where four geochemical populations are found: <10, 10–30, 30–600 and >600 mg Cl/l. Background concentrations of Cl in Danish groundwater is below 30 mg/l. Groundwater with Cl concentrations above the drinking water standard of 250 mg/l is commonly found close to the coastline, especially in the eastern parts of Denmark (Fig. 2). However, elevated concentrations of Cl are also found in inland aquifers.

Trend analyses of the Cl concentration in the groundwater in the greater Copenhagen area show that 38% of the wells have experienced significantly increasing concentrations whereas only 9% have seen significantly decreasing concentrations (95% confidence interval) since the 1960s. Median Cl concentrations in groundwater rose from 40–80 mg/l in 1965–1978 to 80–160 mg/l in 1994–2007. A predominance of inversed ionic exchanged groundwater indicates that infiltration of salt water into a fresher aquifer comes from anthropogenic influenced sources such as road salt or intrusion by sea water due to drinking water abstraction.

Numerical modelling of road salt impact

A numerical assessment tool was developed for a large part of the greater Copenhagen area (274 km^2) in order to evaluate the impact of road salt on groundwater quality. We modelled losses of road salt to the environment at catchment scale from 1967 to 2060 (Fig. 3). The tool combines a surface load model with a well-calibrated 3D numerical groundwater model in MIKE SHE that simulates water flow and solute transport in the subsurface (Kristiansen *et al.* 2009). The surface load model consists of (1) the historic use of road salt since 2001 distributed on the road network where the type of road has been taken into consideration, (2) estimation of the loss of road salt to the groundwater, and (3) simple 1D modelling of the Cl transport through the unsaturated zone.

The loss of road salt to the surroundings is difficult to estimate, but Tvedt *et al.* (2001) estimated that 15–30% of the road salt is lost under Danish conditions. However, not all the lost road salt infiltrates the groundwater as some percolating water is removed by drainage or sewage. In the modelling, we decided to use a loss of 15% of the road salt to groundwater, which can be considered as a best estimate based on available knowledge.

Simulations indicate that with a loss of 15% of the applied road salt, the chloride concentrations below urban areas gen-

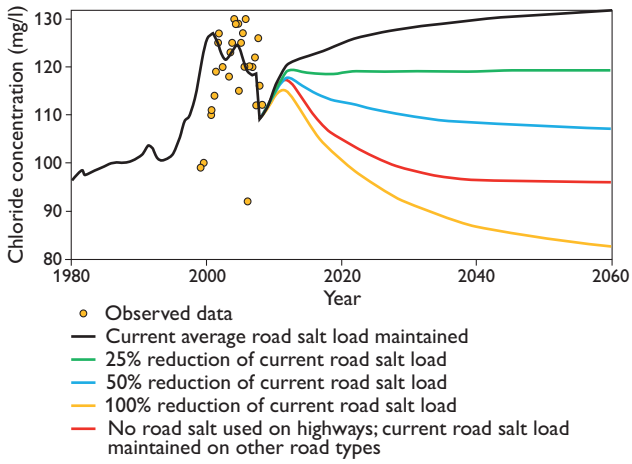

Fig. 4. Modelled and measured chloride concentrations in groundwater in an abstraction well in the greater Copenhagen area. For location see Fig. 3. Breakthrough curves are shown for different scenarios whereby road salt losses to groundwater are reduced.

erally will show a 25–40 mg/l increase, whereas increases can reach 125 mg/l at some major road junctions. Simulated breakthrough curves for a shallow well are shown in Fig. 4 for different scenarios compared to measured values. A background Cl concentration of 80 mg/l is added for the simulated results which contains Cl from natural sources as atmospheric deposition and marine residual water. The upper curve, where the current load of road salt is maintained, shows that it takes decades before a steady state situation is reached. The rest of the curves show the development of the groundwater Cl concentrations at steady state for different reduction scenarios in relation to current road salt usage.

Conclusions

The results show that the upper groundwater Cl concentrations (<80 m below surface) are affected by Cl sources such as road salt, atmospheric deposition and animal manure. Precise identification of the Cl sources at the surface requires more analyses of chemical indicator species in the groundwater. Numerical groundwater modelling in the greater Copenhagen area shows that road salt can result in a significant increase of the Cl concentration in groundwater, particularly near major road junctions. The aquifer used for water supply may be degraded because of the accumulated impact from several Cl sources such as road salt, residual salt groundwater and recent seawater intrusion. The applied model assumes that the loss to groundwater of road salt is 15%. But if the loss was 30%, then the resultant Cl concentration should be doubled. More precise quantification of the loss of road salt and knowledge on Cl sources other than salt applied to public roads are therefore required in order to reduce the uncertainty of the current estimate of the effect of road salt on groundwater quality, for example by establishing study sites in urban areas.

Acknowledgement

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