
The origin of increased salinity in the Cambrian-Vendian aquifer system on the Kopli Peninsula, northern Estonia

Enn Karro · Andres Marandi · Rein Vaikmäe

Abstract Monitoring of the confined Cambrian-Vendian aquifer system utilised for industrial water supply at Kopli Peninsula in Tallinn over 24 years reveals remarkable changes in chemical composition of groundwater. A relatively fast 1.5 to 3.0-fold increase in TDS and in concentrations of major ions in abstracted groundwater is the consequence of heavy pumping. The main sources of dissolved load in Cambrian-Vendian groundwater are the leaching of host rock and the other geochemical processes that occur in the saturated zone. Underlying crystalline basement, which comprises saline groundwater in its upper weathered and fissured portion, and which is hydraulically connected with the overlying Cambrian-Vendian aquifer system, is the second important source of ions. The fractured basement and its clayey weathering crust host the Ca-Cl type groundwater, which is characterised by high TDS values (2–20 g/L). Intensive water abstraction accelerates the exchange of groundwaters and increases the area of influence of pumping. Chemical and isotopic studies of groundwater indicate an increasing contribution of old brackish water from the crystalline basement and rule out the potential implication of an intrusion of seawater into aquifer.

Résumé L'origine de la salinité croissante dans le système aquifère du Cambrien-Vendien dans la péninsule de Kopli, nord de l'Estonie

Le suivi à long terme du système aquifère captif du Cambrien-Vendien utilisé pour l'approvisionnement

d'eaux industrielles dans la Péninsule de Kopli, nord de l'Estonie, révèle de remarquables changements dans la composition chimique des eaux souterraines. Une augmentation de facteur 1.5 à 3 de la TDS et des concentrations de ions majeurs dans l'eau souterraine est la conséquence de pompages intensifs. Les sources principales des charges dissoutes dans les eaux de l'aquifère du Cambrien-Vendien sont le lessivage des roches et d'autres phénomènes géochimiques ayant lieu dans la zone saturée. Le soubassement rocheux cristallin, qui renferme des eaux souterraines salines dans sa partie supérieure altérée et fissurée, et est hydrauliquement connecté avec l'aquifère supérieur du Cambrien-Vendien, est la deuxième importante source d'ions. Le soubassement fracturé et le matériel argileux de l'altération, renferme l'eau souterraine de type Ca-Cl, caractérisée par un haut TDS (2–20 g/l). A cause de la mobilisation intensive de l'eau les échanges d'eau souterraine est sont accélérés et la zone d'influence des pompages augmentent. Les études chimiques et isotopiques indiquent une contribution croissante du drainage des eaux du soubassement cristallin. L'intrusion d'eaux salées de la mer dans le système aquifère n'est pas un phénomène évident.

Resumen El origen del incremento en salinidad en un sistema de acuíferos Cámbrico-Vendiano en la Península Kopli, norte de Estonia

Monitoreo a largo plazo de un sistema de acuíferos confinados, de edad Cámbrico-Vendiano, que se utiliza como fuente de abastecimiento industrial en la Península Kopli, al norte de Estonia, revela cambios notables en la composición química del agua subterránea. Un incremento de 1.5 a 3 veces en TDS y en concentraciones de iones mayores en agua subterránea explotada ha sido ocasionado por bombeo fuerte. Las fuentes principales de carga disuelta en el agua subterránea Cámbrico-Vendiano son la lixiviación de la roca encajonante y los procesos geoquímicos que ocurren en la zona saturada. Basamento cristalino subyacente, que aloja agua subterránea salada en la parte superior intemperizada y fisurada, y está conectado hidráulicamente con el sistema acuífero Cámbrico-Vendiano sobreyacente, es la segunda fuente importante de iones. El basamento fracturado y su corteza de intemperismo arcillosa alojan agua subterránea de tipo Ca-Cl la cual se caracteriza por valores altos de TDS (2–20 g/l). Debido a extracción intensiva se ha acelerado el

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E. Karro (✉) · A. Marandi
Institute of Geology,
University of Tartu,
Vanemuise 46, 51014 Tartu, Estonia
e-mail: ekarro@ut.ee
Tel.: +372-7-375896
Fax: +372-7-375836

R. Vaikmäe
Institute of Geology,
Tallinn Technical University,
Estonia pst. 7, 10143 Tallinn, Estonia

intercambio de agua subterránea y se ha incrementado el área de influencia del bombeo. Los estudios químicos e isotópicos de agua subterránea indican una contribución creciente por filtración derivada del basamento cristalino. Es evidente una intrusión de agua salada hacia el sistema de acuíferos con implicaciones subsecuentes para la calidad del agua.

Keywords Coastal aquifers · Over-abstraction · Salinization · Estonia

Introduction

Overexploitation of aquifers is an issue which is becoming common in water-resources management and which underlines the risks related to groundwater development (Custodio 2002). In practice, an aquifer is often considered as overexploited when some persistent negative results of aquifer development are felt or perceived, such as a continuous water-level drawdown, progressive water-quality deterioration, increase of abstraction cost, or ecological damage.

Intruded saline water may irreversibly change the development of groundwater resources, whether it is seawater encroaching into overexploited aquifers in coastal areas (Chen et al. 1997; Giménez and Morell 1997; Steinhilber et al. 1998; Yakirevich et al. 1998; Cruz and Silva 2000; Martínez and Bocanegra 2002) or older saline groundwater upconing in response to pumping of an overlying layer of fresh water (Karro 1999). Coastal groundwater aquifers are particularly threatened by salt-water intrusion from both sources (Mitrega and Lahermo 1991; Petalas and Diamantis 1999).

Salinization is the most widespread form of water contamination. This process leads to an increase in the content of certain dissolved chemical species, as well as to the overall change in chemical water composition (Richter and Kreitler 1993). An increase in the dissolved components in the groundwater, especially chloride and sodium, has been observed in many wells drilled into bedrock along coastal regions of Estonia (Yezhova et al. 1996; Vallner and Savitskaja 1997; Mokrik 1997, 2000). The most serious consequences of intensive groundwater use in North Estonia include the formation of regional depressions of potentiometric level in the Cambrian-Vendian aquifer system, which is the primary source of public water supply in this region (Perens and Vallner 1997). In Harju county, the share of Cambrian-Vendian groundwater in total groundwater consumption is about 75% (Savitskaja 1999). Overexploitation has caused the changes in the direction and velocity of groundwater flow. Northward regional groundwater flow has been replaced with radial flow towards the centre of the piezometric depression located 10 km to the south from the coast in the Tallinn area. As a result, lateral and rising groundwater flows conduce the transport of brackish water from the deeper portion of the aquifer system and underlying crystalline basement or seawater intrusion to

groundwater intakes (Yezhova et al. 1996; Vallner and Savitskaja 1997; Mokrik 1997; Savitski 2001a).

Thus, the origin of the salinity of Cambrian-Vendian groundwater on the Kopli Peninsula in Tallinn might be due to: (1) intrusion of present-day seawater; (2) pumping-induced upconing of brackish water from below the freshwater or (3) a combination of the two. The purpose of this study is to evaluate the possible causes for the increase in the content of dissolved solids in groundwater.

Geological and Hydrogeological Setting

Estonia is situated in the northwestern part of the East-European Platform. Structurally, its sedimentary beds, lying on the southern slope of the Baltic Shield, are declined southwards at about 3–4 m/km. The Estonian crystalline Paleoproterozoic basement is overlain by Neoproterozoic (Vendian) and Palaeozoic (Cambrian, Ordovician, Silurian and Devonian) sedimentary rocks (Fig. 1) covered by Quaternary deposits (Raukas and Teedumäe 1997).

On the Kopli Peninsula in the northern part of Tallinn City (Fig. 1), the Vendian and Cambrian sedimentary rocks cover the crystalline basement which lies at an approximately depth of 130 m. The crystalline basement, consisting mostly of rapakivi type porphyritic granites, is in its upper portion fractured and weathered. Rämö and Haapala (1995) define rapakivi granite (most widespread type of granite in the bedrock in Finland) as A-type granite, characterised by bimodal (mafic-silicic) magmatic association, and distinctive mineralogy (very high Fe/(Fe+Mg) in the mafic silicates, fluorite as common accessory mineral) and rock chemistry (high K, K/Na, F). Weathering profiles of granites are composed predominantly of kaolinite, illite, chlorite and montmorillonite, depending on the original bedrock composition and the intensity of weathering. Weathered basement rocks are overlain by Vendian and Cambrian siltstone and sandstone, which in northeastern Estonia are divided by a clay layer of the Kotlin Formation into the Voronka and Gdov aquifers (Fig. 2). The upper, Voronka aquifer, consists of quartzose sandstone and siltstone having hydraulic conductivity of 0.6 to 12.5 m/d and transmissivity of 100–150 m²/d (Perens and Vallner 1997). The lower, Gdov aquifer, is formed of mixed-grained sandstone and siltstone, with a hydraulic conductivity varying between 0.5–9.2 m/d and a transmissivity of about 300 m²/d (Perens and Vallner 1997). The thickness of the Kotlin aquitard decreases westward and the unit is not present in the Kopli area. Therefore the Vendian and Cambrian water-bearing rocks here can be handled as one aquifer system with a thickness of 50 to 60 m (Fig. 2).

The Cambrian-Vendian aquifer system is covered by clays of the Lower Cambrian Lontova Formation, which forms the laterally continuous Lontova aquitard (Fig. 2). This aquitard has a strong isolation capacity, as its vertical hydraulic conductivity is predominantly 10⁻⁷–10⁻⁵ m/d (Perens and Vallner 1997). The Lontova clays are 60–

Fig. 1 Schematic map of the study area showing the location of Estonia (a), Kopli Peninsula on the background of the Estonian geological map (b) and the position of the studied wells on the Kopli Peninsula and the line of hydrogeological cross-section (c)

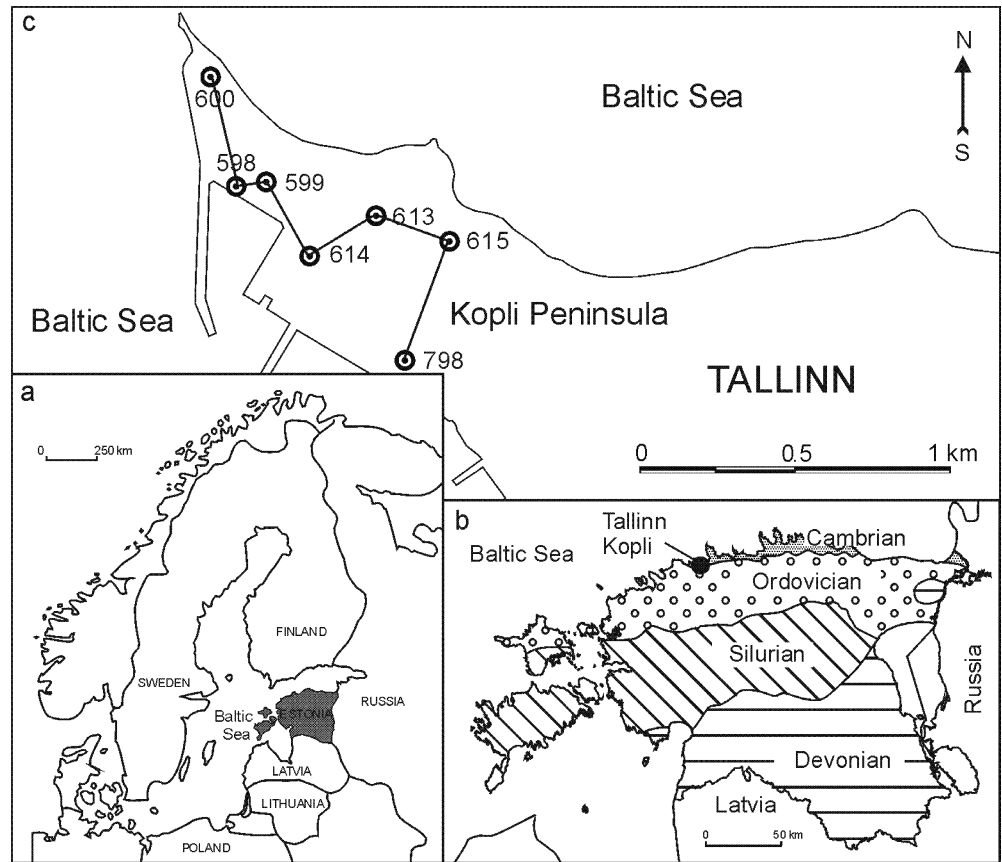
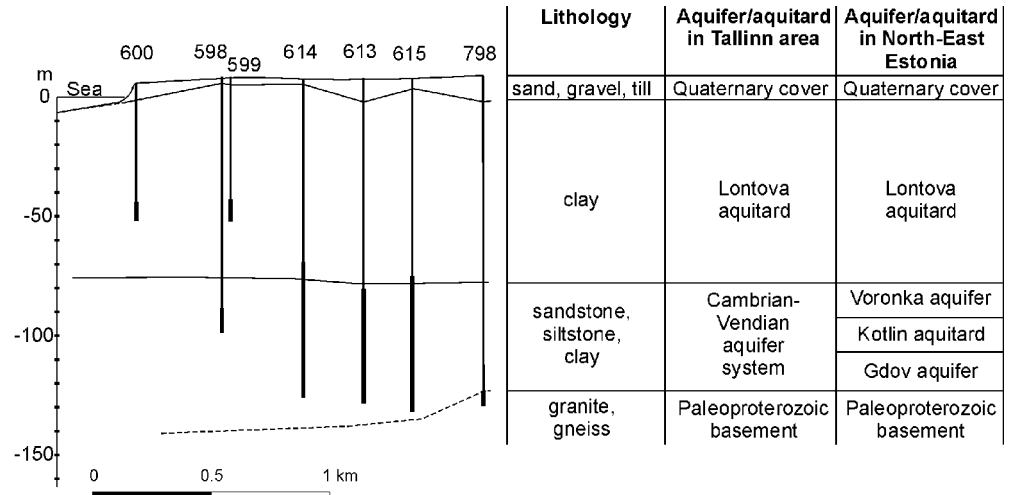


Fig. 2 Hydrogeological cross-section of the Cambrian-Vendian aquifer system and the position of wells at Kopli Peninsula, northern Estonia. Line of section shown in Fig. 1. Segment in *bold* marks the well screen



70 m thick on the Kopli Peninsula (Fig. 2). The crystalline basement of the Baltic Shield is sloping southwards at 3–4 m/km in the study area. Thus, the overlying water-bearing Cambrian and Vendian sedimentary rocks as well as clays of the Lontova Formation pinch out in the Baltic Sea bottom, about 20 km north of the coastline.

Erosional processes in pre-Quaternary time, during interglacial and in late- and postglacial times have formed erosional valleys, cutting through the Lontova aquitard (Tavast 1997). These ancient buried valleys are filled with Quaternary sediments, mostly till, but marine, glacioflu-

vial and glaciolacustrine sediments are also present. The valleys are oriented north-west to south-east, thus being approximately perpendicular to the North-Estonian coastline. Based on stable isotope and radiocarbon analyses, Vaikmäe et al. (2001) have shown that in places, where groundwater is intensively abstracted, these valleys provide the Cambrian-Vendian aquifer system with infiltrated modern water. The intrusion of modern water through the valleys has been detected earlier by the change of Cl^- concentration in groundwater of the Cambrian-Vendian aquifer system (Savitskaja and Viigand 1994). On aver-

age, the chloride concentration in the Cambrian-Vendian groundwater is in the range of 100–600 mg/L. Through the mixing with infiltrating modern water the chlorine concentration in the aquifer has decreased to values less than 100 mg/L.

The Cambrian-Vendian aquifer system recharges in South Estonia and flows northward towards the discharge areas, which are situated in the depressions of the Baltic Sea and the Gulf of Finland. The calculated velocity of groundwater movement (Vallner 1997) in the aquifer system is very low (5×10^{-4} to 5×10^{-3} m/d) and mean residence times are on the order of tens of thousands of years under natural conditions. However, the model calculations showed that intensive groundwater abstraction in North-Estonian coastal areas in the 1980s has enhanced the northward movement of Cambrian-Vendian groundwater (Vallner 2003). Thick clays of the Lontova Formation cover the aquifer system and form the laterally continuous Lontova aquitard, which has a strong isolation capacity. Therefore the groundwater in the Cambrian-Vendian aquifer system, as a rule, is not affected by present day infiltration and the main control on the water chemistry is the geochemistry of the sediment through water-rock interaction.

The Cambrian-Vendian aquifer system can be divided in two main zones containing groundwater with totally different origin and baseline chemical composition.

In southern and central Estonia the aquifer system contains relict saline groundwater of marine origin with TDS values of up to 22 g/L. Cl^- and Na^+ predominates over all other ions in this zone (Karise 1997). In northern Estonia the Cambrian-Vendian aquifer system contains paleogroundwater, which recharged during the last glaciation more than 10,000 years BP by subglacial drainage through the aquifers (Vaikmäe et al. 2001; Piotrowski 1997). This was fresh water with total dissolved solids values mainly below 1.0 g/L. The baseline chemical composition of the water was formed through the water-rock interaction during the last more than 10,000 years. The most characteristic feature of the baseline quality of groundwater of the Cambrian-Vendian aquifer system in northern Estonia is its lightest known oxygen isotopic composition in Europe (Edmunds et al. 2001; Mokrik 1997; Vaikmäe et al. 2001; Yezhova et al. 1996). These waters have $\delta^{18}\text{O}$ values between -18 and -22‰ , while the oxygen isotope composition of groundwater in most of the aquifer systems in Estonia ranges from -11.0 to -12.2‰ (Vaikmäe and Vallner 1989) and the long-term mean annual $\delta^{18}\text{O}$ values in contemporary meteoric water in Estonia are -10.4‰ (Punning et al. 1987). Thus, the isotopic composition of groundwater can be used as an ideal tracer of changes in groundwater baseline quality.

Materials and Methods

This investigation is based mainly on the groundwater monitoring data collected during years 1978 to 2002 from four groundwater production (598, 613, 614, 615) and 3

monitoring (798, 599, 600) wells. Groundwater production wells (598, 613, 614, 615) trapping the Cambrian-Vendian aquifer system at Kopli Peninsula are situated close to the sea (Fig. 1c). The depth of the wells in water supply plants range between 107 to 140 m (Fig. 2) and they are screened in nearly the full thickness of the aquifer system (except well 598). The amount of abstracted groundwater varied from year to year, between 10 to 1,300 m^3/d during 1951–2002. For comparison purposes, groundwater monitoring well 798 (138 m) (Fig. 1 and 2) penetrating into the fractured basement, and monitoring wells 599 (60 m) and 600 (59 m) open in the Lontova Formation were included into study.

Water samples were obtained and the analyses were performed by the Geological Survey of Estonia, the institution responsible for groundwater monitoring using the national observation network and for compiling the registries of groundwater data in Estonia. The historical data include pH, TDS, anions (HCO_3^- , SO_4^{2-} , Cl^-), cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), nitrogen compounds, iron and SiO_2 . One to three chemical analyses per year for each well are available. Seventeen wells of the Cambrian-Vendian aquifer system in northern Estonia were sampled for major and trace ions as well as isotopic investigations in 2001. Six of the sampled wells are located on the Kopli Peninsula and the results of analyses from those wells (598, 599, 600, 613, 614, 615) are used in the current study. In situ, pH, redox potential, electrical conductivity and temperature also were measured. Water samples were taken only after pumping of 2–3 well volumes and stabilisation of field parameters. All samples for ion analysis were filtered and acidified with nitric acid (1%) to stabilise trace elements.

Isotope analyses were conducted in the Laboratory of isotope-palaeoclimatology of the Institute of Geology at Tallinn Technical University. The conventional equilibration technique was used to prepare water samples for oxygen isotope ($\delta^{18}\text{O}$) analyses (Epstein and Mayeda 1953). All measurements were carried out on the Finnigan MAT Delta E mass spectrometre and data are expressed in $\delta\text{‰}$ notation relative to international water standard V-SMOW with standard errors $\leq 0.1\text{‰}$.

Dissolved carbonate samples for radiocarbon (^{14}C) analyses were collected by precipitation of BaCO_3 from 165 to 250 L (depending on carbonate concentration) of groundwater samples, made alkaline with NaOH (Gupta and Pollach 1985). Analyses were performed by liquid scintillation technique on samples converted to benzene, providing an accuracy of about ± 0.5 pmC. Separate samples were collected for $\delta^{13}\text{C}$ analyses and measured by mass spectrometry. These data are expressed in $\delta\text{‰}$ notation relative to international PDB standard with standard errors of $\leq 0.06\text{‰}$.

For data processing, interpretation and hydrogeochemical assessment of the results, MapInfo Professional 6.0 and AquaChem 3.7 were used.

Results and Discussion

Salinity and Hydrochemical Characterisation

The Cambrian-Vendian aquifer system of Kopli Peninsula is very well protected from downward infiltration of modern water by the Lontova aquitard ($K=10^{-7}$ to 10^{-5} m/d), thus anthropogenic contamination does not affect the groundwater chemistry. However, overpumping the aquifer constitutes a potential anthropogenic disturbance of the natural chemical balance in groundwater.

Fresh groundwaters of the Na-Ca-HCO₃-Cl type characterize the upper part of the aquifer system in the study area as well as in the whole Tallinn region (Perens et al. 2001) owing to the hydrochemical differentiation and to stratification due to density differences of water types. The lower part of the Cambrian-Vendian aquifer system and the weathered crystalline basement are characterized by groundwaters of Na-Ca-Cl-HCO₃ and Ca-Na-Cl types with TDS content of 1.4 to 5.0 g/L. The groundwater in the upper part (−80 m a.s.l.) of the aquifer system has 100 mg/L of chlorine, which increases with depth, 100 and 130 m water samples have 350 and 2,500 mg/L, respectively (Savitski 2001a; Boldõreva et al. 2002).

Groundwater abstraction at Kopli Peninsula started in the 1950s, when production wells 613, 614 and 615 were drilled. The amount of abstracted groundwater varied between 400 to 900 m³/d (613, 614) and 200 to 1,300 m³/d (615) during 1951–1992 (Fig. 3). The potentiometric surface of the Cambrian-Vendian aquifer system was lowered 17 m in the Kopli Peninsula by 1992 due to the intensive water abstraction (Savitski 2001a). A decrease in groundwater extraction started in the 1990s (Fig. 3) with the decline of industrial and agricultural production and more sustainable use of groundwater. During the last 10 years the potentiometric surface of the aquifer system has steadily recovered and is now −4.0 m a.s.l (Savitski 2001b). Well 598 was drilled in 1997 and operates with low pumping rate −25–40 m³/d.

Large-scale variations of TDS (0.48–1.55 g/L) and major ion concentrations in the water of production wells (598, 613, 614, 615) are clearly visible during 1978–2002 (Fig. 4, Table 1). Permissible concentrations of major components in water set by the Estonian drinking water standard (Joogivee 2001) and Drinking Water Directive of European Union (98/83/EEC) have been exceeded. The maximum values presented in Table 1 describe the water chemistry in the 1990s. Later, the content of dissolved compounds in groundwater shows a slightly decreasing trend in well 613, reflecting the decrease in pumping rate (Figs. 3 and 4). The most clear and remarkable temporal changes in water chemistry have occurred particularly in well 613, where the content of TDS has reached 1.5 g/L at a rate of 50 mg/L/year. The analogous trends in TDS values can be observed in wells 614, 615 and 598, but with a fairly smoother character. The minimum values in Table 1 mark the “initial” chemical composition of groundwater. Term “initial” is placed into quotation marks due to the fact that the first groundwater samples

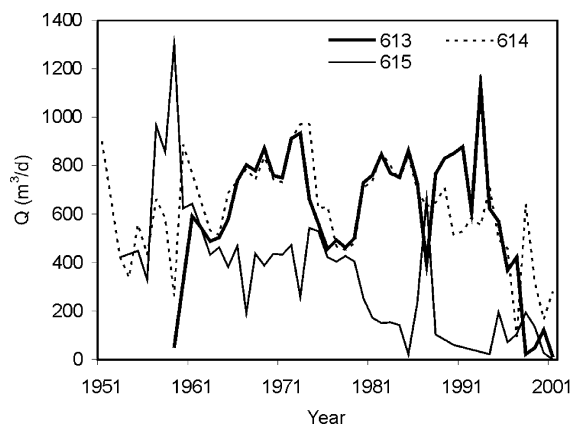


Fig. 3 Groundwater extraction (m³/d) from three production wells on the Kopli Peninsula during 1951–2002

for chemical analyses were taken approximately 25 years after the start of groundwater abstraction (1950s). Thus, it might be only supposed that real initial groundwater in the Cambrian-Vendian aquifer system of the Kopli Peninsula was more dilute than this one analysed in 1978.

The major ions constitute the bulk of the mineral matter contributing to TDS. Accordingly, Na⁺, Ca²⁺ and Cl[−] concentrations in groundwater display the same increasing/decreasing trends as TDS (Fig. 4). The only exception is HCO₃[−], for which values have the narrowest amplitude of fluctuation (Table 1). Quite stable HCO₃[−] concentration is the reason why at high TDS values the bicarbonates remain insignificant in the determination of groundwater chemical types. When TDS exceeds 0.9 g/L, Cl type waters dominate.

Major ion chemistry of sampled groundwater is examined as a whole using the Piper diagram (Fig. 5). It shows slight variations in relations between main cations and anions in the aquifer systems. The change towards the more Ca-Cl dominating groundwater is visible. The water types I to III on the diagram represent an attempt to synthesise the groundwater chemistry. In reality there are no sharp boundaries between water types, and the progression from group I to III represents the evolution of waters with an increasing degree of water-rock interaction and mixing with brackish water from the crystalline basement.

Group I on Piper diagram can be interpreted as “background” water of the Cambrian-Vendian aquifer system, comprising the analytical results of 30 water samples from an area of 400 km² south from Tallinn (Savitskaja 1999). It represents slowly northward flowing Ca-Na-HCO₃-Cl or Ca-Na-Cl-HCO₃ type groundwater, not influenced by heavy pumping. Groundwater at Kopli Peninsula probably had similar chemical character before pumping. Group III describes the water chemistry in the crystalline basement (observation well 798). Water analyses from four abstraction wells (598, 613, 614, 615) open in the Cambrian-Vendian aquifer system at Kopli Peninsula form group II on Fig. 5. In spite of the considerable increase in TDS and major chemical compounds in

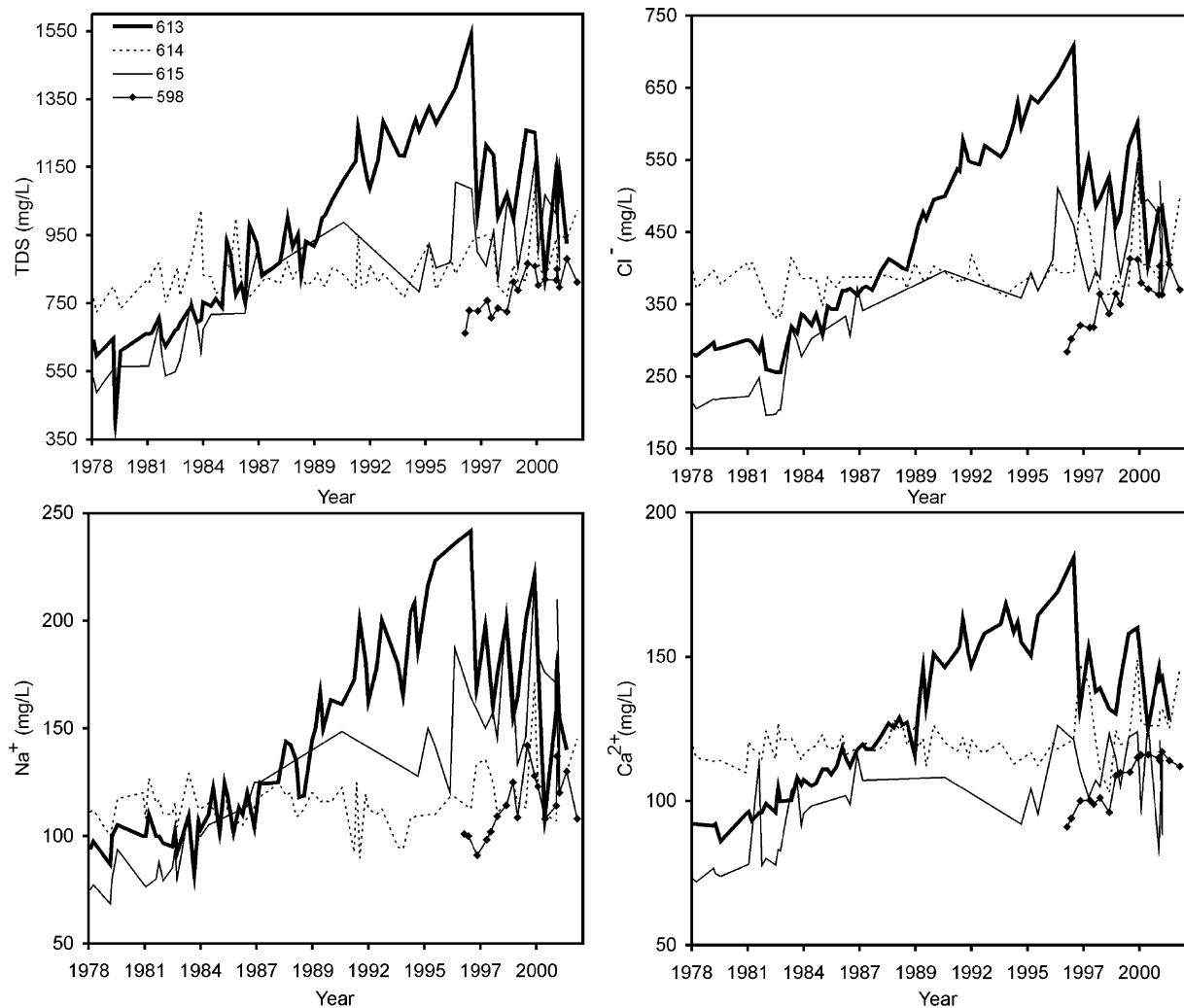


Fig. 4 Temporal changes in TDS, Cl⁻, Na⁺ and Ca²⁺ content in groundwater abstraction wells

Table 1 Statistical summary (range and mean values) of the historical data including concentrations (mg/L) of major chemical compounds and TDS in the studied wells, Koplí Peninsula. Analyses from 1978 to 2002

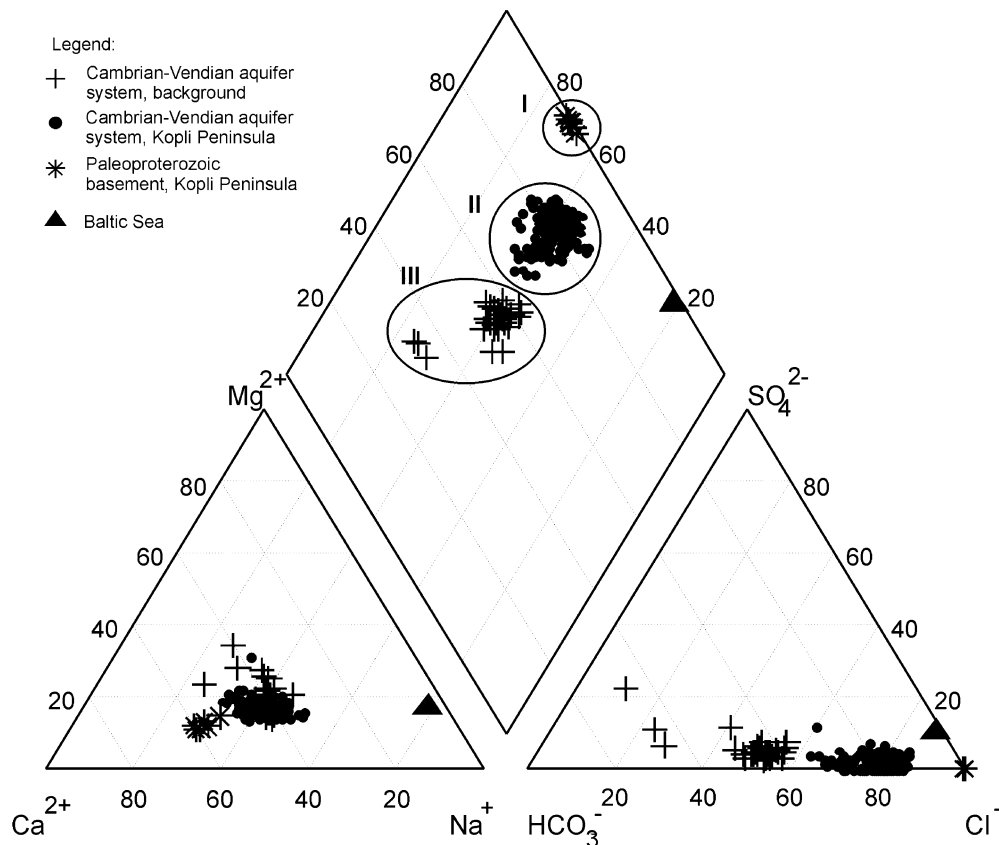
Well no	TDS	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
598	707–1,120	91.0–142.9	8.9–15.0	94.6–117.8	22.6–28.1	302.8–413.0	2.0–17.7	146.4–176.9
	804	114.0	10.7	110.4	25.6	364.1	3.7	158.6
613	624–1,545	96.8–241.7	5.4–13.3	99.0–184.4	21.7–47.6	259.9–707.6	2.0–55.6	146.4–238.0
	1010	160.6	10.0	138.5	31.7	481.6	21.8	170.8
614	724–1,100	89.6–172.2	7.0–20.0	102.8–149.2	23.7–33.0	330.1–546.7	0.0–19.4	121.9–189.2
	832	115.2	10.8	119.6	27.8	387.6	0.0	152.5
615	488–1,170	68.6–222.2	7.8–15.0	71.9–127.3	19.2–40.1	196.1–546.7	0.0–56.4	61.0–189.2
	820	122.5	9.8	101.2	28.6	358.4	24.7	167.8
798	3616–4587	400.0–525.0	16.0–22.5	676.8–836.7	80.4–114.4	2,109.5–2,552.6	0.0–3.7	6.1–18.3
	4347	469.6	20.5	805.1	104.2	2,439.7	2.0	12.2

groundwater, the remarkable scattering of points within group II is not visible. Ca-Na-Cl and Na-Ca-Cl type is governing and the expected evolution (in case of seawater intrusion) towards Na-Cl type (seawater e.g. Baltic Sea composition) does not occur. Slight changes in chemical type within group II are generally caused by relative variation in Ca²⁺ and Na⁺ content.

Ionic Relations and Sources of Major Compounds

The increase of groundwater salinity could be caused by several factors. Thus, it is necessary to use the characteristic ion ratios of the potential source to discriminate between them. Scatter diagrams for the most significant parameters are presented in Fig. 6a–d.

Fig. 5 Piper diagram showing the ionic composition of the Cambrian-Vendian groundwater from wells of northern Estonia (Group I), at Kopli Peninsula (Group II) and in the Palaeoproterozoic basement (Group III). For reference, data of Baltic Sea water are presented



The main diagnostic sign of seawater intrusion into drilled wells on the seaside intake could be the appearance or increase of elements such as sodium and chlorine. The concurrent increase of Na^+ and Cl^- in Kopli wells is very observable (Fig. 4). However, the Na^+/Cl^- plot shows that the groundwater at Kopli Peninsula water works is depleted in sodium relative to seawater (Fig. 6a) and is located below the seawater dilution line (SDL). The depletion of Na^+ relative to seawater in well 615 becomes more evident at higher Cl^- concentrations. The distribution of data is quite linear, suggesting a mixing trend of saline with dilute waters.

Magnesium lies roughly on the SDL with respect to Cl^- in groundwater production wells (598, 613, 614, 615), with small deviations to either side (Fig. 6b). This indicates that Mg^{2+} might have a marine component, modified to some extent (mainly at lower Cl^- values) by dissolution/weathering reactions.

Calcium and potassium are enriched in the groundwater relative to seawater. Potassium concentrations are fairly independent of Cl^- concentrations as shown in Fig. 6d, but Ca^{2+} exhibits a clear increase at high Cl^- values (Fig. 6c). The fact that the points lie mainly above the SDL of Fig. 6b–d reflects the K^+ , Ca^{2+} and Mg^{2+} derived from weathering products.

Palaeoproterozoic bedrock of northern Estonia in the Tallinn area consists mainly of biotite-hornblende gneisses and biotite gneisses (Koistinen et al. 1996; Puura et al. 1997). Mostly NW-SE-trending gneiss belts alternate with

quartz-feldspar and sillimanite-garnet-cordierite gneisses. In the northwestern part of the area gneisses are intruded by rapakivi type porphyritic granites of the Naissaare pluton. Biotite gneisses and biotite-hornblende gneisses are fine- or medium-grained and migmatized by microcline granites. The main minerals of biotite gneisses are plagioclase (An_{30-45}), quartz, biotite and microcline. The major minerals of biotite-hornblende gneisses, which are most basic in composition, are plagioclase (An_{35-50}), quartz, hornblende and biotite. These gneisses have an andesitic chemical composition (SiO_2 55–63 wt%, $\text{Na}_2\text{O} + \text{K}_2\text{O}$ 4.5–6.5 wt %). Typical felsic quartz-feldspar gneisses are fine-grained, rather massive or lineated granoblastic rocks. Quartz (25–40%), plagioclase (An_{20-40}) and potassium feldspar form 85–95% of quartz-feldspar or granite gneisses.

The uppermost part of the crystalline basement was affected by weathering processes before Late Vendian sedimentation. The thickness of the rocks weathered to some degree varies from 0.5–2 up to 100–150 m, if alteration to clay minerals along fracture zones is also considered. The weathered body of basement rocks in the Tallinn area ranges from 3 to 63 m in thickness (Puura et al. 1983). The maturest weathering profiles consist predominantly of kaolinite and other clay minerals, together with some resistant mineral grains including quartz and zircon. In less advanced stages of weathering, depending on original bedrock composition, other clay minerals, such as illite, chlorite and montmorillonite are charac-

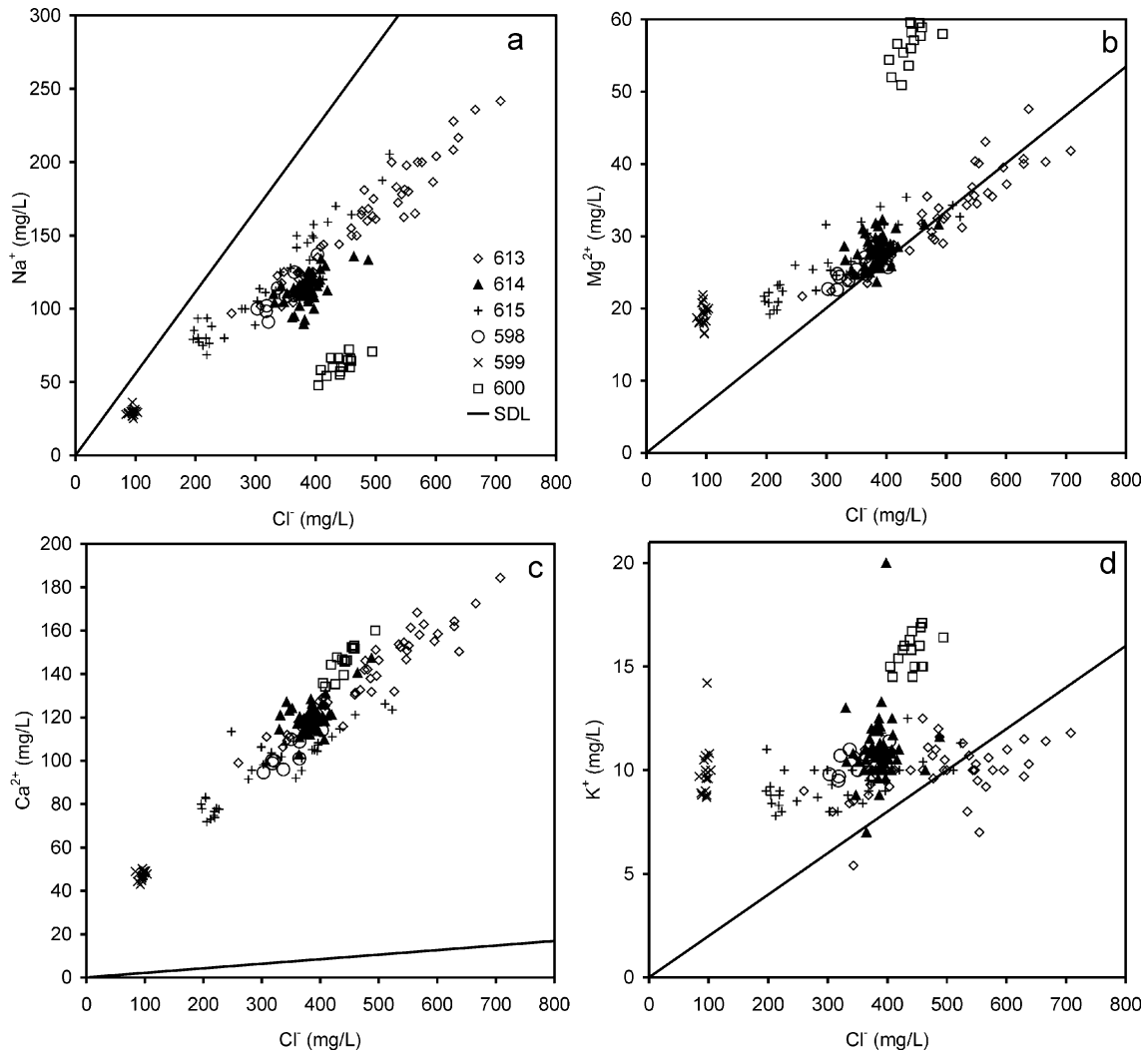


Fig. 6a–d The concentrations of various ions plotted against chloride concentration in groundwater. *SDL* seawater dilution line

teristic (Puura et al. 1983). Thus, the occurrence of high Ca^{2+} and K^{+} contents in deep-seated groundwater can be explained by the mineralogical and chemical characteristics of the reservoir rocks and ion exchange processes with water. The abundant calcium of the gneisses is dominantly present in the plagioclase, which is a less resistant mineral to weathering than potash feldspar. Sodium and potassium occur in chemically fairly resistant potash feldspar and biotite. For this reason, more calcium has been introduced into groundwater. The increases of Ca^{2+} in deep brines in the Canadian Shield are attributed to anorthite reactions (Frape and Fritz 1987). Similarly, anorthite, the Ca-feldspar in the basement of the study area, has been altered to kaolinite with the release of Ca^{2+} into solution.

It is possible that the Na^{+} released during weathering is adsorbed into fine-grained mineral matter or the clay minerals. Preferential adsorption and ion exchange of ions on clay minerals control the distribution and balance of cations in water. Clay minerals have a net negative charge and are therefore unlikely to adsorb anions. Cation

bounding to the basal planes of lattices in clay particles increases with their higher valence and decreasing hydrated ionic radii. This leads to an enrichment of polyvalent cations in adsorbed positions relative to the ionic composition in the liquid phase (Van Olphen 1977). Studies conducted in Norway indicate that adsorbed cations are enriched in Mg^{2+} and Ca^{2+} compared with Na^{+} (Hilmo et al. 1992). Accordingly, the deficit of Na^{+} and low $\text{Na}^{+}/\text{Cl}^{-}$ ratio in groundwater can be explained by the scarcity of a geological source of Na^{+} compared to Ca^{2+} . However, relict seawater trapped in deeper and less permeable parts of the water-bearing complex is the most plausible source of Na^{+} as well as Cl^{-} in groundwater. Na-Cl type groundwater has been detected in the deeper parts of the Cambrian-Vendian aquifer system in southwestern and southeastern Estonia (Perens et al. 2001) and has been interpreted as relict seawater modified by geochemical processes. Besides, Edmunds and Savage (1991) believe that chloride can be derived from the weathering of some minerals such as biotite. They also note, how-

Table 2 Isotopic and chemical parameters determined in 2001. $\delta^{18}\text{O}$ data are expressed in ‰ notation relative to international water standard V-SMOW with standard errors $\leq 0.1\text{‰}$. ^{14}C analyses have the accuracy of about ± 0.5 pmC. $\delta^{13}\text{C}$ data are expressed in ‰ notation relative to international PDB standard with standard errors $\leq 0.06\text{‰}$

Well no	$\delta^{18}\text{O}$ (‰)	^{14}C (pmC)	$\delta^{13}\text{C}$ (‰)	Br^- (mg/L)	Cl^- (mg/L)	Br^-/Cl^-
599	-20.4	2.5	-13.2	0.63	99	0.0064
600	-19.8	5.7	-13.6	2.15	494	0.0044
598	-21.5	3.4	-14.4	3.62	403	0.0090
613	-21.5	3.0	-15.2	3.84	481	0.0080
615	-21.6	2.8	-14.4	3.18	521	0.0061
614	-21.5	5.4	-15.0	3.96	409	0.0097

ever, that in such cases, there is usually a surplus of Cl^- ions over Na^+ .

The corresponding increase of Ca^{2+} and Cl^- concentration in groundwater is a true indicator of water rock interaction (Appelo and Postma 1999), for which different explanations can be proposed. The dissolution of salts is one possible source of chlorides in the deeply seated Cambrian-Vendian groundwater. In comparison, the deep salt waters in the Canadian Shield as well as groundwaters in Stripa granite in Sweden exhibit an increase of Ca^{2+} , which parallels the increase of Cl^- (Frape and Fritz 1987; Nordstrom et al. 1989).

The crystalline basement in Estonia comprises groundwater in its upper weathered and fissured portion, and is hydraulically connected with the overlying Cambrian-Vendian aquifer system. Groundwater in the clayey weathering core of the crystalline basement contains a TDS of 2–20 g/L in northern Estonia (Karise 1997; Perens et al. 2001). In the study area (well 798) Ca-Cl type groundwater with TDS content of 3.6–4.6 g/L and high Cl^- , Ca^{2+} , Na^+ , Mg^{2+} and K^+ concentration occurs (Table 1, Fig. 5).

The screens of most groundwater abstraction wells (613, 614, 615) reach close to the weathered basement (Fig. 2). Thus, as the influence area increases with pumping, the increasing contribution of the upconing water from the underlying bedrock affects the groundwater quality in the Cambrian-Vendian aquifer system.

Br-/Cl- ratio

Ratios of bromide to chloride in some groundwater samples from the Cambrian-Vendian aquifer system were compared to Br^-/Cl^- ratio in seawater and in water of the Finnish Gulf. Bromide and chloride are particularly good indicators for seawater intrusion because both ions are chemically conservative in natural aqueous environments: they do not participate in redox reactions, they are not sorbed onto mineral or organic surfaces, and they do not form insoluble precipitates (Fetter 1993).

Water in the Finnish Gulf is a mixture of seawater from the Baltic Sea and fresh water from streams and groundwater discharge. The most abundant chemical constituent in seawater is dissolved chloride. Bromide, chemically similar to chloride, is also present in seawater but at much lower concentrations. The average chloride and bromide concentrations in seawater are 19,000 and 65 mg/L, respectively (Rankama and Sahama 1950; Hem

1992). The salinity of the present-day Baltic Sea (Finnish Gulf) is considerably lower than that of the Global Seawater (35‰) and ranges from 4 to 6‰ (Perttilä et al. 1980). Thus, the concentrations of Cl^- and Br^- are also lower. Because bromide and chloride are chemically conservative in aqueous medium, the ratio between them is virtually constant with time and locations. Therefore, if dilution is the only process acting on dissolved chloride and bromide in Baltic Sea water, then the Br^-/Cl^- in the Finnish Gulf should equal the Br^-/Cl^- of seawater.

Previous studies have shown that Br^-/Cl^- ratios in groundwater influenced by seawater intrusion are similar to those in seawater (Richter and Kreitler 1993; Andreassen and Fleck 1997). Dissimilar ratios in groundwater and seawater would indicate that the chloride is derived, at least in part, from another chloride source. Nordstrom et al. (1989) note that saline waters in the Precambrian basement tend to have elevated bromide concentrations relative to seawater. Based on the average concentrations of chloride and bromide given by Hem (1992), the Br^-/Cl^- ratio in seawater is 0.0034. The calculations by Hyypä (1984) give the Br^-/Cl^- ratio of 0.0033–0.0035 for Baltic Sea water. The Br^-/Cl^- ratios in the Cambrian-Vendian groundwater abstracted at Kopli Peninsula range from 0.0044 to 0.0097 (Table 2) and are therefore remarkably higher than the seawater ratio, suggesting that additional bromide-rich sources influence the groundwater composition. High Br^-/Cl^- ratios are associated with wells penetrating deep into the aquifer and having a high yield (wells 613, 614). In several regions of Estonia, a high content of bromides in groundwater also has been detected. The crystalline basement comprises groundwater with Br^- concentrations of 51–61 mg/L sporadically in northern Estonia (Karise 1997). Thus, the abundance of bromide in groundwater of the Cambrian-Vendian aquifer system relative to seawater points towards its mixing with saline bedrock groundwater rather than with lateral seawater intrusion.

Isotopic Investigations

Considering the glacial origin of groundwater in the Cambrian-Vendian aquifer system in northern Estonia (Vaikmäe et al. 2001) and its unique isotopic composition, $\delta^{18}\text{O}$ values, and also the ^{14}C and ^3H values in groundwater are the most sensitive indicators of possible modern seawater intrusion into an aquifer system. As

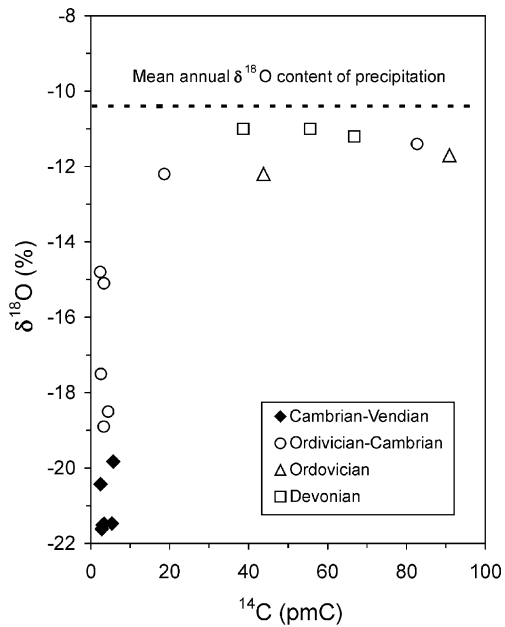


Fig. 7 Distribution of $\delta^{18}\text{O}$ values from the Cambrian-Vendian aquifer system in the Kopli Peninsula as a function of their ^{14}C content. Data from Ordovician-Cambrian, Ordovician and Devonian aquifers (Vaikmäe et al. 2001) are plotted for comparison

mentioned above, $\delta^{18}\text{O}$ values in the Cambrian-Vendian aquifer system in northern Estonia vary from -18 to -22‰ , ^{14}C concentrations are in most cases lower than 5 pmC and the ^3H concentrations are typically below the detection limit (Vaikmäe et al. 2001). According to Punning et al. (1991) the annual mean $\delta^{18}\text{O}$ value of water in the Finnish Gulf is about -7‰ and ^3H concentrations are between 5 to 10 TU. ^{14}C concentrations in Baltic Sea water are close to 100 pmC (Yezhova et al. 1996).

Groundwater samples from six wells in the Kopli Peninsula were analysed for their isotopic composition in 2001. The $\delta^{18}\text{O}$ and ^{14}C values are presented in Table 2 and in Fig. 7. In order to correct the radiocarbon dates for dissolution of aquifer carbonate, $\delta^{13}\text{C}$ values were also measured and the results are presented in Table 2. The $\delta^{18}\text{O}$ and ^{14}C values obtained are typical for groundwater in the Cambrian-Vendian aquifer system in northern Estonia (Mokrik 1997; Mokrik and Mažeika 2002; Vaikmäe et al. 2001) indicating recharge in cool conditions.

In earlier studies several attempts have been made to determine the groundwater ages from the ^{14}C activities of the TIC in Cambrian-Vendian aquifer system. Mokrik (1997) has concluded that the corrected absolute age of groundwater in northern Estonia averages from $23,000$ to $33,000$ years BP. In places, where deep erosional valleys are developed, owing to the infiltration of meteoric water caused by intensive exploitation, the age of groundwater is considerably younger and ranges from $7,000$ to $19,000$ years BP. Yezhova et al. (1996) have presented ^{14}C ages for groundwater in the range of $10,000$ to $15,000$ years BP. In both cases, however, the authors have not described if and how they have corrected the apparent ^{14}C water ages for carbonate dissolution (Clark and Fritz

1997). In earlier studies the conventional correction models have been applied (Ingerson and Pearson 1964; Fontes and Garnier 1979) to convert activity values into ^{14}C ages. The age range for groundwater recharge into the Cambrian-Vendian aquifer system in northern Estonia was found to be $15,000$ – $30,000$ years BP (Vaikmäe 2001). However, based on the above mentioned assumption, that at least part of the groundwater may have infiltrated below the ice sheet, it was concluded, that traditional ^{14}C models may not be appropriate for the conversion of a ^{14}C activity into an age. In the course of recent investigations on formation of carbon composition in the Cambrian-Vendian aquifer system (Raidla 2003) a new dilution model was developed on the basis of existing alkalinity models (Wigley 1975). This model takes into account different sources of carbon in formation of TIC, including the carbon originating from the old organic matter. The ^{14}C ages calculated using this new model fell into the time interval of $10,000$ – $20,000$ years BP, supporting the earlier-stated hypothesis about the glacial origin of the groundwater in northern Estonia. However, in the context of this paper it is not important to calculate and discuss the ^{14}C ages, as the low values of ^{14}C activities (between 2.5 to 5.7 ± 0.5 pmC) found in investigated wells (Table 2) are in good agreement with the results of earlier studies. According to these results, detectable intrusion of modern water (including seawater) into the Cambrian-Vendian aquifer system as a consequence of heavy pumping at Kopli Peninsula has not occurred. This conclusion is confirmed also by the absence of ^3H in all the sampled wells in the coastal areas of Northern Estonia (Vaikmäe et al. 2001).

Conclusions

The overexploitation of fresh-water resources of the Cambrian-Vendian aquifer system in the Kopli Peninsula has resulted in the development of depression of the potentiometric levels and in the increase of water exchange. In turn, it has led to the rise in TDS content and concentration of major ions in groundwater. The lateral seawater intrusion into water intakes can take place at Kopli Peninsula where production wells are situated close to the sea. Taking into consideration the good screening properties of overlying Lontova aquitard, vertical penetration of the seawater from above is hardly feasible.

Also, abstracted groundwater is depleted in sodium relative to seawater and the abundance of calcium, potassium and bromide in groundwater relative to seawater points to mixing of saline groundwater from a deeply seated source rather than laterally from seawater intrusion. The changes in water chemistry can be explained by the mineralogical and chemical characteristics of the reservoir rocks and water exchange with underlying water bearing weathered and fractured crystalline basement, which hosts brackish Ca-Cl type water.

Heavily depleted oxygen isotope composition and low ^{14}C concentrations of the groundwater of the Cambrian-

Vendian aquifer system points to a long residence time of groundwater. Thus, according to the results of isotope analysis, detectable intrusion of modern seawater into the aquifer system is ruled out.

As the non renewable resources of fresh groundwater in the Cambrian-Vendian aquifer system are limited, special regulations for sustainable consumption of the water has to be settled. In order to prevent salt-water intrusion, the fresh-water resources should be exploited by maintaining a balance between groundwater pumping and groundwater recharge. Meanwhile, a more rational distribution and construction of pumping wells should be considered.

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