METALS AND NATURAL RADIOACTIVITY INVESTIGATION OF DANUBE RIVER WATER IN THE LOWER SECTOR

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Abstract. In this paper high-resolution continuum source atomic absorption spectrometry (HRCS AAS) was used for the determination of metal concentrations in Danube water collected in the river lower sector in SE Romania (Braila-Galati-Tulcea). The evaluation of the water natural radioactivity was only performed in Galati sector based on selected radiological parameters: gross alpha/beta activity and radionuclides (210Po, 210Pb, natU, natTh and 226Ra) activity concentrations. The results indicate a temporal and spatial variability of contaminant levels due to anthropogenic inputs and seasonal conditions. For several heavy metals, the registered concentrations exceed the legislated values, imposing a regular monitoring of water quality especially in the case of using the water resource for human consumption, irrigation or aquaculture.

Key words: radioactivity, heavy metals, HR CS-AAS, Danube, SE Romania.
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1. INTRODUCTION

Inorganic environmental pollutants (toxic elements, heavy metals, radionuclides) can pose a threat to ecosystems, groundwater quality, biota and population health, even at very low concentrations [1–5]. In aquatic ecosystems, they originate from polluted soil erosion, atmospheric deposition, use of pesticides and fertilizers on agricultural terrains along the river drainage basin, sewage sludge amendment to soils, technological and domestic wastewaters discharge, industrial and economic activities (chemical industry, iron and steel production, shipbuilding, minerals transportation, corrosion products from vessels) [6–11]. Accurate nuclear and atomic analytical techniques, such as INAA [3, 11–14], XRF [1, 3, 10, 12, 15], PIXE [3, 14, 16], AAS [1, 14, 15, 17–23], ICP-MS [1, 10, 15, 24, 25] and ICP-AES [1, 8, 21],
have been optimized and used in various environmental studies, including analysis of trace elements in surface water, sediments, soils, groundwater, wastewater and sludge, with low limits of detection (LOD).

Danube River is a very important European aquatic artery and the water quality assessment is helpful to the managers of regional monitoring programs for protecting the ecological security of the river basin [1, 2, 18, 26]. Because of specific anthropogenic activities in riverine environments in SE Romania (Braila-Galati-Tulcea), the Danube fluvial ecosystem might exhibit a high level of contamination with metals and radionuclides which could influence the surface water quality in its lower sector [9, 11, 12, 15, 24].

Due to the impact that metals could have upon people’s health, their levels are key water quality parameters for surface waters [8, 27]. Water radioactivity levels are not legislated, but are of outmost importance to be monitored in large rivers, as this constitutes a basic resource for drinking water for riparian population [28, 29], irrigation and aquaculture. Existing seasonal monitoring data for the Lower Danube are very limited in the literature and most of the studies reported physicochemical parameters [7, 20, 30, 31] and levels for a limited number of trace elements, presenting high temporal variability [2, 16, 18, 20, 23, 32]. To the best of our knowledge, for radionuclides and gross alpha/beta activity there is no report published for raw surface water in the Romanian sector of the Danube.

Thus, the determination of the distribution of the natural radionuclides and metals in surface water of Danube River is of great interest for the assessment of public exposure and building an international database with trace metals and radioactivity levels. The aim of this paper was two-fold: 1) to quantify the metals in the Danube water in the river lower sector by High Resolution Continuum Source Atomic Absorption Spectrometry (HRCS AAS) technique and 2) to assess the gross alpha/beta activity and main natural radionuclides ($^{210}$Po, $^{210}$Pb, natU, natTh and $^{226}$Ra) activity concentration by radiometric and instrumental methods.

2. MATERIAL AND METHODS

2.1. SAMPLE COLLECTION AND PREPARATION

Water samples were collected in 2018 in two campaigns. In the first campaign the sampling was performed in four months in the period June-September from five locations in the Lower Danube River, in Galati region, SE part of Romania (samples G1-G5), between the Danube confluence with Siret and Prut tributaries (Fig. 1). In the second campaign (November) the samples were collected from urban and rural sites located in Braila (samples B1-B4) and Tulcea (samples T1-T6) counties, including industrial, agricultural, deltaic and natural protected areas with ecological
value and providing a wide range of ecosystem services [7] (Fig. 1). The characteristics
of the sampling sites and the water physico-chemical quality parameters are presented
elsewhere [7].

The samples were prepared for spectrometric and radiometric analysis at
Laboratory of Atomic Absorption and Laboratory of Experimental Nuclear Physics
and Dosimetry, INPOLDE research center, Dunarea de Jos University of Galati,
Romania. Immediately after sampling, the water samples were filtered using
Whatman filter paper with 45 μm porosity. For the stabilization of the ionic forms
and preservation, the samples were acidified to pH ≤ 2 by adding 5 mL of 65%
superpure HNO₃/1000 mL each and kept in polyethylene bottles at a temperature in
the range 2–5°C.

Fig. 1 – Map of Danube River water sampling sites from the target area, SE Romania
(compilation after [7]).

2.2. ATOMIC ABSORPTION SPECTROMETRY

The dissolved forms of the elements Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb,
Se, Zn were quantified using High Resolution Continuum Source Atomic
Absorption Spectrometry (HR-CS AAS) (ContrAA 700, Analytik Jena, Germany),
equipped with a transversely heated graphite furnace (GF) atomizer, platform type
tube and MPE 60 autosampler. The optical system of this instrument consists of a
xenon short-arc lamp operating in a “hot spot” mode as radiation source, a high-
resolution double echelle monochromator, and a linear CCD array detector with 588
pixels (200 of these pixels are used to measure the absorbance, while the rest are used for internal corrections).

High-purity deionized water with a specific resistivity of 18 MΩ cm obtained from a Milli-Q water purification system (Millipore, USA) was used to prepare all the working solutions. Nitric acid 65% (w/v), Suprapur® (Merck, Germany) was used for the preparation of working standards, modifying solutions and sample preservation. 1000 mg/L standard stock solutions in 2% nitric acid Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se and Zn, TraceCERT® (Merck, Germany) and matrix modifiers (Magnesium, Palladium, Phosphate) for the graphite furnace-AAS, (Merck, Germany) were also employed for the analyses. The gas used was argon 4.8 with a purity of 99.999% (Linde, Romania).

The instrumental parameters, operating conditions and furnace temperature schedule for each element monitored by GF HRCS AAS are presented in Table 1. To reduce the interferences, increase the precision and accuracy of determinations, modifiers-matrix stabilizers were used. Their type and concentration are specific to each element (Table 1). To plot the calibration curves (Fig. 2), working standard solutions were prepared by diluting the reference solutions with 0.5% HNO₃, obtaining the desired concentration, according to the detection thresholds of the analysis instrument.

### Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>Oven parameters</th>
<th>Matrix modifier</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pyrolysis temperature (°C)</td>
<td>Atomization temperature (°C)</td>
<td>Rate of temperature rise to atomization (°C/s)</td>
</tr>
<tr>
<td>Al</td>
<td>309.2713</td>
<td>300</td>
<td>2400</td>
</tr>
<tr>
<td>As</td>
<td>193.696</td>
<td>1100</td>
<td>2200</td>
</tr>
<tr>
<td>Cd</td>
<td>228.8018</td>
<td>600</td>
<td>1200</td>
</tr>
<tr>
<td>Co</td>
<td>240.7254</td>
<td>1200</td>
<td>2100</td>
</tr>
<tr>
<td>Cr</td>
<td>357.8687</td>
<td>1300</td>
<td>2500</td>
</tr>
<tr>
<td>Cu</td>
<td>324.754</td>
<td>1100</td>
<td>2000</td>
</tr>
<tr>
<td>Fe</td>
<td>248.327</td>
<td>1100</td>
<td>2000</td>
</tr>
<tr>
<td>Mn</td>
<td>279.4817</td>
<td>1200</td>
<td>2000</td>
</tr>
<tr>
<td>Ni</td>
<td>232.003</td>
<td>1050</td>
<td>2300</td>
</tr>
<tr>
<td>Pb</td>
<td>283.306</td>
<td>800</td>
<td>1500</td>
</tr>
<tr>
<td>Se</td>
<td>196.0267</td>
<td>1050</td>
<td>2100</td>
</tr>
<tr>
<td>Zn</td>
<td>213.857</td>
<td>300</td>
<td>1300</td>
</tr>
</tbody>
</table>
Fig. 2 – Calibration curves obtained for the metals selected to be investigated by GF HRCS-AAS in river water.
2.3. RADIOMETRIC TECHNIQUES

Various radiometric techniques were employed for the determination of the gross alpha activities, gross beta activities and the activity concentrations of natU, natTh, 210Po, 210Pb, 226Ra in surface water, as described in previous work for drinking water [28, 29] or food items such as bread [33], food supplements [34] and meat [35].

The gross alpha activity and the gross beta activity were determined using a MPC-2000-DP instrument, and the concentrations of natU and natTh were investigated by separation and purification on Dowex-resin followed by the spectrophotometric measurements of arsenazo III-U⁴⁺ complex and arsenazo III-Th⁴⁺ complex, respectively. The concentration of 210Po and 210Pb was determined by the measurement of the gross alpha activity after self-deposition onto nickel disc. The concentration of 226Ra was investigated using a SARAD RTM 1688-2 instrument.

3. RESULTS AND DISCUSSION

3.1. METAL ANALYSIS IN DANUBE RIVER WATER BY GF HRCS-AAS

The results of the elemental analysis (dissolved forms) of Danube water by GF HRCS-AAS for the two campaigns are presented in Figs. 3 and 4 for Galati area, and in Figs. 5 and 6 for Braila and Tulcea areas.

Fig. 3 – Concentrations of Cu, Zn, Al and Fe in the Danube River water samples collected in different months (June-September 2018) from Galati area, SE Romania.
Fig. 4 – Concentrations of Cr, Cd, Pb, Ni and Mn in Danube River water samples collected in different months (June-September 2018) from Galati area, SE Romania.

Fig. 5 – Concentrations of Al, Cu, Fe and Mn in Danube River water samples collected in the second campaign (November 2018) from Braila and Tulcea counties, SE Romania.
Fig. 6 – Concentrations of Cr, Ni, Zn, As and Se in the Danube River water samples collected in the second campaign (November 2018) from Braila and Tulcea counties, SE Romania.

The composition of river water depends on meteorological factors, hydrological regime, human impact and processes of absorption-sedimentation-desorption, which influence the water self-cleaning potential and secondary pollution in the aquatic ecosystem in the given region [8].

Figures 3 and 4 show temporal differences in the metal composition of river water from Galati region, with a tendency of increasing in the autumn month, probably due to the drought conditions in SE Romania which conducted metals to concentrate in water in higher extent. Figures 5 and 6 present spatial differences in Braila and Tulcea areas, depending mainly on the specificity of the technogenic and agricultural activities, erosion processes, mineralogy of suspended solids, efficiency of sewerage systems and naval transport.

Generally, based on recorded metal levels, the Danube water is ranked in the first quality class, according to Romanian Order no. 161/2006 [27]; exceptions are made by: Zn in T6 site (class IV) and G1-G5 in several months (class II or III); Fe in G4 in September (class II); Se in B2 (class II); Cd in G1 and G5 in June (class II) and Pb in G3 in June (class II).

3.2. NATURAL RADIOACTIVITY PARAMETERS OF DANUBE RIVER WATER

The results obtained for gross alpha and gross beta activity and the main natural radionuclides (\(^{210}\)Po, \(^{210}\)Pb, nat\(^{238}\)U, nat\(^{232}\)Th and \(^{226}\)Ra) activity concentrations are presented in Table 2.
The seasonal variation exhibited in Table 2, both of the global activity concentration (alpha and beta) and of the concentration of natural radionuclides, might be due to the variation of alluvial components, biological activity of aquatic vegetation and fauna, temperature and pH.

Table 2
Gross alpha/beta activity and radionuclides’ concentration in river water collected in Galati area

<table>
<thead>
<tr>
<th>Sample code</th>
<th>( \alpha ) (Bq/L)</th>
<th>( \beta ) (Bq/L)</th>
<th>( \alpha_{210Pb} ) (mBq/L)</th>
<th>( \beta_{210Pb} ) (mBq/L)</th>
<th>( \alpha_{nat} ) (mBq/L)</th>
<th>( \beta_{nat} ) (mBq/L)</th>
<th>( \alpha_{226Ra} ) (Bq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>0.016 ± 0.004</td>
<td>0.060 ± 0.009</td>
<td>0.7 ± 0.2</td>
<td>0.030 ± 0.009</td>
<td>13 ± 1</td>
<td>12 ± 1</td>
<td>0.148 ± 0.044</td>
</tr>
<tr>
<td>G2</td>
<td>0.020 ± 0.006</td>
<td>0.065 ± 0.009</td>
<td>0.7 ± 0.2</td>
<td>0.030 ± 0.009</td>
<td>9 ± 0.9</td>
<td>3 ± 0.3</td>
<td>0.166 ± 0.049</td>
</tr>
<tr>
<td>G3</td>
<td>0.012 ± 0.003</td>
<td>0.048 ± 0.007</td>
<td>0.7 ± 0.2</td>
<td>0.077 ± 0.023</td>
<td>8 ± 0.8</td>
<td>11 ± 1</td>
<td>0.124 ± 0.037</td>
</tr>
<tr>
<td>G4</td>
<td>0.021 ± 0.006</td>
<td>0.057 ± 0.008</td>
<td>0.8 ± 0.2</td>
<td>0.061 ± 0.018</td>
<td>9 ± 0.9</td>
<td>13 ± 1</td>
<td>0.100 ± 0.030</td>
</tr>
<tr>
<td>G5</td>
<td>0.02 ± 0.006</td>
<td>0.065 ± 0.009</td>
<td>0.7 ± 0.2</td>
<td>0.030 ± 0.009</td>
<td>9 ± 0.9</td>
<td>3 ± 0.3</td>
<td>0.166 ± 0.052</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample code</th>
<th>( \alpha ) (Bq/L)</th>
<th>( \beta ) (Bq/L)</th>
<th>( \alpha_{210Pb} ) (mBq/L)</th>
<th>( \beta_{210Pb} ) (mBq/L)</th>
<th>( \alpha_{nat} ) (mBq/L)</th>
<th>( \beta_{nat} ) (mBq/L)</th>
<th>( \alpha_{226Ra} ) (Bq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>0.018 ± 0.004</td>
<td>0.088 ± 0.013</td>
<td>0.4 ± 0.1</td>
<td>0.044 ± 0.013</td>
<td>11 ± 1</td>
<td>10 ± 1</td>
<td>0.042 ± 0.011</td>
</tr>
<tr>
<td>G2</td>
<td>0.024 ± 0.005</td>
<td>0.047 ± 0.007</td>
<td>1.2 ± 0.3</td>
<td>0.007 ± 0.002</td>
<td>10 ± 1</td>
<td>4 ± 0.4</td>
<td>0.063 ± 0.017</td>
</tr>
<tr>
<td>G3</td>
<td>0.021 ± 0.005</td>
<td>0.067 ± 0.010</td>
<td>0.5 ± 0.1</td>
<td>0.022 ± 0.002</td>
<td>13 ± 1</td>
<td>9 ± 1</td>
<td>0.051 ± 0.014</td>
</tr>
<tr>
<td>G4</td>
<td>0.010 ± 0.005</td>
<td>0.032 ± 0.005</td>
<td>0.5 ± 0.1</td>
<td>0.017 ± 0.005</td>
<td>10 ± 1</td>
<td>9 ± 1</td>
<td>0.051 ± 0.014</td>
</tr>
<tr>
<td>G5</td>
<td>0.018 ± 0.004</td>
<td>0.023 ± 0.003</td>
<td>1.1 ± 0.3</td>
<td>0.037 ± 0.011</td>
<td>12 ± 1</td>
<td>6 ± 0.6</td>
<td>0.042 ± 0.011</td>
</tr>
</tbody>
</table>

Alluviums and sediments can be washed away or entrained in the water mass depending on the input and flow of the Siret and Prut tributaries that flow into the Danube. Owing to the biological activity, the aquatic flora and fauna can take up and, at the same time, release natural radionuclides into the water - a quantifiable fact, especially in the case of long-lived radionuclides.

Temperature influences the solubility of radionuclides, especially of \(^{226}\)Ra, through the following mechanism: at higher temperatures, a larger amount of radium descendent \(^{222}\)Rn is released from water into the atmosphere and, as a result, its parent, \(^{226}\)Ra, will be found in lower concentration. If less radon is released, the specific concentration of \(^{226}\)Ra remaining in the water subjected to analysis will be higher.

Based on the obtained values, the contribution to the annual effective dose to population through water consuming could be assessed in the case that the raw water is used for potabilization [28, 29].
4. CONCLUSIONS

Accurate atomic and nuclear techniques have been extensively developed worldwide to gain low detection limits of heavy metals in aquatic compartments. High resolution continuum source AAS technique with graphite furnace was employed in this work to quantitatively analyze the metals at trace levels in water collected from the lower sector of the Danube River, in Braila-Galati-Tulcea region, SE Romania. Complementary radiometric methods were used for the assessment of natural radionuclides and gross alpha/beta radioactivity of water samples from Galati area.

The study fills a gap in the database of metal and natural radionuclide concentrations in surface water in the vicinity of a large urban agglomeration in the Danube lower sector in SE Romania. The data are valuable for the freshwater resources management, as well as mapping the water inorganic contaminants and radioactivity in this region and tracking the changes in their levels in the benefit of inhabitants of the river basin and regional authorities.

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