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Chemical composition of bottled mineral waters in Estonia

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ABSTRACT

Five commercially available in Estonia brands of bottled water have been analysed for 59 chemical elements by ICP-QMS and ICP-AES techniques to assess the quality of domestic mineral waters in scope of the European Groundwater Geochemistry Project initiated by the Geochemistry Expert Group of EuroGeoSurveys. Contents of 9 cations and anions, pH and electrical conductivity (EC) were measured in the bottled mineral waters by IC, titration and photometric methods. The data showed a significant difference between natural undiluted mineral water (Värska Originaal) characterised by the highest values of pH, EC and majority of trace elements studied, and other domestic waters sold in Estonia.

The results obtained were compared with the drinking water standards (US EPA, EU and Estonian Permitted Limits). Despite of the wide range of trace element concentrations in all Estonian brands of commercially sold waters the estimated values are generally within defined maximum concentrations allowed for drinking water.

The B concentration assessed in the Värska Originaal water above the maximal permitted values defined as 1 mg/L is a result of long residence time of water due to slow water exchange in the water-bearing Ordovician–Cambrian rocks.

Differences in chemical composition of the bottled waters are linked to host rocks geology in the studied area.

1. Introduction

Mineral water containing various dissolved minerals is used for medicinal aims since a long time. Sharp growth of mineral water consumption has been observed in the last years, and the rising trend is expected to continue. Mineral water is consumed as a drink beneficial for human health and is used for therapeutic purpose in different types of spas and baths. Production of bottled mineral water is increasing in the world and many various brands of mineral water are now available for sale. According to data from European Federation of Bottled Waters (http://www.efbw.eu/bwf.php?classement=07) the average annual consumption of bottled water in the European Union is 105 l per capita. In Europe dominates Italy where consumption of bottled water is approximately 200 l per habitant per year and the minimal consumption is estimated for Finland (16 l per capita a year). Annual consumption of mineral water in Estonia is approximately 30 l per inhabitant a year and it is 18th place in Europe. This amount is approximately 4–5 times less than in the countries with the highest consumption of natural mineral water in Europe (Italy, Germany, France and Spain) (The Association of Cities and Regions for Recycling and Sustainable Resource management; www.acrplus.org/upload/documents/document344.pdf).

Existence of the different types of mineral water in Estonia for the first time was indicated in the last century. Systematic study of mineral water resources was started in the second half of the 20th century. The first deposit of mineral water in Estonia was discovered in Pärnu in 1959 (Karise, 1997). The mineral water was found on the depth more than 500 m and belonged to Cl–Na hydrochemical type with the TDS content of about 22 g/L (Vingisaar 1978). The total reserve of salty and salt water in Estonia reaches hundreds of cubic kilometers. At about 6000 m^3/d of groundwater with TDS 2 g/L or more that is classified in Estonia as mineral water is available now in the country (Karise, 1997).

The mineral water deposits have been found in 16 sites in Estonia (Perens and Vallner, 1997). Locations of wells used for bottling now, locations where the mineral water is used for the curative purposes in baths and spas, and other mineral water deposits are shown in Fig. 1.

There are Kärdla, Kuressaare and Ruhnu located at the Islands Hiiumaa, Saaremaa and Ruhnu. Häädemeeste, Arumetsa, Ikla, and Värska are located in the south from the line Pärnu–Värska on the continental part of the country. Hirvli, Pärispea, Pudisoo, Käsmu and Meriküla are situated on the northern seacoast of Estonia, and Rammu and Põhja-Uhtju are at the islands of the same names in the Gulf of Finland. In Estonia the bottling and marketing of mineral water were started in 1968. Since this time the mineral water was derived from

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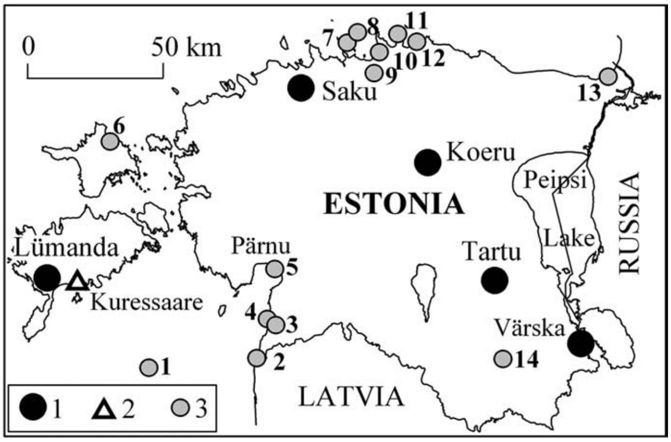

Fig. 1. Location of wells: 1 — used for bottling natural mineral water, 2 — used for extraction of water applied for the curative purposes in spas, 3 — other mineral water deposits: 1 — Ruhnu Island, 2 — Ikla, 3 — Arumetsa, 4 — Häädemeeste, 5 — Pärnu, 6 — Kärdla, 7 — Rammu Island, 8 — Põhja-Uhtju Island, 9 — Hirvli, 10 — Pudisoo, 11 — Pärispea, 12 — Käsmu, 13 — Meriküla, 14 — Võru. Compiled by Perens (Perens and Vallner, 1997), edited by authors.

the wells at Häädemeeste, Arumetsa, Ikla, Kärdla, Pärnu, Värska and Kuressaare. At the present time the mineral water is bottled at five locations: at Saku, Koeru, Värska, in Tartu city and at the Island Saaremaa, in Lümanda settlement.

Despite of mineral water being associated for the people with safer and healthier drink than tap water, the quality and composition of mineral water vary with its origin and require careful monitoring. Five bottled natural waters, which are sold now in Estonia, were evaluated in scope of the European Groundwater Geochemistry Project initiated by the Geochemistry Expert Group of the European Geological Surveys (EGS). The analytical results for the Estonian brands of bottled waters will be presented in the European mineral water atlas (EuroGeoSurveys, 2010) combining high quality geochemical data for 1785 samples analysed for 71 chemical parameters.

2. Methods

The bottles with mineral water shopped from ordinary supermarkets were shipped to the Federal Institute of Geosciences and Natural Resources (BGR) in Hanover, Germany.

Chemical analysis of the bottled water for 59 elements was carried out in the laboratories of BGR by inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS) using an Agilent 7500ce instrument. The F, Cl^-, NO_2, Br^-, NO_3^- and SO_4^{2-} were analysed by ion chromatography (IC) on a Dionex ICS 3000 ion chromatograph. A Thermo Unicam UV 300 was used for ammonium ion measurement by the photometric method. Titration method was applied for determining alkalinity. Applied analytical methods are described in detail in this issue (Birke et al., 2010-this issue).

Because the Värska mineral water was stored up to three days in a large stainless steel cistern before bottling, two additional samples were taken. One directly from the well located at the territory of the A. Le Coq Tartu Õlletehas (2010) and one from the large stainless steel cistern. These samples were analysed for Cr and Ni in the Chemical Laboratory of Geological Survey of Sweden.

The certified international water reference material and standards for trace elements were used as a part of the quality control procedure.

3. Geological setting and main water types

The territory of the country is approximately 45,000 km^2 and in 2009 Estonia had a population of about 1,340,000 (Statistics Estonia, 2009; http://www.stat.ee).

The territory of Estonia is located on the southern slope of the Baltic Shield. On top of the Palaeproterosoic crystalline basement sloping southwards at 3–4 m per kilometre lay the Ediacarian (Vendian) and Palaeozoic (Cambrian, Ordovician, Silurian and Devonian) sedimentary rocks. A sedimentary cover having the thickness of 100–200 up to 500–800 m from north to south of the country is overlaid by the Quaternary deposits (Puura and Raukas, 1997).

Five aquifer systems (Middle Devonian, Middle–Lower Devonian, Silurian–Ordovician, Ordovician–Cambrian and Cambrian–Vendian) that are different in their distributions on the territory of Estonia, geology and chemical composition are the major sources of groundwater in Estonia (Karro et al., 2009).

According to the Estonian standards the groundwater has to contain 2 g/L or more of total dissolved solids to be recognised as a mineral water. Presently in Estonia the mineral water is derived for commercial bottling from all below described aquifers.

The upper Middle Devonian aquifer system extends into the southern portion of Estonia. It is comprised of a sequence of sand- and siltstones with interlayers of clay that thicken to about 250 m in south Estonia. Clayey rocks with low permeability divided the Middle Devonian aquifer system into several local aquifers. In the Middle Devonian aquifer the HCO_3–Ca–Mg (frequently also HCO_3–Mg–Ca) type of groundwater is formed (Karise, 1997) with the TDS content of 0.1–0.6 g/L and most commonly values of 0.3–0.4 g/L.

The Middle–Lower Devonian water-bearing rocks consist of fine-grained weakly cemented sand- and siltstones with interlayers of clayey and dolomitized sandstone. The SO_4–Cl–Ca–Na water with the TDS up to 4.6 g/L occurred in the upper portion (up to 250 m) of the aquifer. Sulphate rich water formed in the passive water exchange zone due to gypsum occurrence in the water-bearing rocks. In the deeper zone the chemical composition of the groundwater is significantly different and the concentrations of SO_4^{2-}, HCO_3^-, and NO_3^- are very low or these compounds are absent (Karise, 1997).

The Middle Devonian and Middle–Lower Devonian aquifer systems are the main sources for water supply in the towns and settlements in the southern Estonia.

The Silurian–Ordovician aquifer is comprised of a sequence of limestones and dolomites interlaid by clays that thicken to about 250 m. The upper, up to a depth of 30 m, part of the carbonate formation is very cavernous and fissured. On the depth from 30 to 100 m the clayey and marl interbeds form low-permeability layers that divided the Silurian–Ordovician system on several aquifers with limited extension (Vallner, 1994). In the upper part of the aquifer the water has the TDS content below 0.6 g/L and is characterised by HCO_3^-Ca–Mg and HCO_3^-–Mg–Ca compositions. In the coastal area and in the deeper part of the system the HCO_3^-–Cl–Na–Mg–Ca type of water with TDS between 0.3 and 1.5 g/L prevailed (Perens et al., 2001). The Silurian–Ordovician aquifer system is the main source of water for the areas north of the Pärnu–Peipsi Lake line and on the islands of the West-Estonian Archipelago.

The Ordovician–Cambrian aquifer system has a thickness increasing to the south from 20 up to 60 m. It includes the Kallavere–Tiskre aquifer (O_1kl–C_1ts) whose depth from the ground is approximately 20 m in the northern Estonia and reaches 500 m in the south of the country. The TDS content ranges from 0.3 to 1.5 g/L and in central and southern Estonia the HCO_3^-–Cl–Na–Mg–Ca water is more widespread. On Hiiumaa Island (Kärdla) the water has a Cl–Na, Cl–Na–Ca and Cl–Ca–Na type (Karise, 1997).

The deepest Cambrian–Vendian aquifer system is formed by Vendian and Cambrian silt- and sandstones lying on top of the crystalline basement consisting of metamorphic gneisses, schists, quartzites and amphibolite. In the northern Estonia the Cambrian–Vendian aquifer is recharged by fresh meteoric water through the ancient buried valleys filled with Quaternary sediments presented by till, and glaciofluvial and glaciolacustrine sediments (Karro and

Marandi, 2003). The Vendian deposits are declined to the west of Estonia and on the Estonian islands the water-bearing rocks are presented by the Cambrian sand- and siltstones interlayed by thin clay layers. In the eastern and southern parts of Estonia the Cambrian–Vendian aquifer system is subdivided into Voronka (V_2vr) and Gdov (V_2gd) aquifers composed by quartzose sand- and siltstones, and mixed-grained sand- and siltstones, respectively (Perens and Vallner, 1997). In northern Estonia groundwater has the TDS values lower than 1 g/L and is characterised by Cl–HCO_3^-–Na–Ca and HCO_3^-–Cl–Ca–Na compositions (Perens et al., 2001). In northeastern, southwestern and southeastern Estonia the water with TDS values up to 22 g/L and the domination of Cl and Na^+ is widespread (Karise, 1997). The results of isotope investigations showed that the water in the Cambrian–Vendian aquifer system was recharged during the last glaciation (Vaikmäe et al., 2008).

4. Results and discussion

Five brands of bottled natural mineral waters are now sold in Estonia. These are pumped from wells drilled into various aquifers at different depths in the sequences of sedimentary rocks (Table 1).

The most famous mineral water in Estonia is the water at Värska situated in Põlva County in East-southern Estonia. The mineral water at Värska occurs in Devonian, Ordovician–Cambrian and Cambrian–Vendian aquifer systems. The bottling of the best-known mineral water under the brand name Värska derived from the Ordovician–Cambrian aquifer system from the depth of 463 m was started since 1968. Already in 1987 its annual production reached 17 million 0.5 L bottles. This Cl–Na–Ca–(Mg) water registered under the trademark “Värska Originaal” and bottled by the AS Värska Vesi is used largely for treatment of chronic digestive tract diseases (hypoacidity) and some metabolic diseases. In 2005 water Värska Originaal was certified in Estonia as a natural mineral water and is officially recognised as a mineral water in Estonia.

One more type of mineral water produced by Tartu Brewery Ltd (now A. Le Coq Company) is the Värska mineralized water. On the production of this bottled water it used the Middle–Lower Devonian groundwater of HCO_3–Mg–Ca-type and 0.4 g/L TDS (Karise, 1997) pumped from the depth of 200 m. According to published information some amounts of salts are added to the derived water prior to its bottling (http://www.alecoq.ee/drinks/water/varska).

The mineral water bottled in the settlement Lümanda at Island Saaremaa (Saaremaa Vesi) is obtained from the well opened to the Silurian–Ordovician aquifer system on the depth of 45 m. In the depth of up to 30–50 m in this aquifer the HCO_3^-Ca–Mg and HCO_3^-–Mg–Ca water with a low content (less 0.6 g/L) of dissolved solids prevailed (Karro et al., 2009).

Mineral water used for the production of Võluvesi water is derived from the Ordovician aquifer and pumped from the depth of 120 m in settlement Koeru in the central Estonia (Järva County).

Mineral water under the brand Saku water is produced from the water extracted from the Cambrian–Vendian aquifer system from the depth of 235 m and is filtered prior to bottling. In the formation of the groundwater composition of this confined aquifer the processes of host rocks leaching and leakage from the upper weathered part of crystalline basement play an important role (Marandi, 2007).

The obtained results (Table 2) indicated that there are considerable variations among the examined bottled waters with respect to their chemical constituents and physicochemical parameters.

The electrical conductivity (EC) can be used as an indirect measurement of total dissolved solids (TDS) in the water. EC in µS/cm can be converted to TDS in mg/L with multiplication by factor of 0.65 (Harter, 2010; http://groundwater.ucdavis.edu/Publications/Harter_FWQFS_8084.pdf). The EC ranges from 175 to 4370 µS/cm and reflects the high variability of the total dissolved solids (TDS) content (Lloyd and Heathcote, 1985) in the Estonian bottled waters. The highest EC values were estimated for the bottled Värska Originaal and Värska mineralised waters (4370 µS/cm and 2130 µS/cm). Other bottled waters in Estonia have EC values significantly lower like Saaremaa (588 µS/cm) and Võluvesi (588 µS/cm) mineral waters. The lowest EC (175 µS/cm) was determined in the water Saku.

The pH values of both sold under brands Värska Originaal and Värska mineralised waters are significantly low (4.7 and 5.3 respectively) because they are treated by the addition of carbon dioxide for carbonation prior to bottling. Estimated pH values are significantly lower than recommended by the USA EPA pH level between 6.5 and 8.5 for drinking water. Water with a low pH may cause corrosion of metal pipes, resulting in the release of metals, including the toxic ones such as Cd, Cu, Pb, Zn etc. that may pose a negative health effect (Laluraj and Gopinath, 2006). Other types of Estonian bottled waters are slightly basic (the pH value is between 7.55 and 7.7) (Figs. 2 and 3).

Comparison of bottled water showed a significant difference in the concentrations of HCO_3^-, SO_4^{2-} and SiO_2 that are substantially higher in the waters from upper aquifers composed by carbonates than in the deeper Ordovician–Cambrian and Cambrian–Vendian aquifers where the water-yielding portion consists of generally sand- and siltstones.

The HCO_3^- concentration in the upper aquifer systems consisted of limestone and dolomite with clayey interlayers is in the limit of 200–400 mg/L marked as balanced for the water having pH values between 7.2 and 7.6 (Karise, 1997). The waters from the wells tapping the silt- and sandstones of Ordovician–Cambrian and Cambrian–Vendian aquifers contain 96.4 and 41.8 mg/L of HCO_3^-, respectively.

The Värska Originaal and Saku waters from Ordovician–Cambrian and Cambrian–Vendian aquifers are characterised by a lowering in

Table 1
General data regarding wells used for bottling mineral water and lithology of water-bearing aquifers in Estonia.

Brand of bottled water	Bottling location	Aquifer system	Depth of well, m	Water-bearing rocks
Värska, mineralised	Tartu	Middle–Lower Devonian	200	Sandstone, limestone and dolomite
Saaremaa Vesi	Lümanda	Silurian–Ordovician	45	Limestone and dolomite, often cavernous, with clayey interlayers
Võluvesi	Koeru	Silurian–Ordovician	120	Limestone and dolomite
Värska Originaal	Värska	Ordovician–Cambrian	463	Sandstone and siltstone
Saku	Saku	Cambrian–Vendian	235	Sandstone and siltstone

Table 2
The pH, electrical conductivity (EC), concentration of main cations and anions in the bottled mineral waters in Estonia and and tap water from Tallinn (Nõmme district).

	Unit	Värska Originaal	Värska	Saaremaa Vesi	Võluvesi	Saku	Tallinn (Nõmme), tap water
pH		4.7	5.3	7.55	7.7	7.55	7.76
EC	m	4370	2130	588	596	175	727
HCO_3^-	mg/L	96.4	429	322	340	41.8	154
NH_4^+	mg/L	0.113	<0.005	<0.005	<0.005	<0.005	<0.005
NO_2^-	mg/L	<0.005	<0.005	0.349	0.058	<0.005	<0.005
NO_3^-	mg/L	0.65	24.3	0.01	2.47	0.29	0.72
PO_4^{3-}	mg/L	0.08	0.18	0.04	0.03	0.02	<0.01
SO_4^{2-}	mg/L	16.1	49.4	37.6	37.1	6.03	99.9
SiO_2	mg/L	6.8	9.1	9.6	6.2	2.2	4.49
Br^-	mg/L	9.25	0.09	0.054	0.011	0.222	0.556
Cl^-	mg/L	1338	444	13.4	7.33	27.1	138
F^-	mg/L	0.106	0.18	0.644	0.399	0.271	0.365

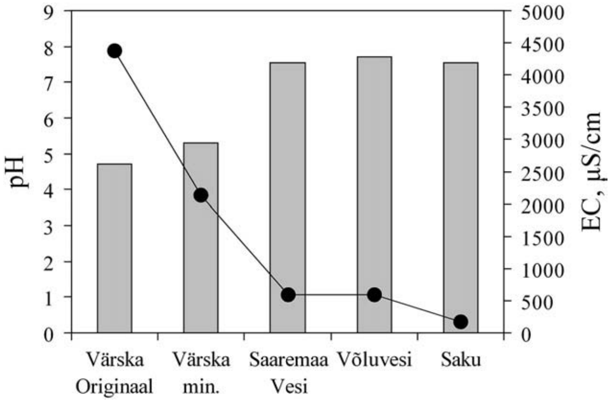

Fig. 2. pH and electrical conductivity (EC) variation in bottled mineral waters in Estonia. Filled circles are the pH values, and shaded columns showed the electrical conductivity values.

sulphate ion content (16.1 and 6.03 mg/L) in comparison with water derived from Devonian sandstones or Silurian and Ordovician carbonate rocks where SO_4^{2-} concentration ranges from 37.1 up to 49.4 mg/L. All of them are well below the current Estonian and international drinking water regulations of 250 mg/L SO_4^{2-}.

In the Värska Originaal high water concentrations of Cl^- (1338 µg/L) typical for water from the Ordovician–Cambrian aquifer at the great depth (Perens et al., 2001) were found. Exceeding Cl^- concentration in the Värska mineralised water could be explained by high Cl^- content in the derived groundwater used for the bottled water production as well as potassium and sodium chlorides added (private communication) to this water prior to the bottling. Fluoride concentrations in the bottled water are lower than its permissible concentration in drinking water in Estonia (1.5 mg/L) (Estonian Drinking Water Standards, 2001) and do not pose a health risk to individuals.

The highest concentration of Br in the bottled waters studied (9.25 mg/L), which was revealed for the Värska Originaal, is significantly lower than it was estimated in the groundwater of the Ordovician–Cambrian aquifer derived from the depth of 520 m and deeper (Karise, 1997). Br is not covered by standard limits but with the groundwater quality criterion is suggested to be 1 mg/L (Brindha and Elango, 2010). However, several studies showed that daily intake doses of 1 mg/kg body weight do not lead to changes observed in physical examination and only 1000 or more milligrams of Br taken daily can be potentially harmful for living organisms and lead to the negative health effect.

In general, despite of the significant difference in the contents of major constituents the natural water bottled in Estonia has concentrations of major measured nutrients in the limits of established local legislation and international standards. Data regarding major constituent contents reported at the labels on the bottles and available only for Värska Originaal and Võluvesi waters are very similar to measured concentrations for Värska Originaal and close to data for Võluvesi waters.

The chemical composition of natural mineral water depends on many factors, including the mineralogy/lithology of the aquifer, residence time of the water (Grošelj et al., 2010), amount of solids and trace elements which are soluble under the given pH and redox conditions and originated from the local water source (Banks et al., 1995; Misund et al., 1999) etc. In spite of mineral water's consumption growth the data on the abundance and potential risk on the health of trace elements are very limited (Reimann et al., 2003; Krachler and Shotyk, 2009). In Estonia the concentrations that exceeded the permitted values by the EU regulations were indicated for cadmium (Cd), lithium (Li), manganese (Mn) and lead (Pb) in Värska groundwater derived from the Ordovician–Cambrian aquifer system (Karise, 1997; Marandi, 2007).

The chemical composition of Estonian bottled mineral waters is summarized in Table 3. There are also indicated detection limits for the 59 elements measured.

Chemical element concentrations were compared (Table 3) with relevant national and international drinking water standards including European Directive 98/83/EC (EEC, 1998), European Union Commission Directive (EU2003/40/EC, 2003), United States Environmental Protection Agency (EPA, 2002), and Estonian Permitted Limits for drinking water (2001). At the same time the allowable values for quite a number of elements measured for bottled water including the hazardous ones are not estimated. Only for 23 among 68 measured elements maximum acceptable concentrations including the secondary maximum contaminant levels (SMCL) are defined by international controlling organizations. The SMCL which are guidelines established by the US EPA (2002) are marked in Table 3 by the asterisks.

The results showed a significant variation of trace element concentration among bottled mineral waters. The highest difference in element concentrations is observed for Al, As, B, Ca, Co, Cr, Cu, Dy, Fe, Ho, K, Li, Mn, Mg, Na, Ni, Rb, Sb, U, Y, Zn and Zr that may be attributed generally to the difference in dissolution and ion exchange processes in water-bearing rocks. With respect to other studied bottled waters the Värska Originaal water is characterised by the higher contents of the majority of trace elements studied and shows clearly higher concentrations of B, Bi, Ca, Co, Cr, Cs, Ge, I, Li, Mg, Mn, Nb, Pb, Rb, Sn, Sr, Ta, Te, Ti and W. The lowest concentrations of the majority of measured elements in the water studied were estimated for Saaremaa and Saku mineral waters. It could be noted that Saku water originated from the Cambrian–Vendian aquifer whose water is

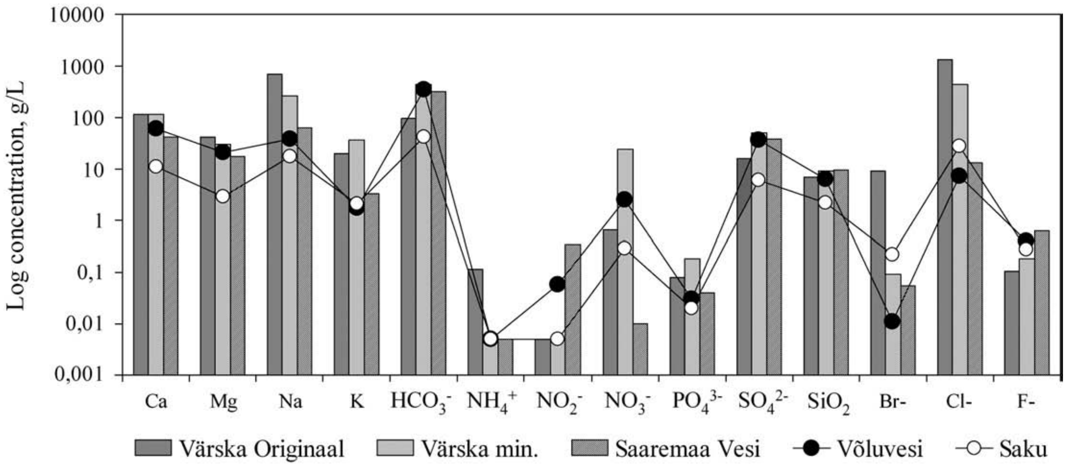

Fig. 3. Concentrations (log-scale) of main cations and anions in bottled mineral waters in Estonia.

Table 3

Trace element concentrations in bottled mineral waters in Estonia and tap water from Tallinn (Nõmme district). Element limit values for drinking water given by the European, US EPA and Estonian regulations and standards are listed for comparison.

Element	Unit	Detection limit	Värska Originaal	Värska mineralised	Saaremaa Vesi	Võluvesi	Saku	Tallinn (Nõmme), tap water	EEC standards (1998)	EU2003/ 40/EC (2003)	EPA MCL	Estonian PL, 2001
Ag	µg/L	0.001	0.00109	<0.001	<0.001	<0.001	<0.001	<0.001			100*	
Al	µg/L	0.05	1.27	0.728	0.829	11.4	<0.3	0.791	200		200*	
As	µg/L	0.01	0.0965	0.247	0.146	0.184	<0.01	0.023	10	10	10	10
B	µg/L	0.1	1180	54.1	85.9	31.8	119	75.2	1000			1000
Ba	µg/L	0.005	0.182	0.267	0.056	0.117	0.039	178		1000	2000	1000
Be	µg/L	0.001	<0.001	<0.001	<0.001	0.0517	<0.001	0.0042			4	
Bi	µg/L	0.0005	0.00314	<0.0005	<0.0005	<0.0005	<0.0005	0.0008				
Ca	mg/L	0.01	117	116	41.2	61.1	10.9	82.2				
Cd	µg/L	0.001	0.00245	0.00245	0.00206	0.00268	0.00247	0.0143	5	3	5	5
Ce	µg/L	0.0005	0.000722	0.00137	0.0016	0.00815	<0.0005	0.00133				
Co	µg/L	0.002	0.21	0.0316	0.0244	0.126	<0.002	0.0127				300
Cr	µg/L	0.01	16.5	1.77	0.0537	0.0327	0.0891	0.0947	50	50	100	50
Cs	µg/L	0.0005	0.0678	0.00535	0.011	0.00694	0.00466	0.0107				
Cu	µg/L	0.001	0.504	0.276	0.646	2.08	0.561	4.46	2000	1000	1000*	2000
Dy	µg/L	0.0002	0.000797	0.00149	0.000801	0.01	0.0002	0.000305				
Er	µg/L	0.0002	0.000219	0.000655	0.000551	0.00873	0.00011	0.000169				
Eu	µg/L	0.0002	0.0128	0.0187	0.00413	0.0089	0.00237	0.0166				
Fe	µg/L	0.01	86.1	2.2	1.89	0.741	0.114	2.66	200		300*	
Ga	µg/L	0.0005	<0.001	<0.001	0.0032	0.0112	0.00479	3.54				
Gd	µg/L	0.0002	0.00343	0.00208	0.000826	0.00775	0.000225	0.00313				
Ge	µg/L	0.005	0.0728	0.0106	0.0201	0.0579	0.083	0.167				
Hf	µg/L	0.0001	0.00158	0.00108	0.00197	0.00193	0.000501	0.000718				
Hg	µg/L	0.001	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	1	1	2	1
Ho	µg/L	0.0001	0.000255	0.000575	0.00029	0.0027	0.000277	0.000293				
I	µg/L	0.01	31.5	6.7	10.8	6.31	9.54	35.9				
K	mg/L	0.1	19.6	36	3.3	1.7	2.1	5.7				
La	µg/L	0.0001	0.00275	0.00277	0.00135	0.00652	0.000549	0.00165				
Li	µg/L	0.01	84.4	5.55	3.95	11.8	3.48	6.93				
Lu	µg/L	0.00005	0.00031	0.000286	0.0000605	0.00139	<0.0001	0.000111				
Mg	mg/L	0.01	41.7	30.4	17.3	20.5	2.88	23.1				
Mn	µg/L	0.005	0.012	0.001	0.004	0.002	<0.001	0.317	50	50	50*	50
Mo	µg/L	0.001	0.883	0.401	1.07	0.901	1.42	5.99				70
Na	mg/L	0.1	677	267	62.4	38.8	17	46.6	200			
Nb	µg/L	0.001	0.00321	0.00147	0.00155	0.00276	<0.001	0.00192				
Nd	µg/L	0.0001	0.000892	0.00119	0.0012	0.00907	0.000374	0.00141				
Ni	µg/L	0.005	21.6	0.199	0.112	1.59	0.163	0.0669	20	20	100	20
Pb	µg/L	0.001	0.143	0.0802	0.108	0.089	0.0254	0.00504	10	10	15	10
Pr	µg/L	0.0005	0.000321	0.00016	0.000215	0.00196	0.0000941	0.000171				
Rb	µg/L	0.001	10.8	0.728	1.66	1.28	0.883	2.18				
Sb	µg/L	0.001	0.395	0.541	0.269	0.407	0.00711	0.0172	5	5	6	5
Sc	µg/L	0.001	0.081	0.084	0.0518	0.138	0.0153	0.0647				
Se	µg/L	0.005	0.0187	0.341	<0.01	0.202	<0.01	<0.01	10	10	50	50
Sm	µg/L	0.0001	0.00365	0.0031	0.00119	0.00304	0.000459	0.00144				
Sn	µg/L	0.001	0.0463	0.00749	0.00575	0.00889	0.0176	0.00423				
Sr	mg/L	0.001	2.19	0.133	0.124	0.114	0.141	0.525				
Ta	µg/L	0.005	0.00492	0.00205	0.00101	0.00193	0.00109	0.00258				
Tb	µg/L	0.00005	0.000263	0.000215	0.000108	0.00119	<0.0001	0.000185				
Te	µg/L	0.001	0.0271	0.00902	0.0103	0.00798	<0.005	0.00989				
Th	µg/L	0.0001	0.000587	0.000586	0.000788	0.000691	0.000295	0.00051				
Ti	µg/L	0.005	0.123	0.0826	0.0209	0.193	<0.01	0.0803				
Tl	µg/L	0.0005	0.00249	0.0444	0.00188	0.00845	0.00136	0.00908			2	
Tm	µg/L	0.00005	0.000141	0.000188	0.000119	0.00119	0.0000593	0.000114				
U	µg/L	0.00005	0.00933	4.72	0.0283	2.39	0.0056	0.0238				
V	µg/L	0.01	0.24	0.293	0.0871	0.283	0.0606	<0.01				
W	µg/L	0.002	0.102	0.0274	0.0117	0.0233	0.0897	0.0229				
Y	µg/L	0.00005	0.0103	0.0059	0.00297	0.144	0.000594	0.0032				
Yb	µg/L	0.0001	0.000213	0.00106	0.000698	0.00822	0.000269	0.000329				
Zn	µg/L	0.01	2.13	0.792	1.19	28.8	2.22	53.4			5000*	5000
Zr	µg/L	0.001	0.00682	0.0782	0.0889	0.102	0.0013	0.00462				

characterised in the northern Estonia by a relatively low (0.4–1.0 g/L) content of dissolved solids (Karise, 1997) but due to the occurrence in the passive water exchange zone (Karise, 1997; Vaikmäe et al., 2008;) is usually rich in trace elements. However, the Saku bottled water has the lower concentration of the majority of elements measured (excepting Cr, Ge and some other elements) relative to other analysed waters. In the case of the Saku water, taking into account the purification of water before bottling, it is possible to suggest some lowering of element contents accompanying this treatment process.

Bottled Saaremaa mineral water originated from the carstic limestone and dolomites with K-bentonite layers. Trace element abundances are generally low in carbonate rocks and they are poor with respect to leaching to groundwater. At the same time in the Saaremaa mineral water relatively high concentrations of fluoride and boron are analysed. As showed in sequential leaching experiments (Karro et al., 2009) fluoride up to ten times most intensively leached from bentonite in comparison with carbonate owing to that the bentonite beds could be the potential source of F for the water in the

Silurian aquifer. Content of B in Saaremaa mineral water is the average (85.9 μg/L) among the waters studied.

Võluvesi water extracted from the depth of 120 m of the Silurian–Ordovician aquifer showed some increase of Cu, Mo, U, V, Y and Zn concentrations relative to other waters. This combination of elements is typical for dark argillite (so-called Dictyonema shale), rich in a large number of trace elements (Petersell, 1997), and that interbeds occurred in the lower portion of the Ordovician sequence.

Saaremaa and Võluvesi waters derived from the Silurian–Ordovician aquifer and Saku water extracted from the deepest Cambrian–Vendian aquifer have close to neutral pH and are characterised by a lower level of trace elements relative to Värska Originaal and Värska mineralised bottled waters. It could be caused by the fact that metal migration ability decreases significantly with increasing pH (Malinovskii, 2002) and the low concentrations of elements are ascribed to the neutral and basic pH reduced metal mobility.

Thus, the current study allowed to significantly enlarge the set of measured elements and did not reveal concentrations of any elements significantly exceeding permitted values for the drinking water established both at local and at international scales.

To estimate the effect of pumped water storage in stainless steel cistern before bottling on the water chemistry the water derived at Värska was sampled after pumping from the bedrock and prior to the bottling. The data obtained from the Chemical Laboratory of Geological Survey of Sweden showed that the water prior to the bottling has exceeding contents of Cr and Ni. Natural water taken directly from the well has contents of 0.5 μg/L of Cr and 2 μg/L of Ni. Storage of water in the cistern leads to the contamination by these elements which concentrations exceed up to 16.5 μg/L and 21.6 μg/L for Cr and Ni, respectively. Detected value of Cr in the bottled water is below the maximum permitted values. The Ni concentration is near to the allowed value and only negligibly exceeds it. According to information from Värska Vesi Ltd a stainless steel cistern for water storage was substituted with the plastic one in the first quarter of 2010 and contamination of bottled water was not observed after this event.

Trace element concentrations of Estonian bottled water were compared with tap water derived from the Cambrian–Vendian aquifer system, which is the main source of drinking water in northern Estonia including the capital of the country, Tallinn, in order to determine whether the differences in element contents of tap water and bottled waters are significant. Element concentrations of the tap water from Tallinn (Nõmme district) analysed at the Federal Institute for Geosciences and Natural Resources (BGR) are given for comparison in Tables 2 and 3. The EC value for tap water (727 μS/cm) exceeds considerably the respective data (175 μS/cm) for Saku bottled water derived from the same Cambrian–Vendian aquifer system. Concentrations of Cl (138 mg/L), Br (0.556 mg/L) and F (0.365 mg/L) in drinking water are in 5, 2.5 and 1.5 times higher, respectively, than in Saku water and considerably lower than permissible concentrations according to the EU regulations and Estonian drinking water standards. Tap water contains the Al, As, B, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, I, K, La, Li, Lu, Mn, Mg, Mo, Na, Nb, Nd, Pr, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Te, Ti, Tl, Tm, U, Y, Yb and Zn concentrations higher than in Saku mineral water purified prior to bottling. At the same time the concentrations of B, Ni, Pb, V and W are remarkably higher in bottled water that assumes that these elements' contribution has been attributed to purification process.

Tap water has significantly higher concentrations of Ba, Cd, Cs, Cu, Ga, Ge, I, Mn, Mo and Zn (also as Li, Rb and Sr except Värska Originaal) than in domestic mineral waters sold in Estonia. The main sources of trace elements in the Cambrian–Vendian tap water are leaching from the host rock and underlying crystalline basement, which comprises saline groundwater in its upper weathered zone and is hydraulically connected with the Cambrian–Vendian aquifer system (Vaikmäe et al., 2008). Tested tap water meets all standards for drinking water listed in Tables 2 and 3 and is suitable for municipal water supply.

6. Conclusions

The results of the chemical analysis of natural mineral waters showed an obvious difference in the total dissolved solids content in the bottled water in Estonia. The Värska Originaal and Värska mineralised waters have a high content of total dissolved solids and acidic pH due to carbonatisation of the bottled waters. Värska Originaal is characterised by highest concentrations dominated by Cl^- and NH_4^+ ions. Other mineral waters are weakly mineralised and dominated by the HCO_3^- and SO_4^{2}-ions. The lowest concentrations of main constituents including Ca, Fe, K, Mg and Na were determined in Saku mineral water that is purified (filtered) before bottling.

Trace element concentrations in mineral waters studied are in compliance with the requirements described in the Estonian, EU and EPA documents that imposed respective drinking water standards. The B value in the Värska Originaal mineral water (1180 μg/L) is slightly above the Estonian and European drinking water standards of 1000 μg/L. The elevated levels of Ni and Cr in this mineral water seem to be due to the contamination from storage in a stainless steel cistern prior to bottling. In the first quarter of 2010 this problem was solved because the cistern was replaced with a plastic one. None of these values pose threat to public health.

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References

A. Le Coq Tartu Õlletehas AS. Accessed via the internet http://www.alecoq.ee/drinks/water, March 2010.

Banks, D., Reimann, C., Røyset, O., Skarphagen, H., Sæther, O.M., 1995. Natural concentrations of major and trace elements in some Norwegian bedrock groundwaters. Appl. Geochem. 10, 1–16.

Birke, M., Reimann, C., Demitriadis, A., Rauch, U., 2010. Determination of main and trace elements in European bottled mineral water — analytical methods. J. Geochem. Explor. 107, 217–226 (this issue).

Brindha, K., Elango, L., 2010. Study on bromide in groundwater in parts of Nalgonda District, Andhra Pradesh. e-J. Earth Sci. India 3, 73–80 Accessed via the internet http://www.earthscienceindia.info/, March 2010.

Commission Directive 2003/40/EC of 16 May 2003. Annex 1. Constituents naturally present in natural mineral waters and maximum limits which, if exceeded, may pose a risk to public health. Official Journal of the European Union, 22.05.2003.L 126/37. Accessed via the internet (http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2003:126:0034:0039:EN:PDF), January 2010.

EEC, 1998. Council Directive 98/83/EC of 3 November 1998 on the Quality of Water Intended for Human Consumption. Official Journal L 330/32, 05.12.1998.

EPA (U.S. Environmental Protection Agency), 2002. List of Contaminants & their MCLs. Inorganic Chemicals. . EPA 816-F-09-0004, May 2009. Accessed via the internet (http://www.epa.gov/safewater/contaminants/index.html), January 2010.

Estonian Drinking Water Standard, 2001. The Quality and Monitoring Requirements for Drinking Water and Methods of Analysis. SOMm RTL 2001/100/1369 (in Estonian).

European Federation of Bottled Waters. Accessed via the internet (http://www.efbw.eu/bwf.php?classement=07), December 2009.

Grošelj, N., van der Veer, Grishja, Tušar, M., Vracˇko, M., Novicˇ, M., 2010. Verification of the geological origin of bottled mineral water using artificial neural networks. Food Chem. 118, 941–947.

Harter, T., Groundwater Quality and Groundwater Pollution. ANR Publication 8084. Accessed via the internet http://groundwater.ucdavis.edu/Publications/Harter_FWQFS_8084.pdf, March 2010.

Karise, V., 1997. In: Raukas, A., Teedumäe, A. (Eds.), Composition and Properties of Groundwater Under Natural Conditions. : Geology and Mineral Resources of Estonia. Estonian Academy Publishers, Tallinn, pp. 152–156.

Karro, E., Marandi, A., 2003. Mapping of potentially hazardous elements in Cambrian–Vendian aquifer system, northern Estonia. Bull. Geol. Soc. Finland 75, 17–27.

Karro, E., Marandi, A., Vaikmäe, R., Uppin, M., 2009. Chemical peculiarities of Silurian–Ordovician and Cambrian–Vendian aquifer systems in Estonia: an overview of hydrochemical studies. Estonian J. Earth Sci. 58, 342–352.

Krachler, M., Shotyk, W., 2009. Trace and ultratrace metals in bottled waters: survey of sources worldwide and comparison with refillable metal bottles. Sci. Total Environ. 407, 1089–1096.

Laluraj, C.M., Gopinath, G., 2006. Assessment of seasonal variation of groundwater quality of phreatic aquifers — a river basin system. Environ. Monit. Assess. 117, 45–57.

Lloyd, J.W., Heathcote, J.A., 1985. Natural Inorganic Hydrochemistry in Relation to groundwater. Clarendon Press, Oxford, England.

Malinovskii, D.N., 2002. Strontium migration in groundwater of fluvioglacial sediments in the Khibiny Massif. Water Resour. 29, 252–255.

Marandi, A., 2007. Natural chemical composition of groundwater as a basis for groundwater management in the Cambrian–Vendian aquifer system in Estonia. Ph. D Thesis, Tartu Univ.

Misund, A., Frengstad, B., Siewers, U., Reimann, C., 1999. Variation of 66 elements in European bottled mineral waters. Sci. Total Environ. 243/244, 21–41.

Perens, R., Vallner, L., 1997. Hydrogeology. In: Raukas, A., Teedumäe, A. (Eds.), Geology and Mineral Resources of Estonia. Estonian Academy Publishers, Tallinn, pp. 137–145.

Perens, R., Savva, V., Lelgus, M., Parm, T., 2001. The Hydrogeochemical Atlas of Estonia. Geological Survey of Estonia, Tallinn.

Petersell, V., 1997. Dictyonema argillite. In: Raukas, A., Teedumäe, A. (Eds.), Geology and Mineral Resources of Estonia. Estonian Academy Publishers, Tallinn, pp. 327–331.

Puura, V., Raukas, A., 1997. Estonia. In: Eldridge, E.M., Fairbridge, R.W. (Eds.), Encyclopedia of European and Asian regional geology. Springer, pp. 193–201.

Reimann, C., Bjorvatn, K., Frengstad, B., Melaku, Z., Tekle-Haimanot, R., Siewers, U., 2003. Drinking water quality in the Ethiopian section of the East African Rift Valley I —data and health aspects. Sci. Total. Environ. 311, 65–80.

Statistics Estonia. Accessed via the internet (http://pub.stat.ee/), November 2009.

The Association of Cities and Regions for Recycling and Sustainable Resource management. Accessed via the internet (www.acrplus.org/upload/documents/document344.pdf), January 2010.

Vaikmäe, R., Kaup, E., Marandi, A., Martma, T., Raidla, V., Vallner, L., 2008. The Cambrian–Vendian Aquifer, Estonia. In: Edmunds, W.M., Shand, P. (Eds.), The Natural Baseline Quality of Groundwater. Blackwell Publishing, pp. 353–371.

Vallner, L., 1994. Problems of groundwater quality management in Estonia. groundwater quality management: In: Kovar, K., Hofrichter, J. (Eds.), Proceedings of the GQM 93 Conference, Tallinn, IAHS Publ. 220, pp. 449–460.

Vingisaar, P., 1978. In: Heinsalu, Ü. (Ed.), Eesti mineraalveed ja nende kasutamine: Põhjavee kasutamisest ja kaitsest Eesti NSV-s. Eesti NSV Tead. Akad., Tallinn, pp. 54–71 (in Estonian).