

## HEAVY METAL CONTENTS IN DEEP AQUIFERS FROM THE REPUBLIC OF MOLDOVA.

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### Introduction

The Republic of Moldova has a large spectrum of underground mineral waters (16 reservoirs). The deep aquifers with mineral waters of different ages are situated at 200 –1,000 m depth: Vendian crystalline basement rocks (V), Silurian crystalline limestone (S<sub>1</sub>), Cretaceous limestone (K), Baden-Sarmatian limestone and clay-sand deposits (N<sub>1b-s1</sub>), middle Sarmatian limestone and clay-sand deposits (N<sub>1s2</sub>). [1,3-5]. The hydro-geochemical features of the main aquifers and the possible sources of trace elements in groundwaters were discussed elsewhere [1-6]. Other aquifers showed no significant mineralization, i.e. upper Sarmatian-Meotian (N<sub>1s3-m</sub>), Pontian (N<sub>2p</sub>), and alluvial (A<sub>3</sub>) horizons. The principal aquifer for potable and balneological purposes is in the Baden-Sarmatian horizon. The mineralization of these groundwater systems is between 1 and 120 g L<sup>-1</sup>. The therapeutically mineral waters are found to S and NE of the country and contain relatively high contents of H<sub>2</sub>S (30-80 mg L<sup>-1</sup>), I<sup>-</sup> (1-60 mg L<sup>-1</sup>), Br<sup>-</sup> (20-250 mg L<sup>-1</sup>), Li, Rn., Sr and B. Thermal waters, situated in SW part of the country (Prut River Valley) have temperatures from 22 – 32 °C. The quality of groundwater is largely affected by the local geological features that are likely responsible of relatively high concentrations of F<sup>-</sup>, Sr and Se, whose contents vary between 0.2 to 18.0, 0.1 and 17.0 mg L<sup>-1</sup> and 10 to 170 µg L<sup>-1</sup>, respectively. Contents of NH<sub>4</sub><sup>+</sup> are as high as 20 mg L<sup>-1</sup> [3,5].

The aim of this study, carried out in the framework of a bilateral project between the Moldova Academy of Sciences (Institute of Geology and Seismology, IGS) and the Italian National Council of Research (Institute of Geosciences and Earth Resources, IGG), was that to determine the heavy metal and micro-component concentrations from the Baden-Sarmatian aquifer and assess their source(s) by comparing our results with those of previous investigations.

### Methods

Water sampling and trace element analysis were carried out according to the protocols used in the accredited ISO 17025 laboratories of the Institute of Chemistry (Academy of Science of Moldova) in cooperation with IGS and CNR-IGG. The main physico-chemical parameters and chemistry were also determined. Five pilot areas were studied (Fig. 1): Cahul, Hirjauca, Gotesti and Congaz are mineral water resorts whereas at Dubasari this aquifer is used for potable water supply.

## Results

The depth and mineralization of the Baden-Sarmatian aquifer are, as follows: Cahul 430-530 m, 68.59 g L<sup>-1</sup>, Gotesti 450-520 m, 5.76 g L<sup>-1</sup>, Congaz 450-520 m, 5.04 g L<sup>-1</sup>, Hirjauca 250 m, 1.47 g L<sup>-1</sup>, Dubasari 40-150 m, 0.86 g L<sup>-1</sup>. The results are presented in Table 1. Pb, Cr, Mn, As, Se and Fe have low contents in the most of the studied sites with the exception of Dubasari where Fe and As are up to 2.8 mg L<sup>-1</sup> and 13.8 µg L<sup>-1</sup>, respectively. High values of Cd are found in the Cahul waters while Ni has high concentrations in the most mineralized waters and those of Dubasari. Li and Sr are slightly enriched at Congaz and Gotesti while F<sup>-</sup>, I<sup>-</sup> and Br<sup>-</sup> show high contents (up to 13.2, 23.7 and 140.5 mg L<sup>-1</sup>, respectively) in the most mineralized waters.

**Table 1.** Trace element concentrations (in g L<sup>-1</sup>) in the Baden-Sarmatian aquifer (N<sub>1</sub>b-s<sub>1</sub>).

Metal	Pilot areas (mineralization, g L <sup>-1</sup> )				
	Cahul (68.59)	Gotesti (5.76)	Congaz (5.04)	Hirjauca (1.47)	Dubasari (0.86)
Cd, µg L <sup>-1</sup>	<0.2–12.0/4.85*	<0.2–0.5/0.4	<0.2	<0.2	<0.2
Pb, µg L <sup>-1</sup>	<1.0	<1.0	<1.0	<1.0	<1.0–14.3/3.4
Cr, µg L <sup>-1</sup>	<0.8–1.5/1.1	<0.8	<0.8–3.0/1.75	<0.8–1.25/1.15	<0.8–1.8/1.3
Ni, µg L <sup>-1</sup>	<1.0–26.2/1.1	<1.0	<1.0–20.0/10.75	<1.0–5.0/3.2	<1.0–43.0/7.0
Mn, µg L <sup>-1</sup>	23.4–224.1/123.7	10.0–40.0/28.3	30.0–130.0/70.0	<1.0–2.0/1.5	<1.0–48.0/17.0
As, µg L <sup>-1</sup>	<1.0	<1.0	<1.0,0	<1.0	<1.0–13.8/4.3
Se, µg L <sup>-1</sup>	<1.0	<1.0	<1.0,0	<1.0	<1.0–8.7/4.2
Fe, mg L <sup>-1</sup>	<0.05	<0.05	<0.05	<0.05	<0.05–2.80/0.54
Li, mg L <sup>-1</sup>	0.05	1.5–2.4/1.97	0.70–1.84/1.21	0.04	n.d.**
Sr, mg L <sup>-1</sup>	1.00	1.5–2.9/2.3	1.61–9.79/4.93	0.08	n.d.**
F, mg L <sup>-1</sup>	n.d.**	8.10–13.20/10.0	5.70–7.60/6.60	<6.20–7.50/7.00	0.14–2.77/0.85
I, mg L <sup>-1</sup>	9.5–23.7/21.32	0.10–2.03/1.34	1.50–7.20/4.43	0.08	n.d.**
Br, mg L <sup>-1</sup>	25.86–140.5/115.2	2.26–4.00/3.29	3.50–19.4/11.48	0.13	n.d.**

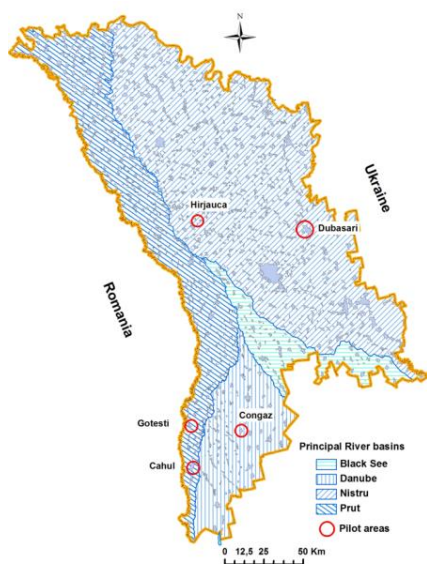
\*concentration range/average value; \*\*n.d. not determined; single values are with no interval and average value.

## Conclusion

The mineralized waters from the Baden-Sarmatian aquifer have naturally occurring high contents of F<sup>-</sup>, I<sup>-</sup>, Br<sup>-</sup>, Sr, Li and Mn, while other heavy metals, with a few exceptions, are below the main admissible contents for potable waters. It is noteworthy to mention that samples from Dubasari, whose waters are intensively used for potable purposes is apparently contaminated by waters from shallower aquifers that are likely affected by anthropogenic sources.

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**Figure 1.** Location of pilot areas.