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Trace metals in recharge and discharge ground waters at two sites at the Baltic coast of Sweden

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ABSTRACT

The distribution and controls of trace elements (Cd, Cr, Cu, Ni, Pb, Zn and U) in shallow groundwater in discharge and recharge zones were analysed at two sites on the Baltic coast of Sweden; one granite-dominated and one with a significant addition of calcite. Although the study sites differ in overburden geochemistry and groundwater trace metal concentrations, which were well reflected in the general groundwater composition, the relative hydrochemical differences between recharge and discharge ground waters were similar at both sites, and temporally stable. The concentrations of Cd, Cu, Ni and U were higher in soil tubes in recharge areas, but Cr was higher in discharge zones. Also concentrations of HS, Fe, Mn and NH_4 were higher in discharge samples, which in combination with increased ^{34}S values provide strong evidence of a transition from oxidizing to more reducing conditions along the groundwater flow gradient. In terms of trace metals, this might mean either mobilisation due to dissolution of trace-metal carrying Fe(III) and Mn(IV) phases, or immobilisation caused by precipitation of discrete trace-metal sulfides or co-precipitation with Fe sulfides. The results from this study show that the latter is dominant in both the carbonate and granite environments for the metals Cd, Cu and Ni. Chromium concentrations were likely coupled to organic complexation and were higher in discharge groundwater, where DOC was also more abundant. As the concentration of several potentially toxic trace metals were found to differ between recharge and discharge areas, a climate driven change in hydrology might have a substantial impact on the distribution of these metals.

1. Introduction

The pressing debate on the future climate situation has brought to the fore a broad spectrum of questions regarding possible environmental consequences, among which are changes in hydrological regimes. Ground and surface waters might be affected through altered speciation of a wide range of substances and their consequent redistribution between environmental compartments.

Climate change scenarios for the Nordic region have been constructed within the Swedish climate modelling program SWECLIM (Rummukainen et al., 2004). Within this platform, various climate models were used to generate scenarios on temperature development, precipitation and evapotranspiration, and these were brought together in hydrological models. With a reference interval between 1961 and 1990, simulations for a projected time slot in 2071–2100 showed substantial hydrological responses for the Swedish mainland. The common patterns found were decreases in precipitation and runoff in southern Sweden during summer and increases during spring, winter and fall (Xu, 2000; Andréasson et al., 2004). The change was found to be most pronounced during the winter period, with precipitation increases of up to 60% but no significant effect on evapotranspiration (Xu, 2000).

Although the SWECLIM simulations should be treated with caution, it is essential to define what effect such hydrological changes might have on for example water geochemistry. The essential assumption is that local groundwater regimes are likely to respond to the hydrological changes by an expansion of discharge areas during the more moist seasons and the contrary during summer, hence amplifying the seasonal variations already shown in boreal regions. The content of dissolved elements should theoretically differ between recently infiltrated and discharging groundwater, as the latter is usually older and the time factor is essential to kinetically controlled processes such as weathering reactions and microbial transformations. Important differences in groundwater composition between infiltrating and discharging areas could also arise from the differing content of e.g. O_2 and organic substances. There are studies which have dealt with geochemical evolution of deep (in the bedrock) groundwater along regional water flow gradients (Smedley and Edmunds, 2002; Edmunds et al., 2003; Smedley et al., 2003; Coetsiers and Walraevens, 2006; Tang and Johannesson, 2006). Studies on similar changes in local and shallow systems have been conducted in a French catchment

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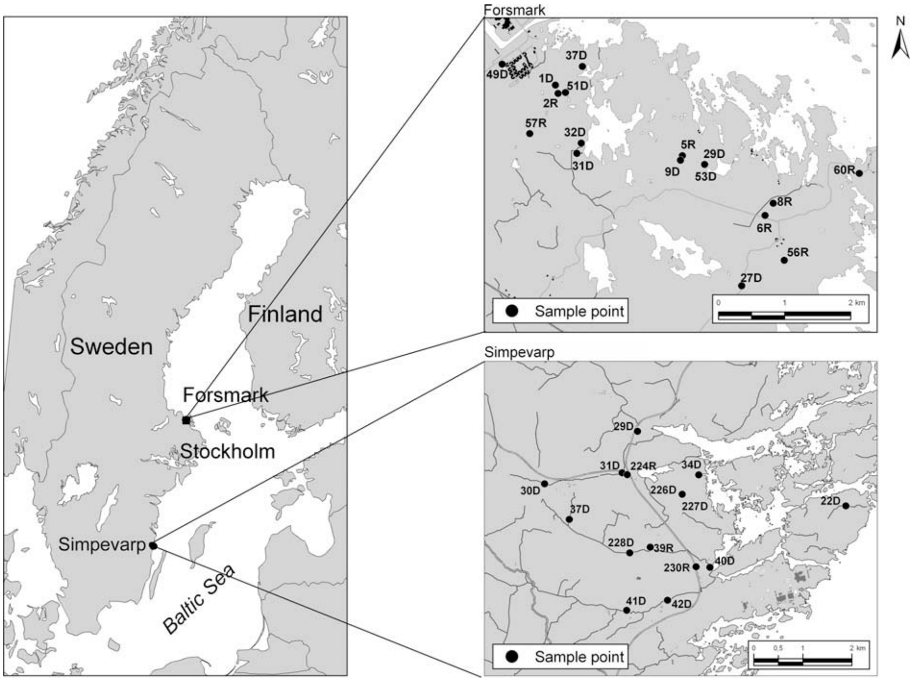


Fig. 1. Map of Sweden showing the study areas of Forsmark and Simpevarp. Sampling points are in the SKB SICADA database and in SKB reports given the prefix SFM000 in Forsmark and SSM000 in Simpevarp. The letter D indicates that the soil tube is located in a discharge area, and R indicates recharge. ©Lantmäteriet, SKB, Fredrik Hartz, 2009-03-03.

(Dia et al., 2000; Gruau et al., 2004), with the focus on the distribution of redox sensitive elements and rare earth elements (REEs). Little is still known about shallow systems of the boreal zone with its clear seasonal contrasts, in particular concerning the behaviour of trace metals.

Identification of climate induced changes in groundwater composition is also relevant in monitoring of spatial and temporal groundwater development. The European Groundwater Directive (GWD, 2006), for example, aims at protecting groundwater resources from pollution and requires a common union framework for control of groundwater quality and development over time. As the directive exclusively sets out to control anthropogenic impact, the risk of misjudgement due to insufficient consideration of the soil and bedrock lithology has been addressed. To provide an aid for uniform consideration of the soil and bedrock influence, a European aquifer typology map has been presented (Wendland et al., 2008). However, if climate is also an important factor for natural fractionation between groundwater and the solid phase, this is something to also consider when a temporal groundwater development is monitored.

This paper focuses on discrepancies in chemical composition between shallow groundwater (found in Quaternary deposits) in areas of recharge character and areas with discharge attributes at two pristine sites in Sweden; Forsmark and Simpevarp. These two sites are proposed geological repositories for storage of nuclear waste, and their hydrogeochemical prerequisites are therefore of special interest. The sites have been extensively studied within the framework of a site investigation programme carried out by The Swedish Nuclear Fuel and Waste Management Company (SKB). This paper aims to show the differences in groundwater chemistry that were detected between the two hydrological type areas, in both Forsmark and Simpevarp, focusing on trace metals, and to suggest processes that bring forth these discrepancies. The ecotoxicologically relevant trace metals Cd, Cr, Cu, Ni, Pb, Zn and U were chosen, and to aid in the interpretation of their behaviour, an initial evaluation of selected major and minor water constituents and stable isotopes was conducted.

2. Study areas

Forsmark and Simpevarp (Fig. 1) are located on the Swedish east coast, about 140 km north and 300 km south, respectively, of the Swedish capital Stockholm. Both sites belong to sparsely populated regions and are thus suitable for studies on natural hydrogeochemical processes. The nearness to the Baltic Sea means that the two areas are situated well below the highest Holocene shoreline and have relatively young soils. Forsmark extends from sea level to approximately 20 m.a.s.l. and the Simpevarp area reaches 50 m.a.s.l. The ground water tables generally follow the silhouette of the underlying bedrock and are found at depths between 0 and 1.5 m.

In Forsmark, the bedrock is dominated by Proterozoic metagranitoids (Stephens et al., 2005), and the soil overburden, which was deposited during or after the latest (Pleistocene) glaciation, rests directly on the bedrock. The surface deposits have been mapped for a $\sim$40 km^2 model area (Sohlenius et al., 2004), showing that 85% of the land is covered by Quaternary deposits with maximum depths of 17 m, and approximately 13% of the area represented by bedrock outcrops, mostly occurring at higher altitudes. The deposits are dominated by sandy till, followed by clay, gyttja and peat. The upper soil layers often classify as immature regosol profiles (Lundin et al., 2004). The mineralogy of the overburden partly reflects the granitoid composition of the bedrock, but also shows a significant addition of $CaCO_3$ (10–30%), originating from limestone that was carried to the site from the Bothnian sea floor by the Pleistocene ice sheet (Lundin et al., 2004). In lower areas, high frequencies of wetlands, lakes and streams are found.

In Simpevarp, the bedrock is composed of Proterozoic medium grained granitoids, which is mirrored also in the overburden, dominated by sandy or gravely till and covering approximately 40% of a $\sim$100 km^2 model area (Rudmark et al., 2005). The overburden is however thinner than at Forsmark; seldom more than 4 m, with the deepest soil deposits found in the valleys and the highest settings dominated by exposed bedrock or thin layers of till and peat. About 35% of the area shows exposed bedrock or only has very thin soil coverage (Rudmark et al., 2005). Compared to Forsmark, more developed soil profiles are found in Simpevarp, and less wetlands.

Both areas correspond to the boreo-nemoral zone with a rather heterogeneous mosaic picture of deciduous and coniferous forests and a clear climate seasonality. The mean annual temperature in Forsmark is 5.0 °C, and in Simpevarp 6.5 °C. Precipitation minus evapotranspiration leaves some 200 mm a^{-1} to runoff in Forsmark, and approximately 150–160 mm a^{-1} in Simpevarp (SKB, 2005a,b). The largest difference is found in snow cover duration, where Forsmark has about twice as many days with snow cover (100–125) as Simpevarp (50–75) (Sveriges nationalatlas, 2004).

More complete descriptions of the Forsmark and Simpevarp study areas are given in, e.g. SKB (2005a,b). But to summarize, both areas are underlain by granitoid bedrock, although differing geochemically (primarily in the abundance of calcite in the soil) and in overburden extension. The flat topographical characteristics in combination with shallow ground water surfaces imply the existence of local groundwater flow systems at both sites, overlying deeper and more regional groundwater systems. Drier recharge areas are found at topographical high-points, and wetter discharge zones in lower locations.

3. Materials and methods

3.1. Data retrieval

Chemical data for this study was retrieved in November 2007 from the database SICADA (Sicada_07_427), which is owned, quality checked and supervised by SKB. In the present study of groundwater composition, only soil tubes which have repeatedly been sampled for both major elements and the selected trace metals were chosen. The minimum number of samples required to include a soil tube was set to three. In Forsmark, 24 soil tubes were included, sampled between 4 and 14 times during a 5-a sampling period (July 2002–April 2007). In Simpevarp, 36 soil tubes were included (sampled 3–9 times), corresponding to 3 a of sampling (September 2004–May 2007). The entire material was used for a general comparison of the groundwater geochemistry between the two sites and for the analysis of temporal trends.

3.2. Recharge/discharge classification

Data files with detailed inventory material from a field recharge/discharge classification of the 100 × 100 m vicinity of the soil tubes were received from SKB. Further information on the classification has been given by Werner et al. (2007) and by Emma Bosson (pers. comm.). The basis for the categorization consisted of seven comprehensive parameters: local topography, distance to surface water, vegetation of the ground, field, bush and tree layers and, finally, site hydrology. Each parameter was determined from a set of inventoried or measured field characteristics and allotted a number, after which the seven parameters were ultimately combined to generate a hydrological class identity.

For the evaluation of chemical groundwater discrepancies between hydrological subareas, the complete dataset was reduced to include only soil tubes that had been classified as recharge or discharge. Samples from these soil tubes were then selected based on time of sampling, with the aim of including the same number of samples from each soil tube, and with samples from different soil tubes taken during the same 2-week periods. In Forsmark, these criteria gave 10 discharge-classified and seven recharge-classified soil tubes, originating from five periods (2004-01, 2004-04, 2004-07, 2004-10 and 2005-04). In Simpevarp, 12 discharge soil tubes were identified and three recharge-classified. These samples were collected during five other periods; 2004-09, 2005-06, 2005-09, 2005-12, 2006-03 and 2006-05.

3.3. Water sampling and analyses

Information on installation and design of the soil tubes is presented in Claesson and Nilsson (2003a–c, 2004); Johansson (2003); Johansson and Adestam (2004a,b) and Werner et al. (2004), and a more thorough description of sampling and analysis methodology, with analytical measurement uncertainties, is given by Nilsson and Borgiel (2005). To summarize, groundwater samples were collected at a level corresponding to the upper limits of the soil tube filter tip, about 1 m above the bedrock surface and well below the groundwater table. Although soil depths are generally larger in discharge areas and groundwater tables shallower, no significant difference between sampling depths existed between the selected soil tubes in recharge and discharge areas. Sampling was conducted using a submersible pump, and 3–5 times the pump volume was discarded before sampling. In Forsmark, disposable filters (Millipore, 0.40 μm) were placed at the pump outlet to separate colloidal and suspended material when waters were taken for analysis of trace metals and DOC. Samples for other determinants were filtered in the laboratory, as were all samples in Simpevarp. ICP-AES/ICP-MS were used for the highlighted trace metals (Cd, Cr, Cu, Ni, Pb, Zn and U), base cations (Na, K, Ca and Mg) and total concentrations of Mn, Si and Sr. The bicarbonate content was determined by alkalinity titration, pH by potential measurement, Cl by Mohr-titration or ion chromatography, depending on concentration, and SO_4 by ion chromatography. Spectrophotometry was used for concentrations of total Fe and Fe(II), HS, NO_3 and NH_4. TOC and DOC were determined using the IR Carbon analysator Shimadzu TOC5000. The isotopes ^{2}H, ^{18}O and ^{34}S were analyzed by mass spectrometry.

Analysis results below detection limit were set to half the detection limit. The concentrations most frequently found below detection limit were those of HS (in 21% of the samples in Forsmark and 4% in Simpevarp).

Since most elements exhibited positively skewed distributions, often fairly well described by a lognormal function, the central tendency of concentrations in individual soil tubes are discussed in terms of median values and non-parametric statistical tests are used; Mann–Whitney to compare single variables between Forsmark and Simpevarp, and Spearman rank correlations to evaluate connections between elements. These analyses were performed with the MS Excel application XLstat. The variation in recharge/discharge data was summarized by principal component analysis (PCA) using "The unscrambler v9.1" from CAMO Process AS. Prior to the multivariate analysis, variables were fitted to normal distributions and all data were scaled to unit variance and mean centered.

4. Results

The main groundwater source was infiltrated meteoric precipitation, deduced from the ^{2}H and ^{18}O values, which for all groundwater samples plotted along the global meteoric water line (GMWL). Both Forsmark and Simpevarp showed stable groundwater systems, where variations in chemistry over time were small and differences between soil tubes being greater than any seasonal fluctuations within individual tubes. Therefore, only spatial variations are discussed in detail below, based on the following figures; Fig. 2 summarizes raw data and illustrates differences between, firstly; Forsmark and Simpevarp, and, secondly; recharge and discharge zones. Fig. 3 presents the results from the PCA analysis and illustrates the most central differences when all variables were included, while Fig. 4 summarizes differences only in major ionic composition.

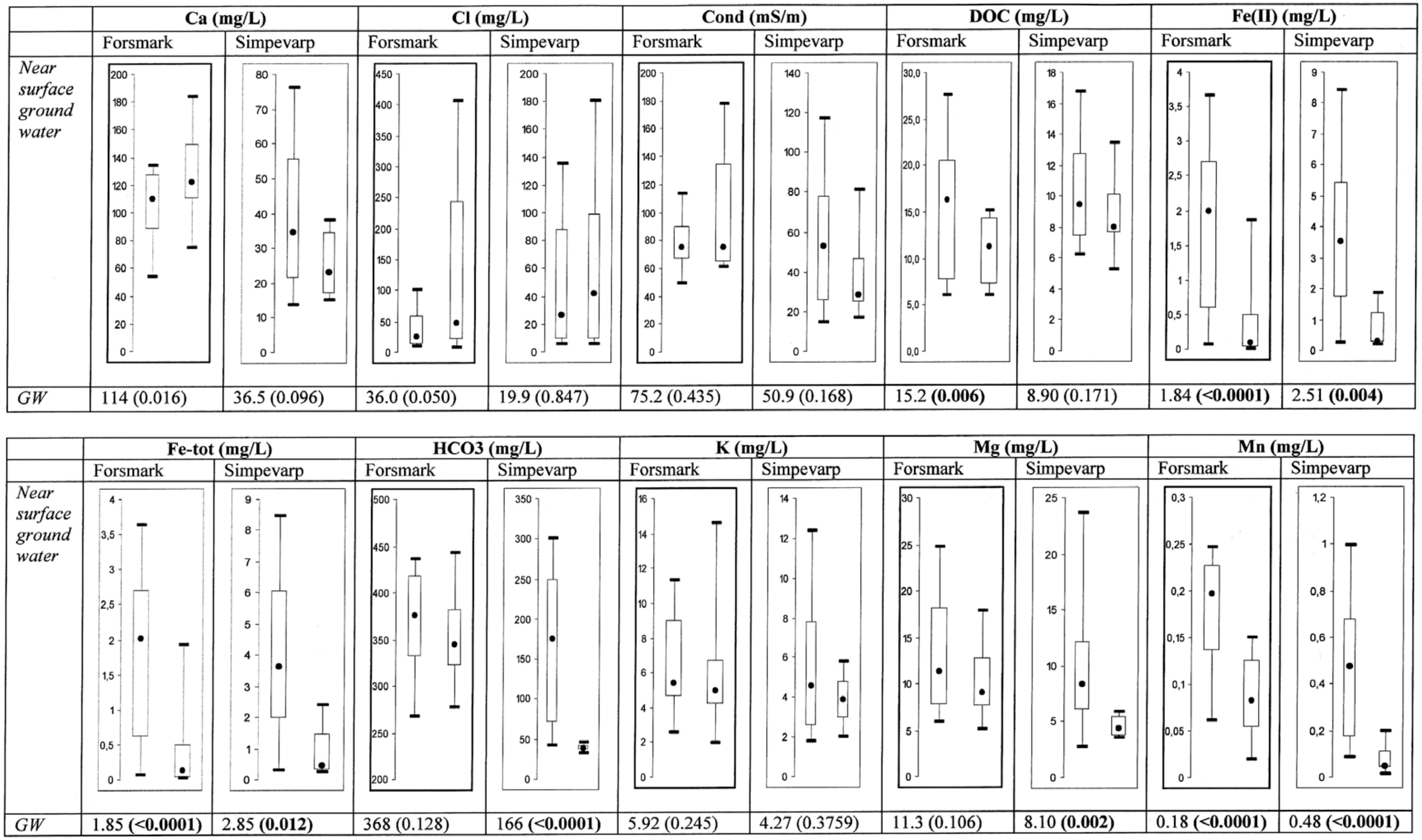


Fig. 2. Groundwater concentrations in soil tubes in discharge (boxplot to the left) and recharge (to the right) areas in Forsmark and Simpevarp. The boxes are delimited by the 1st and 3rd quartile of the data, with the horizontal line representing the median value. The lowest and highest values correspond to the 10th and 90th percentile, respectively. Note that the axis scale can differ between the sites! GW = groundwater median concentrations in Forsmark and Simpevarp. Given in brackets behind are the p-values of the two-tailed Mann–Whitney test. Bold p-values indicate significant differences between recharge and discharge soil tubes ($\alpha = 0.05$).

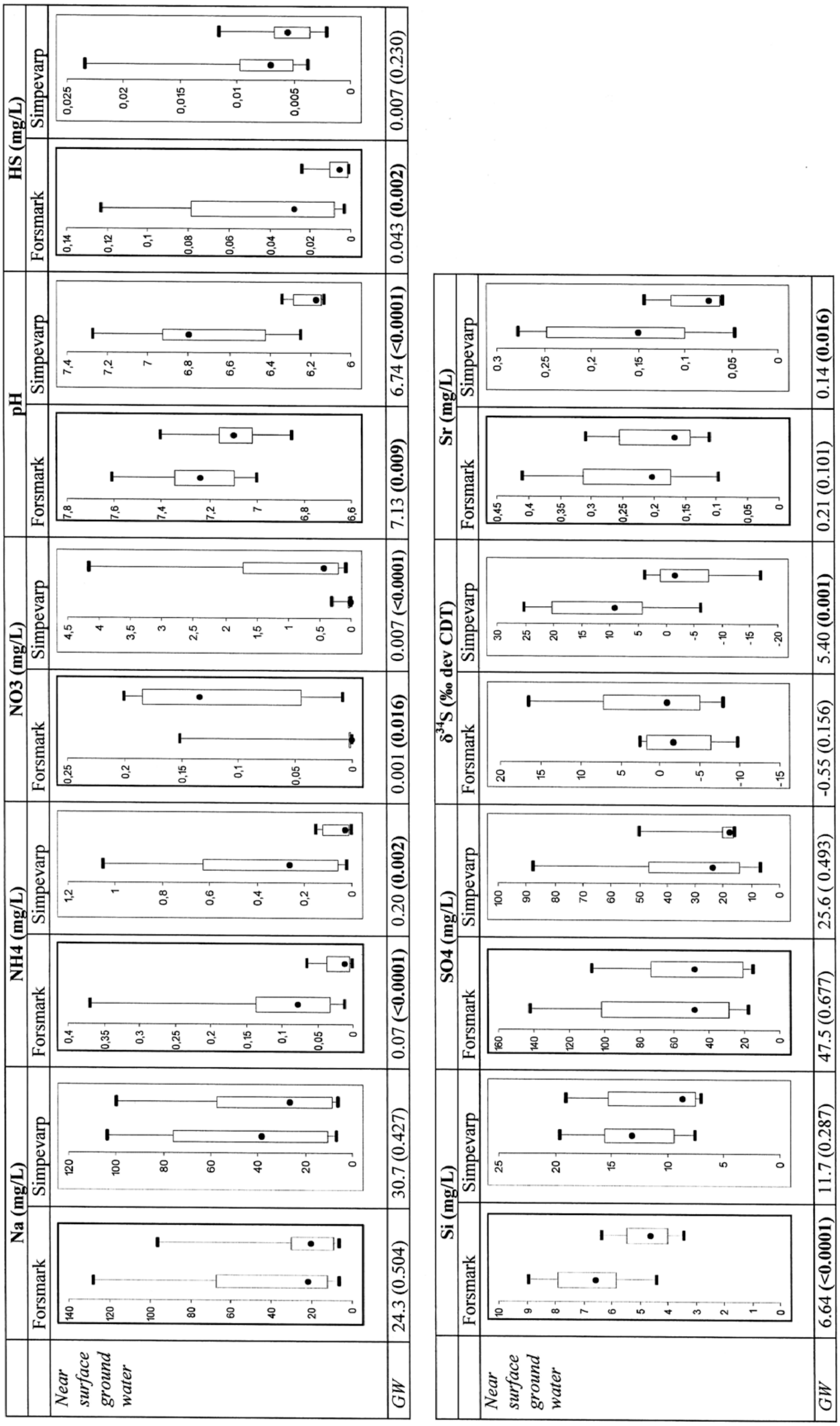
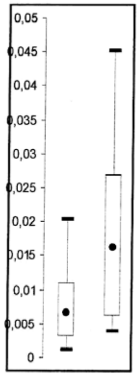
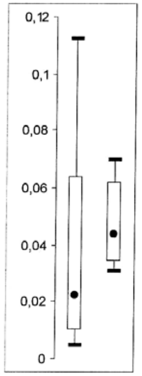
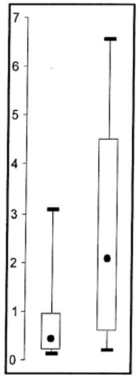
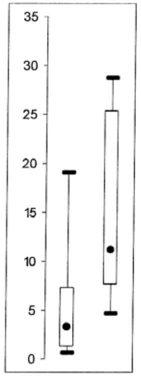
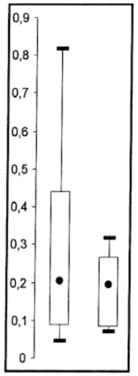
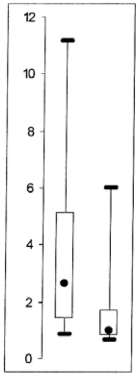
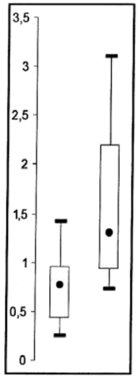
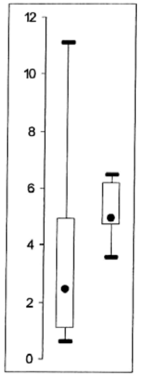
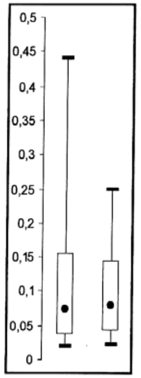
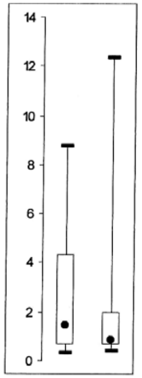


Fig. 2 (*continued*)

	Cd (µg/L)		**Cu (µg/L)**		**Cr (µg/L)**		**Ni (µg/L)**		**Pb (µg/L)**	
	Forsmark	Simpevarp	Forsmark	Simpevarp	Forsmark	Simpevarp	Forsmark	Simpevarp	Forsmark	Simpevarp
Near surface ground water										
GW	0.006 **(0.003)**	0.022 (0.101)	0.50 **(<0.0001)**	3.20 **(0.001)**	0.24 (0.475)	2.06 **(0.017)**	0.84 **(<0.0001)**	2.78 **(0.019)**	0.09 (0.817)	1.30 (0.579)

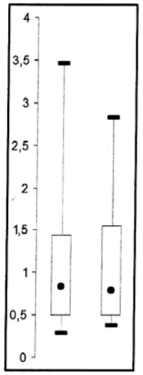
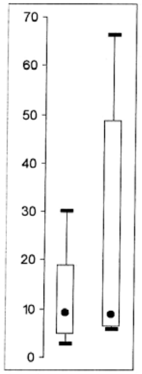
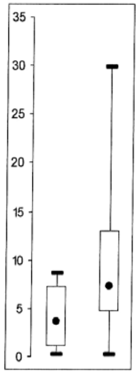
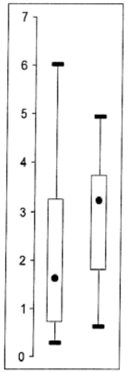
	Zn (µg/L)		**U (µg/L)**	
	Forsmark	Simpevarp	Forsmark	Simpevarp
Near surface ground water				
	0.85 (0.837)	7.92 (0.149)	3.82 **(0.006)**	1.76 (0.104)

Fig. 2 (*continued*)

The groundwater chemistry differed substantially between Forsmark and Simpevarp, as can be seen from the first principal component (PC1) of the PCA score plot in Fig. 3a. This principal component separated soil tubes in Forsmark (plotted to the right in the figure) from those in Simpevarp (to the left) and accounted for 32% of the total variance in the data set. PC1 was described by the strongest negative factor loadings for the trace metals and positive ones for HCO_3, pH and Ca (Fig. 3b), which establishes the importance of calcite weathering on groundwater chemistry in Forsmark, and the generally inverse correlations between trace metals and most of the major elements. In more detail, the differences in general groundwater chemistry (Fig. 2) between Forsmark and Simpevarp were portrayed by higher pH values in Forsmark and elevated concentrations of most major ions (Ca, Mg, K, Sr, HCO_3, Cl and SO_4) and U, while groundwater in Simpevarp showed strongly elevated trace metal (Cd, Cu, Cr, Ni, Pb and Zn) concentrations and higher concentrations of Na, Si, Fe, Mn and N. Similar concentrations at both sites were found only for organic material, where the values from unfiltered samples (TOC) were essentially the same as for filtered (DOC), which proves a strong prevalence of dissolved forms. The major ion proportions in Forsmark and Simpevarp (Fig. 4) show that the groundwater samples from Forsmark were exclusively of Ca–HCO_3 type, while in Simpevarp all ions except Mg were important.

The second principal component (PC2) of the PCA accounted for 24% of the total variance and separated soil tubes in recharge areas (assigned negative factor scores) from those in discharge areas (positive scores). So, a hydrological division was the second most effective data arrangement to describe the total variance, after the separation of samples from Forsmark and Simpevarp (Fig. 3a). The second principal component was described by positive weights for Fe, Mn and NH_4 and negative weights for NO_3 and U (Fig. 3b), and was consequently most likely representing a redox gradient. However, not only the redox sensitive elements differed between recharge and discharge zones, as can be seen in Figs. 2 and 4. For the ionic proportions in recharge and discharge areas (Fig. 4), a slightly different pattern was observed in Forsmark and Simpevarp. At the former site, Ca contributed with a larger percentage in soil tubes at recharging locations, while at the latter site the largest differences were found among the anions with recharging sites plotting towards higher proportions of SO_4 and Cl in the piper diagram. When focusing on absolute concentrations (Fig. 2), recharge areas in both Forsmark and Simpevarp exhibited higher values for NO_3 and most trace metals (Cd, Cu, Ni and U), while a trend of lower concentrations was found for major cations (Ca, Mg, K, Na, Si and Sr), HCO_3, pH, DOC, Fe, Mn, HS, NH_4 and the trace metal Cr (Fig. 2). An exception from this general pattern was the behaviour of Ca, which in Forsmark was higher in recharge areas. Uncorrelated with the hydrological parameter were Cl, SO_4, Pb and Zn.

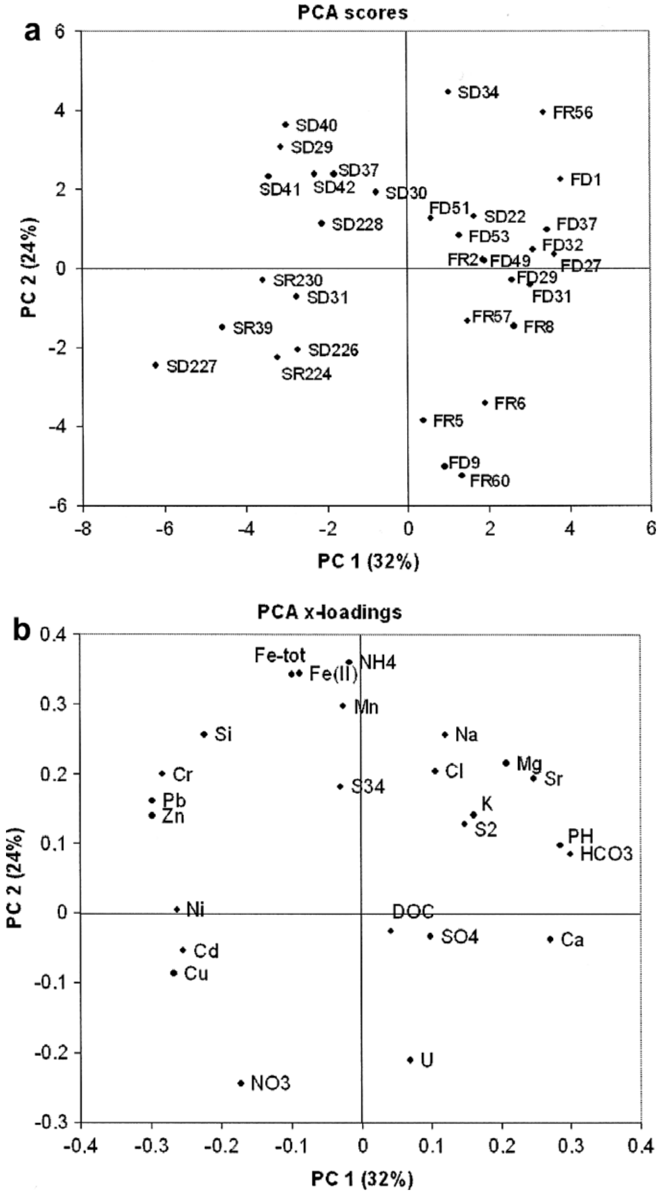


Fig. 3. Scores (a) and loadings (b) of the first two principal components (PC1 and PC2) for groundwater chemistry in recharge and discharge areas. Abbreviations in the score plot specify soil tube identity, with site (F = Forsmark and S = Simpevarp), hydrological class (R = recharge and D = discharge) and numbers from the SKB sampling program of shallow groundwater. The analysis was run on median values for each analyzed soil tube. In the PCA score plot, soil tube FR56 and FD9 plotted outside the general recharge and discharge clusters. For FR56, missing analyses for all redox sensitive elements might be an explanation of this deviation, as PC2 is defined mainly by those variables.

5. Discussion

The ground waters in Forsmark and Simpevarp, despite showing substantial differences in terms of both absolute and relative concentrations of many variables, evolved along the flow path from recharge to discharge areas in an overall similar manner, as summarized in Fig. 5. To get the overall picture, the discussion is started with a summary on the general differences between the groundwater systems in Forsmark and Simpevarp.

5.1. Differences between Forsmark and Simpevarp

The differences in trace metal concentrations (Cd, Cr, Cu, Ni, Pb and Zn) constituted the first obvious difference between the two study sites. In Simpevarp, the concentrations were comparable to the levels found in groundwater of the capital of Sweden (Stockholm), while in Forsmark they were below average for Swedish groundwater (Bertills, 1995; Aastrup and Thunholm, 2001; Ek et al., 2007). Lead is enriched in the relatively young granites north of Simpevarp (Andersson and Nilsson, 1992), and is therefore likely to originate mainly from that source. For the other metals, however, available information does not point to matching soil enrichments (SKB SICADA database; Melkerud et al., 1992). Nonetheless, soil and bedrock mineralogy are often important for the groundwater trace element composition (Ledin et al., 1989; Banks et al., 1995; Frengstad et al., 2001; Zelewski et al., 2001), and the imperfect geographical correspondence between soil sampling points and groundwater soil tubes begs for some caution before a lithological control is definitely ruled out. Alternative explanations for

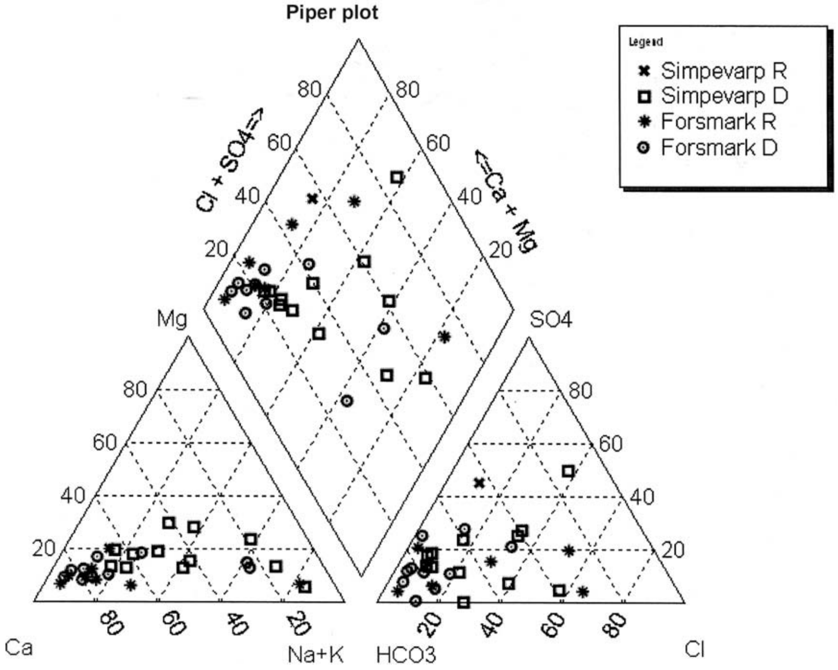


Fig. 4. Proportions of major ions in groundwater, indicated for Forsmark and Simpevarp and with a separation between soil tubes in recharge (R) and discharge (D) areas.

the higher trace metal concentrations in Simpevarp might be: (1) less carbonate ions and organic molecules capable of adsorbing metals; (2) significantly lower pH values in the upper soil layers, where the median pH in the O-horizon was 4.5, while in Forsmark it was 6.5 (Lundin et al., 2005; Tröjbom and Söderbäck, 2006). The only moderate difference in terms of groundwater median pH (6.7 in Simpevarp compared to 7.1 in Forsmark) is though unlikely to be a major explanation for the much higher trace metal concentrations at the latter site; (3) redox driven dissolution of Fe and Mn oxyhydroxides in the absence of sulfides and (4) more intense chemical weathering. Further investigations would have to be carried out in order to determine the relative contribution of each of these processes.

In contrast to the other trace metals, U was higher in Forsmark. This might be due to relatively high U concentrations in the soil of this region (Salminen et al., 2004). In addition, the elevated concentrations of both inorganic and organic C in Forsmark may contribute to the high U concentrations in solution. The occurrence of calcite suggests formation of aqueous Ca uranyl carbonate species at circumneutral pH values, and the formation of these complexes effectively suppresses adsorption (Zheng et al., 2003; Dong et al., 2005; Fox et al., 2006). Also organic complexation can be significant for U, and high DOC concentrations favor soluble species.

The higher calcite content of soils in Forsmark is the second most important reason for the chemical divergence between the two groundwater systems, as reflected by circumneutral pH values and Sr enriched Ca–HCO_3 water. The elevated SO_4 concentration in groundwater from Forsmark is an additional difference of importance, likely to derive from sulfide-bearing post-glacial sediments which frequently occur in coastal areas below the highest shoreline. Sohlenius et al. (2004) suggest that a small percentage of the Forsmark drainage area might be covered with such sediments. Saline water intrusion is less likely as the SO_4/Cl ratio in the groundwater is about 10 times as high as in marine water and, secondly, because the δ^{34}S value is close to zero. In marine and brackish water, the δ^{34}S value of SO_4 is stable and close to +20, while in fresh waters that carry sulfide-derived SO_4, the δ^{34}S values are lower; often between −5 and +5 (Åström and Spiro, 2000). A final difference between the two study sites might be higher redox potentials in groundwater in Forsmark, as indicated by lower water concentrations of Mn and Fe, although similar concentrations occur in the mineral soil (Melkerud et al., 1992; SGU, 2007), and a much lower contribution of reduced N (NH_4) in relation to oxidized N (NO_3).

5.2. Differences between recharge and discharge areas

5.2.1. Redox stable elements

The concentration of dissolved elements in groundwater is known to change with time after infiltration, as the time factor is essential for kinetically controlled processes such as weathering reactions and microbial transformations. Generally increasing concentrations of cations (Na, K, Mg, Ca, Si, Li and Sr) along the groundwater flow gradient (Edmunds et al., 2003; Coetsiers and Walraevens, 2006) and with sampling depth (Schürch et al., 2004) have been observed elsewhere. Schürch et al. (2004) did, however, indicate similar or slightly decreasing Ca concentrations with depth in a groundwater borehole. Similar results were found in Forsmark in the present study, where Ca concentrations were highest in groundwater from infiltrating areas. Since calcites are more readily dissolved than most other minerals, the higher Ca concentration in recently infiltrated water likely reflects weathering discrepancies in the upper soil horizons. Along the groundwater flow route, Ca is exchanged for other cations, causing the Ca concentrations in groundwater to decrease and other cations to increase. This ion exchange process is shown in the major ionic composition, with a transition from groundwater of Ca–HCO_3 type in recharge areas to more of a Na–HCO_3 character in discharge locations. The simultaneous pH increase in discharge soil tubes is also likely to derive from cation exchange, and obviously exceeds the proton release that can be expected from the oxidation of organic material, which was more abundant in soil tubes in discharge zones. Besides calcite dissolution and cation exchange, silicate weathering also contributes to the signature of the slightly more mature discharge groundwater, as postulated by the parallel increase in Si concentration in discharge groundwater. The pattern with increasing cation concentrations and pH along the groundwater flow direction was the same in

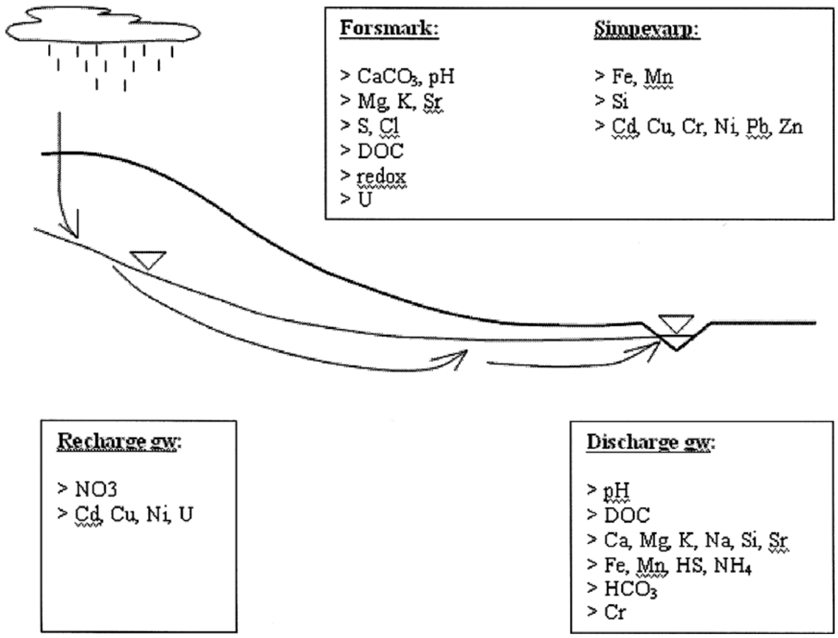


Fig. 5. Summary of differences in groundwater chemical composition between Forsmark and Simpevarp (upper text box) and common groundwater differentiation between soil tubes in recharge and discharge areas, applicable to both sites (lower boxes).

Forsmark and Simpevarp, with the only difference being that in Simpevarp, Ca was also higher in discharge areas, as well as the other cations. The difference in Ca occurrence can be explained by the much lower calcite content in Simpevarp, where other minerals might also be of importance for the Ca supply, or where dissolution of the marginal carbonate pool is not enough to show effects on the composition of groundwater in recharge areas.

The higher cation concentrations in discharge areas as compared to recharge locations were paralleled by high concentrations of DOC and HCO_3. As the groundwater table is shallower in discharge areas, it periodically penetrates the upper organic soil layers, and this is the likely explanation for the higher DOC concentrations in groundwater at these sites (as also suggested by Gruau et al., 2004). The higher HCO_3 concentrations in discharge zones were most marked in Simpevarp, and may reflect an increase in dissolution of carbonic acid produced during respiration and decomposition of soil organic matter, calcite dissolution (Ca increased along the flow route in Simpevarp), proton consumption during silicate weathering, or a combination of these possible explanations. Although a higher organic content was found in discharge groundwater in Forsmark as well, the main source of HCO_3 here is carbonate minerals, and hence alkalinity differences between recharge and discharge soil tubes were not as marked.

5.2.2. Redox sensitive elements

Groundwater maturation along the flow gradient sometimes also involves O_2 consumption. Within the SKB sampling program, concentrations of dissolved O_2 have only been determined for Forsmark, but relatively few samples were analyzed and a large proportion of the results were near or below the detection limit. So, the uncertainty in this parameter is large and the results have to be interpreted with care. However, samples with values below detection limit (0.1 mg/L) were clearly more frequent in discharge soil tubes. If these values were set to half the detection limit, the median values of dissolved O_2 concentrations were 3.70 mg/L in recharge groundwater and 0.10 mg/L in discharge groundwater. This indicates an actual decrease in available O_2. The consumption of O_2 with the simultaneous decreases in redox potential is often illustrated by altered concentrations and proportions of redox sensitive species such as Fe(II)/Fe(III), Mn(II)/Mn(IV), NH_4, NO_3 and SO_4 (Smedley and Edmunds, 2002; Edmunds et al., 2003; Coetsiers and Walraevens, 2006; Tang and Johannesson, 2006). However, different elements are reduced at different redox values, which means that readily reduced species may occur in reduced form while others are still oxidized. As an example of this succession, Coetsiers and Walraevens (2006) identified a zone of O_2 and NO_3 reduction in the uppermost meters below ground surface, reduction of Fe and Mn oxyhydroxides occurring from a few meters depth to approximately 75–100 m, and SO_4 reduction below that. In both Forsmark and Simpevarp, the most obvious difference between soil tubes in discharge and recharge areas was found for redox sensitive elements (Fig. 4), where discharge zones showed higher concentrations of Fe-tot, Fe(II), Mn, NH_4 and HS, and lower concentrations of NO_3. This is strong evidence of a significant decrease in redox potential along the groundwater flow route at both sites, resulting from O_2 consumption during the successive decomposition of organic molecules originating from recharge areas and a further intensified O_2 consumption in discharge areas due to the elevated organic matter content at these locations. Higher Fe, Mn and DOC concentrations in groundwater in wetlands than in uplands was also observed in a French catchment by Gruau et al. (2004), and interpreted as indicative of more reducing conditions in the wetland.

Even though the SO_4 concentrations were similar in recharge and discharge areas (Fig. 3), it is also likely that sulfates are reduced some time after infiltration or upon groundwater arrival in typical discharge zones. This is suggested by the data from Simpevarp, where the median $\delta^{34}S_{(sulfate)}$ values were just below zero in recharge soil tubes. In contrast, for the discharge tubes in Simpevarp, the corresponding value was significantly higher; close to +10, and the higher $\delta^{34}S$ values in discharge areas were accompanied by high HS concentrations. The high isotope values are not explained by intrusion of marine water, as there was no associated increase in Cl (Fig. 3) and since the Na/Cl ratio did not match that of marine water. In fact this ratio was even higher in discharge than in recharge groundwater (if the groundwater in discharge areas were influenced by saline water, the Na/Cl ratio would have decreased). Sulfide oxidation is also unlikely since that is a process which commonly delivers SO_4 with low (or negative) $\delta^{34}S$ values. The most likely explanation is therefore that along the flow path in Simpevarp, the conditions get sufficiently reducing not only to release Fe(II), but also to reduce a significant amount of SO_4. The microbes that carry out the reduction of SO_4 favor the light S isotope (^{32}S). This results in low $\delta^{34}S$ values of the sulfide produced, and as the lighter isotope is removed from the SO_4 pool, the remaining SO_4 gains increased $\delta^{34}S$ values. The higher HS concentrations in discharge areas fit nicely into this conceptual explanation. The similar SO_4 concentrations in recharge and discharge areas are somewhat intriguing, but is most likely explained by reduction of a SO_4 pool that is not large enough to produce changes in concentrations but still large enough to produce significant shifts in the isotope ratio. The microbial isotope fractionation is often as high as 40‰ (Goldhaber, 2003). This means that reduction of only a small part of the SO_4 pool can be enough to cause a shift in the $\delta^{34}S$ value by several ‰. It is likely that the same mechanism is operating in Forsmark, as indicated by the clearly elevated HS concentrations in discharge as compared to recharge areas (Fig. 3). However, the SO_4 concentrations are overall too high to cause a visible shift in the isotopic composition.

5.2.3. Trace metals

Chromium and U are among the trace metals most frequently described in studies of groundwater chemistry. The chemistry of both these metals is highly sensitive to changes in pH and redox status. At circumneutral pH, the oxidized hexavalent forms are found as anionic species which are easily dissolved and, unless sorption occurs, mobile. At lower redox potentials, the reduced forms (Cr (III) and U (IV)) precipitate as insoluble oxides, mainly UO_2 and $Cr(OH)_3$ or Cr_2O_3. As would be expected from this redox dependence, the concentrations of Cr and U have repeatedly been shown to decrease in natural groundwater systems as the redox potential declines (Smedley and Edmunds, 2002; Edmunds et al., 2003; Smedley et al., 2003; Tang and Johannesson, 2006). The results from Forsmark and Simpevarp are in accordance with these findings for U, which were found in higher concentrations in soil tubes in recharge areas.

Chromium did, however, act in the opposite way from that which is usually reported, with higher concentrations in discharge zones. This was established with statistical significance only in Simpevarp, but the same trend was also observed in Forsmark. Icopini and Long (2002) recognized that concentrations of reduced Cr in natural, anaerobic environments can be higher than would be expected if the primary Cr(III) forms were the commonly identified oxyhydroxide species. They postulated that the explanation for this might be complexation by dissolved organic material. The physical form of the organic material is crucial, as complexes with particulate organic matter would generally promote attenuation, as has been shown by Hellerich and Nikolaidis (2005). Puzon et al. (2005) also acknowledged the phenomenon of complex formation between Cr(III) and dissolved organic molecules and pointed to the widespread overlooking of the fate of Cr(III) following bacterial Cr(VI) reduction, which arises from the common assumption that reduced Cr is immobile. In both Forsmark and Simpevarp, the vast majority of the organic material in the groundwater was found to be dissolved, and among the studied trace metals, Cr was the element with by far the strongest correlation to DOC. The positive correlation to DOC and the dominance of dissolved organic material may indicate that the speciation of Cr is controlled by the formation of aqueous organo-Cr(III) complexes. The higher Cr concentrations in discharge groundwater could then be explained by the elevated DOC levels. This effect might arise even if reduction of Cr(VI) has occurred, as suggested by the references given above. It is, however, not likely that the increase in DOC in discharge zones is the only, or even not the most important, reason for the higher Cr concentrations. This is suspected since the difference in Cr concentrations between recharge and discharge soil tubes was most evident in Simpevarp, which was the site with the weakest correlation between Cr and DOC (*R*s in Simpevarp = 0.28; Forsmark = 0.81) (Fig. 6). In Forsmark, where the correlation was strongest, several soil tubes with high Cr concentrations were found in recharge groundwater. An alternative explanation for the higher Cr concentrations in discharge areas could be dissolution of Fe and Mn oxyhydroxides, with a simultaneous release of Cr(VI). Adsorption onto Fe hydroxides is a recognized attenuation mechanism for the otherwise generally soluble Cr(VI) species (Nikolaidis et al., 1994). If this mechanism is acting in the studied groundwater systems, the dissolution of these hydroxides along the flow gradient would not only cause an increase in soluble Fe but also in Cr. This is supported by positive correlations between Cr and Fe in both Forsmark (*R*s = 0.64) and Simpevarp (*R*s = 0.61). In Forsmark, seven outliers with Cr concentrations between 7 and 43 μg/L were found (Fig. 7). All these were from discharge groundwater, and these samples were also represented in the top 10 Fe concentrations measured. When focusing on the concentration interval up to 1 μg Cr/L, where all the other samples were found, it remained clear that most of the samples with both high Cr and Fe concentrations had been collected from discharge soil tubes. A similar pattern was seen in Simpevarp. The same correlation was found with Mn, and hence oxyhydroxides of this element are also important. The slow kinetics of the Cr(VI) reduction (Henderson, 1994) following the dissolution of Fe and Mn hydroxides might keep a significant part of the Cr(VI) in solution. Although further speciation analysis would have to be conducted in order to better distinguish between the role of organic complexation and that of Fe and Mn hydroxides, it is suggested that the latter control is more important for the differentiation of Cr in these groundwater systems.

The trace metals Cd, Cu and Ni were, in a manner similar to U, depleted in samples from the discharge areas. The correlations to Fe and Mn were weak, which indicates that Fe and Mn oxyhydroxides are less important for the occurrence of Cd, Cu and Ni in these two groundwater systems. Significant negative correlations were though found to dissolved sulphide. This pattern indicates that Cd, Cu and Ni are controlled to a large extent by precipitation of metal sulfides. This is consistent with the isotopic data for Simpevarp, which provided strong evidence of SO_4 reduction in the discharge zones. There was thus a strong divergence among the chalcophilic metals, as Fe(II) and Mn(II) increased while several trace metals (Cd, Cu and Ni) decreased as sulfides obviously precipitated in the discharge zones. This is most likely explained by extensive release of Fe and Mn from dissolved oxyhydroxide, and rapid depletion of dissolved sulfide, causing Fe(II) and Mn(II) but not the trace elements to build up in solution. In the case of Forsmark and Simpevarp, the same results were found although large differences applied to both trace metal concentrations and S content, where lower sulfide concentrations and higher trace metal levels in Simpevarp generated a much lower sulfide to metal ratio.

5.3. Impact of climate change on trace metal transport

Before data analysis, it was suspected that possible geochemical responses to variations in hydrology might be detectable on a seasonal basis, as Forsmark and Simpevarp are located in a region of strong seasonal contrasts and since seasonal variations in shallow groundwater chemistry have been observed in other locations. It has, for example, been recognized in groundwater of areas with sulfide mining activities, with increased acidity and concentrations of metals and SO_4 during snowmelt (e.g. Herbert, 2006). Montlucon and Sanudo-Wilhelmy (2001), who measured groundwater concentrations of trace metals, nutrients and organic material in a

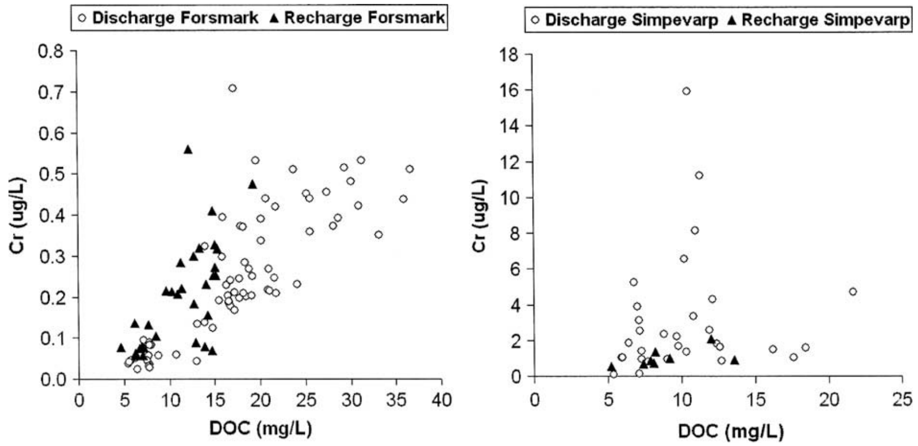


Fig. 6. Scatter plots of Cr concentration as a function of DOC, with discharge and recharge soil tubes separated. The left figure from Forsmark, and the right one from Simpevarp.

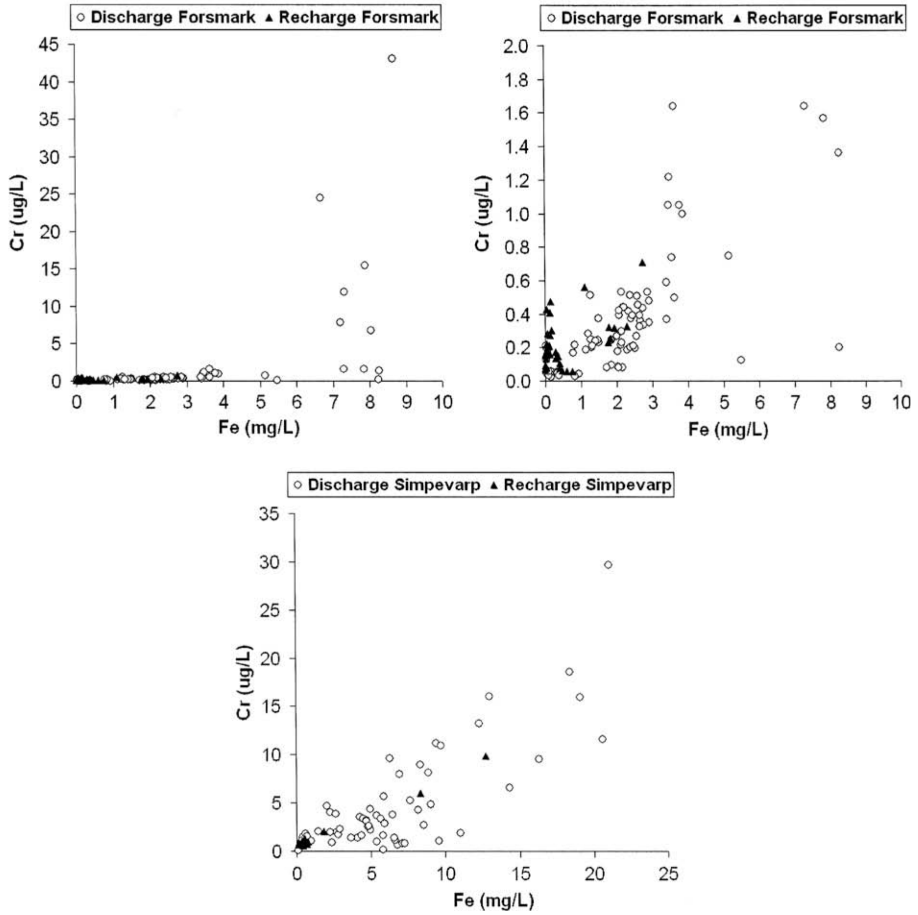


Fig. 7. Scatter plots of Cr concentration as a function of total Fe, with discharge and recharge soil tubes separated. The upper two plots are from Forsmark, where the first one comprises all data points, and the second one excludes the six highest values. The bottom plot is from Simpevarp.

coastal aquifer on two occasions; during a dry period with low groundwater discharge and after a rainy period with high groundwater discharge, also found significant differences for most elements. In contrast, however, Zelewski et al. (2001), who sampled eight soil tubes in shallow groundwater with relatively large groundwater table fluctuations during a 2-a period, could not see any seasonal variability. Neither did they observe any correlation between metal concentrations (of Hg, Cu and Zn) and groundwater table elevation. In the case of Forsmark and Simpevarp, the temporally stable data showed that none of the studied elements varied significantly over the year, and hence the established differences between soil tubes in recharge and discharge areas were constant over the studied period. It seems that hydrological changes that happen over relatively short time intervals, for example recurring fluctuations of the groundwater table or varying groundwater flow rates, are not sufficient to affect the main chemical differences between recharge and discharge areas at these two sites. Therefore, in the longer time perspective, the annual net change is of greater relevance.

As the S redox transitions were essential for the fractionation of metal concentrations in recharge and discharge zones (for Cd, Cu and Ni), the first step to broaden the understanding of how these trace metals might be affected in the longer perspective should be to define what effect climate change would have on the redox potential. Besides the general decrease in O_2 dissolution that a temperature increase will give, the most important control on O_2 availability in groundwater is the concentration of organic material. Several studies, made on various ecosystems, have already indicated that increased atmospheric CO_2 levels and/or a temperature increase have the potential to enhance the net primary production (NPP), given that the conditions are not too dry (Norby and Cotrufo, 1998; Oren et al., 2001; Bergh et al., 2003; Fröberg, 2004). Thus, a transition towards a generally wetter and warmer climate in Forsmark and Simpevarp could increase the concentration of organic compounds in both groundwater and the adjoining soil. In combination with an expansion of the wet discharge areas, this ought to result in a general decrease in redox potential, followed by precipitation of sulfides and decreased metal mobility. However, just as important as NPP is the decomposition rate, where climate might interfere in several steps; on microbial and soil fauna activity, O_2 supply, litter chemistry and plant community composition, but where the net result is still uncertain (Norby and Cotrufo, 1998; Tipping et al., 1999). Moreover, the net increase in precipitation that has been simulated for Scandinavia within the SWECLIM program is not universally applicable. It is therefore of great relevance to study the transition between recharge and discharge chemistry also in settings that are assumed to become drier. Several studies have shown that pulses of SO_4-enriched water are drained from watersheds after dry periods, and not only in areas were sulfide minerals are especially common (Yan et al., 1996; Sommaruga-Wögrath et al.,1997; Devito and Hill, 1999; Eimers and Dillon, 2002). This is likely due to oxidation of sulfides, where the drought-induced release of SO_4 is likely paralleled by a release of sulfide-associated metals.

Finally, U is one of the most important trace metals in this specific study where data comes from two areas that are under investigation to be used as deep repositories for spent nuclear fuel. This study confirms the results from other, similar studies which show that the mobility of U is diminished in anaerobic environments. In this particular case it is therefore a significant result that the shallow groundwater zone is likely to act as a sink for U that could be migrating towards the surface after an accidental rupture of a deep repository capsule.

6. Conclusions

Despite different overburden geochemistry in Forsmark (calcareous) and Simpevarp (granitoid), and although trace metal concentrations were much higher in Simpevarp for all metals except U, both sites showed a similar chemical division between recharge and discharge groundwater. In addition, both systems were temporally stable, and differences between recharge and discharge areas did not show any seasonal variations. Discharge areas were characterized by higher concentrations of cations (Mg, K, Na, Si and Sr), DOC, HCO_3 and pH. Lower redox potentials at discharging locations were mirrored by higher concentrations of Fe, Mn, HS and NH_4, and lower concentrations of NO_3.

For the trace metals, the following main observations were made when recharge and discharge zones were compared:

- Concentrations of U were higher in recharge areas. This was expected due to the oxidized U(VI) form being more soluble than reduced U(IV).
- Concentrations of Cr were higher in the anaerobic environment (discharge zones), which was the opposite from what was expected. The most likely explanations are formation of aqueous organo-Cr(III) complexes and redox driven dissolution of Fe and Mn oxyhydroxides that releases coprecipitated Cr(VI).
- Concentrations of Cd, Cu and Ni were higher in recharge areas, and likely originated from dissolution of metal-bearing sulfides. This mechanism was valid in both Forsmark and Simpevarp, although the S content differed between these sites.
- Lead and Zn were uncorrelated with the hydrological parameter.

As hydrology is strongly coupled to climate factors, the grouping of trace metals between recharge and discharge zones within the same catchments indicate that a climate change might have a substantial impact on groundwater trace metal concentrations, and from this study it seems that the redox potential is the factor to trigger a redistribution between aqueous and solid phases. As either Forsmark or Simpevarp will be used for deep storage of nuclear waste, an important finding is the lower U concentrations in discharge areas at these two sites. In a wider context, the net precipitation increases that have been simulated for the Scandinavian countries by SWECLIM is likely to lower the redox potential of many shallow groundwater systems and hence decrease the total soluble pool of U, Cd, Cu and Ni. In several regions outside Scandinavia, where simulations of future climate show radical decreases in annual net precipitation, the effect might be the reverse. As the understanding of toxic metal distribution in the environment has important applications in the field of risk assessments and management of contaminated sites, additional studies on this subject are of great relevance.

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