

Origin of brackish groundwater in a sandstone aquifer on Bornholm, Denmark

N. O. Jørgensen and J. Heinemeier

ABSTRACT

A multi-isotope approach in combination with hydrochemical data and borehole logging is applied to identify the source of brackish groundwater in a borehole in the well field of Neksø Municipal Waterworks in Bornholm, Denmark. The aquifer lithology consists of fractured Lower Cambrian sandstones resting on Proterozoic crystalline basement. The water body in the studied borehole is significantly stratified with respect to the hydrochemical and isotopic signatures and reveal a Na–Ca–Cl–HCO₃ water type and TDS values > 1,000 mg/L below a halocline at 40–55 m below measurement point (bmp). The occurrence of brackish groundwater is remarkable for this aquifer, which otherwise yields potable groundwater of good quality. The stable isotope (¹⁸O and ²H) compositions indicate a meteoric origin of the brackish groundwater, which rules out seawater intrusion into the aquifer. ¹⁴C activities show apparent ¹⁴C ages of the brackish groundwater in the range 2200–4300 yr (BP), whereas the freshwater samples above the halocline indicate modern age. Hydrochemical (Cl/Br and Sr) and isotopic studies (¹⁸O, ²H and ⁸⁷Sr/⁸⁶Sr) of the brackish groundwater point to a well-mixed and homogeneous water body reflecting long water–rock interaction and suggest a contribution of palaeowater from the fractured crystalline basement which has intruded into the Lower Cambrian sandstone aquifer.

Key words | brackish groundwater, palaeowater, stable isotopes, strontium isotopes

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INTRODUCTION

Enhanced electrical conductivities (>2,100 μS/cm) are recorded in a 118 m deep borehole (DGU 247.248) in the well field of Neksø Municipal Waterworks on the east coast of Bornholm, Denmark (Figure 1). The water type can be classified as slightly brackish water (TDS >1,000 mg/L) according to the classification of Drever (1997). The aquifer is confined to semi-confined and the lithology consists of fractured ortho- and protoquartzitic Lower Cambrian sandstones resting on Proterozoic crystalline basement. The occurrence of enhanced electrical conductivity (EC) is remarkable for this aquifer, which otherwise yields potable groundwater of good quality (EC < 500 μS/cm). However, slightly enhanced EC in the range from 600 to 1,000 μS/cm are observed in the bottom of some other boreholes in the well field and

a number of wells in the vicinity of the study area have been abandoned in the past for that reason.

The geological setting in the coastal areas of eastern Bornholm, Denmark consists of a pre-Cambrian basement comprising granites and gneisses overlain by a Lower Cambrian uniform red protoquartzitic Nexø Sandstone Formation which gradually gives way to the shallow marine orthoquartzitic Hardeberga Sandstone Formation. The Lower Cambrian sandstone formations are overlain by a thin cover (1–5 m) of Quaternary glaciogenic deposits. The pre-Quaternary sandstones and bedrock have been exposed to extensive block faulting.

The main aquifer in the area is found in the Nexø Sandstone Formation which is a c. 115 m thick uniform red protoquartzitic sandstone, quartz-cemented, with

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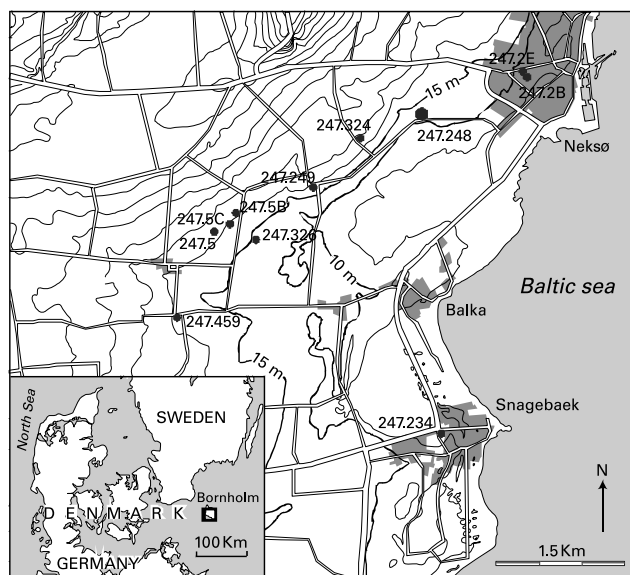


Figure 1 | Map of the study area at the east coast of Bornholm, Denmark, showing the location of well DGU 247.248 and other production wells in the well field of Neksø Municipal Waterworks. The equidistance between contours is 5 m.

subordinate contents of weathered feldspar. Primary intergranular porosity is insignificant and the main part of the porosity is found in numerous fractures, either parallel to bedding planes or at steep angles in individual sandstone beds (Skjernaa & Jørgensen 1993). A large number of shallow and deep water wells have been established in the area over time and most groundwater in the region is abstracted from the uppermost 20 m of the most fractured part of the sandstone.

Brackish groundwater and high salinity brines have been known since at least the turn of the 20th century from a large number of locations in the Fennoscandian (Baltic) Shield. Brackish groundwater has been observed in shallow wells (<200 m) drilled into the bedrock of the coastal areas of the Baltic Sea in both Finland and Sweden and Estonia. Most of these occurrences of brackish groundwater are located below the highest shorelines of the postglacial Flandrian transgression (7000–3000 yr BP) and owing to influence from the Baltic Sea and its precursors (Lindewald 1985; Kankainen 1986; Kankainen *et al.* 1987; Nurmi *et al.* 1988; Négrel *et al.* 2005). However, upconing of brackish formation water or high salinity brines from the crystalline basement has also been suggested (Karro *et al.* 2004; Négrel *et al.* 2005). It is the objective of the present study to evaluate the possible sources of brackish groundwater in

the fractured sandstone aquifer by combining hydrochemical characteristics and environmentally stable isotopes (^{18}O and ^2H), strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) and ^{14}C activities in the groundwater.

METHODOLOGY

Flow logs were carried out using a SEBA Mini Current Meter M1. A caliper log was performed with an MGX II Portable Digital Logger. Partial yield was calculated on the basis of corresponding well diameter and measured velocity flow using a velocity distribution factor of 1.5. Electrical conductivity logs were carried out by a WTW conductivity meter LF 197 standardised to 25°C. Electrical conductivities (EC) of groundwater samples and seawater were measured in the field by a WTW conductivity meter LF 197.

Water samples were collected in pre-rinsed polyethylene bottles. Water samples for major and minor ion analyses were filtered through a 0.45 μm pore diameter filter. Major cations (Na, K, Ca and Mg) were determined by atomic absorption spectrophotometry (AAS). Analyses of anions were carried out on a Dionex DX120 ion chromatograph. The accuracy of the analyses was estimated from electroneutrality (EN (%)) (Appelo & Postma 1996):

$$\text{EN}(\%) = (\sum \text{cations} + \sum \text{anions}) / (\sum \text{cations} - \sum \text{anions}) \times 100\% \quad (1)$$

which is within $\pm 5\%$ for all samples.

Twelve depth-specific water samples were collected for oxygen, hydrogen and strontium isotope analyses. The oxygen isotope ratio was determined by equilibration of 5 ml of sample with CO_2 gas as described by Epstein & Mayeda (1953). The analyses were carried out on a VG Sira 10 mass spectrometer with automatic inlet. The deuterium measurements on the water samples were carried out on a EuroVector elemental analyser (EA; EuroPtrOH-3100) with a EuroVector liquid autosampler (LAS; EuroAS-300) coupled to a Micromass IsoPrime isotope ratio mass spectrometer (IRMS) according to the method described by Morrison *et al.* (2001). The method uses the continuous flow technique where a constant flow of helium carries the water samples from EA to the mass spectrometer. The results for both isotopes are expressed in permil (‰) deviation from the VSMOW (Vienna Standard Mean

Ocean Water) standard using the δ scale according to the equation

$$\delta\text{‰} = [(R_{\text{sample}} - R_{\text{vsmow}})/R_{\text{vsmow}}] \times 1000 \quad (2)$$

where R is the particular isotopic ratio (i.e. $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$) for the sample and standard (Fritz & Fonte 1980). Reproducibility (1 SD) is better than $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and about $\pm 1\text{‰}$ for $\delta^2\text{H}$. Strontium for $^{87}\text{Sr}/^{86}\text{Sr}$ ratio analyses was separated from a 2.5N HCl solution by conventional ion exchange. Approximately $1\ \mu\text{g}$ SrCl_2 was mounted on tantalum filaments with phosphoric acid. The Sr isotopic composition was measured on an 8-collector Fisons Sector 54-30 mass spectrometer. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalized to an $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194. Within-run precision was typically ± 0.000005 (1 SD) on $^{87}\text{Sr}/^{86}\text{Sr}$ and always better than ± 0.000007 . In the course of data acquisition, the average value and precision of measured values of the international standard material NBS 987 were $^{87}\text{Sr}/^{86}\text{Sr} = 0.710245 \pm 0.000001$ (1 SD), $n = 12$.

The measurements of ^{14}C activities were performed on CO_2 gas expelled from the water samples by acidification with phosphoric acid (Boaretto *et al.* 1998). The CO_2 was converted to graphite and measured by accelerator mass spectrometry (AMS) at the tandem accelerator mass spectrometer at the AMS ^{14}C Dating Laboratory, Institute of Physics and Astronomy, Aarhus University.

The oxygen isotope analyses were determined at the Geophysical Institute, Copenhagen University. The hydrogen isotope analyses were performed at the Institute of Physics and Astronomy, University of Aarhus. Standard hydrochemical analyses of groundwater samples from production wells, Nexø Municipal Waterworks, were performed by Steins Laboratorium A/S. Determinations of major ions in groundwater samples collected from DGU 247.248 and strontium isotope ratios were made in the laboratory facilities at the Geological Institute and the Danish Centre for Isotope Geology at the University of Copenhagen.

RESULTS AND DISCUSSION

Flow log and caliper log

The well DGU 247.248 is 118m deep. The borehole lithological log shows 112m of Lower Cambrian Nexø

sandstone overlain by approximately 6 m of Pleistocene glaciogene till and fluvial sediments (Figure 2). The borehole is equipped with a 15 cm diameter steel casing in the unconsolidated glaciogene sediments, with open hole conditions in the Nexø Sandstone section. A caliper log was carried out in the open hole part of the section, i.e. 6–118 m below measuring point (bmp) (Figure 2). The borehole diameter is remarkably constant (Figure 2), i.e. 15–17 cm throughout the section studied. However, a few significant cavities are recorded at 112–116 m bmp, 97–98 m bmp and 48–50 m bmp and in the uppermost 5 m below the casing. The cavities found in the lower part of the sequence most likely represent fractures as the result of disintegration of intercalating layers of silts and clays in the sandstone, a phenomenon which is frequently observed in outcrops. The irregular cavities observed in the uppermost part of the sandstone reflect the pre-glacial weathered surface of the sandstone formation.

A flow log was performed with the fixed installation of a submersible pump at a depth 26 m bmp and with a constant yield of $16.3\ \text{m}^3/\text{h}$. The flow log covers only the interval 26–100 m bmp due to the limitation of the instrument and the position of the pump. The flow log indicates a partial yield of approximately $3\text{--}5\ \text{m}^3/\text{h}$ at a depth of 100 m bmp (Figure 3). There is a steady increase in the partial yield from 5 to $6\ \text{m}^3/\text{h}$ in the depth interval 100–75 m bmp, which reflects the fractures recorded in the lower part of

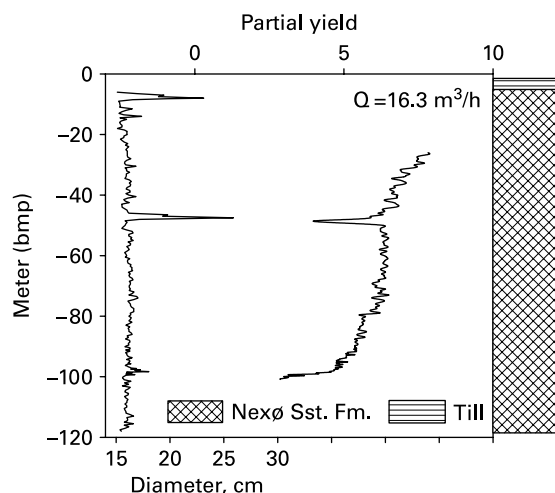


Figure 2 | Lithology, caliper log and flow log of well DGU 247.248, Nexø Municipal Waterworks. bmp: below measuring point.

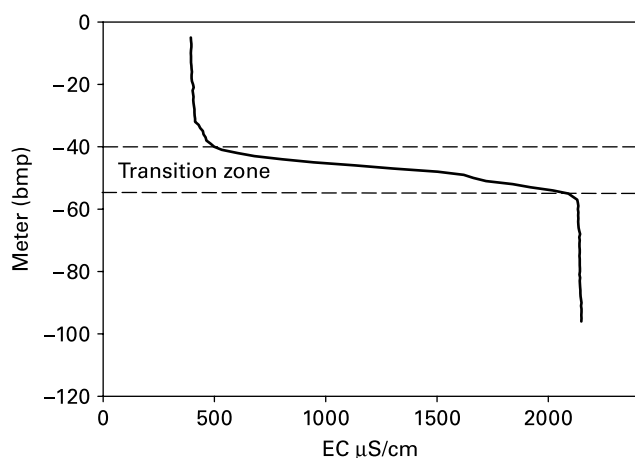


Figure 3 | Electrical conductivity log of well DGU 247.248, Neksø Municipal Waterworks. Note the significant halocline at 40–55 m bmp.

the sandstone sequence. The yield is relatively stable at $6\text{ m}^3/\text{h}$ in the depth interval 75–50 m bmp. At 48 m bmp there is a significant drop in flow velocity, which corresponds to the large cavity at this level shown by the caliper log (Figure 2). From 45 m to 26 m bmp, corresponding to the position of the pump, there is an increase in partial yield from 6.5 to $7.8\text{ m}^3/\text{h}$. The partial yield immediately below the pump is recorded as $7.85\text{ m}^3/\text{h}$, which corresponds to 48% of the total yield. It is believed that the occurrence of the cavity and the increase in partial yield from 46 m bmp and from 26 m bmp and upward represents the intensively fractured upper part of the aquifer. The results from the flow log indicate that 60% of the yield derives from this part of the aquifer, which is in accordance with our general understanding of the hydraulic properties of the sandstone aquifer (HOH Water Technology 1998).

Electrical conductivity log

Electrical conductivity logs in well DGU 247.248 were carried in the interval 6–96 m bmp. The electrical conductivity log reveals a significant stratification of the standing water body (Figure 3). The groundwater at shallow depth above c. 50 m bmp reveal an electrical conductivity at $400\text{--}500\text{ }\mu\text{S}/\text{cm}$ which is similar to what is generally recorded from other production wells in the study area. The depth interval 40–55 m bmp appears to be a transitional zone, a halocline, where the electrical conductivity

increases from $500\text{ }\mu\text{S}/\text{cm}$ to $1,900\text{ }\mu\text{S}/\text{cm}$. The electrical conductivity of the groundwater at greater depths is relatively stable but reveals a slightly increasing tendency with depth and reaches a maximum of $2,175\text{ }\mu\text{S}/\text{cm}$ at 96 m bmp (Figure 3). The position of the halocline is relatively stable over time although periodically influenced by pumping activities. However, it is assumed to be controlled by the major fracture observed at ~ 48 m bmp.

HYDROCHEMISTRY OF MAJOR IONS

The major ion hydrochemistry of groundwater samples obtained from well DGU 246.248 and from other boreholes in the well field are shown in Table 1. This can be divided into water types according to AQUACHEM and the distribution of major ions in the Piper diagram (Piper 1944) in Figure 4. Generally, groundwater from the well field is of the Ca-HCO_3 , Ca-Mg-HCO_3 water types. Two water wells (DGU 247.2e and DGU 247.326) show relatively high content of sulfate and are of the $\text{Ca-Na-HCO}_3\text{-Cl-SO}_4$ or $\text{Ca-HCO}_3\text{-SO}_4\text{-Cl}$ water types (Figure 4). The groundwater collected above the halocline in well DGU 247.248 is of the Ca-HCO_3 water type, corresponding to the general hydrochemical composition of the groundwater in the well field. However, groundwater samples collected below the halocline differ significantly from all other water samples, being of the Na-Ca-Cl-HCO_3 water type (Figure 4).

A plot of Na concentrations versus Cl concentrations is shown in Figure 5. The Na/Cl ratio is close to modern seawater composition for all the studied water samples. The relationship between the Na and Cl contents in water samples from above the halocline in well DGU 247.248 and from other boreholes in the well field corresponds to the seawater ratio of Na/Cl. Corresponding values of Na and Cl recorded from water samples below the halocline cluster around the seawater ratio, but it is important to note that the Na concentrations are rather constant in these samples whereas the Cl contents show a wide range of values (Figure 5).

Plots of the Ca/Na , Mg/Na and Cl/Na ratios versus depth in well DGU 247.248 are shown in Figure 6. The Cl/Na ratios are relatively constant and close to the seawater composition throughout the water column.

Table 1 | Major ion hydrochemistry of groundwater samples from well DGU 247.248 and other production boreholes in the well field of Neksø Municipal Waterworks. EN (%) (electroneutrality %) (Appelo & Postma 1996)

Well DGU no.	EC ($\mu\text{S/cm}$)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	HCO ₃ (mg/L)	Br (mg/L)	Sr (mg/L)	EN (%)
247.2E	756	36	6.3	90	23	46	73	320	0.75		0.24
247.5	653	14	5.2	102	10	29	47	274	0.48		2.91
247.5B	671	15	5.7	108	11	31	49	278	0.48		4.45
247.5C	586	15	4.0	93	8.1	30	52	216	0.53		4.98
247.249	702	27	3.3	99	16	47	53	323	0.37		-1.12
247.326	873	38	4.4	136	13	73	110	302	0.33		1.55
247.459	704	22	4.9	111	16	31	78	309	0.29		2.54
247.604	641	20	6.2	89	18	22	25	350	0.40		0.56
247.248 (meter bmp)											
5	435	10	1.8	87	6.3	18	42	256	0.15	0.2	-2.16
10	445	10	1.9	88	6.3	20	34	248	0.16	0.2	0.54
20	440	12	2.0	87	6.7	18	37	251	0.17	0.3	0.72
30	456	14	2.3	90	7.2	20	49	261	0.16	0.6	-0.86
40	540	24	2.7	93	8.7	32	51	312	0.21	0.8	-4.37
50	1850	229	12.6	99	30	405	41	319	2.91	2.8	0.60
60	2090	285	14.8	104	33	495	39	328	3.47	3.2	1.37
65	2120	290	14.9	100	34	460	43	333	3.34	3.4	3.50
70	2120	291	15.0	99	32	488	41	441	3.37	3.4	-2.61
75	2130	292	15.0	106	33	540	47	337	3.79	3.5	-1.42
80	2140	290	14.9	100	33	535	37	332	3.87	3.5	-1.36
85	2135	294	15.0	103	34	545	45	342	3.90	3.6	-1.99

The water samples above the halocline show an increase of the Ca/Na and Mg/Na ratios caused by the contribution from the overlying glacial deposits. The Ca/Na and Mg/Na ratios for the water samples below the halocline are remarkable constant, reflecting a homogeneous and well-mixed water body.

THE CHLORIDE/BROMIDE RATIO

The relatively inert and conservative elements, bromide and chloride, may be used to determine the likely origins and evolutions of groundwater and a bivariate diagram Cl/Br (wt) ratio vs Cl concentration may identify sources of salinity (Davis *et al.* 1998; Hernández-García & Custodio 2004; Rao *et al.* 2005). The Cl/Br (wt) ratio of modern seawater is ~290 (Davis *et al.* 1998) and the conservative behaviour of these two elements will result in values close to

this level for water types in near-coastal environments influenced by seawater intrusion and/or marine aerosols. Compared to oceanic seawater, Baltic Sea water is brackish, showing a wide range of salinities. However, the Cl/Br (wt) ratio is reported in the range 290–295, similar to that of oceanic seawater (Wilson 1975; Hyppä 1984). Groundwater affected by subsurface brines, dissolution of halites or anthropogenic influence may have characteristic Cl/Br ratios. A thorough discussion of the geochemistry of chloride and bromide in groundwater is presented by Davis *et al.* (1998).

It appears that groundwater in the Neksø Sandstone aquifer is remarkably enriched in Br compared to seawater composition (Figure 7). Two water types can be distinguished according to the Cl/Br ratios observed, suggesting different Br-rich sources that influence the groundwater composition in the aquifer. One water type has relatively constant Cl/Br ratios in the range from 100–150 and

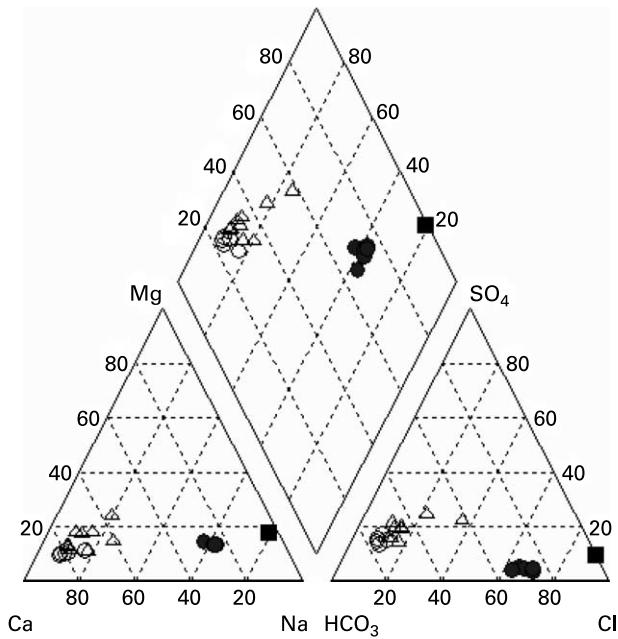


Figure 4 | Piper (1944) diagram showing the major ion hydrochemical compositions of the studied water types from the well field of the Neksø Municipal Waterworks. (●) Groundwater samples from below the halocline in well DGU 247.248. (○) Groundwater samples from above the halocline in well DGU 247.248. (Δ) Groundwater samples from other production wells in the well field. (■) Normal oceanic seawater composition (Hem 1985) is shown for comparison.

includes water samples from DGU 247.248 and the production wells DGU 247.249 and DGU 247.459. Only one borehole, DGU 2487.326, has a higher Cl/Br (wt) ratio of 223, which may indicate anthropogenic contributions of Cl to this sample (agricultural/fertilizer run-off). There are

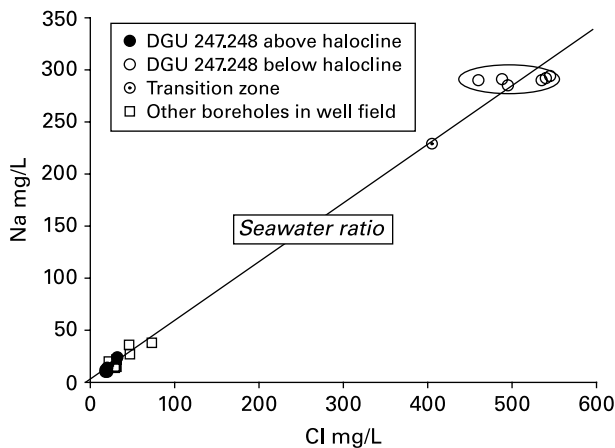


Figure 5 | Na concentrations versus Cl concentrations in DGU 247.248 and other boreholes from the well field of the Neksø Municipal Waterworks.

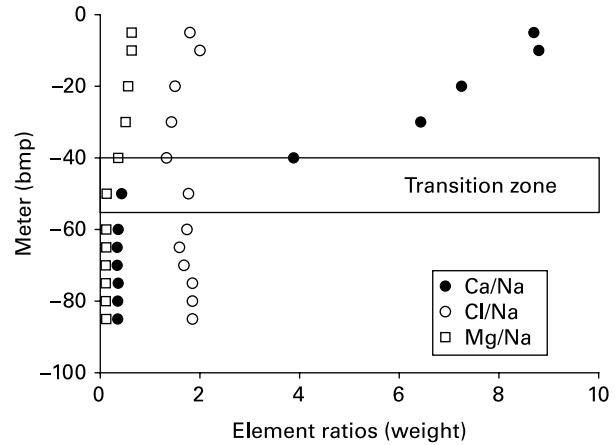


Figure 6 | Variations with depth of selected element/Na ratios in well DGU 247.248.

no significant differences in the Cl/Br ratios from water samples above and below the halocline in DGU 247.248. But it is worth noting that the Cl/Br ratios in water samples below the halocline are remarkably constant (Cl/Br (wt) ~ 140), which suggest that they have a common source.

The second water type reveals typically low Cl/Br ratios (Cl/Br (wt) 55–65) and are recorded in groundwater from the production wells DGU 247.2E, DGU 247.5, DGU 247.5B, DGU 247.5C and DGU 247.604 (Figure 7).

The Cl/Br (wt) ratio in a natural groundwater system typically has a wide range from 40–300 (Davis et al. 1998; Rao et al. 2005). Extraordinarily low Cl/Br ratios may indicate

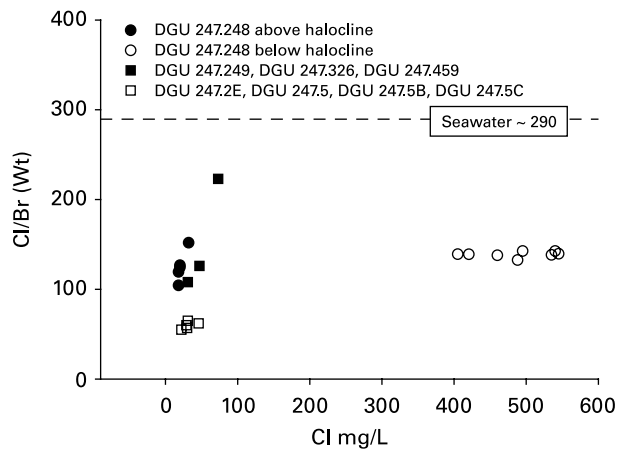


Figure 7 | Cl/Br (weight) ratios vs. Cl contents of water samples from well DGU 247.248 and other production boreholes in the well field of Neksø Municipal Waterworks. The Cl/Br (weight) ratio of normal oceanic seawater is shown for comparison.

degradation of Br-bearing organic matter or the presence of residual brines rich in Br in the subsurface. High Cl/Br (wt) ratios > 300 are considered to be the result of re-dissolution of evaporites as the source of Cl in the aquifer.

However, there are no lines of evidence for degradation of organic matter or residual brines rich in Br in the subsurface of the Neksø Sandstone aquifer. The Cl/Br (wt) ratios in the interval 100–150 are similar to ratios found by extracting Cl and Br from granites and metamorphic rocks (Davis *et al.* 1998) and, furthermore, it is noted that saline formation waters from the Scandinavian crystalline basement tend to have elevated Br concentrations relative to modern seawater (Nordstrom *et al.* 1989). Therefore, the concentration of Br in groundwater of the Neksø Sandstone aquifer points to the influence of saline formation water from the bedrock rather than seawater intrusion.

STABLE ISOTOPE (^2H AND ^{18}O) DISTRIBUTION

The vertical distribution of the stable oxygen and hydrogen isotopes is shown in Figure 8 and the results are given in

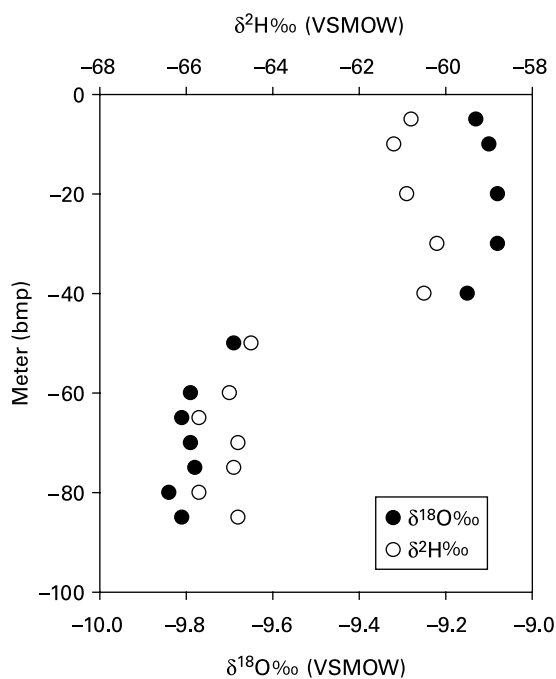


Figure 8 | Oxygen and hydrogen isotopic distributions in groundwater samples collected from well DGU 247.248, Neksø Municipal Waterworks. Note the differences in the isotopic compositions between the upper fresh groundwater body and the brackish groundwater below the halocline in the bottom of the well.

Table 2. Both isotopes reveal a significant stratification of the standing water body which is consistent with the results of the electrical conductivity logs and the major ion hydrochemistry. The relationship between oxygen and hydrogen isotopic compositions is shown in Figure 9. The Global Meteoric Water Line: $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$ (Craig 1961) and the isotopic compositions of seawater from the Baltic Sea and the North Sea are shown for comparison. The groundwater samples show isotopic values that plot slightly above the Global Meteoric Water Line and reveal two significant groups according to the stratification of the water body. The isotope compositions are fairly constant in groundwater samples above the halocline, i.e. $-9.1\text{‰} \delta^{18}\text{O}$

Table 2 | Stable isotope ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) compositions, strontium isotope $^{87}\text{Sr}/^{86}\text{Sr}$ ratio distributions and strontium contents in depth-specific water samples collected in well DGU 247.248, Neksø Municipal Waterworks

Well DGU no.		$\delta^{18}\text{O}$ (VSMOW) (‰)	$\delta^2\text{H}$ (VSMOW) (‰)
247.2E		-9.3	-62
247.5		-9.2	-61
247.5B		-9.2	-60
247.5C		-9.1	-62
247.249		-9.1	-61
247.326		-9.1	-62
247.459		-9.2	-61
247.604		-9.3	-62
247.248	$^{87}\text{Sr}/^{86}\text{Sr} \pm 2\text{SD}$		
5	$0.713\ 069 \pm 0.000\ 008$	-9.1	-61
10	$0.712\ 947 \pm 0.000\ 009$	-9.1	-61
20	$0.711\ 569 \pm 0.000\ 009$	-9.1	-61
30	$0.710\ 573 \pm 0.000\ 010$	-9.1	-60
40	$0.710\ 311 \pm 0.000\ 008$	-9.2	-61
50	$0.709\ 832 \pm 0.000\ 007$	-9.7	-65
60	$0.709\ 780 \pm 0.000\ 009$	-9.8	-65
65	$0.709\ 743 \pm 0.000\ 010$	-9.8	-66
70	$0.709\ 728 \pm 0.000\ 007$	-9.8	-65
75	$0.709\ 748 \pm 0.000\ 007$	-9.8	-65
80	$0.709\ 733 \pm 0.000\ 006$	-9.8	-66
85	$0.709\ 676 \pm 0.000\ 007$	-9.8	-65
Baltic Sea 1	$0.709\ 353 \pm 0.000\ 006$	-7.3	-54
Baltic Sea 2	$0.709\ 378 \pm 0.000\ 010$	-7.4	-53
North Sea	$0.709\ 232 \pm 0.000\ 008$	0.0	1

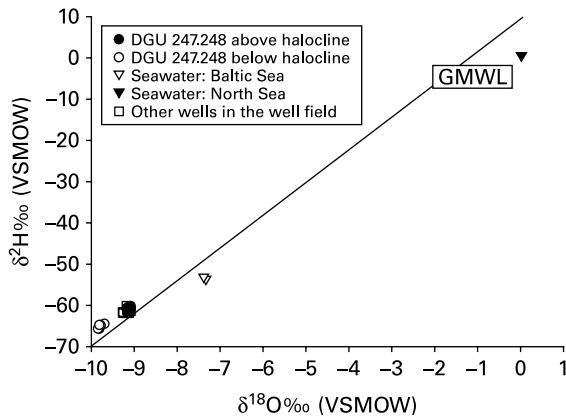


Figure 9 | Relations between $\delta^{18}\text{O}\text{‰}$ and $\delta^2\text{H}\text{‰}$ distributions for fresh and brackish groundwater collected from well DGU 247.248 and from other production wells in the well field. The Global Meteoric Water Line (GMWL) and the isotopic compositions of seawater from the present North Sea and Baltic Sea are shown for comparison.

and -61‰ $\delta^2\text{H}$, whereas groundwater samples collected below the halocline are slightly depleted showing $\delta^{18}\text{O}$ values between -9.7‰ and -9.8‰ $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the range from -64‰ to -66‰ $\delta^2\text{H}$ (Figures 8 and 9). The trend observed suggests that the brackish groundwater is infiltrated under cooler climatic conditions.

The relationship between the distributions of $\delta^{18}\text{O}$ and Cl concentrations is shown in Figure 10. The distributions of $\delta^{18}\text{O}$ and Cl in water samples above the halocline resemble the compositions recorded in other boreholes in the well field whereas the proportions in the water samples below the halocline are significantly different. No correlation exists between the two parameters, which suggests

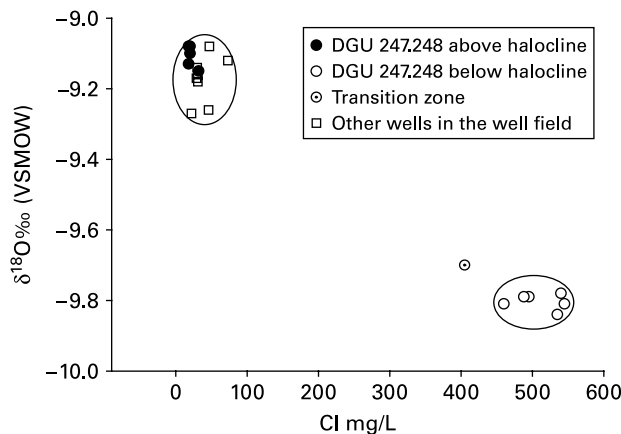


Figure 10 | The relation between $\delta^{18}\text{O}\text{‰}$ distributions and Cl concentrations in water samples collected in well DGU 247.248 and other production wells in the well field of Neksø Municipal Waterworks.

that the water bodies have different origins and that the compositional differences observed are not due to simple mixing processes between fresh water and brackish water.

The isotopic composition of North Sea seawater is close to the normal oceanic composition ($\sim 0\text{‰}$ δ for both isotopes), whereas the Baltic Sea water is significantly isotopically depleted (i.e. -7.4‰ $\delta^{18}\text{O}$ and -53‰ $\delta^2\text{H}$) in accordance to the brackish water conditions found in the shallow water body in the central part of the Baltic Sea off Bornholm as a result of the mixing of oceanic North Sea water and surface water run-off from the continents (Friedman *et al.* 1964; Ehhalt 1969; Fröhlich *et al.* 1988).

The stable isotopes are generally considered as being sensitive parameters to unveil possible mixing with seawater and seawater intrusion in groundwater systems. However, the stable isotopic compositions of the brackish groundwater below the halocline show no evidence of seawater influence.

STRONTIUM ISOTOPE ($^{87}\text{Sr}/^{86}\text{Sr}$) DISTRIBUTION

The vertical distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in water samples collected in well DGU 247.248 is presented in Table 2 and is shown in Figure 11. The Sr isotope ratios decrease significantly from 0.7131 to 0.7106 from the top of the water column downwards to 40 m bmp at the interface between fresh and brackish groundwater. The Sr isotope ratio is fairly stable but slightly decreasing below the

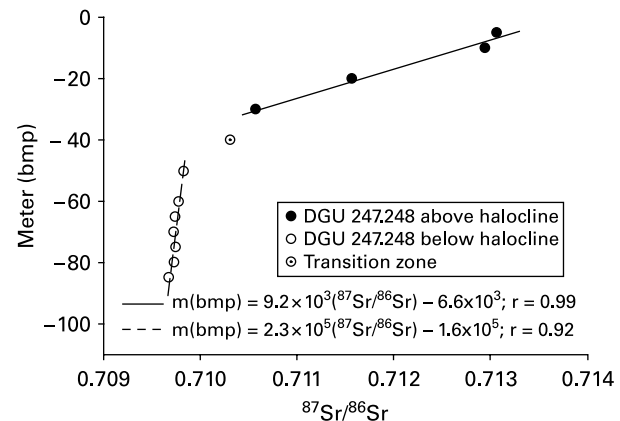


Figure 11 | The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio distributions with depth in groundwater samples collected from well DGU 247.248, Neksø Municipal Waterworks.

halocline from 0.7098 to 0.7097. The water sample in the transition zone at 40 m bmp reveals an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7103. The water samples above the halocline show a relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and depth that fit a regression line with the equation

$$M(\text{bmp}) = 9.2 \times 10^3 (^{87}\text{Sr}/^{86}\text{Sr}) - 6.6 \times 10^5 \quad (r = 0.99, n = 4) \quad (3)$$

The water samples below the halocline show a relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and depth that fit a regression line with the equation

$$M(\text{bmp}) = 2.3 \times 10^5 (^{87}\text{Sr}/^{86}\text{Sr}) - 1.6 \times 10^5 \quad (r = 0.92, n = 7) \quad (4)$$

There is a lack of correlation between the distributions of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios above and below the halocline which indicates the occurrences of two well-defined water bodies of different origins in well DGU 247.248. However, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for all groundwater samples are higher than that of seawater, which indicates that the major source of the Sr is the result of continental weathering of radiogenic Sr released from Sr-bearing silicate minerals in the host rocks like K-feldspar, plagioclase, hornblende and mica found in the protoquartzitic Neksø Sandstone and the underlying Proterozoic granitic crystalline basement. The greatest range in the Sr contents and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are observed in groundwater above the halocline and are assumed to be the result of a mixture of Sr derived from different sources with different Sr isotope compositions which also include contributions from the superjacent carbonate bearing glacial deposits (see Figure 6).

The relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $1/\text{Sr}$ is shown in Figure 12. It appears that the Sr concentrations in the water samples above the halocline fit a mixing line with the equation

$$^{87}\text{Sr}/^{86}\text{Sr} = 6.7 \times 10^{-4} (1/\text{Sr}) + 0.7094 \quad (r = 0.99; n = 4) \quad (5)$$

The data suggest that the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of groundwater in contact with the glacial deposits might be one of the end members of the mixing line. The other end member is most likely Sr released from weathered K-feldspar in the Neksø Sandstone, considering the shallow flow regime in the freshwater system.

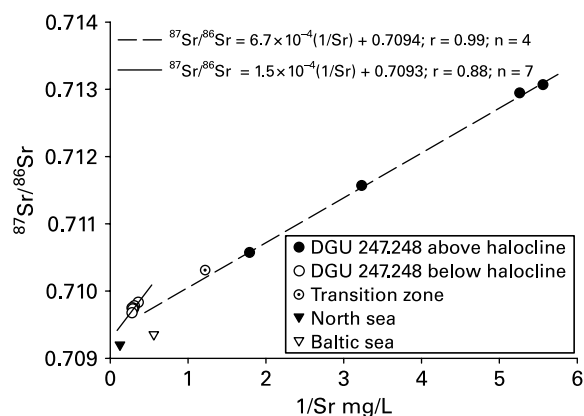


Figure 12 | Relation between $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and $1/\text{Sr}$ mg/L for groundwater samples collected from well DGU 247.248, Neksø Municipal Waterworks. The mixing line (regression line) and the Sr isotopic compositions of modern seawater from the North Sea and the Baltic Sea are shown for comparison.

The water samples below the halocline show a relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $1/\text{Sr}$ that fit a mixing line with the equation

$$^{87}\text{Sr}/^{86}\text{Sr} = 1.5 \times 10^{-4} (1/\text{Sr}) + 0.7093 \quad (r = 0.88; n = 7) \quad (6)$$

The end members of the mixing line cannot be identified. However, the low and constant Ca/Na ratios at ~ 0.35 that characterize the brackish groundwater (Figure 6) are in agreement with the Ca/Na ratio as a result of silicate weathering (Négre *et al.* 1993; Gaillardet *et al.* 1997) and the low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios may be indicative for plagioclase dissolution (Négre *et al.* 2003). The high Sr concentrations and the relatively constant $^{87}\text{Sr}/^{86}\text{Sr}$ signature of the brackish groundwater may represent the result of long-term water-rock interaction and suggest the occurrence of a large and well-mixed homogeneous deep reservoir in the crystalline basement. The trend is supported by Figure 13 that illustrates the relationships between $^{87}\text{Sr}/^{86}\text{Sr}$ and Cl/Na ratios. The groundwater above the halocline shows large fluctuations in both $^{87}\text{Sr}/^{86}\text{Sr}$ and Cl/Na ratios whereas the brackish groundwater is characterized by fairly constant values.

The Sr isotope ratios for North Sea seawater and seawater from the Baltic Sea off Bornholm are shown for comparison (Figure 12; Table 2). The North Sea seawater has an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.709194, which is in accordance with the composition of normal oceanic seawater at

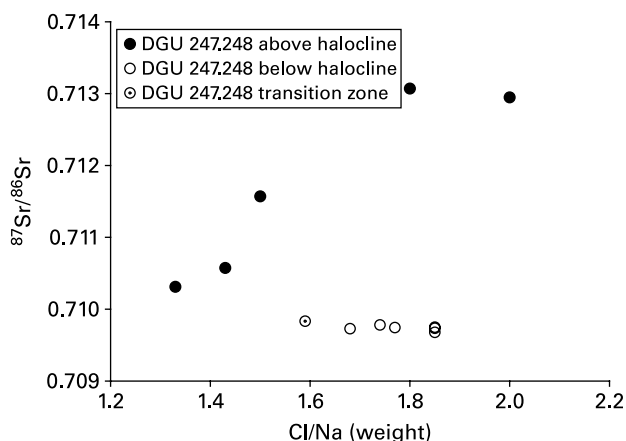


Figure 13 | Relationship between ⁸⁷Sr/⁸⁶Sr ratios and Cl/Na ratios in water samples from well DGU 247.248. The seawater ratio is shown for comparison.

~0.7092 (Faure 1986). Seawater samples from the Baltic Sea off Bornholm have Sr isotope ratios (⁸⁷Sr/⁸⁶Sr) of ~0.7094 and can be related to the Sr isotope values in the dissolved load from rivers draining the Precambrian Fennoscandian Shield in a mixing with normal oceanic seawater. The ⁸⁷Sr/⁸⁶Sr ratios presented in this study are consistent with the findings of Négrel *et al.* (2005) in a study of Baltic seawater. However, there is no obvious relationship between the ⁸⁷Sr/⁸⁶Sr compositions of modern seawater and the Sr isotope ratios in the two water bodies in well DGU 247.248 (Figures 12 and 13).

¹⁴C ACTIVITIES

The determination of ¹⁴C activities in dissolved inorganic carbon (DIC) was performed on water samples collected from above and below the halocline in well DGU 247.248 in order to estimate the groundwater ages. Furthermore, the

¹⁴C activities were measured in water samples collected from two other boreholes in the well field, well DGU 247.5 and well DGU 247.5B.

However, groundwater ages determined from measured ¹⁴C activities in (DIC) are based on the estimate of the initial concentration of ¹⁴C at the time of recharge and the subsequent modification of DIC during transport within the aquifer. Generally, these modifications dilute the ¹⁴C signal, which results in overestimation of the groundwater age. A number of correction models have been used to estimate groundwater ages (Clark & Fritz 1999; Kalin 2000) but they are all subject to uncertainties since substantial correction requires a profound knowledge of carbonate hydrochemistry in the recharge area, which generally is not available. Therefore, it is emphasized that the calculated apparent ¹⁴C ages are considered as residence time indicators and the values should not be taken at face value.

In this study the δ¹³C mixing model (Pearson & Hanshaw 1970) is adopted according to the application in Boaretto *et al.* (1998). The measured ¹⁴C activities are corrected for “dead” fossil carbonate dissolution assuming values of δ¹³C = 0‰ of formation carbonates (marine limestone) and δ¹³C = -25‰ for the root-zone CO₂. Furthermore, the dissolution processes is assumed to take place in a “closed system” scenario. In such case the corrected ¹⁴C concentrations are calculated from

$$^{14}C_{cor} = ^{14}C_{mes}(-25)/\delta^{13}C_{mes} \tag{7}$$

and the apparent ¹⁴C groundwater age is calculated from

$$A = A_0 e^{-\delta t} \tag{8}$$

The results are presented in Table 3. The measured stable carbon isotope ratios are given as δ¹³C in permil (‰)

Table 3 | ¹⁴C activities and δ¹³C distributions and calculated apparent ¹⁴C ages of groundwater samples collected from well DGU 247.248 and two other production boreholes in the well field of Neksø Municipal Waterworks

Well no.	Depth (meter bmp)	δ ¹³ C (VPDB) (‰)	¹⁴ C conc. pMC% measured	¹⁴ C conc. pMC% corrected	¹⁴ C age BP calculated apparent age
DGU 247.248	15	-16.3	78.0 ± 0.5	119	Modern
	49	-13.0	39.8 ± 0.3	77	2210
	85	-14.1	33.6 ± 0.3	60	4280
DGU 247.5	10	-13.5	66.3 ± 0.4	123	Modern
DGU 247.5B	10	-12.6	75.2 ± 0.5	149	Modern

relative to the VPDB standard. The measured ^{14}C concentrations are given in pMC (percent Modern Carbon) and the calculated apparent ^{14}C groundwater ages are relative to BP (Before Present: 1950). However, it is emphasized that the apparent groundwater age should be regarded as an estimated mean DIC age as result of groundwater mixing in the reservoir.

The ^{14}C activities of water samples from above the halocline and from other boreholes in the well field with comparably low EC values ($<700\ \mu\text{S}/\text{cm}$) reveal high ^{14}C concentrations, indicating post-bomb origin and, therefore, a relatively young groundwater generated not earlier than 1950. This figure is in accordance with CFC dating of groundwater samples from wells DGU 247.5, DGU 247.5b and DGU 247.5c, which yielded dates in the range 1970–1990 (HOH Water Technology 1998). However, groundwater samples collected below the halocline are found to be significantly older, with estimated apparent ^{14}C ages in the range from 2200 to 4300 yr BP and confirm the occurrences of two water bodies of different origins in the aquifer.

SOURCES OF THE BRACKISH GROUNDWATER

Occurrences of brackish groundwater and high salinity brines from a large number of locations in the Fennoscandian (Baltic) Shield have been known since at least the turn of the 20th century. High salinity brines have been described in particular from a number of locations in crystalline environments in Sweden and Finland, e.g. Äspö, Stripa and Palmottu, and hydrochemical and isotope geochemical investigations have been carried out to elucidate the origin of deep-seated saline groundwater in the basement (Nordstrom *et al.* 1989; Négrel *et al.* 2003, 2005). A comprehensive overview is given by Négrel *et al.* (2005). These studies confirm that high salinity brines are present below the depth of active groundwater flow systems in many crystalline environments.

Brackish groundwater has also been observed in shallow wells ($<200\ \text{m}$) drilled into the bedrock of the coastal areas of the Baltic Sea in Finland, Sweden and Estonia. These occurrences of brackish groundwater are below the highest shorelines of the postglacial Flandrian transgression (7000–3000 yr BP) and generally related in

origin to Holocene seawater trapped in the bedrock (Lindewald 1985; Kankainen 1986; Kankainen *et al.* 1987; Nurmi *et al.* 1988). However, it is also known that deep-seated brines may influence active aquifer systems in the basement and the overlying sandstone reservoirs (Karro *et al.* 2004; Négrel *et al.* 2005). The wide range of chemical and isotopic compositions of these saline formation waters and the different mixing trends observed have been explained by local water–rock interaction and several mixing scenarios of glacial to post-glacial meteoric water types and Baltic Sea water types (Négrel *et al.* 2005).

The groundwater samples collected below the halocline in DGU 247.248 show stable isotope compositions that plot close to the global meteoric water line (Craig 1961) and there is no trend in the stable isotopic compositions that may indicate affinity to a marine source. Furthermore, the Cl/Br ratio of the groundwater is appreciable lower than the seawater ratio and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios observed are again not consistent with a present-day marine origin. Therefore, the results indicate a meteoric origin and rule out seawater intrusion for the present-day brackish water environment of the Baltic Sea and its precursors.

The stable isotopic compositions of the brackish groundwater below the halocline are slightly depleted in comparison to the fresh groundwater and normal isotopic compositions of present-day Danish groundwater (Jørgensen & Holm 1994; Jørgensen 2002). Considering the apparent ^{14}C ages observed, the reason for the depleted isotopic composition of the brackish groundwater compared to fresh groundwater may reflect a slightly different and cooler climatologically regime during recharge conditions in the past. European palaeowaters are generally depleted in comparison to present-day groundwater, but significant depletion, up to $\sim 12\text{‰}$ $\delta^2\text{H}$, is primarily observed beyond c. 10,000 yr BP during the transition between the Holocene and the last glaciations (Rozanski 1985) as a result of colder climate recharge during the retreat of the Weichselian ice sheet. Isotopically depleted groundwater is recorded from many sites in the Baltic Shield and assumed to be the result of the influence of glacial melt water or cold climate recharge (Laaksoharju *et al.* 1999; Vaikmäe *et al.* 2001; Karro *et al.* 2004). Therefore, the isotopic depletion observed in water samples from below the halocline in DGU 247.248 is assumed to represent cold climate recharge.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for all groundwater samples are relatively high, indicating the major source of the Sr is relatively radiogenic Sr released from Sr-bearing silicate minerals found in the protoquartzitic Neksø Sandstone and the underlying Proterozoic crystalline basement. It is worthwhile to note that the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.713) are recorded in water samples collected in the uppermost part of the borehole in contact with the highly fractured and weathered part of the sandstone sequence. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ~ 0.7098 , which characterize the brackish water samples below the halocline, also show affinity to weathering processes of the crystalline basement rather than lateral intrusion of modern seawater. The appreciably higher Sr contents recorded in this water body point at long residence time and long-term effects of water–rock interaction. However, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of brackish water deviates significantly from that of fresh groundwater and may represent another source of Sr in the basement and different geochemical weathering conditions than the present-day scenario. Brackish groundwater has not been recorded at similar depth in any other borehole in the well field. Therefore, water–rock interaction is assumed to be the main source of the brackish groundwater and appears to be controlled by upward migration of mineralized palaeowater from the fractured crystalline basement.

CONCLUSIONS

The standing water column in well DGU 247.248 is stratified showing a freshwater/brackish water interface at approximately 40–55 m bmp. The stratification of the water body is a function of density variations and the position of the halocline is determined to a large extent by the flow pattern in the well primarily controlled by the significant fracture zone recorded at 48–50 m bmp.

The occurrence of two different water bodies in the aquifer is confirmed by hydrochemical investigation, the isotopic distributions (^{18}O , ^2H and $^{87}\text{Sr}/^{86}\text{Sr}$) and the ^{14}C activities in the water column. The water body above the halocline is of Ca– HCO_3 /Ca–Mg– HCO_3 water types and the stable isotope composition is similar or close to that of the fresh young groundwater in the aquifer. The brackish groundwater below the halocline is characterized by an

Na–Ca–Cl– HCO_3 water type reaching a maximum of 550 mg/L Cl and show deviating isotopic signatures.

The groundwater is remarkably enriched in Br compared to the seawater composition and the low Cl/Br ratios exclude marine origin and re-dissolution of evaporites as the source of Cl in the aquifer. The Cl/Br (wt) ratio of the brackish groundwater is remarkably constant at ~ 140 and is similar to ratios found by extracting Cl and Br from granites and metamorphic rocks and at a size of the order of that recorded from saline waters from the Scandinavian crystalline basement. Thus, the concentration of Br in groundwater of the Neksø Sandstone aquifer points at the influence of saline formation water from the bedrock.

The stable isotopic compositions (^{18}O and ^2H) indicate a meteoric origin of the brackish groundwater and again rule out seawater intrusion from the present-day Baltic Sea and its precursors. The brackish groundwater is slightly depleted in comparison to normal Danish groundwater and, furthermore, shows apparent ^{14}C ages in the range from 2200 to 4300 yr BP. The positive association is assumed to reflect a cooler climatologically regime during recharge conditions in the past.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the fresh as well as the brackish groundwater is distinctly higher than that of seawater. The enhanced EC and the high Sr contents and the low ^{14}C concentrations suggest that the brackish groundwater in the deeper part of the aquifer is the result of long residence time and the effects of long-term water–rock interactions. Furthermore, the fairly constant and specific $^{87}\text{Sr}/^{86}\text{Sr}$ signature at ~ 0.7098 and high constant Sr concentrations demonstrate the occurrence of a large and well-mixed homogeneous deep water reservoir in the Neksø Sandstone and/or in the crystalline basement. Brackish groundwater has not been recorded at similar depth in any other borehole in the well field. Therefore, it is assumed that the contribution of brackish groundwater is due to local derived upward migration of mineralized palaeowater in the fractured aquifer matrix rather than lateral intrusion of modern seawater.

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