TRACE ELEMENT CONTENT, SOURCE AND DISTRIBUTION REGULARITIES IN GROUNDWATER OF BALTIC ARTESIAN BASIN

I. RETIKE, A. KALVANS, A. DELINA, A. BABRE, B. RAGA, E. PERKONE, AND J. BIKSE

Faculty of Geography and Earth Sciences, University of Latvia, Riga, Latvia ,e-mail: inga.retike@lu.lv

INTRODUCTION

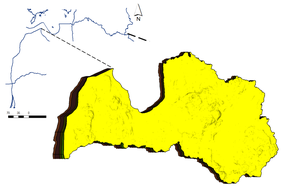

Figure 1. **Map of study area**

The territory of Latvia is a part of the Baltic Artesian (Sedimentary) basin which considering water chemistry and intensity of water connection between aquifers can be divided into three major water exchange zones: **freshwater** (active water exchange), **saline** (delayed exchange), and **brines** (stagnant water exchange zone) (table 1).

Table 1.

Stratification of hydrogeological cross-section (Levins et al. 1998); existing data and new results

Hydrogeological Zones	Multi-aquifer system	Main aquifers	Prevailing sediments	Existing data (Gosk et al., 2006)	New results and planned sampling sites
Active water exchange (freshwater)	Kvartārs Q		Sand, till, etc.	612	45
	Augšperma P_2		Limestone, dolomite	4	
	D_3fm	C_1	Sandstone, dolomite	2	
		Mūru-Ketleru D_3mr-ktl		5	5
		Jonišķu-Akmens D_3jn-ak	Dolomite, sandstone		
	D_3pl-aml	Stipiņu D_3st	Dolomite, marl	1	
		Katlešu-Ogres D_3kt-og	Sandstone, marl	12	3
		Daugavas D_2dg	Dolomite	12	2
		Salaspils D_2slp	Marl, gypsum	18	5 2 2
		Pļaviņu D_2pl	Dolomite	45	10
	D_{2-3}ar-am	Amatas D_2am	Sandstone, siltstone	14	13
		Gaujas D_2gj		39	28 1
		Burtnieku D_2br		19	8
		Arukilas D_2ar		3	3
Regional Narva aquitard D_2nr					
Delayed water exchange (saline)	D_{1-2}	D_2pr	Sandstone, siltstone	1	4
		D_2rz	Marl,sandstone		
		D_1km	Sandstone, siltstone		15
		D_1gr			
Ordovician and Silurian water proof formation O-S					2
Stagnant (brines)	C	Kembrija			1
Lontova water proof formation C_1ln					

Only two types of data sources are available on groundwater trace element concentrations in Latvia: **1)** the data from geological mapping and hydrogeological exploration during Soviet times and **2)** recent studies, particularly „Agricultural influence on groundwater in Latvia" (Gosk et al. 2006).

It is impossible to test the quality of the first; therefore, the old data is incomparable to data obtained by modern methods. The second data source is mainly limited to Quaternary sedimentary aquifer susceptible to agricultural influence.

AIM OF THE STUDY

The aim of this study is to determine the distribution and sources of trace elements in groundwater in Latvia and compare the results with WHO and EU potable water standards.

MATERIALS AND METHODS

Groundwater samples from monitoring and supply wells as well as boreholes and springs were analyzed by **total x-ray fluorescence** (TXRF) and **atomic absorbtion spectroskopy** to determine the concentrations of trace and major elements (cations).

The major **benefits** of **using TXRF analysis** is a simple multi-element analysis without external calibration, low maintenance and operating costs, and a small amount of groundwater sample needed (micrograms range). **Disadvantage** of TXRF analysis is a lower sensitivity compared to ICP-MS,it is impossible or unprecise to measure light elements with atomic number <13. Because of Mo excitation source is used it is impossible to measure Mo, Zr, Cd and other elements of interest. There are also some restrictions in detection of several elements because of the overlapping of the energy lines of elements.

Table 1.

Certified (ERM CA011b- Hard Drinking water UK) and by Röntec PicoTAX spectrometer measured values

Constituent	Certified value (µg/l)	Uncertainty (µg/l)	Measured values by TXRF (µg/l)	Coeficient of variation (µg/l)	Relative error, %
Al	209	11	<ZNR		
As	10,15	0,34	8,83	1,45	13
Ba	115,2	3,7	83,6	11,0	27
Be	5,01	0,41	N		
B	952	48	N		
Cr	48,2	1,6	45,5	1,39	6
Co	4,82	0,28	4[a]		
Cu	1936	75	1916	41	1
Fe	186	11	193	4	4
Pb	24,51	0,52	18,25	3,10	26
Mn	48,3	1,6	43,8	1,4	9
Mo	5,45	0,33	N	0,00	
Ni	19,27	0,68	15,83	1,91	18
Se	9,91	0,41	7,17	0,65	28
Sr	471	21	462	8	2
Zn	597	19	563	13	6
Br			62,25	3,48	

Constituent	Certified value (µg/l)	Uncertainty (µg/l)	Measured values by TXRF (µg/l)	Coeficient of variation (µg/l)	Relative error, %
Ca	73	2,7	60	1,2	18
Mg	14,78	0,48	N		
K	5,11	0,16	4,43	0,10	13
Na	22,77	0,78	10,38[c]	4,80	54

UDL- under detection limit
N- impossible to measure
a- element was detected only in one case from twelve replicates
b- $t_{0,95}$, n=12
c- $t_{0,95}$, n=4

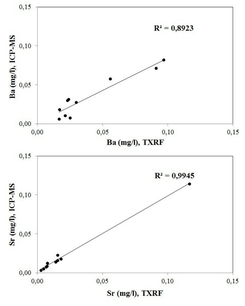

Figure 2. **Linear correlation between TXRF and ICP-MS results for barium and strontium**

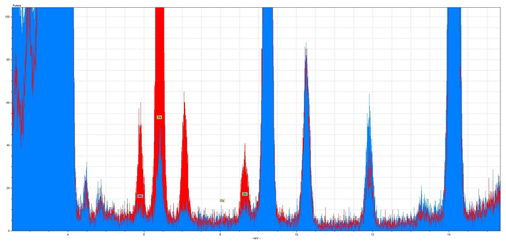

Figure 3. **TXRF spectra of acidified and not acidified groundwater sample : «red»- acidified, «blue»- not acidified (Murjāņi 99)**

CONCLUSIONS

1. This study confirmed that highlited calcium and strontium values occur in sulphate calcium saline groundwater (Levins and Gosk 2007), but also showed, that gypsum dissolution can result in highlited boron concentration to.
2. Barium values strongly depends on sulphate ion presence, therefore the sulphate ion rich groundwater (e.g. D3slp) mainly show smaller barium values.
3. There has been found several interesting connections between some trace elements (e.g. strong connection between K, Rb, Mn and Cu and connection between As and Fe in PCA analysis), but the existing data stilla areinsufficient to interpret and statistically prove all hypothesis.

References

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- Levins I., Levina N., Gavena I. 1998. *Latvijas pazemes ūdeņu resursi.* Valsts ģeoloģijas dienests, Rīga. 24 lpp.
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RESULTS

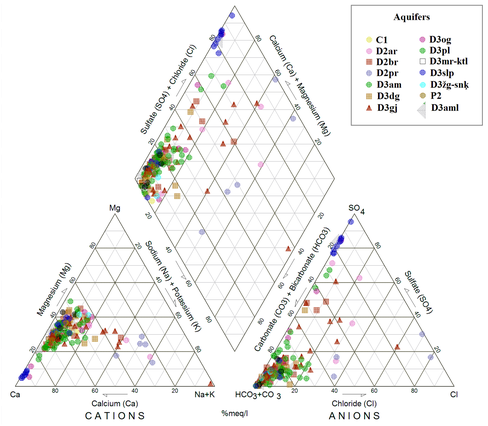

Figure 4. **Piper plot showing the composition of groundwater in the study area**

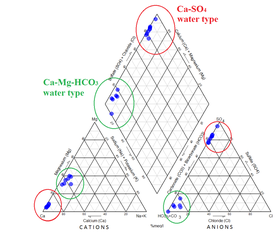

Figure 5. **Piper diagram reflecting the chemical type of groundwater in Salaspils (D3slp) aquifer**

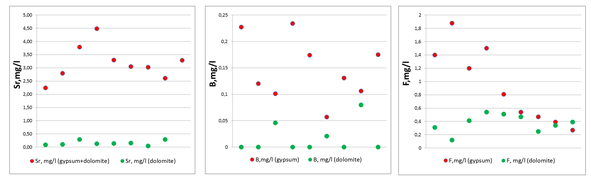

Figure 6. **Differences between trace element content in different water types within Salaspils (D3slp) aquifer**

Piper plot (Fig.4) shows that there ar three different types of water observed: 1) **Ca-Mg-HCO_3**, 2)**Ca-SO_4** and 3) and weakly approaching to **Na-CO_3** water type. All water types are reflecting the prevailing sediments in water bearing aquifers, e.g. dolomite or gypsum (table 1), but the third type possibly shows the freshening of groundwaters reflecting the chemistry of waters under the regional Narva aquitard.

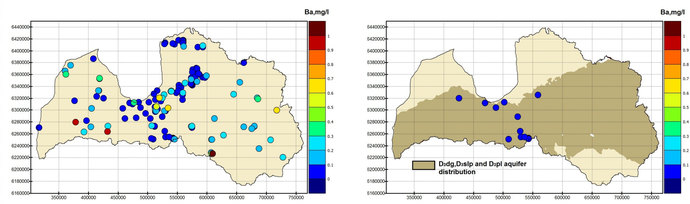

Figure 7. **a) Ba^{2+} values (>DL =0,001mg/l) in groundwater of Latvia b) Ba^{2+} values in gypsum containing dolomite sediments**

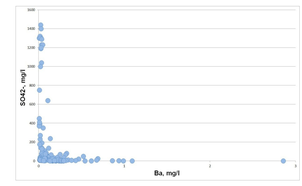

Figure 8. **The Ba^{2+} and SO_4^{2-} content in the groundwater within Latvia**

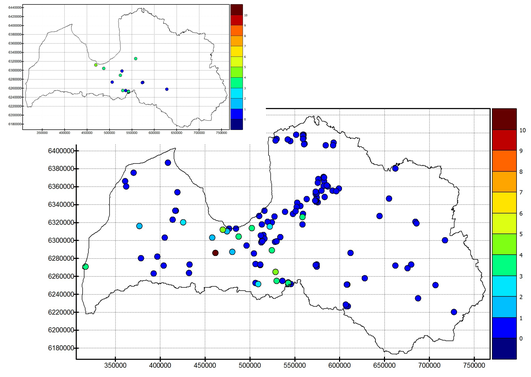

Figure 9. **a) B values (>DL =0,002mg/l) in groundwater of Latvia b) B values in gypsum containing dolomite sediments**

Barium naturally are common in igneous and sedimentary rocks, also in shale and coal and most frequently as a component of minerals baryte ($BaSO_4$) and witherite ($BaCO_3$) (Edmunds and Shand 2008; Marandi et al. 2004). The content of Ba within territory of Latvia varies from the analythical detection limit (1µg/l) to 2,86 mg/l (WHO guideline 0,3 mg/l).

The results from previous studies (Marandi et al. 2004) show that SO_4^{2-} and HCO_3 ions are the main compounds that precipitate the barium ion out from solution. This study confirmed that high SO_4^{2-} content in groundwaters can limit dissolved Ba^{2+} content in groundwater (Fig.8).

Teritorially, a higher concentration of Ba^{2+} can be clearly seen in eastern part of Latvia (Fig.7a) The lowest values more often are found in groundwater samples collected from gypsium containing dolomite or sandstone sediments compared with samples collected from dolomite or limestone sediments (Fig.7b). It is importatant to remember that Ba^{2+} can be strongly adsorbed on clay minerals and by metal oxides and hidroxides (Edmunds and Shand 2008).

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