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EVALUATION OF ARSENIC SPECIATION IN GROUNDWATER SAMPLES FROM THE WESTERN ROMANIAN AQUIFER

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Introduction

Across Europe, numerous groundwater systems contain naturally occurring arsenic (As) at concentrations exceeding the 10 µg/L limit set by the WHO and the EU Drinking Water Directive. Nearly one million Europeans are exposed through drinking water, mainly in the Pannonian Basin, where elevated As levels reflect specific hydrogeochemical conditions. In rural western Romania, geogenic arsenic contamination affects deep groundwater sources supplying small and medium-sized communities.

Arsenite (As(III)) and arsenate (As(V)) are the main inorganic As species, with As(III) prevailing under the reducing conditions typical of groundwater. As(III) is reported to be up to 60 times more toxic than As(V). Because As(III) is more mobile and less strongly adsorbed onto Fe/Al (oxyhydr)oxides than As(V), oxidation of As(III) to As(V) enhances arsenic removal.

The aim of this study is to quantify total arsenic concentrations in these groundwater sources and to determine the predominant arsenic species, As(III) and As(V).

Materials and methods

Groundwater quality was investigated at 10 sampling points in Timis County, western Romania. The sampling campaign was conducted during 2024-2025. All groundwater sources were located in rural areas and had depths ranging from 120 to 180 m. General and specific analytical methods were employed to investigate the inorganic constituents of the groundwater and to identify and quantify potentially toxic pollutants. Particular attention was paid to ammonium, nitrite, nitrate, iron, manganese, and selected heavy metals (Pb, Cr, Cd, Cu, Zn and Ni).

The concentrations of Mn, Fe, Cu, Zn, Cr, Cd, Pb and Ni were determined by flame atomic absorption spectrometry (FL-AAS).

The detection technique used for As total was Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES Avio 500, Perkin-Elmer) and the concentration of ammonium, nitrite and nitrate were determined with a Spectrofotometer UV-VIS (Specord 205, Analytik Jena). The detection and quantification of arsenic species (As(III) and As(V)) in groundwater samples were performed using an Agilent 1260 Infinity II HPLC system coupled to an Agilent 7850 ICP-MS. Agilent MassHunter software, version D.01.01 (SI 637) was used for data processing and quantification of arsenic species. The optimized operating parameters for arsenic speciation analysis by HPLC–ICP-MS are presented in Table 1.

Table 1 - The optimal parameters of HPLC-ICP-MS

HPLC Parameters	ICP-MS Parameters
Pre-column: Agilent G315 4-65002, 4.6 mm×10 mm	RF Power: 1400 W
Column: Agilent G3154-65001, 4.6 mm × 150 mm	Nebuliser pump: 0.4 rps
Column temperature: ambient	Nebuliser gas flow: 1.10 L/min
Volume injected: 50 µL	Plasma gas flow: 15 L/min
Mobile phase flow rate: 1.0 mL/min	Auxiliary gas flow: 0.9 L/min
Time/sample: 16 min	He collision gas flow: 4.3 mL/min

Results and conclusions

In this study, we systematically assessed the pollution status of ten selected deep groundwater sources in Timis County, Romania, in accordance with the requirements of Directive (EU) 2020/2184. The physicochemical characterization revealed that iron, manganese, ammonium, and arsenic concentrations exceeded the applicable drinking-water parametric values in all ten groundwater sources analyzed. In contrast, the concentrations of Zn, Cu, Cr, Cd, Ni, and Pb remained below the respective permissible limits in all ten sources. For example, iron (Fe) concentrations ranged from 0.4 to 1.2 mg/L, thus exceeding the drinking-water parametric value of 0.2 mg/L, in all groundwater samples analyzed. Total As concentrations ranged from 19 to 236 µg/L, exceeding the parametric value of 10 µg/L by up to 24 times. Arsenic speciation analysis performed on four selected wells revealed that As(III) was the predominant species, accounting for 55–95% of total arsenic. Figure 1 presents the arsenic speciation results for the four groundwater wells analysed. Therefore, oxidation of As(III) to As(V) should be considered a key step in the treatment process to enhance arsenic removal efficiency.

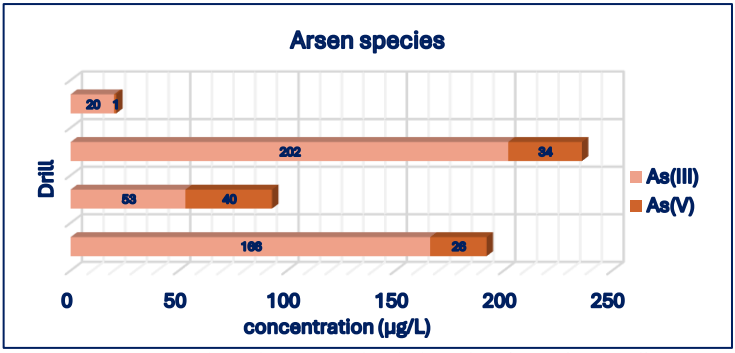


Figure 1 - Arsenic species concentrations in four selected groundwater wells in Timis County, Romania

Characterizing arsenic concentrations and speciation will provide essential insights into arsenic occurrence and behavior in the affected groundwater sources, thereby supporting the design and development of an effective water treatment protocol for arsenic removal.

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