POLLUTION SOURCES ASSESSMENT OF THE ENVIRONMENT WITH NATURAL RADIONUCLIDES AND HEAVY METALS IN *ARIEȘ* RIVER BASIN

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The present work is performed to obtain information on sources of pollution of the river Arieș with heavy metals and naturally occurring radionuclides. This paper is a first step to build a reference map of radioactive background level and also a database to assess future physical-chemical changes of surface water and sediments in the studied area.

Potential sources of pollution with radionuclides and heavy metals are represented by the four uranium mining perimeters and three metal mining exploitations drained by the Arieș river or its tributArieș.

Keywords: environmental pollution, uranium, radium, radioactivity, heavy metals

1. Introduction

The pollution is the most serious of all environmental problems, representing a major threat to the health of millions of people and global ecosystems. In recent years, pollution becomes a principal problem with human activities. Natural and artificial radionuclides as radiation sources in surface water and sediments captured the attention of many researchers in the last three decades, especially after the Chernobyl disaster in 1986 [1]. Radionuclides most widespread natural radioactive series are those of potassium (K^{40}), uranium (U^{238}) and thorium (Th^{232}) [2,3]. The majority of radionuclides has a low solubility in water and tends to be adsorbed, therefore to accumulate in the sediment. Heavy metal pollution of aquatic ecosystems is increasing, due to the effects of urbanization and industrialization [4-6].

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Also, the levels of contamination in the aquatic environment with heavy metals can be estimated through analysis of water and sediments. Heavy metals are considered major contaminants in marine coastal environments and worldwide [7]. They represent a serious threat to human health, living organisms and natural ecosystems [8]. Many heavy metals are known to be toxic or carcinogenic to humans [9]. Metals such as copper (Cu), zinc (Zn) and manganese (Mn) in small concentration are essential, playing an important role in biological systems, but when are in high amount these metals become toxic elements [10]. There are non-essentials metals such as lead (Pb), cadmium (Cd) which are toxic and their bio-accumulation in tissue results in intoxication, decreased fertility, cell and tissue damage, cell death and dysfunction of a variety of organs [11,12]. Heavy metals can contribute to the degradation of aquatic ecosystems by reducing species diversity and accumulation of metals in living organisms [13].

Investigation of heavy metals in water and sediments can be used to estimate the anthropogenic impact of mining industries and the risks posed by discharges of waste on ecosystems [14-16]. Therefore, it is important to measure the concentrations of heavy metals in water and sediment [17].

This paper presents potential sources of pollution with heavy metals and natural radionuclides of hydrographic network corresponding to Arieș river basin.

Arieș river (Fig.1) has a length of 167 km and an area of 2970 km^2 drainage, flows from the Bihor Mountains, crossing Cluj and Alba counties and drains into Mures river near Gura Arieș village. The territory crossed by Arieș has a petro graphic complexity that resulted in a wide range of underground deposits and a large number of natural reservations: geological, forest and mixed (have been identified 44 natural reservations). Thus, the tourism potential of the Arieș basin is special, its territory is propitious for various types of tourism (mountain climbing and winter sports, cultural, eco - and rural tourism, hunting and fishing, speological turism, gastronomy) [18].

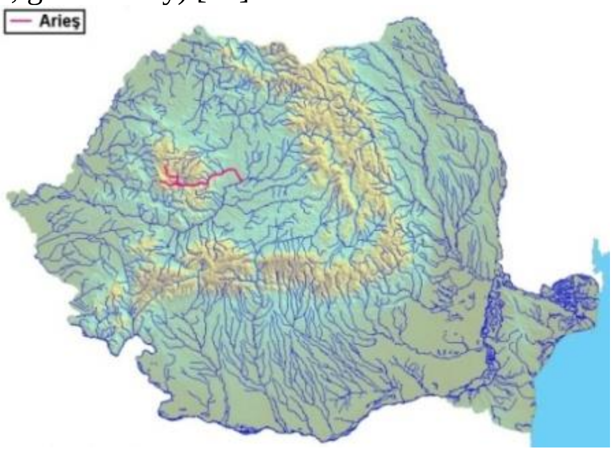

Fig. 1. *Arieș* river on the Romania map

Potential sources of pollution with radionuclides are geological exploration perimeters of uranium ores located on tributArieş of the river Arieş or right on its valley, namely Arieşeni - Galbena, Garda, Avram Iancu and Lupsa perimeters. Potential sources of heavy metal pollution are metalliferous mining perimeters which are located on tributArieş of the Arieş river, namely Rosia Poieni mining, Rosia Montană and Baia de Arieş.

Regarding the water quality parameters, Arieş river and tributArieş are generally characterized by a lower mineralization, the amount of dissolved mineral salts being below 400 mg/L. The content consists of bicarbonates, chlorides and sulfates of sodium, potassium, calcium and magnesium. Total water hardness is generally less than 15 degrees, and it is formed for the most part in the bicarbonate hardness.

The hydrogen ion concentration (pH) is placed around neutral, pH being in the range 6.8-7.8. Dissolved gases are present, such as dissolved oxygen saturation between 65-95% and free carbon dioxide, generally below 10 mg/L. The main feature of watercourse presents variable charging with suspended solids and organic matter, loaded proportionally related to weather and climate.

It is known that natural radioactivity of water content in rivers and lakes vArieş by the presence of radioactive elements with an activity of 0.37 Bq/L. In mineral waters, these values are approximately 100 times higher than the water in rivers and lakes, respectively 37 Bq/L [19].

Regarding the sediments radioactivity, the main factors influencing the solubility and sediment content in radioactive elements are related to the nature of rocks through which the waters flows, their temperature regime, general hydrogeology and hydrodynamic regime of groundwater. Uranium (U) and radium (Ra) from rocks are leached intense by water containing salts and depending of pH and oxygen is oxidizing the uranium (IV) to uranium (VI) species, causing an intense leaching and distribution and mobility thereof. In addition to atmospheric oxygen, other gases such as carbon dioxide, dissolved in the water, favor the distribution and mobility of uranium. If these waters are enriched in radon (Rn) and radium, the water becomes radioactive water.

Due to the different geochemical characteristics, precipitation of U and Ra species is produced in a different way. Thus, uranium is retained extensively in sediments riched in organic matter, and radium is adsorbed by clay sediments and hydroxides of iron and manganese [20]. Also, the formation of insoluble tetravalent uranium compounds in a reducing environment leads to the precipitation and removal of uranium from the water. For radium, on the other hand, reducing conditions favors the growth of concentration in the water, in comparison with uranium. Uranium in oxidizing conditions can be mobilized; in conditions of low pH values (2-3) uranium and radium pass intensely in solution, being able to be in balance. For waters with pH 4.5-6.5 there is a relative shift of radium in water, and at pH greater than 7, uranium shows a higher percentage [21].

As above shown, the main sources of rivers water pollution are the mining water from the extraction process/mining closing (mine water) as well as water from mineral processing processes in preparation plants.

2. Materials and methods

For soil samples were collected 250 g of dump material and the analyzed elements were uranium and radium. For water samples were collected 1000 mL of mine water and the analyzed elements were uranium (U), radium (Ra), lead (Pb), copper (Cu), magnesium (Mg), calcium (Ca), iron (Fe) and nickel (Ni).

Gamma dose rate was measured at 1 meter from dump surface with flowmeter FH40G-L10 (manufacturer Thermo, Germany); measuring range was from 10 nSv/h to 10 mSv/h. Radon was measured in the mouth galleries with the device RAD 7 (manufacturer DURRIDGE, USA), by sucking air into the unit, in four cycles of 5 minutes each. The analysis results are printed using the embedded printer. The sensitivity was 0.013 Bq/m^3.

Analysis of natural radionuclides in soils and sediments was made by multi DART gamma spectrometry with high performance detector hyperpure Germanium analyzer (manufacturer ORTEC, USA). Radium was dosed after emitted gamma lead lines - 214 (Pb^{214}) and bismuth - 214 (Bi^{214}) after complete radioactive equilibrium established between radium and its descendants. Uranium was dosed after the line gamma 63 and 186 KeV. The measurement consists in recording the energy spectrum of gamma radiation and to identify specific energy gamma emission lines of the analyzed element. Limits of detection are 1 mg/kg and 25 Bq/kg for U_{nat} and 1.5 mg/kg and 0,015 Bq/g for Ra^{226}, respectively.

Spectral analysis of heavy metals in water and soil was conducted with SpectrAA 220 flame absorption spectrophotometer (VARIAN, UK). Determination of uranium in water was made using a spectrophotometric method with UV-VIS CECIL 1011 spectrophotometer (CECIL, UK) for samples containing uranium up to 2 g/L.

3. Results and discussions

Potential sources of pollution with radionuclides are presented in Table 1. The maximum reference for annual effective dose representing the weighted sum of equivalent doses from external and internal exposure performed on all tissues and organs of the body resulting from exposure to ionizing radiation is 1 mSv/year [22], as is indicated in Romanian NSR-01.

Table 1

Radionuclides in perimeters related to uranium mining in the Arieş river basin

Nr. crt.	Uranium mining perimeter	Number of ore deposits	Sample of mine water	Debit gamma dose (μSv/h)	Rn^{222} (Bq/m^3)	U_{nat} (ppm)	Ra^{226} (Bq/g)
1	Arieşeni Galbena	4	G4 Galbena G1 Vârciorog	0.18–1.5	45-315	5-15	0.07-0.27
2	Gârda	9	G 8, G 9	0.16–5	32-138	14-400	0.19-400
3	Avram Iancu	9	G XII G Arieş G XI Arieş	0.18–1.9	35–1266	4–850	0.05-11.87
4	Lupşa	8	G 6, G 5, G 7	0.18–1.5	30-214	5– 30	0.07- 0.39

Maximum limits for Rn^{222} in air is 55 Bq/m^3 [23] for public exposure and 1110 Bq/m^3 for profesional exposure, according to safety rules of radiological on operational radiation protection in mining and preparation of uranium and thorium (Romanian NMR-01).

The results of analysis of mine water from abandoned uranium mining perimeters that can pollute the Arieș river are presented in Table 2.

Table 2

The analysis results of mine water samples

Sample	Mine water	pH	Radioactive elements		Metals (mg/L)					
			U_{nat} (mg/L)	Ra^{226} (Bq/L)	Pb	Cu	Ca	Mg	Fe	Ni
Arieșeni – Galbena mining perimeter										
1	G4 – Galbena	5.8	0.2140	0.05	0.004	0.004	20.14	30.18	0.063	0.01
2	G1 – Vârciorog	6.7	0.024	0.01	0.004	0.003	21.81	27.42	0.048	0.05
Garda perimeter										
3	G 8	6.99	0.011	0.010	0.063	0.009	22.08	14.15	0.017	0.03
4	G 9	6.74	0.22	0.010	0.051	0.022	24.74	29.6	0.004	0.04
Avram Iancu perimeter										
5	G XII	6.7	0.105	0.070	0.080	0.020	19.23	15.83	0.092	0.12
6	G. Arieş	6.21	0.008	0.009	0.020	0.004	8.16	16.92	0.056	0.08
7	G. XI Arieş	5.95	0.075	0.059	0.070	0.050	21.32	56.42	0.009	0.06
Lupsa perimeter										
8	G 6	7.43	0.0072	0.005	0.027	0.045	19.13	35.22	0.088	0.03

9	G 5	7.16	0.0036	0.0002	0.008	0.008	21.88	26.18	0.076	0.11
10	G 7	7.37	0.084	0.051	0.045	0.061	3.35	19.14	0.008	0.04
NTPA 001/2005		**6.5-8.5**	-	-	0.2	0.100	300	100	5	0.5
Alert limit (according to the Government Ord. 756/1997			-	-	0.14	0.070	210	70	3.5	0.35

In Romania, the surface water quality is assessed in accordance with the provisions of the Normative 161/2006 ("Surface water quality classification to determine the ecological status of water bodies") which indicate the classification of ecological and chemical water for all surface. Mine water analysis results are reported according to Government Order 352/2005 containing previsions on limit values for pollutants loading of industrial and municipal wastewater discharged into natural receivers. The Order 756/1997 of the Ministry of Water, Forests and Environmental Protection with subsequent amendments concerning environmental pollution assessment, determines the alert thresholds for the content of heavy metals in surface waters. The concentration of metals in waters falling studied limit values laid down in Norm 161/2006 and below the alert in accordance with Order 756/1997.

The results showed that mine water pH is normal, except mine water from the G4 Galbena, G. Arieșeni and G XI Arieșeni which have a weak acid character.

Limit values for activity U_{nat} and Ra^{226} are derived limits set by the National Commission for Nuclear Activities Control (CNCAN) in the authorization process.

4. Conclusions

Radioactive pollution is generated by the uranium mining industry as processing plants and by the abandoned uranium mining perimeters.

Gamma dose rate measured in the uranium mining perimeters related to Arieș river basin were up to 1.9 μSv/h and even a value of 5 μSv/h for stockpile gallery G8 Garda. Natural background value was of 0.12 μSv/ h.

Rn concentrations varied between 30 and 1266 Bq/m^3, the highest values being recorded in the mouths of galleries. U_{nat} and Ra^{226} contents in soil varied between 5 and 850 ppm for U_{nat} and from 0.05 to 400 Bq/g for Ra^{226}, respectively; values over levels of exclusion of 16 ppm for U_{nat} and 0.040 Bq/g for Ra^{226} were provided in NMR 01 CNCAN. The presence of U_{nat}, Ra^{226} and heavy metals rich effluents in mine waters and industrial waters led to river system pollution.

Heavy metal pollution was generated by the uranium mining, metal mining and the presence of waste dumps and tailings dams. All concentrations of heavy metals species (anions, cations, metal traces) from mine waters were below the maximum permissible concentration (MPC) and below the alert as NTPA 001/2005 and the ion concentrations were below 2 mg/L.

The pH of the mine water was between 5.8 and 7.43. Mine waters from the Yellow G4 Galbena and G. XI Arieșeni samples have a weak acid character, with pH values below the normal of 6.5, according NTPA 001/2005.

It follows that in order to determine the level of contamination by natural radionuclides and heavy metals in Arieș river, it is necessary to know the migration process of chemical species and their concentration both in river water and in sediment.

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