

Barium anomaly in the Cambrian-Vendian aquifer system in North Estonia

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Abstract A barium anomaly with a maximum Ba^{2+} concentration of 6.37 mg/l was distinguished in a Cambrian-Vendian (Cm-V) aquifer system that is widely used as a drinking water source in the towns Kunda, Rakvere and Kohtla-Järve of North-Estonia. The modelling results show that at low sulphate concentrations (below 3 mg/l) Ba^{2+} contents can exceed the limit values for drinking water (such as 2 mg/l set by US EPA). Bicarbonate ions in their common concentration range in groundwater cannot limit Ba^{2+} at its content below 10 mg/l. The probable natural sources of the anomaly are the crystalline basement and its weathering zone. Groundwater in the clayey weathering core is hydraulically connected with the overlying Cm-V aquifer system, thus the upconing of deeper-seated groundwater, caused by intensive exploitation of wells, is possible.

Introduction

Usually, the concentrations of barium in natural waters are low (less than 1 mg/l), mainly because its dissolution is limited by baryte ($BaSO_4$) and witherite ($BaCO_3$) solubility products (Ball and Nordstrom 1991). Although the soluble salts of barium ($BaCl_2$, $Ba(NO_3)_2$) are known to be toxic in high concentrations, the Drinking Water Directive of the European Union (98/83/EEC) does not limit its concentration. Presumably, this is due to a lack of historical evidence and experience in Europe of the appearance of high barium concentrations in groundwaters.

In the water of deep wells of the North Estonian water supply systems, anomalously high concentrations of dissolved barium were first recorded in 1996 (Otsa and Tamm 1997; Tamm 1998), as only for that year laboratory techniques had developed to the level that application of routine controls could be accomplished. A study of trace elements in the Cambrian-Vendian (Cm-V) aquifer system was also performed in 1994, but did not include barium (Savitskaja and Viigand 1994). According to the findings in 1996, the barium concentration exceeded the limit value of the previous Estonian drinking water standard - 0.7 mg/l - (Joogivesi 1995) 2–13 times in 3 sampling locations, with maximum concentrations found in the water supply of Kohtla-Järve town - as high as 9 mg/l. The new Estonian drinking water standard (Joogivee 2001), which came into force in June 2002, does not limit barium concentration. The Environmental Protection Agency of the United States (EPA 1995) has set the maximum concentration limit (MCL) for barium in drinking water at 2.0 mg/l. Based on an epidemiological study according to which no significant health risks were followed at 7.3 mg/l (Brenniman and Levy 1985), the World Health Organisation has published a guideline value 0.7 mg/l for barium in drinking water, that includes an uncertainty factor of 10 accounting for intraspecies variation (WHO 1996). According to the EPA, if people are exposed to barium at levels above the MCL for relatively short periods of time, gastrointestinal disturbances and muscular weakness may result. A lifetime exposure at levels above MCL may lead to high blood pressure diseases. The EPA regulation for barium became effective in 1992. Between 1993 and 1995, the EPA required water suppliers to check for wells with barium levels above 2 mg/l and, if present, continuous monitoring was required. If contaminant levels were found to be consistently above the MCL, the water suppliers had to use water treatment methods for barium removal (EPA 1995). This study provides scientific evidence on the barium anomaly in North Estonian (Fig. 1) groundwater, maps the territory of the anomaly, analyses the geological settings and provides hydrogeochemical considerations for the reasons of the occurrence. It is suggested that because the geological settings of New Member States are different from the Old EU Members the experience on natural water quality studies, such as the data on barium in Estonia, has to be accounted for in further development of EU legislation.

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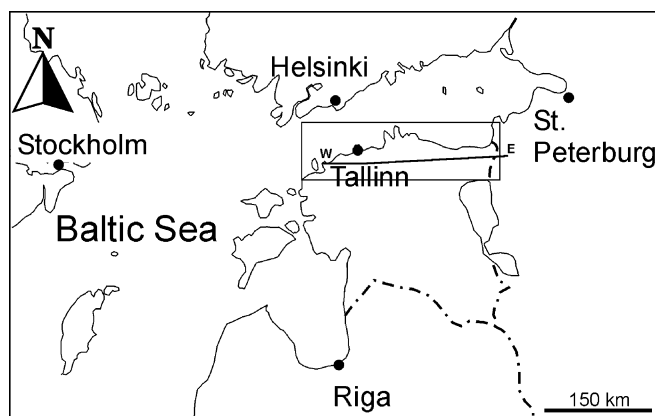


Fig. 1
Location of the study area and the line of the hydrogeological cross-section

Study area

Estonia is situated in the northwestern part of the East-European Platform. Structurally, its sedimentary beds have a thickness of 150 to 750 m, and lie on the southern slope of the Baltic Shield, with a dip of 0.1 to 0.3° (3–4 metres per kilometre) southwards. Crystalline Palaeoproterozoic (PP) basement is overlain by Vendian and Palaeozoic (Cambrian, Ordovician, Silurian and Devonian) sedimentary rocks covered by Quaternary deposits (Fig. 2). Terrigenous and carbonate Palaeozoic and Proterozoic rock form porous fissured and karstified, mostly confined aquifers. The deepest economically important Cambrian-Vendian aquifer system (Cm-V) is distributed throughout Estonia, except in the Lokno-Mõniste uplift area in South Estonia (Tšeban 1975). The water-yielding portion of the aquifer system consists of sand- and siltstones with interlayers of clay. The aquifer system is covered by

Fig. 2
Hydrogeological cross-section of North Estonia. Q – Quaternary sediments, D_{2nr} – Narva aquitard, O – Ordovician aquifer system, O-Cm – Ordovician-Cambrian aquifer system, Cm_{1ln} – Lontova aquitard, Cm-V – Cambrian-Vendian aquifer system, V_{2vr} – Voronka aquifer, V_{2kt} – Kotlin aquitard, V_{2gd} – Gdov aquifer, PP – Palaeoproterozoic crystalline basement

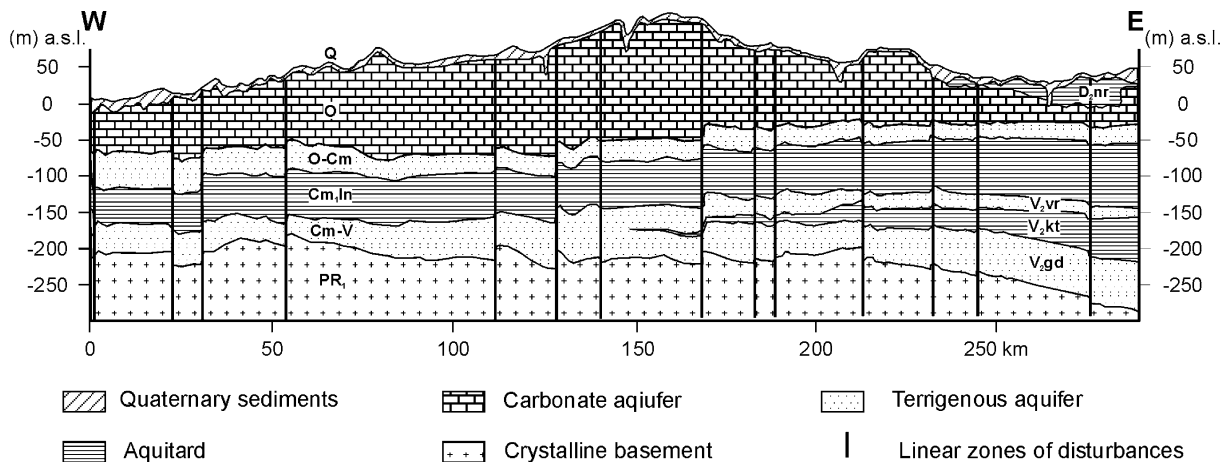


Table 1
Significant reactions in the aqueous phase used in modeling

Reactions defining the speciation	log K
$\text{H}_2\text{O} = \text{OH}^- + \text{H}^+$	-14.0
$\text{Ba}^{2+} + \text{CO}_3^{2-} = \text{BaCO}_3$	2.71
$\text{Ba}^{2+} + \text{HCO}_3^- = \text{BaHCO}_3^+$	0.982
$\text{Ba}^{2+} + \text{SO}_4^{2-} = \text{BaSO}_4$	2.7
$\text{BaCO}_3 = \text{Ba}^{2+} + \text{CO}_3^{2-}$	-8.562
$\text{BaSO}_4 = \text{Ba}^{2+} + \text{SO}_4^{2-}$	-9.97
$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3$	3.224
$\text{Ca}^{2+} + \text{HCO}_3^- = \text{CaHCO}_3^+$	1.106
$\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4$	2.3
$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.48
$\text{CO}_3^{2-} + 2\text{H}^+ = \text{CO}_2 + \text{H}_2\text{O}$	16.681
$\text{H}^+ + \text{CO}_3^{2-} = \text{HCO}_3^-$	10.329
$\text{Mg}^{2+} + \text{HCO}_3^- = \text{MgHCO}_3^+$	1.07
$\text{Mg}^{2+} + \text{SO}_4^{2-} = \text{MgSO}_4$	2.37
$\text{NO}_3^- + 10\text{H}^+ + 8\text{e}^- = \text{NH}_4^+ + 3\text{H}_2\text{O}$	119.077
$\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- = \text{NO}_2^- + \text{H}_2\text{O}$	28.57

50–100 m thick Cambrian clays (Fig. 2) that form laterally continuous Lontova aquitard (Cm_{1ln}) having a strong isolation capacity as its transversal conductivity is predominantly 10^{-7} ... 10^{-5} m/d (Perens and Vallner 1997). The aquifer system is underlain by the up to 50 m thick clayey weathering zone of the crystalline basement (PP). In the eastern part of Estonia, the up-to 50-m-thick clays of the Kotlin Formation (V_{2kt}) divide the aquifer system into two aquifers (Fig. 2). Westwards the Kotlin clays pinch out and the Cambrian and Vendian water-bearing rocks form the steady aquifer (Perens and Vallner 1997). The upper, Voronka aquifer (V_{2vr}), consists of quartzose sand- and siltstone with a thickness of up to 45 m in northeastern Estonia. The conductivity of rocks ranges from 0.6 to 12.5 m/d. Transmissivity decreases from 100–150 m²/d in northern Estonia to 50 m²/d and less in the southern direction. The lower, Gdov aquifer (V_{2gd}), is formed of an up to 68-m-thick complex of mixed-grained sand- and siltstone. In northern Estonia, the conductivity of water-bearing rocks of the Gdov aquifer is 0.5–9.2 m/d. Transmissivity in northeastern Estonia (300–350 m²/d) decreases in a southerly and westerly direction to 100 m²/d or less.

The Cambrian-Vendian aquifer system recharges in South Estonia and flows northward towards the discharge

Table 2

Selected hydrochemical properties of groundwater in Cambrian-Vendian aquifer system compared to the limit values set by standards

Well no.	Location	Aquifer	T (°C)	Eh (mV)	pH	Hardness (meq/l)	COD (mgO/l)	TOS (mg/l)	Concentration (mg/l)			
									Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
602	Vääna-Jõesuu	V ₂ vr	7.4	38	8.3	2.0	<1	304	26.0	8.5	26.5	6.0
603	Vääna-Jõesuu	V ₂ gd	9.1	-13	8.3	2.2	<1	224	30.0	8.5	34.0	7.0
3274	Jägala	V ₂ gd	9.2	57	7.9	6.0	2.0	866	84.0	22.0	97.5	8.0
1090	Kiiu	V ₂ vr	9.6	78	7.6	12.4	3.6	1450	188.0	36.0	150.4	8.5
1092	Kiiu	V ₂ vr	10.8	52	7.7	8.0	3.2	936	116.0	27.0	115.8	9.0
6777	Rakvere	V ₂ vr	12.1	88	7.7	3.0	<1	396	34.01	16.0	96-0	8.5
2738	Rakvere	V ₂ gd	8.3	-22	7.7	6.4	<1	1020	88.0	24.0	128.0	10.0
2776	Kunda	V ₂ vr	10.9	40	7.8	6.5	2.8	936	87.0	26.0	140.0	8.0
2772	Kunda	V ₂ gd	11.2	-30	8.3	6.1	1.2	866	80.0	26.0	130.0	8.0
2384	Aseri	V ₂ vr	11.0	159	7.8	4.9	2.8	658	61.1	23.0	115.0	8.5
2387	Aseri	V ₂ gd	12.0	147	8.0	4.8	2.5	843	62.1	20.3	115.0	8.0
2256	Püssi	V ₂ vr	12.0	129	7.9	3.6	1.3	640	44.3	16.9	130.0	7.5
2329	Püssi	V ₂ gd	13-0	124	7.9	3.4	1.8	578	42.3	15.8	130.0	7.5
2369	Kohtla-Järve	V ₂ vr	10.0	81	7.9	3.6	1.5	696	56.1	9.1	200.0	7.0
2184	Kohtla-Järve	V ₂ gd	12.0	120	8.1	4.1	1.3	740	53.1	17.1	130.0	8.0
2266	Ahtme	V ₂ gd	13.0	-27	7.7	2.6	2.7	722	29.4	13.2	240.0	7.0
2379	Vasavere	V ₂ vr	8-0	-38	8.2	1.3	2.0	543	12.8	7.8	170.0	4.0
2632	Vasavere	V ₂ gd	12.0	117	7.9	5.2	1.5	1531	57.3	28.4	375.0	9.5
2217	Sillamäe	V ₂ vr	11.0	138	7.9	0.9	1.6	536	12.0	3.6	195.0	5.5
2207	Sillamäe	V ₂ gd	12.0	101	7.8	1.6	1.6	1174	16.4	9.5	405.0	7.0
2083	Narva-Jõesuu	V ₂ vr	12.0	-47	7.9	0.6	0.7	517	6.6	3.2	195.0	4.0
20841	Narva-Jõesuu	V ₂ gd	10.0	-52	7.9	0.7	0.9	531	7.6	3.6	200.0	4.0
	Min		7.4	-52	7.7	0.6	0.7	224	6.6	3.2	26.5	4.0
	Max		13.0	159	8.3	12.4	3.6	1531	188.0	36.0	405.0	10.0
	Median		11.0	67.5	7.9	3.6	1.7	677	48.7	16.5	130.0	7.8
	MCL*				6.5-9.5		5				200	
	98/83/EC				6.5-9.5		5				200	
	Number of wells exceeding MCL				0		0				3	

*MCL, maximum concentration limit of the Estonian drinking water standard (Joogivee 2001). In Ba case, the old drinking water limits are used (Joogivesi 1995)

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 ($5 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ m/d) and mean residence times are of the order of tens of thousands of years under natural conditions. A thick formation of Cambrian clays 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 into 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 palaeo-groundwater, which recharged during the last glaciation more than 10,000 y BP by subglacial drainage through the aquifers (Piotrowski 1997; Vaikmäe and others 2001). In North Estonia, the aquifer has a characteristic Cl-HCO₃-Na-Ca and HCO₃-Cl-Ca-Na mineralisation mainly below 1.0 g/l (0.4-1.1 g/l) (Savitskaja and Viigand 1994). The baseline chemical composition of the water was formed through the water-rock interaction during the last more than 10,000 y (Yezhova and others 1996; Mokrik

1997; Edmunds and others 2001; Vaikmäe and others 2001).

The Cambrian-Vendian aquifer system is a major source of the public water supply in northern Estonia. In Ida-Virumaa and Harju counties, the share of Cambrian-Vendian groundwater consumption is about 75% and in Lääne-Virumaa, almost 50% (Savitskaja 1999).

Materials and methods

During autumn 2001, 22 groundwater samples were collected. The sampling points were selected according to following criteria: (1) assurance of a good areal representation; (2) sampling of both Gdov and Voronka aquifers at every sampling point; and (3) the possibility of comparison with data from previous studies. All sampled groundwater production wells are under operation at the moment. In the field, pH, redox potential, electrical conductivity and temperature were measured. Water samples were taken only after the stabilising of field parameters. All samples were filtered and acidified with nitric acid (1%) to stabilise trace elements. In the laboratory the concentrations of NH₄⁺, NO₂⁻, NO₃⁻, PO₄³⁻, Cl⁻, SO₄²⁻, HCO₃⁻, Ca²⁺, Mg²⁺, Fe_{tot}, Si, F⁻, Al³⁺, As³⁺, Ba²⁺, K⁺, Mn²⁺ and Na⁺ were determined. For Fe_{tot}, NH₄⁺, NO₂⁻, PO₄³⁻, Si, SO₄²⁻ a spectrophotometer was used, HCO₃⁻ content was measured by potentiometric titration, K⁺ and Na⁺ were measured by flame photometers, Cl⁻ was

														Water type
HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	Si	F ⁻	NH ₄ ⁺	NO ₂ ⁻	NO ₃ ⁻	PO ₄ ³⁻	Fe _{1pt}	Mn ²⁺	Al ³⁺	As ³⁺	Ba ²⁺	
115.9	19.0	46.0	1.3	0.85	0.17	0.001	0.08	0.004	0.59	<0.02	<0.003	<0.001	0.123	Ca-Na-Mg-HCO ₃ -Cl
103.7	22.0	62.0	3.2	0.78	0.29	0.001	0.04	0.017	0.56	0.06	0.014	<0.002	0.202	Ca-Na-Cl-HCO ₃
176.9	<1	804.9	3.4	0.45	0.74	0.002	0.03	0.011	1.30	0.10	0.009	0.002	0.345	Na-Ca-Cl-HCO ₃
152.5	<1	815.0	2.9	0.40	1.10	0.003	0.07	<0.002	7.50	0.21	0.029	0.003	0.505	Ca-Na-Cl
183.0	<1	184.0	3.2	0.36	0.50	0.002	0.03	0.002	1.90	0.16	0.007	<0.001	0.432	Ca-Na-Mg-Cl-HCO ₃
201.3	<1	150.0	3.1	0.52	0.19	<0.001	0.05	<0.002	0.35	0.07	0.037	<0.001	0.786	Na-Ca-Cl-HCO ₃
201.3	<1	345.0	2.7	0.91	0.24	0.001	0.05	0.005	6.70	0.14	0.055	0.001	2.410	Na-Ca-Cl-HCO ₃
237.9	<1	323.0	1.4	0.96	0.64	0.002	0.05	0.006	2.00	0.12	0.603	0.003	5.410	Na-Ca-Cl-HCO ₃
262.4	<1	323.0	1.1	1.00	0.64	0.004	0.06	0.008	3.30	0.10	0.011	0.003	6.090	Na-Ca-Cl-HCO ₃
242.8	2.0	220.0	3.3	1.07	0.36	0.040	<0.2	0.047	1.10	0.11	0.039	0.001	3.770	Na-Ca-Cl-HCO ₃
247.7	2.0	235.0	3.3	1.14	0.37	0.040	<0.2	0.040	0.89	0.11	<0.003	0.001	3.970	Na-Ca-Cl-HCO ₃
151.3	2.0	233.0	3.2	0.86	0.19	0.020	<0.2	<0.01	0.92	0.10	0.004	<0.001	0.735	Na-Cl-HCO ₃
183.6	<2	231.0	3.3	0.86	0.17	0.010	<0.2	<0.01	0.94	0.10	0.004	<0.001	0.810	Na-Ca-Cl-HCO ₃
150.1	<2	316.0	2.5	0.76	0.11	0.0101	<0.2	<0.011	0.62	0.12	0.021	<0.001	0.826	Na-Ca-Cl-HCO ₃
196.4	<2	231.0	3.2	0.92	0.19	0.010	<0.2	0.045	0.88	0.09	<0.003	<0.001	6.370	Na-Cl-HCO ₃
169.0	<2	384.0	3.4	0.69	0.14	<0.01	<0.2	<0.01	0.46	0.09	0.012	<0.001	0.216	Na-Cl-HCO ₃
190.3	<2	197.0	3.5	0.58	0.15	<0.01	<0.2	0.010	0.79	<0.02	0.020	<0.001	0.262	Na-Cl-HCO ₃
181.0	2.0	700.0	2.7	0.66	0.15	0.020	<0.2	<0.01	0.77	0.22	0.025	<0.001	0.096	Na-Cl
251.3	<2	201.0	3.2	0.65	0.11	<0.01	<0.2	0.010	0.38	<0.02	0.070	<0.001	0.317	Na-Cl-HCO ₃
162.3	<2	640.0	2.3	0.67	0.14	<0.01	<0.2	<0.01	0.35	0.10	0.034	<0.001	0.530	Na-Cl
205.0	<2	202.0	2.6	0.47	0.06	<0.01	<0.2	0.016	0.38	<0.02	0.054	<0.001	0.072	Na-Cl-HCO ₃
207.4	<2	208.0	2.2	0.52	0.12	<0.01	<0.2	0.016	0.48	0.04	0.112	0.001	0.077	Na-Cl-HCO ₃
103.7	2.0	45.0	1.1	0.36	0.06	0.001	0.03	0.002	0.35	0.04	0.004	0.001	0.072	
262.4	22.0	700.0	3.5	1.14	1.10	0.040	0.08	0.047	7.50	0.22	0.603	0.003	6.370	
187.0	2.0	232.0	3.2	0.73	0.19	0.004	0.05	0.011	0.84	0.10	0.025	0.002	0.518	
	250	250		1.5	0.5	0.5	50		0.2	0.05	0.2	0.01	0.7	
	250	250		1.5	0.5	0.5	50		0.2	0.05	0.2	0.01		
	0	9		0	4	0	0		22	17	1	0	10	

analysed by argentometric titration and for NO₃⁻ automated flow injection analysis was used. The content of trace elements (Al³⁺, As³⁺, Ba²⁺ and Mn²⁺) was detected by using the graphite furnace AAS.

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

Theoretical background

Geochemistry of barium

Barium is a naturally occurring component of minerals (e.g. baryte, witherite) that are found in small but widely distributed amounts in the Earth's crust, especially in igneous rocks, sandstone, shale and coal (Miner 1969; Kunesh 1978). Under natural conditions, barium is stable in the +2 valence state and is found primarily in the form of inorganic complexes. Conditions such as pH, Eh, cation exchange capacity and the presence of sulphate, carbonate, and metal oxides will affect the partitioning of barium and its compounds in the environment.

The primary source of naturally occurring barium in drinking water results from the leaching and dissolution of rocks into groundwater (Kojola and others 1978). The concentration of barium in natural waters is very low, because its dissolution is limited by equilibrium with baryte (BaSO₄) and witherite (BaCO₃) solubility products

(Ball and Nordstrom 1991). The data by Monnin and others (2001) show an overall symmetrical behaviour between barium and sulphate, suggesting that the sediment pore water barium content is controlled by equilibrium with barium sulphate (baryte). The solubility of BaSO₄ increases considerably in the presence of chloride (Cl⁻) and other anions (NO₃⁻ and CO₃²⁻), and at pH levels of 9.3 or below, the barium ion (Ba²⁺) is the dominant species (NAS 1977; Bodek and others 1988).

Barium is strongly adsorbed by clay minerals (Kabata-Pendias and Pendias 1984, Lagas and others 1984) and reacts with metal oxides and hydroxides in soil (Hem 1959; Rai and others 1984). The cation exchange capacity of the sorbent largely controls the retention of barium in soils (Bodek and others 1988). The ionic radius of the barium ion in its typical valence state (Ba²⁺) makes isomorphous substitution possible with strontium and potassium but not with the smaller ions of sodium, iron, manganese, aluminium and silicon (Kirkpatrick 1978). Barium can also form salts with acetate, nitrate, chloride, and hydroxide ions and the mobility of barium in soils increases upon formation of these water-soluble salts (Bodek and others 1988).

Hydrogeochemical modelling

The solubility of baryte is defined in the WATERQ4F database (Ball and Nordstrom 1991) as

$$[\text{Ba}^{2+}] * [\text{SO}_4^{2-}] = 10^{-3.97}$$

where $[\text{Ba}^{2+}]$ and $[\text{SO}_4^{2-}]$ are activities of ions expressed in mmol per kg of water.

Assuming at low ionic strengths the concentrations approximated to activities, the maximum content of sulphate ion (mg/l) can be defined according to

$$[\text{SO}_4^{2-}]_{\text{max}} = \frac{10^{-3.97} * 96}{\frac{[\text{Ba}^{2+}]}{137.34}}$$

However, this calculation does not express total sulphate as aqueous complexes such as CaSO_4° and MgSO_4° give significant contribution to the total sulphate concentration. PHREEQC simulation was used to account for the whole range of aqueous species. The simulation was made by titration of a water sample from well 603 with BaCl_2 solution. The thermodynamic data relevant to modelling are presented in Table 1.

Results and discussion

Groundwater chemistry and its accordance to quality requirements

The chemical type of groundwater is determined by Na^+ , Ca^{2+} , Cl^- and HCO_3^- in the studied aquifer system, while Na^+ and Cl^- are the most abundant ions in water. Magnesium is present in minor quantities (3.2–36.0 mg/l) and the content on SO_4^{2-} is mostly below the limit of quantification (Table 2). Thus, the chemical type of groundwater in the Cm-V aquifer system (Voronka and Gdov aquifers) varies from Ca-Na- HCO_3 -Cl to Na-Cl-type (Table 2, Fig. 3).

Groundwater sampling points are listed in Table 2 in the following sequence: samples from the eastern part of the study area are placed in the uppermost rows, and the results of analyses reflecting groundwater composition in western Estonia occupy the lowermost positions. If groundwater from both the Gdov and Voronka aquifer has been sampled in the same location, results of analyses in Table 2 are marked by indexes V_{2gd} and V_{2vr} , respectively. General lateral changes in the chemical composition as well as in the type of groundwater are remarkably bigger than those in vertical direction in certain sampling points. Prevailing of Ca^{2+} and HCO_3^- ions in groundwater decreases eastwards where Na^+ and Cl^- ions become dominant in the Gdov aquifer (Table 2, Fig. 4). Approximately the same trend can be observed in the overlying Voronka aquifer. The content of Na^+ and Cl^- in the Cm-V aquifer system varies from 26 to 405 mg/l and 46 to 700 mg/l, respectively, exhibiting the highest values in the eastern part of the country. The concentrations of Ca^{2+} (6–188 mg/l) and HCO_3^- (103–264 mg/l) show somewhat higher values in the western part of the study area. The highest SO_4^{2-} values are also detected from the western margin of the area (Vääna-Jõesuu) – 19 and 22 mg/l. The content of total dissolved solids (TDS) in

analysed groundwater samples varies from 224 to 1,531 mg/l (Table 2).

Groundwater abstracted from studied wells is directly, without any purification, distributed between consumers. As an exception, the mixing of groundwater originated from Cambrian-Vendian and Quaternary aquifers is used to lower the content of TDS in Kohtla-Järve. Thus, it might be supposed, that the groundwater chemistry is in accordance with the limit values set by drinking water standards (98/83/EC 1998; Joogivee 2001). Table 2 shows the number of wells where the concentrations of certain chemical compounds exceed MCL. Generally, the groundwater has a good quality, but the problems are associated with elevated Fe_{tot} and Mn^{2+} contents. Highest Fe_{tot} contents reach up to 6–7 mg/l, crossing limit values 30–35 times. Manganese is above the permitted value in 17 wells. Groundwater does not always fulfil the requirements of drinking water standards in the case of Cl^- and Na^+ (Table 2). The content of Al^{3+} , As^{3+} , F^- and nitrogen compounds in the water is low; Ba^{2+} is the only toxicant whose content in the water is much higher than permitted in water abstracted for drinking purposes.

Distribution and hydrogeochemical behaviour of barium

The content of Ba^{2+} in analysed water samples varies from 0.07 to 6.37 mg/l. Detected Ba^{2+} values do not show any certain trend in vertical direction – if there is high Ba^{2+} in the Gdov aquifer, it is in elevated amounts also in the overlying Voronka aquifer. Laterally a clear pattern in the distribution of Ba^{2+} can be observed (Fig. 5). Barium content is obviously lower in marginal parts of the studied area than in the centre. The highest Ba^{2+} values are associated with the Kunda-Rakvere-Kohtla-Järve area, which can be defined as the Ba-anomaly in the Cm-V aquifer system.

The results of geochemical modelling showed that the aqueous complexes CaSO_4 and MgSO_4 contribute to the increased solubility of total SO_4^{2-} , so that in the solubility product, the pK value of –3.64 could be used in calculations instead of –3.97. In addition, the presence of high Cl^- (at 700 mg/l, highest measured in the Cm-V aquifer system in this study) increases the solubility even more, to pK –3.42. The equilibrium line presented on Fig. 6 corresponds to a pK value of –3.42. The four water samples with the highest concentration of Ba^{2+} are close to the equilibrium, as well as two with the highest SO_4^{2-} concentration. It is obvious, that at SO_4^{2-} concentrations below 3 mg/l, the limit value set for Ba^{2+} (2 mg/l) can be exceeded. Also, at Ba^{2+} levels of 10 mg/l, HCO_3^- concentration of 100 mg/l and pH 8.2, witherite (BaCO_3) is still well under saturation (saturation index –0.8). So, witherite cannot limit the concentration of Ba^{2+} into an acceptable range even at the usual concentrations of HCO_3^- in the groundwater. The results of chemical analyses and modelling suggest a geological source for elevated barium content in groundwater in the central region of North Estonia. Proterozoic bedrock in the northeastern part of Estonia, cut through by numerous linear zones of disturbances, consists mainly of

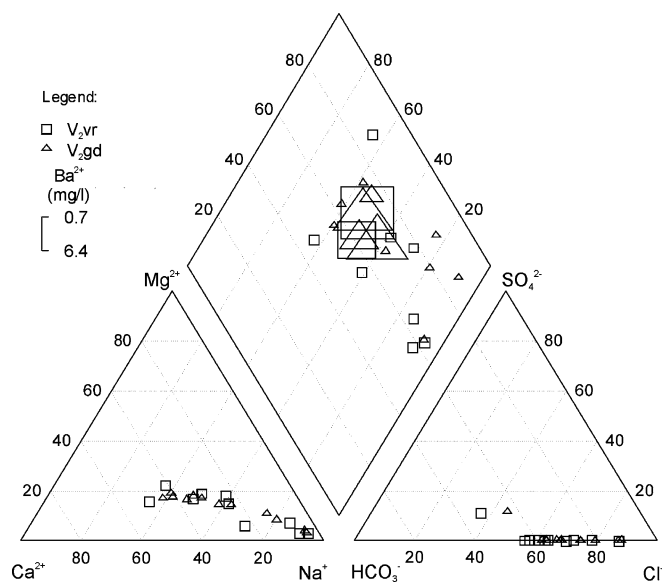


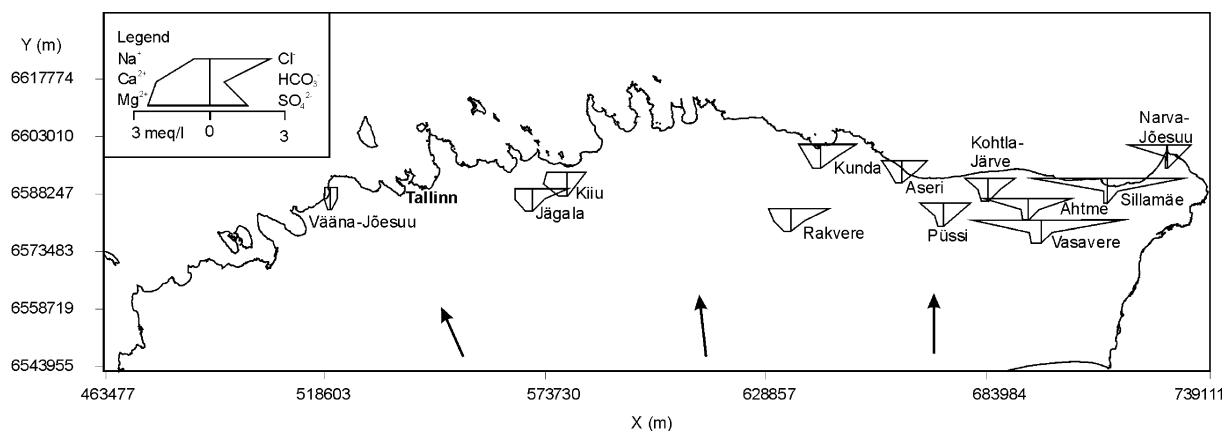
Fig. 3

Piper diagram reflecting the chemical type of groundwater in study area and proportional content of Ba^{2+} . V_2vr – Voronka aquifer, V_2gd – Gdov aquifer

gneisses and biotite gneisses. In the uplifted areas of bedrock in the vicinity of Kunda and Rakvere, there are sulphidic black schists, quartzites, amphibole and pyroxene gneisses (Koistinen and others 1996). During magmatic differentiation barium is removed from silicate melts when potassium minerals crystallize, and in rocks it is present especially in micas and potassium feldspar. Hydrothermal solutions and the late differentiates of silicate melts contain sulphate, which precipitates barium as insoluble baryte (BaSO_4). According to Klein and others (1983) the content of barium in the gneisses of the Estonian crystalline basement is 700 ppm. The highest average Ba^{2+} concentration (1,000 ppm) of northeastern Estonian bedrock has been detected in silicate marbles (Koppelmaa and Kivisilla 1997), which are associated with hydrothermal pyrrhotite-pyrite ore mineralisation in the Kunda and Rakvere region.

Fig. 4

Stiff diagram showing the lateral changes in the chemical composition of groundwater in the Gdov aquifer in North Estonia. Regional groundwater flow direction after Perens and Vallner (1997) is marked with arrows



On the other hand, barium is strongly adsorbed by clay minerals (Kabata-Pendias and Pendias 1984) and by metal oxides and hydroxides (Hem 1959). The weathering zone of Estonian basement rocks is composed predominantly of kaolinite, illite, chlorite and montmorillonite providing adsorption sites also for Ba -ions.

The crystalline basement comprises groundwater in its upper weathered and fissured portion and is in places hydraulically connected with the overlying Cambrian-Vendian aquifer system. Fracture zones with an interconnected network of open fractures can conduct significant groundwater flow. Groundwater in the clayey weathering zone of the crystalline basement contains TDS 10–20 g/l (Karise 1997) in northern Estonia being the probable source of chemical compounds in the Gdov aquifer. Thus, one of the potential barium sources is advection between the water bearing underlying weathering zone. Besides, the working intervals of groundwater abstraction wells opening the Gdov aquifer often locate close to the weathered basement and as the influence of pumping increases, the upconing of the water from underlying bedrock may take place. However, the exact identification of the geological source of the barium needs detailed sampling and chemical analysis of crystalline basement rocks and the weathering zone.

Conclusions

A barium anomaly with a maximum Ba^{2+} content of 6.37 mg/l was distinguished in the Cm-V aquifer system of Estonia. Anomalously high barium values are associated with groundwater supply wells of Kunda, Rakvere and Kohtla-Järve cities in North Estonia.

The modelling results show that sulphate and bicarbonate ions are the main compounds that precipitate the barium ion out from solution, although the bicarbonate ion has practically no influence when barium ion concentrations are low (<10 mg/l). The content of chloride ions, vice versa, contributes to increased solubility of the barium ion. The results also showed that in the case of a low (<3 mg/l) concentration of sulphate ions the barium ion content in the Cm-V aquifer system can be higher than the limit value (2 mg/l) set for drinking water by the EPA.

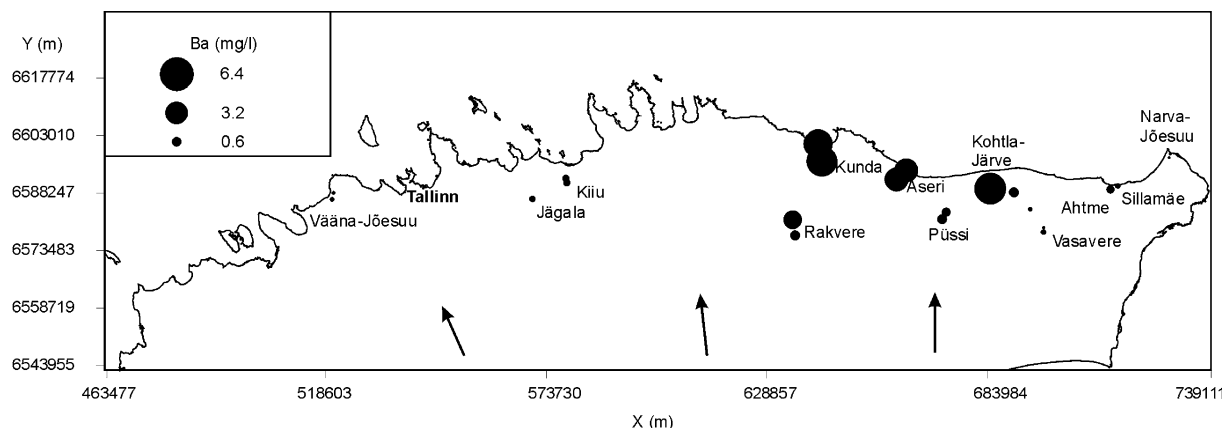


Fig. 5

The content of Ba^{2+} in the Cambrian-Vendian aquifer system in North Estonia. Regional groundwater flow direction after Perens and Vallner (1997) is marked with arrows

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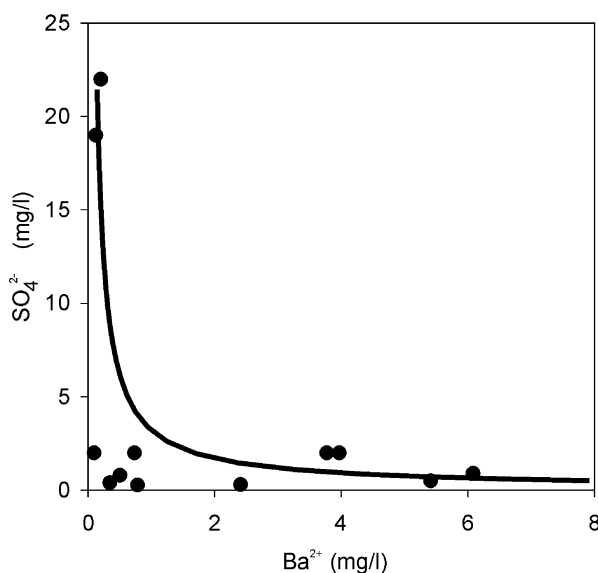


Fig. 6

The Ba^{2+} and SO_4^{2-} content in the groundwater of the Cambrian-Vendian aquifer system and the equilibrium line of baryte solubility modelled by PHREEQC

The crystalline basement and its weathering zone are the probable sources of barium in groundwater draining Vendian and Cambrian terrigenous rocks. Groundwater in the clayey weathering zone of the crystalline basement is hydraulically connected with the overlying Cm-V aquifer system, thus the capturing of deeper-seated groundwater by intensive exploitation of wells is possible.

High concentrations of the Ba-ion in natural waters are uncommon, but the anomalies exist in the conditions, where a Ba^{2+} source is available and sulphate concentration is low. The attention of policy-makers and health organisations should be turned towards the scientific evidence of such anomalies, and the work of natural scientists should be integrated with health and legislation development issues.

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